Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

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Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Introduction chapter

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Background

The main instrument for the reduction of VOC emissions from industrial installations using organic solvents in the European Union is Council Directive 1999/13/EC[1] of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations (SE Directive).

Article 7 ("Substitution") of the SE Directive requires the Commission to ensure "that an exchange of information between Member States and the activities concerned on the use of organic substances and their potential substitutes takes place".

The present guidance documents are the result of a Commission project to provide sector specific information on VOC substitution and reduction measures for each of the activities covered by the SE Directive and listed in its Annexes I and II(A). This project was carried out by a consortium of consultants including BiPRO and ÖKOPOL under the management of AEA Technology.

The guidance documents contain detailed information on the use of substances and techniques that have the least potential effects on air, water, soil, ecosystems and human health. Each guidance document gives a short overview on the activity and the related industry sector covered, describing the solvents used, the related VOC emissions and their possible impact on the environment and on human health. Subsequently, they give a comprehensive overview of VOC-free alternatives to conventional systems, of systems with a reduced VOC use, and of other VOC emission prevention measures and abatement techniques. Particular attention is given to substitution of VOCs classified as CMR substances and halogenated VOCs carrying risk phrases R40/R68. Some practical "good practice" examples are discussed to show opportunities and barriers to the successful implementation of VOC prevention and reduction measures. Finally, relevant emerging techniques and promising research approaches are presented.

The information in the guidance documents draws on the STS BREF[2] (Best Available Techniques Reference document on Surface Treatment using Solvents) developed under the IPPC Directive (2008/1/EC) as adopted by the European Commission in 2007. In addition, numerous publications and web sites have been reviewed, interviews have been conducted with experts of the industries concerned, researchers and industry suppliers have also been contacted. Several stakeholders and competent authorities have been consulted and given the opportunity to provide inputs to the project. All of their contributions have been of outstanding value for the project and are very much appreciated.

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[1] OJ L 85, 29.3.1999, p.1

[2] http://eippcb.jrc.es/reference/

How to use the guidance documents

These documents are intended to:

- Provide information for operators and permitting authorities of activities under the scope of the SE Directive;
- Give a short, and easy to use overview of VOC reduction and VOC substitution measures;
- Raise awareness and interest in recent developments that provide further opportunities to reduce the use of organic solvents and their associated VOC emissions.

It should be noted, however, that:

- These documents do not have the status of a BREF document and do not define BAT;
- By focussing on VOC relevant issues, the guidance is equally applicable to large and small installations and the documents are thus not restricted to IPPC installations;
- The documents aim to avoid undue detail, their description of technologies has been limited to a level suitable for a general readership;
- The documents do not aim to reflect a full life cycle assessment and cost-benefit analysis of the options presented or to contain exhaustive assessment of all cross-media effects as these will be situation specific.

General issues to be considered when implementing VOC reduction and substitution measures

It is important, when selecting VOC emission prevention/reduction measures, to consider the impacts on the environment as a whole on a case-by-case basis. Options should be selected on the basis of a balanced assessment of cross-media effects (water, soil, energy use, waste). Life Cycle Assessment can be a useful tool for such decision-making process[3].

When considering substitution options, it should be remembered that REACH[4] requires that harmful substances are not substituted by more harmful substances (see Articles 60(5) and Article 64(4)).

Selection of good practice examples

The information provided seeks to reflect practical experience. The good practice examples have been collected from actual companies to illustrate particular substitution/prevention/abatement techniques applied. Their selection does however not imply that the techniques cited are necessarily the best with respect to the minimisation of all possible environmental impacts.

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[3] For more information about life cycle assessment see: http://lca.jrc.ec.europa.eu/EPLCA/deliverables.htm or http://lca.jrc.ec.europa.eu/.,

[4] OJ L 396, 30.12.2006, p. 1–849, http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2006:396:0001:0849:EN:PDF

Overview of guidance documents and good practice examples

No	Topic of Guidance	Good practice examples for VOC reduction and substitution
0	Introduction chapter	
1	Heatset web offset printing	a) Printing without isopropanol in the dampening solution b) Waterless heatset offset printing
2	Publication rotogravure	a) Achieving a low toluene emission using a closed loop system and high frequency toluene recovery with steam from a CHP gas turbine
3	Other rotogravure, flexography, rotary screen printing, and laminating or varnishing units	a) High efficiency waste gas treatment by adsorption wheel b) Use of VOC emissions to fuel engines for electricity production
4/5	Surface cleaning	a) Sealed single chamber installation using perchloroethylene as cleaning agent b) Vacuum system to reduce VOC losses c) Plasma cleaning technology for degreasing and surface activation of plastic parts
6.1	Vehicle coating (< 15 t/y) and vehicle refinishing	a) Coating of aluminium wheel rims: Changing to water-based metallic-effect base coat and a powder coating top coat b) Coating of trailers: Changing to a high-solid product. Reduced cleaning with shorter material supply ducts c) Trailer coating: Use of automatic washing machines for equipment cleaning d) Coating of brake pads: Reduced overspray from optimized arrangement of work pieces for spray coating
6.2	Vehicle coating (large series)	a) Increased use of powder coating
7	Coil coating	a) Use of Reduced Solvent Polyester Paints b) Use of Water Reducible Epoxy Baker
8.1	Other metal coating	a) Changing from solvent based to water based systems; change of application and drying techniques b) Use of automatic washing machines for cleaning of equipment
8.2	Other coating - plastic, textile, fabric, film and paper coating	a) Changing from solvent based system to water based systems b) Use of water based coatings - drying with dehumidified air c) Use of Plastic extrusion coating
9	Winding wire coating	No examples available
10	Coating of wooden surfaces	a) Replacing solvent borne polyurethane paint with water-borne paint b) Substituting solvent based paints with water based paints c) VOC reduction: Results of an overview study on furniture producing companies
11	Dry cleaning	a) Liquid silicone cleaning b) Liquid CO2 cleaning c) Perchloroethylene cleaning with a refrigerated condenser

No	**Topic of Guidance**	**Good practice examples for VOC reduction and substitution**
12	Wood impregnation	a) Use of EN 13991 Grade C creosote b) Thermal treatment of wood c) Water based preservatives
13	Coating of leather	a) Change to water based systems b) Improvement of spraying technique
14	Footwear manufacture	a) Increased use of high-solid products, water based systems, reactive coatings and adhesive systems; installation of a waste gas scrubber. b) Improved handling of VOC containing products
15	Wood and plastic lamination	No examples available
16	Adhesive coating	a) Solvent/water based coating machines b) Abatement technologies: Refrigerated cooling, Regenerative thermal oxidation and Recuperative thermal oxidation c) Hot melt coating
17	Manufacturing of coatings, varnishes, inks and adhesives	a) Improved housekeeping and enclosed manufacturing process b) Enclosed production and improved cleaning technique
18	Rubber conversion	a) Automotive tyre production: Overview on measures to reduce VOC emissions b) Agricultural tyre production: Overview on measures to reduce VOC emissions
19	Vegetable oil and animal fat extraction and vegetable oil refining activities	No examples available
20	Manufacturing of pharmaceutical products	a) Use of effective abatement technologies for VOC emission reduction

Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Guidance 1:

Heatset web offset printing

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses heatset web offset printing and the related cleaning of equipment, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emission Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
Printing is defined by the Directive as ‘any reproduction activity of text and/or images in which, with the use of an image carrier, ink is transferred onto whatever type of surface. **It includes associated varnishing, coating and laminating techniques.**’
Heatset web offset is defined as ‘a web-fed printing activity using an image carrier in which the printing and non-printing area are in the same plane, where web-fed means that the material to be printed is fed to the machine from a reel as distinct from separate sheets. The non-printing area is treated to attract water and thus reject ink. The printing area is treated to receive and transmit ink to the surface to be printed. Evaporation takes place in an oven where hot air is used to heat the printed material.’
Varnishing is defined as ‘an activity by which a varnish or an adhesive coating for the purpose of later sealing the packaging material is applied to a flexible material.’
Coating is defined as ‘any activity in which a single or multiple application of a continuous film of a coating is applied.’
Laminating associated to a printing activity is defined as ‘the adhering together of two or more flexible materials to produce laminates.’

Other common printing techniques like sheet fed offset printing, cold set offset printing, digital printing, letter set printing or sheet fed screen printing do not fall under the scope of the SE Directive.

The following printing activities, covered by the SE Directive, are addressed in separate guidance documents: publication rotogravure see guidance 2, packaging printing using flexography or gravure printing and rotary screen printing see guidance 3.

The SE Directive lays down the following activity specific emission limit values for heatset web offset printing:

Table 2: Emission limit values of the SE Directive

<table>
<tr><th colspan="4">SE Directive – Emission limit values (ELVs)
(Annex II A – activity No. 1)</th></tr>
<tr><th>Activity</th><th>Solvent consumption threshold [tonnes/year]</th><th>ELVs in waste gases [mg C/Nm³]</th><th>Fugitive emission values [% of solvent input]</th></tr>
<tr><td rowspan="2">Heatset web offset printing</td><td>> 15 - 25</td><td>100</td><td>30 (1)</td></tr>
<tr><td>> 25</td><td>20</td><td>30 (1)</td></tr>
<tr><td colspan="4">Special provisions:
(1) Solvent residue in finished product is not to be considered as part of fugitive emissions</td></tr>
</table>

The SE Directive applies to heatset web offset printing if a solvent consumption of 15 tons per year is exceeded.

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

According to the SE Directive, a VOC shall mean any organic compound at 293.15 K (20°C), a vapour pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use.

For heatset web offset the second part of the VOC definition is relevant because ink oils are heated in the dryer and under those conditions have a similar volatility as substances with a vapour pressure ≥ 0.01 kPa at 20°C.

Specific requirements apply for VOCs classified as CMR substances[1] as well as for halogenated[2] VOCs that are assigned the risk phrases R40 or R68[3]. There is a general obligation to replace CMR substances – as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated VOC with R40 or R68 the emission limit values in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.

However, heatset web offset printing normally does not use VOC classified as CMR substances or halogenated VOC with the risk phrases R40 or R68.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

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[1] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

[2] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine or iodine.

[3] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: ‘Possible risk of irreversible effects’. The new wording is: ‘Limited evidence of a carcinogenic effect’. In the ‘old’ version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: ‘Possible risk of irreversible effects’. This new risk phrase does not include carcinogenicity. The ‘new’ version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to reflect this change a final decision on which version applies can only be given by the European Court

2 Summary of VOC substitution/reduction

The main sources of VOC emissions are the ink drying process and the use of solvents (usually isopropanol) in the dampening solution and for cleaning the machinery.

VOC EMISSION REDUCTIONS CAN BE ACHIEVED BY SUBSTITUTION OF SOLVENTS FROM THE DAMPENING SOLUTIONS AND CLEANING SYSTEMS AS WELL AS BY USING EFFICIENT WASTE GAS TREATMENT

Emissions can be minimized by reducing the proportion of isopropanol in the dampening solution system, by using low-volatility or non-volatile cleaners and by deploying efficient waste gas treatment for VOC emissions from inks (substitutes for VOC emitting inks are under development).

When isopropanol is substituted in the dampening solution, personnel training may be required in order to avoid printing errors that occur when the isopropanol level is low (< 3 vol.-%).

The reduction of the volatility of the cleaning products leads to reduced VOC emissions. VOC-free cleaning products can be used for automatic roller cleaning systems and for manual cleaning of rollers and ink reservoirs.

Regular machine cleaning can be done with VOC-free systems.

3 Description of the activity and related industry sector

Heatset web offset printing is used throughout Europe, mainly for printing products with a circulation of over 10,000 copies. About 50 % of all catalogues and 40 % of all magazines are produced by heatset printing (the remainder being produced by publication rotogravure printing) [ERA 2008]. Other typical products of heatset printing are travel brochures, advertising material and coloured books.

Heatset printing machines are able to print from 8 to 40 magazine pages per revolution. The press prints on both sides (resulting in up to 80 magazine pages per revolution), using the four standard inks: black, blue, yellow and magenta. In some machines additional colours (e.g. for brand marks) and varnishes can be applied.

TYPICAL HEATSET PRINTING IS DONE WITH FOUR STANDARD INKS.

In Europe, 2144 heatset web offest machines are installed [KBA-1 2008] with the following distribution of size (pages per revolution on one or both sides):

Table 3: Size distribution of heatset offset machines in Europe

8 pages	11.0 %	32/40 pages	15.9 %
16 pages	54.4 %	48 pages	9.6 %
24 pages	3.6 %	64-80 pages	5.5 %

[KBA-1 2008]

Ink consumption data of the graphical printing sector (here illustrated with data from Germany) show the sector is dominated by the use of publication gravure printing technique (~50 %), followed by heatset web offset (~25 %), coldset offset (~15 %) and sheet fed offset (~10 %). [German EPA 1999]

AFTER PUBLICATION ROTOGRAVURE, HEATSET PRINTING IS THE MOST IMPORTANT PRINTING TECHNIQUE FOR THE PUBLICATIONS SECTOR

Companies using heatset web offset may also employ sheet fed offset printing (not in the scope of the SE Directive) for short runs and cover printing or, for long runs, publication rotogravure (in the scope of the SE Directive).

The market in Europe is dominated by three printing machine producers who use similar technology. Ancilliary equipment and materials, such as dampening solution circuits, coated rollers, roller cleaning systems, dryers and integrated waste gas cleaning systems are provided by a limited number of suppliers.

4 Technical process description

The printing and non-printing areas of the image carrier plates used in offset printing have different material properties: hydrophobic (lipophilic) areas that attract ink and hydrophilic areas that attract water based ‘dampening solution’ and repel ink (this approach contrasts with other printing techniques where the printing and non-printing areas have either embossed or engraved surfaces).

Heatset web offset is characterised by

- Printing onto material from a roll or ‘web‘ (not single sheets),
- Passage of the ink *indirectly* from the image carrier plate via a rubber coated cylinder to the printed material. This ‘off-set‘ technique avoids abrading of the image carrier plate.
- Application of heated air (180°- 300°C) to hasten drying of inks. (Other offset printing techniques use ‘cold set‘ inks where drying is via ink diffusion into the paper and ink oxidation with ambient air).

HEATSET OFFSET PRINTS ONTO PAPER FROM A ROLL. INKS ARE DRIED WITH HEATED AIR.

Heatset web offset machines print on paper, at a speed of ~10-17 m/s. The speed determines the dryer length (up to 18 m) to allow the retention time of 1 second needed for the ink to dry.

4.1 Process flow and relevant associated VOC emissions

Figure 1 shows the main relevant solvent inputs and VOC outputs (arrows indicate the relevance of the VOC amount) [German EPA 2003]:

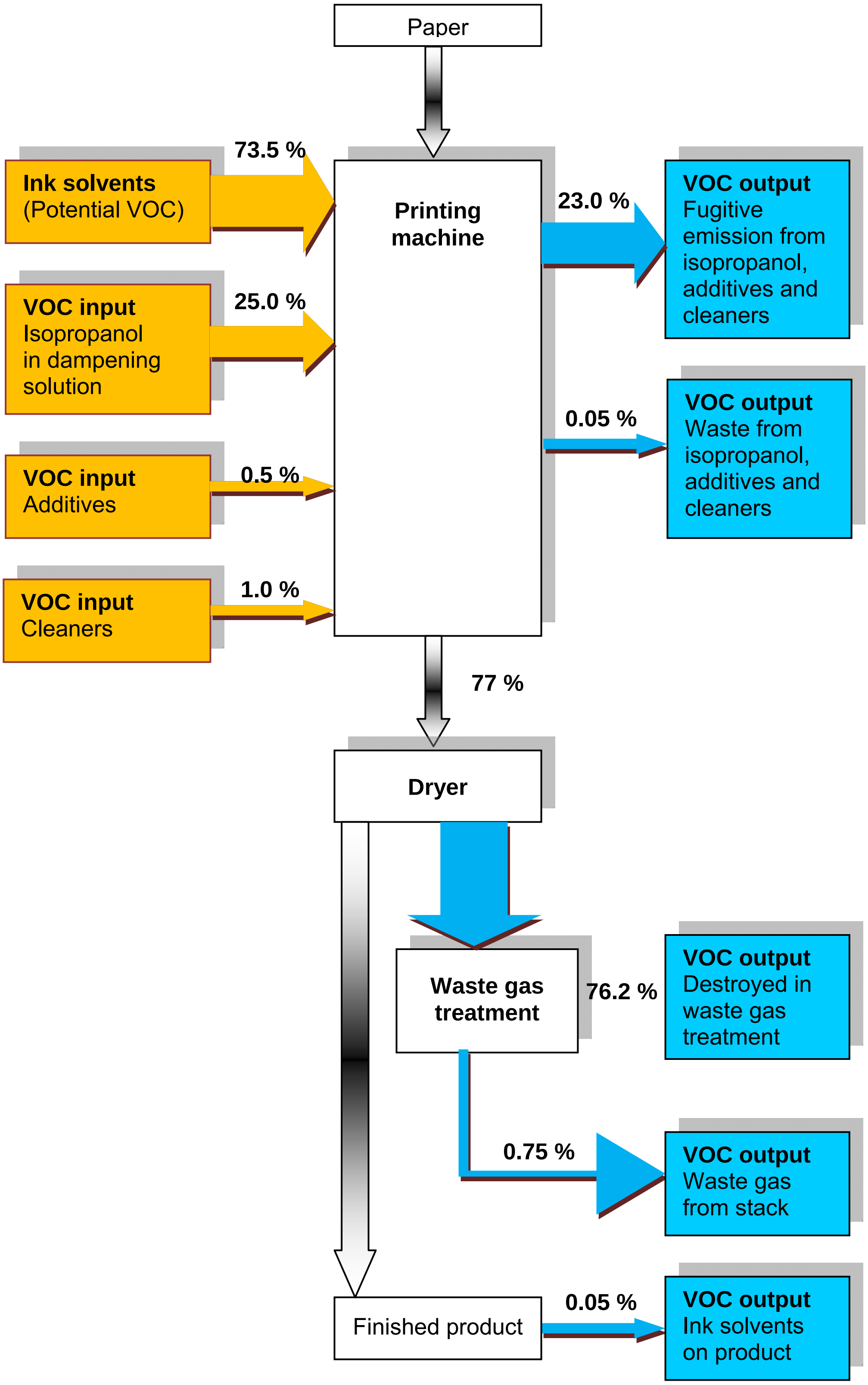

Figure 1: Main VOC input and output of heatset web offset printing

4.2 Process description

Heatset printing machines have ‘double printing units‘ for each colour on both sided of the web. Ink and dampening solution are automatically pumped to each unit. Ink rollers and dampening solution rollers transport the materials from separate reservoirs to the image carrier roller. Several roller coatings are used that provide different hydrophilic properties.

INK AND DAMPENING SOLUTION ARE PASSED (‘OFF-SET’) FROM THE IMAGE CARRIER TO A RUBBER ROLLER WHICH PRINTS ON THE PAPER

As dampening solution during printing is constantly being contaminated with paper dust and ink spots, circulated dampening solution has to be passed via an effective filter before fresh water, isopropanol and other additives are added to obtain the desired characteristics for printing.

Dampening solution circuits use various decontamination systems - usually cloth filtration. They are equipped with systems for cooling as well as for measuring and dosing with isopropanol and additives. If fresh water contains high or variable concentrations of alkaline salts then de-salting is used to adjust the composition of the dampening solution.

VOC EMISSION IS INFLUENCED BY DAMPENING CIRCUIT SYSTEM, BY TYPE OF ROLLERS AND CLEANING SYSTEMS AS WELL AS BY EFFICIENCY OF WASTE GAS COLLECTION AND TREATMENT.

When an operator becomes aware of printing errors, the image carrier plate and the rubber rollers are cleaned to remove paper dust or excess ink. Roller cleaning may be done manually or by automatic cleaning systems. Automatic systems apply cleaning solvents using spray, brush or tissue/wipe mechanisms. Besides such 'ad-hoc' roller cleaning, general machine cleaning is carried out regularly (e.g. once a week).

After printing, the paper passes through an oven to dry the ink. The waste gases are ducted to a waste gas treatment system.

Heatset printing machines are often enclosed, mainly for noise protection reasons.

[EGTEI 2003] [BREF STS 2007] [Ökopol 2008]

4.3 Inks

Inks for heatset web offset need to be based on oils. That is because the technique uses printing plates that attract lipohilic substances (oils) for colour areas and hydrophilic substances (water based) for colourless areas.

Heatset offset printing inks are based on high boiling mineral oils that do not evaporate at ambient air temperature and thus do not dry quickly. Therefore they can rest without harm in the machine for several hours, e.g. during stops for maintenance.

The majority of images are created using the three standard colours and black. Therefore cleaning the colour systems is only necessary if additional colours are used (e.g. for brand marks) or during routine machine cleaning. Heatset inks usually contain about 35 % oil. About 85 % of the oil content of the inks evaporates in the dryer at 180°-300°C. Hence, about 30 % of total heatset ink input evaporates in the dryer. [German EPA 2003]

IN GENERAL ABOUT 30 % OF THE HEATSET INK AMOUNT IS EVAPORATED IN THE DRYER

At the conditions of use (in the dryer), the volatility of the organic solvents in the heatset inks is comparable with the volatility of substances having a vapour pressure of > 0.01 kPa at 20°C. Therefore, according to the VOC definition of the SE Directive these ink solvents are VOC.

According to the SE Directive, solvent residue in finished product is not to be considered as part of fugitive emissions (see table 2 on page 4).

VOC are emitted in the dryer from inks, dampening solution and – in the case of cleaning during paper transport – from cleaners. They are ducted to a thermal oxidiser to be abated. If there is insufficient VOC in the waste gases to maintain the minimum flame temperature (about 2 g/m^3), natural gas is used as an additional fuel.

4.4 Dampening solution system

For conventional plates the process water must adhere strongly to the surface to separate printing from non-printing area. This requires a constant pH-level. Therefore additives are used in the process water to stabilise the water-ink-balance on the plate and to lower the surface tension of the water.

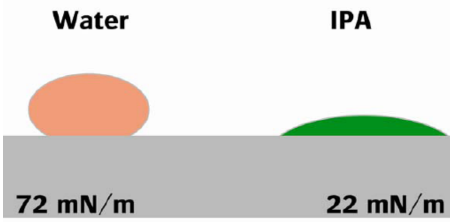

Figure 2: Different surface tensions of water and isopropanol

Two main additives are commonly used:

- isopropyl alcohol (‘isopropanol’ or ‘IPA’) to lower the surface tension
- salts to regulate the pH-level.

ISOPROPANOL AND ETHANOL ARE MOST COMMONLY USED SOLVENTS IN THE DAMPENING SOLUTION

Less frequently ethanol is used instead of isopropanol. Other additives are phosphoric acid, gum arabic, corrosion inhibitors, wetting agent, drying stimulator, fungicide, antifoaming agent. [IMPEL 2000]

Isopropanol and ethanol not only lower the surface tension when dampening solution is transported onto the printing plate but also cool the printing system when they evaporate; they also prevent the growth of microorganisms in the dampening solution.

4.5 Cleaning system

Volatile organic solvents are commonly used for cleaning the machine and all of its parts (mainly the plate, the ink reservoirs and numerous cylinders).

WEEKLY MANUAL CLEANING IS USED AS GOOD MAINTENANCE PRACTICE

Most heatset web offset machines have automated roller cleaning systems. Additional weekly manual cleaning of the entire machine is considered good maintenance practice. [KBA-2 2008]

5 Solvent use, emissions and environmental impact

5.1 Solvents used

The following VOC relevant substances are used [German EPA 2003], [Ökopol 2008]:

1. **Inks** are based on about 33-35 % aliphatic hydrocarbons (solvents). The solvents are made of mineral oil. They are not volatile at ambient temperatures but are volatile in the dryer. About 85 % of the oil fraction is evaporated in the dryer as VOC (equivalent to about 30 % of the total ink amount). Solvent residue in the finished product is not considered as part of fugitive emissions (see table 2) because it is not volatile at ambient temperatures.

ABOUT 85 % OF SOLVENTS IN INKS EVAPORATE IN THE DRYER

2. **Dampening solution** consists mainly of water. It generally contains about 3 % dissolved salts and from 0 % up to 20 % isopropanol (= isopropyl alcohol or IPA). Less commonly, dampening solution can contain ethanol instead of isopropanol. At 20°C, isopropanol has a vapour pressure of about 4 kPa and ethanol of about 5.9 kPa. Both are therefore classified as VOC under the SE Directive.

ISOPROPANOL IS CLASSIFIED AS VOC

3. **Other additives,** based on less volatile or non-volatile organic compounds (often glycols), have been used to reduce the isopropanol content of dampening solution. The VOC content of these additives can vary from 0 % up to 30 %. The dosage is about 3 %, resulting in a final concentration of 0 - 1 % VOC in the dampening solution.

ADDITIVES FOR ISOPROPANOL SUBSTITUTION MAY CONTAIN SUBSTANCES CLASSIFIED AS VOC

4. **Cleaners** are mainly based on hydrocarbons. Aromatic hydrocarbons have good cleaning properties but their use has been restricted for health protection reasons. Common cleaners are mainly aliphatic hydrocarbons with vapour pressures of 0.1 - 11 kPa at 20°C (100 % VOC, flash points of 30° - 80 °C). To a lower extent aromatic hydrocarbons are contained. Oily cleaning products, introduced in the nineties, are based on natural oils, high boiling mineral oils or mixtures thereof (0 % VOC, vapour pressure < 0.01 kPa at 20°C, flash point > 100°C).

CLEANING AGENTS ARE MAINLY BASED ON HYDROCARBONS

5.2 Solvent consumption and emission levels

One tonne of ink allows printing about 330,000 m^2 (both sides) or 100,000 catalogues (48 pages DIN A4). [Ökopol 2008]

The ink consumption of the smallest heatset web offset printing machines (printing 8 pages in one revolution) is about 30 kg/h. [Ökopol 2008]. If such a machine is operated with one shift for 5 days a week, the annual VOC consumption from inks alone is about 20 tonnes, exceeding the SE Directive threshold of 15 tonnes per year (if inks contain about 35 % of VOC and not taking into account VOC from dampening solution and cleaners).

EVEN SMALLEST HEATSET MACHINES REGULARLY EXCEED THE SOLVENT CONSUMPTION THRESHOLD OF 15 TONNES PER YEAR

Thus heatset web offset activities generally exceed the VOC threshold of 15 t/a. [Ökopol 2008]

Many companies have installed more than one machine. Most machines print 16 pages or more (up to 80). As machine costs are high, they are often operated for 3 shifts/day and 6 days/week. [Ökopol 2008]

HEATSET WEB OFFSET CAN BE REALISED WITH 0 – 3 VOL.-% ISOPROPANOL

The best performing heatset web offset installations add only 0 - 3 vol.-% isopropanol to dampening solution [Ökopol 2008]. Without efficiency optimisation the isopropanol content is typically around 10 vol.-% but can be as high as 20 %.

Most heatset web offset printing machines are equipped with automatic washing systems. The best performing installations use non-VOC cleaners (with a vapour pressure < 0.01 kPa, flash point > 100°C) for automatic cleaning and low volatile or non-VOC cleaners for manual cleaning (with a vapour pressure < 0.2 kPa, flash point > 60°C). [German EPA 2003]

VOC-FREE CLEANERS CAN BE USED. LOW VOLATILE CLEANERS HAVE VAPOUR PRESSURES < 0.2 KPA.

The application of best available techniques is associated with a VOC emission of 2.5 – 10 % for new machines and 5 – 15 % for existing machines, related to total ink consumption. [BREF STS 2007, p. 570]

In order to comply with the waste gas emission limit values of 20 or 50 mgC/m^3 (see table 2 on page 4), heatset web offset installations have to apply thermal waste gas treatment. The best performing thermal oxidisation systems achieve levels < 15 mgC/m^3. [BREF STS 2007, p. 518] [Ökopol 2008]

5.3 Key environmental and health issues

In heatset web offset printing a broad range of solvents are used, mainly isopropanol, ethanol, glycols as additives of the dampening solution and predominantly aliphatic hydrocarbons for cleaning.

Process emissions of solvents, together with NOx emissions, are precursors of ground level ozone formation in the presence of sunlight.

EMISSIONS TO AIR OCCUR FROM STORAGE, PROCESS AND CLEANING OPERATIONS.

Emissions of VOC to air may occur from:

- the storage of the solvents
- the process (mainly from dampening solution)
- cleaning operations (automatic and manual)

Existing occupational workplace limits should be taken into consideration.

Emissions from thermal oxidisation systems will contain organic compounds that have not been destroyed or are only partly destroyed, as well as CO_2, CO, and NOx. When natural gas is used as additional fuel, emissions may also contain unburned methane (CH_4).

Emissions of VOC to water occur from the disposal of dampening solution (local regulations have to be considered). Spills and leaks from storage areas may result in emissions to soil and groundwater.

The process generates waste containing solvents which need to be disposed in a way that emissions to air, soil and groundwater are prevented or limited.

Cleaners may contain aromatic hydrocarbons such as xylene and toluene. These substances have higher impacts on human health than aromatic hydrocarbons. Toluene is classified with the risk phrase R40 (“may cause cancer”).

6 VOC substitution

The following sections describe potential substitutes for VOC (using VOC-free and reduced-VOC systems). There are also descriptions of the application technologies or special conditions needed and the advantages and disadvantages compared to systems that use solvents with a high VOC content.

WATERLESS WEB OFFSET PRINTING IS APPLICABLE FOR VOC REDUCTION

VOC emissions result from the forced drying of the oily hydrocarbon solvents in the inks. These emissions can only be avoided by adapting the printing process (see chapter 10 for information on the state of development of water based offset inks). UV inks (drying by using ultraviolet light, without VOC emissions) cannot be used in heatset machines because the printing speed is too high.

Substitution is possible for the other two major emission sources:

VOC-FREE DAMPENING SOLUTION AND VOC-FREE CLEANERS CAN BE USED

- isopropanol in dampening solution and
- VOC based cleaners (for parts and machinery)

This can be done by:

VOC CAN BE SUBSTITUTED BY USING WATERLESS OFFSET

BY REDUCING ISOPROPANOL IN DAMPENING SOLUTION

BY VOC-FREE CLEANERS

1. Avoiding the use of dampening solution altogether by using waterless offset. This has to be combined with tempering of rollers, use of adapted inks, plates and plate development equipment.
2. Reducing the isopropanol content in the dampening system by replacing it with special additives. This requires the use of exact measurement of all additives, special roller materials, keeping the process water cool, clean and with a constant salt content, and controlling temperature and humidity of the ambient air in the press room.
3. Using non-volatile products for parts and machine cleaning,
   for rollers and reservoir cleaning - substituting volatile cleaners with organic substances having a vapour pressure of < 0.01 kPa;
   for regular manual machine cleaning - using dry ice (CO_2).

6.1 VOC-free systems

This section describes the ways that VOC-free products or systems can be used to replace the organic solvents currently used.

6.1.1 Substitution of dampening solution by waterless heatset

Substitution of the entire dampening water system (and related VOC emissions from isopropanol and other additives) may be achieved with ‘waterless offset’.

Waterless offset needs specialised image carrier plates and related developing equipment and adapted inks.

Waterless plate developing chemicals, besides avoiding VOC emissions, have a reduced wastewater impact. Shorter start-up times are needed to obtain the correct printed image which reduces personnel costs and minimizes paper waste. [Nienstedt 2007]

Whilst Japan has long used waterless heatset web offset printing [EWPA 2008], the technology has had little commercial uptake in Europe until 2004, with the exception of a few sheet fed applications. Printers have feared becoming dependent on one printing plate supplier and were concerned that investment in disparate systems would reduce their flexibility to produce the same job on different machines (because waterless plates differ from conventional plates). Additionally, it was feared that the market would not pay more for improved quality.

In 2004, however, waterless cold set web offset for newspaper printing has become commercially viable, due to the higher prices paid for high quality advertisements and lower operational costs due to shorter start-up times. Meanwhile these cold set newspaper machines have been equipped also with heatset dryers in two companies in Belgium and Denmark, printing semi-commercial magazins. Another company in France will install waterless offset with the option to be complemented with a heatset dryer (as long as the machine is used for coldset, it is not covered by the SE Directive). [KBA-2 2008]

When using waterless heatset offset, production costs are reduced by about 7 - 12 %. At present, the product range is reduced to about 70 % of the total range achievable using conventional heatset printing because ‘high-end’ products (like top quality catalogues) can not be produced, yet. [KBA-2 2008]

WATERLESS WEB OFFSET REDUCES PRODUCTION COSTS SIGNIFICANTLY

6.1.2 Full substitution of isopropanol in dampening solution

Substituting isopropanol in the dampening solution may be more practical than changing to waterless offset printing systems. To do so, however, several pre-conditions have to be met. Isopropanol reduction to zero, without loss of printing quality, is only possible on new machines (installed after 2000) as older machines do not have appropriate cylinder acclimatising systems and older rollers cannot be adjusted with adequate precision.

ATTENTION HAS TO BE PAID TO THE COMPOSITION OF ADDITIVES FOR ISOPROPANOL REDUCTION AS THESE MAY CONTAIN VOC

Special additives have been developed to facilitate the substitution. These additives also lower the surface tension of the water and prevent the growth of micro-organisms. The additives contain up to 30 % organic hydrocarbons (mainly glycols) and some of these are classified as VOC; so to achieve a 100 % VOC-free dampening solution system, the composition of additives has also to be considered.

For more information about improving the pre-conditions for isopropanol reduction see chapter 7.1.

6.1.3 Substitution of VOC cleaners by non-VOC cleaners

VOC-free, high boiling, cleaning agents ('HCA') or VOC-free vegetable oil based cleaning agents ('VCA') can be used in place of conventional volatile products (usually having vapour pressures of 0.1 – 11 kPa). Smaller quantities are needed for effective cleaning and they can be diluted with up to 50 % water. The resulting reduction in consumption fully compensates for their higher price [Ökopol 2008].

VOC-FREE OILY CLEANERS CAN BE MIXED UP TO 50 % WITH WATER

These cleaning products require new working practices. Products with low volatility often do not work immediately when applied to the surface to be cleaned. They have to be rinsed off using water - as a second step. Therefore, switching to non-volatile substances for cleaning will require workers to adjust their working practices.

When non-volatile cleaners are manually applied they have to be used sparingly because if dripped into the machine they may cause printing errors.

Automatic cleaning systems often have to be adapted to allow the use of non-VOC cleaners because much lower quantities (about 50 %) are needed and ducts and openings have to be adapted so as to provide equal quantities over the entire length of the rollers. Some elastic tube materials are not resistant to the use of oily cleaning agents. Providers of washing machinery can deliver lists of appropriate cleaning agents.

AUTOMATIC WASHING SYSTEMS MAY HAVE TO BE ADAPTED TO VOC-FREE CLEANERS

Blanket coated rollers for automatic cleaning are usually applied in combination with spray cleaning of printing rollers. Instead of spraying the cleaners for later absorption in the blanket, pre-impregnated blankets are available, impregnated with non-VOC cleaners.

<u>Economic and cross-media effects</u>

VOC-free cleaners not only avoid emissions but also significantly improve the health and safety of the work place because of their reduced flammability risks. Storage too is less costly.

Non-volatile cleaners, being oily substances, should be handled with care. Workers should use gloves when using these materials. Spillages can make floors slippery and lead to a higher risk of accidents. Spillage can also result in the contamination of the dampening solution and of the plate. This can cause printing errors and may necessitate re-printing and related increase of environmental impacts. Appropriate staff training can help to avoid spillage.

VOC-FREE CLEANERS ARE OILY AND THEREFORE SPILLAGE TO THE FLOOR LEADS TO ACCIDENT RISKS

While VOC-free spray systems for automatic cleaning generate liquid waste (cleaning agents mixed with water and dirt), pre-coated VOC-free blanket cleaning systems generate solid waste (textiles with dirty cleaning agents). Handling and appropriate treatment of waste is often easier for solid than for liquid waste.

Membrane filtration is more energy efficient than distillation for recovery of non-VOC cleaners because of the high boiling point of non-VOC cleaners.

6.2 VOC-reduced systems

If the complete substitution of organic solvents is impractical then changing to systems with a reduced VOC content, such as those described in this section, can decrease emissions.

6.2.1 Partial substitution of isopropanol in dampening solution

The extent to which isopropanol reduction is possible depends on each individual machine. The proportion of organic compounds in dampening solutions should generally not exceed 10 wt.-%[4] in the case of existing presses and 5 wt.-% in the case of new presses. [DEFRA 2008] Further reductions can be achieved if process conditions are optimised (see chapter 7.1) [Ökopol 2008].

Reductions are best established in small steps, guaranteeing that each reduction step is tested for at least a 2 - 3 month period, while observing the printing characteristics at each reduction level. Suppliers of additives and roller materials often support the testing of reduced isopropanol level operation.

For isopropanol reduction it is essential that the characteristics of the dampening solution are kept constant. The fresh water composition must be stable. Cooling equipment is needed to keep the temperature constant. For more information about improving the pre-conditions for isopropanol reduction see chapter 7.1.

The emission reduction resulting from isopropanol substitution depends on the initial levels used. Since the major part of VOC from inks is destroyed in the thermal treatment of the waste gases, fugitive emissions from isopropanol represent about 80 % of VOC emissions (the remaining 20 % is from cleaners). Thus, by isopropanol substitution, a major part of the VOC emissions can be avoided. If, for example, the isopropanol concentration level in the dampening solution is reduced from 10 vol.-% to 5 vol.-%, a 40 % emission reduction can be achieved.

REDUCTION OF IPA CONCENTRATION FROM 10 % TO 5 % CAN LEAD TO 40 % REDUCTION OF VOC EMISSIONS

Economic and cross-media effects

Isopropanol substitution not only has direct health benefits: storage of non-flammable substitutes carries less risk and thus requires less safety measures.

When using substitutes, more energy is consumed in the process for cooling of the working space and rollers as isopropanol evaporation has a cooling effect in the machine. Additionally, energy is needed for more accurate measurement and filtering of the dampening solution to ensure printing quality.

Substitutes are more corrosive to ferrous machine parts and may cause damage if not handled properly - this risk may be avoided by appropriate spillage management.

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[4] wt.-%: weight percent, vol.-%: volume percent

Isopropanol substitutes, like anti-fouling substances and some glycols, may have harmful human health effects. Therefore, special attention should be given to safety data sheets to ensure that least harmful products are used for substitution.

6.2.2 Substitution of VOC cleaners by low-VOC cleaners

Low volatility organic solvents can be used (with vapour pressures of around 0.1 kPa at 20°C and flash points of about 60°-80°C) instead of traditional cleaners having a high volatility (vapour pressure of 3 – 11 kPa at 20°C).

As with non-VOC cleaning agents the switch to low volatility organic substances requires flexible working practices but there are off-setting operational benefits. These products can be diluted with up to 50 % water leading to less consumption and reduced costs.

Automatic cleaning systems may have to be adapted to use low volatile cleaning agents as flexible tube materials and dose metering volumes may not be adequate. Providers of washing machinery have lists of suitable low volatility cleaners and are able to adapt their systems for their use.

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements and abatement techniques can be used to reduce VOC emissions if VOC substitution as described in section 6 is not possible. The following measures are commonly applied for heatset web offset.

7.1 Process improvements

In order to obtain low isopropanol levels precise dosing is needed for additives as well as for isopropanol. This requires the use of accurate measurement and dosing devices, traditional density measurement methods and conventional dosing without measurement are insufficent. There are infrared and ultrasonic measurement systems on the market that are suitable.

Whereas traditional dosing was done by calibrated volumetric pumping systems, the best performing systems now use conductivity measurements of the incoming water before and after dosing with additives.

LOW IPA LEVELS REQUIRE MORE PRECISE DOSING

Accumulated dust and ink contamination in the dampening solution can be a problem because at low isopropanol levels there is a risk of more frequent printing errors. High efficiency filters reduce contamination but are prone to blockage, so parallel filters with automatic switching are commonly used. Alternatively membrane filters with automatic purging systems can be used.

CONTROL OF ROLLER PERFORMANCE IS A PRECONDITION FOR IPA REDUCTION

It is essential to maintain a constant roller performance when working at reduced isopropanol levels. This requries regular maintenance, including calibration, as well as ensuring that the hydrophilic properties of the roller surfaces are high to guarantee a constant water supply to the plate cylinder.

To achieve reduced isopropanol concentration in the dampening solution, conventional rollers can be substituted by rollers coated with a special hydrophilic rubber surface or with hydrophilic ceramic.

In order to optimise results with automatic cleaning, various types of brushes can be used in the different sections of the cleaning device.

A general reduction of VOC emissions from isopropanol and cleaners can also be achieved by applying good practice measures [IBU 2008, DEFRA 2008]:

TRAINING OF PERSONNELL CAN LEAD TO VOC REDUCTION

- Training of workers to first assess and improve the process conditions before increasing the isopropanol level in dampening solution.
- Training of workers to use as little cleaner as necessary during manual cleaning of image carrier plates, machine parts and machinery.
- Training of workers to avoid spillage of cleaners.
- Training of workers in how to avoid emissions from spillage during bottling or transport and from open containers (virgin material as well as used cleaners and rags).
- Keeping pre-impregnated rags in an enclosed container prior to use.

7.2 Waste gas abatement

Installation of waste gas treatment systems is necessary to comply with the waste gas emission limit values of the SE Directive.

7.2.1 Efficient use of solvent emissions

Thermal treatment and energy recovery for ink drying is commonly used. Solvent recovery is no efficient option as the recovered fraction would need further treatment for re-use, containing isopropanol from the dampening solution and a mixture of hydrocarbons from inks and cleaners, besides water from the dampening solution.

MOST EFFICIENT WASTE GAS ABATEMENT SYSTEMS DESTROY > 99 % OF VOC

The most efficient abatement technique for destroying VOC in heatset web offset waste gases has an efficiency of > 99 % - resulting in emission levels below 20 mgC/m^3 [BREF STS 2007, p. 566].

EXCESS HEAT FROM THERMAL OXIDISATION CAN BE USED FOR ROOM/WATER HEATING

For higher energy efficiency the best systems use the energy content of the incoming VOC and recover energy in the waste gases for heating the dryer (heat recuperation). This ‘integrated’ system can also be installed in existing installations equipped with non-recuperative thermal oxidation.

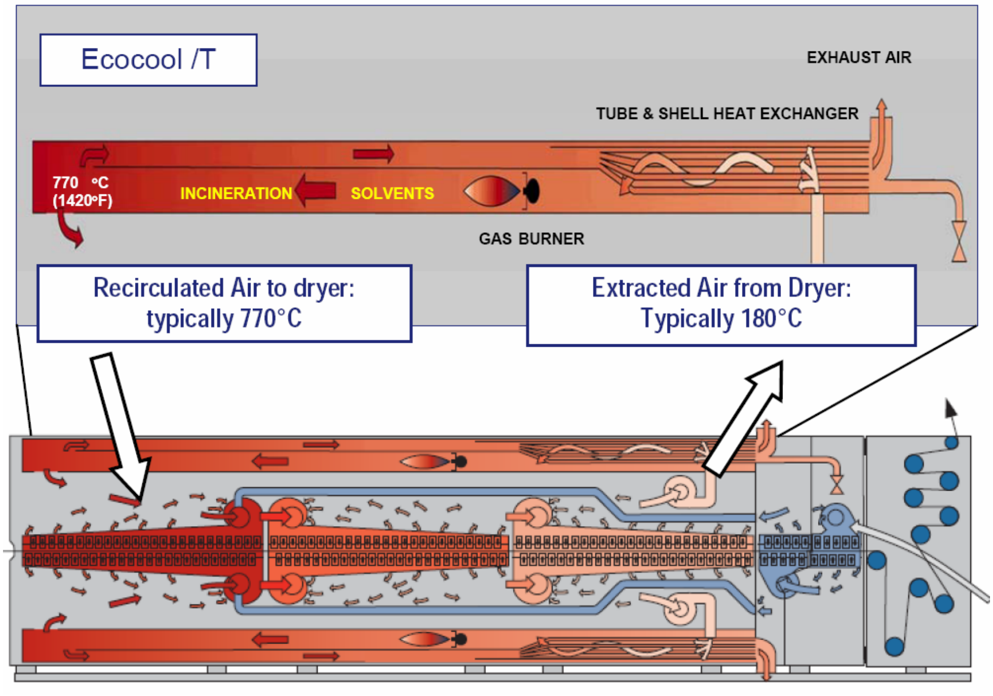
Authothermic combustion is difficult to achieved with machines printing 16 pages per revolution, but possible for larger machines (cylinder length of 1.80 m – 2.25 m). [MAN Roland 2008]

In dryers, following the heating zones, there are drying zones with a temperature of around 180°C. In the last zone before the cooling zone of the dryer, the concentration of evaporated ink solvents is at its highest. For effective oxidisation this solvent vapour must be heated to a minimum of 770°C.

To avoid explosion, dilution air must be introduced to prevent solvent concentrations exceeding 25 % of the lower explosion limit. Solvent concentration measurement can be used to optimise the dilution, and the dilution air can be preheated in a heat exchanger using the exhaust gases. The energy from the burnt solvents minimises the fuel gas needed to reach the necessary minimum temperature of 770°C. [GOSS 2008]

HEAT EXCHANGER PRE-HEATS INCOMING FRESH AIR WITH HOT AIR EXTRACTED FROM THE DRYER

MEASURING SOLVENT CONCENTRATION IN THE DRYER MINIMISES THE ADDITIONAL FUEL REQUIREMENTS



[GOSS 2008]

Figure 3: Dryer with integrated thermal waste gas treatment and heat exchanger

Energy produced from oxidisation leads to excess heat, which is available for other purposes such as room/water heating via an effective heat exchange (also applicable in combination with integrated systems using VOC combustion for ink drying). [Company-1 2008]

Enclosed machinery reduces fugitive emissions, especially when combined with an air conditioning system that extracts all ambient air from the printing room through the waste gas cleaning system.

Cleaning agents are difficult to capture in the waste gas treatment systems for safety reasons and the dryer is usually turned off during cleaning periods (the temperature of the dryer is too high and an explosion might occur if it were running). Some 10 % of isopropanol emissions (dampening solution) are captured and routed to the dryer and then treated in the incinerator. [EGTEI 2005]

7.2.2 Minimisation of fugitive emissions

INTEGRATED DRYER AND NEGATIVE PRESSURE IN ENCLOSED MACHINE ROOMS HELP TO DESTROY MOST VOC EMISSIONS

If machines are enclosed and dryers work with integrated waste gas treatment, all air extraction of the encapsulated machine can be via the dryer and the waste gas treatment system. In such a case, the extraction rate can be regulated to ensure that fugitive emissions are minimised. [Ökopol 2008]

8 Summary of VOC emission reduction measures

The following table summarizes the various approaches to substitute or reduce VOC emission as described in chapters 6 and 7.

Table 4: Measures for VOC substitution and VOC reduction in heatset web offset

Objectives	**Description**	
VOC-free systems	VOC-free cleaners	Use of cleaners with a vapour pressure of < 0.01 kPa at 20°C.
	Waterless heatset web offset printing	Use of specific printing plates and adapted inks that enable printing without dampening solution.
	VOC-free dampening solution	Use of specific VOC-free additives, in combination with process improvement measures (see below).
VOC-reduced systems	Reduction of isopropanol in dampening solution	Stepwise reduction of the isopropanol content in the dampening solution to < 5 %, in combination with process improvement measures (see below).
		Use of specialised additives for the dampening solution that mimic the functionality of isopropanol.
	Less volatile cleaners	Use of cleaners with a vapour pressure of around 0.1 kPa at 20°C.
		Use of dry ice (CO_2) for regular machine cleaning
Process improvement	Optimised dosing and measurement	Use of precise measuring and dosing systems for isopropanol and additives.
	Optimised dampening solution quality	Use of temperature control, effective particle filters, fresh water treatment.
	Optimisation of rollers of dampening system	Use of special roller surfaces (ceramic, special rubber).
	Optimised cleaning	Use of automatic cleaning systems for all rollers.
	Optimised use of isopropanol	Training of workers to improve process conditions instead of increasing the isopropanol level.
	Optimised handling of cleaners and cleaning waste	Training of workers to avoid excess use, spillage and emissions from storage handling.
Abatement technologies	Thermal oxidisation	Treatment systems with efficiency > 99 % and emission values < 20 mgC/m^3. Recovery of waste heat (for integrated system and for water and/or room heating system).
	Air extraction via abatement system	Machine containment, extraction of cabin air via abatement system.

9 Good practice examples

9.1 Printing house 1

A heatset web offset printing company uses 4 heatset offset machines, mainly for publications. A new 16-pages machine has been purchased that is able to print without the use of isopropanol.

GOOD PRACTICE 1: PRINTING WITHOUT ISOPROPANOL IN DAMPENING SOLUTION

The new machine is equipped with ceramic coated rollers for better dampening solution transport to the plate. The dampening solution is connected with a high efficiency dust filtering system. The machine is equipped with water-based cooling system for the ink rollers. A VOC-free additive is used, in place of isopropanol, at no additional costs.

Compared with the former machine, the new machine avoids the use of ~17,500 litres isopropanol consumption per year (13.8 t/a) with an annual costs savings of about 17,500 Euro (at ~1 €/litre of isopropanol).

There are no cross-media effects, it has a similar energy requirement to that of conventional heatset web offset printing, cooling of the rollers and dampening solution leads to increased printing stability.

[Ökopol 2008]

9.2 Printing house 2

Two web offset printing companies in Belgium and Denmark use waterless heatset web offset. Each machine saves yearly ~ 12,000 – 15,000 liters isopropanol and ~130,000 – 150,000 liters water due to the waterless system.

GOOD PRACTICE 2: WATERLESS HEATSET OFFSET PRINTING

The quality of the printing products is better than the quality of conventional coldset printing (used for newspaper production); mainly semi-commercial magazins are printed. The machine investment costs for the machine are similar as for a conventional machine.

[KBA-2 2008]

10 Emerging techniques and substitutes under development

VOC-free cleaning agents

New water based cleaning agents (VOC-free), suitable for manual and automatic cleaning, are currently undergoing testing in pilot plant. The residues from these cleaners do not need to be rinsed off after cleaning because they do not lead to oily spots that would cause printing errors. Therefore, they have the advantage over high boiling organic cleaning agents that no second cleaning step with water is needed. [Ökopol 2008]

VOC-FREE WATER BASED CLEANERS ARE UNDER DEVELOPMENT

Inks without organic solvents

While there have been development projects for sheet fed offset printing using water based inks (results were presented at the international DRUPA trade fair in 2004), no comparable work is known for heatset web offset. [Ökopol 2008]

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Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive

(Directive 1999/13/EC)

Guidance 2:

Publication rotogravure printing

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses publication rotogravure printing and the related cleaning of equipment, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emission Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
Printing is defined by the Directive as 'any reproduction activity of text and/or images in which, with the use of an image carrier, ink is transferred onto whatever type of surface. It includes associated varnishing, coating and laminating techniques.'
Rotogravure is defined as 'a printing activity using a cylindrical image carrier in which the printing area is below the non-printing area, using liquid inks which dry through evaporation. The recesses are filled with ink and the surplus is cleaned off the non-printing area before the surface to be printed contacts the cylinder and lifts the ink from the recesses.'
Publication rotogravure is defined as 'a rotogravure printing activity used for printing paper for magazines, brochures, catalogues or similar products, using toluene-based inks.'

The following printing activities, covered by the SE Directive, are addressed in separate guidance documents: heatset web offset printing (guidance 1), packaging rotogravure printing, flexography printing and rotary screen printing (guidance 3).

The SE Directive lays down the following activity specific emission limit values for publication rotogravure printing:

Table 2: Emission limit values of the SE Directive

SE Directive – Emission limit values (ELVs) (Annex II A – activity No. 2)				
Activity	**Solvent consumption threshold [tonnes/year]**	**ELVs in waste gases [mg C/Nm^3]**	**Fugitive emission values [% of solvent input]**	
			New	Existing [1]
Publication rotogravure	> 25	75	10	15

THE SE DIRECTIVE APPLIES TO PUBLICATION ROTOGRAVURE IF A SOLVENT CONSUMPTION OF 25 TONS PER YEAR IS EXCEEDED.

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

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[1] Existing installation shall mean an installation in operation or, in accordance with legislation existing before the date on which this Directive is brought into effect, an installation which is authorised or registered or, in the view of the competent authority, the subject of a full request for authorisation, provided that the installation is put into operation no later than one year after the date on which this Directive is brought into effect [SE Directive, Article 2 No. 2]

Specific requirements apply for VOCs classified as CMR substances[2] as well as for halogenated[3] VOCs that are assigned the risk phrases R40 or R68[4]. There is a general obligation to replace CMR substances – as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated VOC with R40 or R68 the emission limit values in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.

Publication rotogravure printing does not use VOC classified as CMR substances or halogenated VOC with the risk phrases R40 or R68. Although toluene is classified with R40, it is not covered by the restrictions of the SE Directive as it is not a *halogenated* VOC.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

The main organic solvent used in publication rotogravure is toluene. Substitution of toluene based inks by water based inks could not be achieved so far.

VOC EMISSION REDUCTION CAN BE ACHIEVED BY USING FAST DRYING INKS, BY DRYING FINISHED PRODUCTS UNDER CONTAINED CONDITIONS AND BY INCREASING WASTE GAS TREATMENT EFFICIENCY

Toluene is emitted from the finished product, from 'leaky' installations and through the waste gas after recovery (adsorption). No substitutes for toluene in the process are currently available.

VOC-free systems exist for regular machine cleaning.

Emissions can be reduced by drying finished products as long as possible under contained conditions and by increasing the efficiency of the waste gas extraction and the waste gas solvent recovery system.

Capture of toluene inside the installation – to avoid fugitive emissions - can be obtained by using inks with specific fast drying properties (‘retention inks’). It can also be achieved by increasing temperature in the press room and by increasing dryer length (applicable only at new installations).

For many of the proposed measures, cross-media effects, in particular the increased energy con sumption, have to be taken into account.

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[2] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

[3] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine or iodine.

[4] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: ‘Possible risk of irreversible effects’. The new wording is: ‘Limited evidence of a carcinogenic effect’. In the ‘old’ version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: ‘Possible risk of irreversible effects’. This new risk phrase does not include carcinogenicity. The ‘new’ version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to reflect this change a final decision on which version applies can only be given by the European Court

3 Description of the activity and related industry sector

Publication rotogravure printing is used in most countries of Europe. As shown in Table 3, 232 machines were installed in 2003 in EU 15 [EGTEI 2003]. For 2004, twelve out of EU 15 Member States reported a total of 44 existing and 7 new installations[5] [Implementation 2006].

Table 3: Number of publication rotogravure machines and related cylinder width

Cylinder min. width [mm]	Cylinder max. width [mm]	Number of machines
900	1999	63
2000	2449	39
2450	2749	77
2750	3179	25
3180	4320	28
Total		232

[EGTEI 2003]

Compared with other printing techniques, publication rotogravure is associated with the highest investment costs for machinery and the highest costs of producing the image carrier. Therefore, publication rotogravure printing is generally used by large companies, sometimes also operating heatset web offset in the same plant to be able to print different runs.

MORE THAN HALF OF ALL MAGAZINES AND CATALOGUES ARE PRINTED WITH PUBLICATION ROTOGRAVURE

About 60 % of all magazines and 50 % of all catalogues are printed using the publication rotogravure technique, the remainder are produced with heatset web offset printing [ERA 2008].

Products printed with publication rotogravure have a circulation of at least 200,000 copies, substantiating the extra costs of making rotogravure cylinders over those of making printing plates for heatset web offset printing [BREF STS 2007, FGI 2007]. Most runs are of more than 500,000 copies. A cylinder can print more than 10 million copies without quality loss.

Publication rotogravure generally prints on paper. Compared with heatset web offset, publication rotogravure can also print with very good results on partially coated or non-coated paper surfaces. [BREF STS 2007]

4 Technical process description

Publication rotogravure printing is characterized by the use of engraved cylinders, toluene based inks and a solvent recovery system for toluene in the waste gas.

The printing technique works with the highest production speed of the sector (~ 15 m/s). It uses the longest cylinders (max. 4.32 m) and is therefore able to print the widest paper web.

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[5] No data from Italy and Sweden, and no specific data on publication rotogravure from France.

Installations for publication rotogravure printing consist mainly of

- Printing units (ink fountain, gravure cylinder, impression roller)
- Drying units (operating at ~ 35° - 40°C)
- Air extraction system with solvent recovery units (activated carbon).

4.1 Process flow and relevant associated VOC emissions

Figure 1 shows the main relevant solvent inputs and VOC outputs (arrows indicate the relevance of the VOC amount). [BREF STS 2007] [Ökopol 2008]

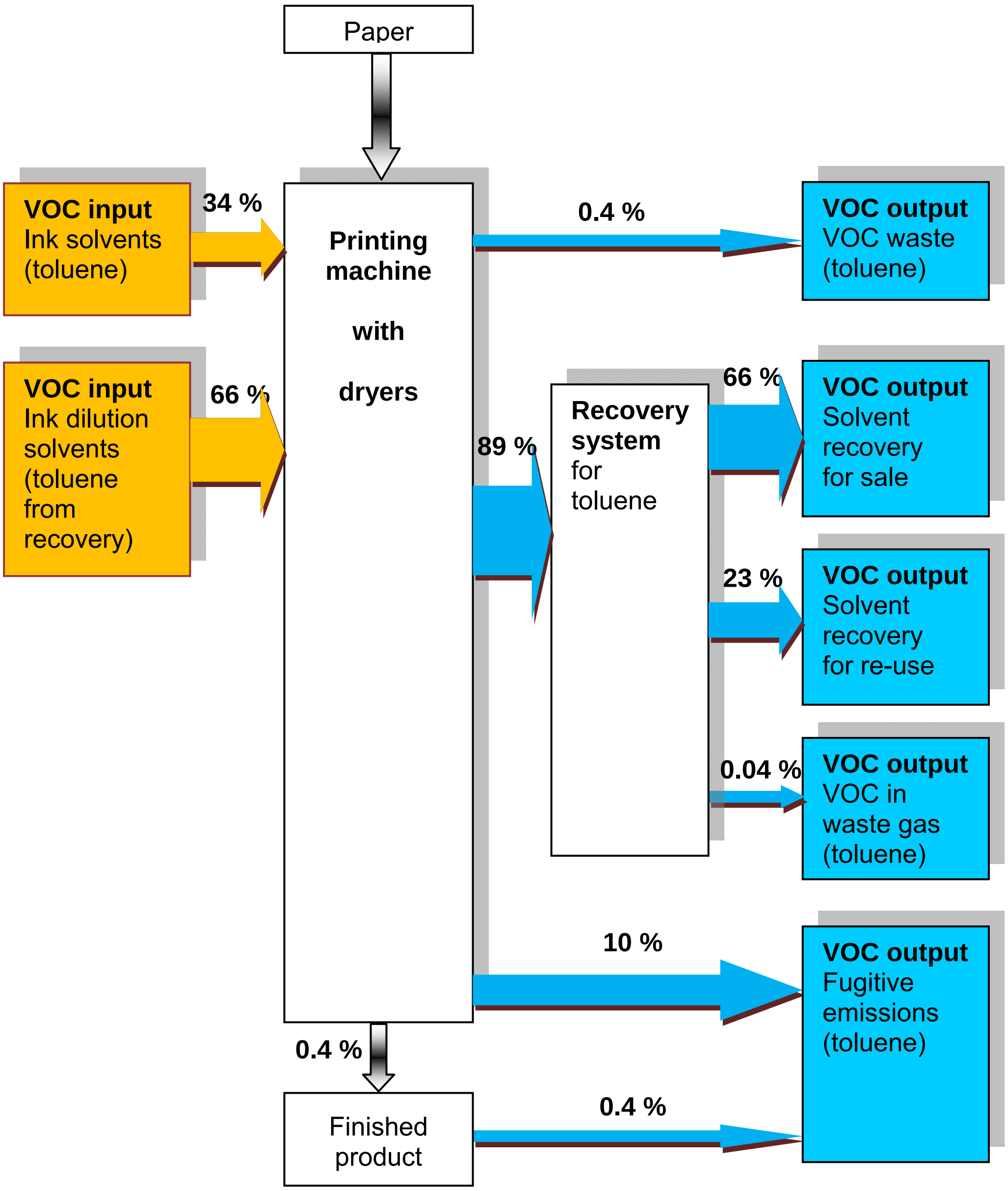

Figure 1: Main VOC input and output of publication rotogravure printing

4.2 Process description

Publication rotogravure machines use cylinders consisting of a steel base with a copper surface. The image is engraved into the copper layer, mainly by digital laser-engraving, less frequently with electromechanical engraving. To resist long runs, the image is protected by electroplating a thin layer of chromium onto the cylinder surface.

For printing, the circulating cyclinder is first flooded with ink, afterwards the surface is scrapped clean with a ‘blade’ to leave ink only in the engraved areas for its transport onto the paper. The image transfer takes place when the transpassing paper is pressed between the gravure cyclinder (image carrier) and the impression roller.

The amount of ink transferred to the paper is controlled by variation of the depth and size of the recessed cells ('dots'). The ink is transferred via a process of pressure, osmosis, and electrostatic pull.

PUBLICATION ROTOGRAVURE PRINTING IS DONE WITH FOUR STANDARD INKS

Publication rotogravure machines print on both sides in one run, using the four standard inks: black, blue, yellow and magenta. Only a few machines are equipped with an additional ink unit for customer specific colours. Each printing unit is followed by a dryer.

After printing one colour, the paper web is transferred into the dryer to evaporate ink solvent (toluene) before entering the next colour unit. The drying usually takes place without heating the air flow to prevent dimension changes of the paper web.

Sufficient air must be introduced into the work place to avoid toluene concentrations exceeding 50 % of the lower explosion limit. For this purpose solvent concentration measurements are executed at least at the outlet to the solvent recovery system. To optimise acclimatisation of the work place, additional measurements can be executed near the machine.

[CITEPA 2003] [UK 2004] [BREF STS 2007] [Siegwerk 2008] [KBA 2008]

4.3 Inks

Inks for publication rotogravure are all based on toluene. Toluene based inks have a very low viscosity, allowing a fast ink transfer from the engraved cells onto the paper.

FOR PRINTING, PUBLICATION ROTOGRAVURE INKS CONTAIN 70 – 75 % OF TOLUENE

Publication rotogravure inks usually contain ~ 50 - 55 % toluene. The viscosity of the inks is adapted inside the ink reservoirs of the machines, which are equipped with mixers. For printing, the toluene content is adjusted to ~ 70 – 75 %.

Most of the toluene content of the inks evaporates in the dryer and is routed to the solvent recovery system. Recovery is realised with adsorption on several activated carbon units (e.g. during 70 min), desorption of toluene by passing hot steam (~45 min) and carbon drying with extracted air (1-7 min). Hot steam is cooled, advantageously with heat exchange, and toluene – as it is lighter than water – can be separated in a gravitational separation system.

Recovered toluene is partly used for dissolving inks in the plant, partly sold to the ink manufacturer. [German EPA 2003-2] [UK 2004] [Siegwerk 2008]

4.4 Cleaning system

As the majority of printed products are produced with the three standard colours and black, cleaning of reservoirs is only necessary during routine machine cleaning.

TOLUENE IS THE MAJOR CLEANING AGENT USED IN PUBLICATION ROTOGRAVURE

Once dried inside the machine, inks can be dissolved with toluene again. Therefore toluene is the major solvent used for machinery cleaning (e.g. printing cylinders, impression rollers and ink reservoirs). Additionally, acetone may be used.

[German EPA 2003-1] [BREF STS 2007]

5 Solvent use, emissions and environmental impact

5.1 Solvents used

Toluene is the major solvent used for publication rotogravure printing. For cleaning, in rare cases, acetone is used.

5.2 Solvent consumption and emission levels

For printing one part of solids, about four parts of toluene are used. Table 4 shows the average ink and solvent consumption associated with different cylinder widths of publication rotogravure printing:

Table 4: Ink and solvent consumption of different publication rotogravure cylinders

Cylinder min. width [mm]	Cylinder max. width [mm]	Ink consumption* [t/y]	Average toluene input [t/y]
900	1999	430	860
2000	2449	640	1280
2450	2749	920	1840
2750	3179	1130	2260
3180	4320	1330	2660
* Inks non diluted (50 wt.-% solvent content) as delivered to the printing plant			

[EGTEI 2003]

The solvent consumption of publication rotogravure printing generally exceeds the SE Directive solvent consumption threshold of 25 tonnes per year and the capacity of the installations usually also exceeds the solvent consumption capacity threshold of 200 tonnes per year of the IPPC Directive 2008/1/EC. [Ökopol 2008]

As investment costs are high, machines are often operated for 3 shifts/day and at least 6 days/week. [Ökopol 2008]

TOTAL VOC EMISSIONS OF LESS THAN 2 % OF THE SOLVENT INPUT CAN BE ACHIEVED

The application of best available techniques is associated with a VOC emission of 4 – 5 % for new plants and 5 – 7 % for existing plants, related to the total solvent input [BREF STS 2007, p. 575]. Some installations have been able to achieve even less than 2 % VOC emissions related to the solvent input (tables 5 and 6). [Ökopol 2008].

Table 5: Total emission levels of three German publication rotogravure printing installations using solvent recovery systems

	Unit	Installation 1	Installation 2	Installation 3
2003	[%]	2.7	1.8	2.4
2004	[%]	2.3	3.9	1.6
2005	[%]	1.7	2.1	1.1
2005	[%]	1.9	1.6	-

[BURDA 2006] [PRINOVIS-1 2007] [PRINOVIS-2 2007]

Table 6: Specific emission levels of three German publication rotogravure printing installations using solvent recovery systems

	Unit	Installation 1	Installation 2	Installation 3
2003	[mg/m^2]	71	39	59
2004	[mg/m^2]	63	80	37
2005	[mg/m^2]	46	43	25
2006	[mg/m^2]	51	28	-

[BURDA 2006] [PRINOVIS-1 2007] [PRINOVIS-2 2007]

Best performing solvent recovery systems within the sector achieve yearly average emission levels of < 15 mgC/m^3. [Schott 2008]

BEST PERFORMING SOLVENT RECOVERY SYSTEMS ACHIEVE EMISSION VALUES OF LESS THAN 15 MGC/M^3

Toluene emissions from the final product are about 0.5% of toluene input or 300 mg per kilogramme of printed product.[6] Best operating installations achieve emission levels below both values. [Germany 2003] [KBA 2008] [Ökopol 2008]

5.3 Key environmental and health issues

In publication rotogravure printing toluene is used as solvent for inks and for cleaning.

Process emissions of solvents, together with NOx emissions, are precursors of ground level ozone formation in the presence of sunlight.

Emissions of VOC to air may occur from:

- the printing process and its cleaning operations,
- the solvent recovery system,
- the printed product.

The process generates very little waste containing solvents that needs to be disposed in a way that emissions to air, soil and groundwater are prevented or limited.

Toluene is irritating to the skin. Vapours may cause drowsiness and dizziness. Toluene is classified with the risk phrases R40 (“possible risk of cancer”) and R63 (“possible risk of harm to unborn child”). Therefore the work station has to be well ventilated to ensure workplace safety. Existing occupational workplace limits have to be taken into consideration.

OCCUPATIONAL WORK PLACE LIMITS HAVE TO BE TAKEN INTO CONSIDERATION

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[6] Measurement can be done following the Danish method COWI No 2

6 VOC substitution

The following two sections describe potential substitutes for VOC (VOC-free systems and reduced-VOC systems). There are also descriptions of the application technologies or special conditions needed.

6.1 VOC-free systems

It is not possible to run publication rotogravure printing with VOC-free ink systems. VOC-free systems can only be applied for cleaning because due to their high production speed rotogravure printing machines need inks with low viscosity and fast drying properties. This is difficult to achieve with other solvents or with water-based inks (see chapter 10 on emerging techniques).

VOC-FREE CLEANING SYSTEMS CAN BE USED FOR REGULAR MACHINE CLEANING

CO_2 (‘dry ice’) can be used for regular machine cleaning. Pellets of dry ice are blown, with pressurized air, at about 300 m/s onto the surface to be cleaned. A high degree of cleanliness is achievable and no residue is left.

Cleaning machines cost about 9,000 to 14,000 € and the dry ice about 0.6 €/kg. Dry ice consumption is about 30 - 50 kg/h. If dry ice use exceeds ~60,000 t per year it is economic to rent a pelletizing machine at a cost of about 900 €/month. [ASCO 2008]

Cross-media effects

Noise and dust protection of operators has to be assured. As high carbon dioxide concentrations are a health risk, sufficient ventilation is needed at closed workplaces to maintain workplace safety.

6.2 VOC-reduced systems

As complete substitution of organic solvents is impossible in publication rotogravure, the use of systems described in this section can decrease emissions.

6.2.1 Retention ink systems

Retention inks have been developed to reduce emissions from the final product (outside of the installation), aiming at a toluene content of < 300 mg per kilogramme of printed matter.

RETENTION INKS REDUCE TOLUENE CONTENT IN THE FINAL PRODUCT, REDUCING TOTAL VOC EMISSION BY ABOUT 15 %

The ink system differs from conventional inks by forming a dried film surface later than conventional inks do. This effect enables higher evaporation rates of ink solvents inside the plant (recovered by the adsorption system). As a result the toluene content in the final product is lower and accordingly fugitive VOC emissions are reduced.

Compared with conventional inks, 30 – 50 % toluene emission from the final products can be reduced with retention inks. If the total emission from products is ~ 1 % of the solvent input with conventional inks, total emissions of < 0.5 % can be achieved by using retention inks.

Assuming total VOC emissions of about 5 – 7 % of the solvent input, retention inks can reduce total emissions by about 10 %.

Economic and cross-media impacts

Less ink is needed if retention inks are used [BREF STS 2007]. Retention inks have the same price as conventional inks [BREF STS 2007] [German EPA 2003-1].

Greater toluene emission inside the plant necessitates more efficient adsorption to prevent increasing emissions at the stack. Higher adsorption of toluene requires more energy for desorption, but leads to increased benefits from sale or reuse of recovered solvents. [BREF STS 2007]

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements and abatement techniques can be used to reduce VOC emissions in addition to VOC substitution as described in section 6. The following measures can be applied for publication rotogravure.

7.1 Process improvements

7.1.1 Increased length of the dryer

By increasing the length of the dryer, a prolonged retention time of the web for toluene evaporation is achieved. This is only applicable to new installations as retrofitting is not possible. [BREF STS 2007]

INCREASED DRYER LENGTH REDUCES EMISSIONS TO AIR

Economic and cross-media impacts

Additional energy is needed for increased dryer capacity. Higher toluene emissions will need more energy for desorption but will lead to economic benefits from increased toluene recovery.

7.1.2 Installation of storage places with extraction systems

AIR EXTRACTION AT STORAGE OF RAGS AND WASTE INKS CAN REDUCE AIR EMISSIONS

Separate storage places for rags and waste inks inside the workplace can be equipped with efficient hood extraction, connected with the solvent recovery system. This prevents air emissions when handling toluene loaded cleaning rags and ink waste. [German EPA 1999]

Economic and cross-media impacts

Sufficient ventilation at separate storage places is needed to maintain workplace safety. Greater toluene emission inside the plant necessitates more efficient adsorption to prevent increasing emissions at the stack. Higher adsorption of toluene requires more energy for desorption, but leads to increased benefits from sale or reuse of recovered solvents. [BREF STS 2007]

7.1.3Continuous air extraction from machines and dryers

Continuous air extraction from the machines and the dryers provides extraction not only during production times but also when machines are stopped for preparation, maintenance or cleaning.

Continuous air extraction systems are able to constantly maintain negative pressure at inlet and outlet of the paper web. With this measure, VOC emissions from ink reservoirs and cylinders are reduced.

[BREF STS 2007]

7.1.4 Continuous air extraction from machines, dryers and press room

CONTINUOUS AIR EXTRACTION FROM ALL VOC RELEVANT AREAS LEADS TO ADDITIONAL EMISSION REDUCTION

Additional VOC emission reduction can be achieved if air is not only extracted from the enclosed machine and the dryer but also for the entire press room. By routing press room air to the adsorption system, the toluene content is recovered. [BREF STS 2007]

This system needs an adaptation of the activated carbon system to be able to adsorb and desorb lower toluene concentrations effectively.

Economic and cross-media impacts

Desorption of activated carbon is less effective (more energy intensive) because low waste gas concentrations cannot achieve the same loading.

7.2 Waste gas abatement

7.2.1 Efficient adsorption and desorption

A high level of adsorption of toluene sent to solvent recovery can be achieved. The most efficient abatement techniques for recovering toluene from publication rotogravure printing recover > 98 % of incoming toluene and about > 96 % of the solvent input. Annual average emission levels < 15 mgC/m^3 are obtained. [German EPA 2003-1] [Schott 2008].

These levels are achieved by installing more activated carbon and by operating desorption in shorter intervals, i.e. before toluene emissions have started to increase significantly (“break-through”).

The intervals of desorption can be optimised with constant monitoring of output concentration of air flows of the recovery system, routing extraction air to a second, unloaded adsorption unit if determined emission levels are exceeded.

Both input and output monitoring of the adsorption unit can also be used for controlling adsorption capacity and determining the moment when extraction air should be routed to another adsorption unit.

Economic and cross-media impacts

Desorption of activated carbon is energy intensive. Although efficient systems lead to higher toluene recycling rates and less emissions, energy effort to achieve this (and its related environmental impact) has to be balanced with the benefits of increased recovery efficiency.

7.2.2 Capturing of air emissions during drying of activated carbon after desorption

When desorption of VOC from activated carbon takes place, the activated carbon becomes wet and needs about 30 – 60 seconds drying time to recover its adsorption capacity.

During this time, extraction air from the installation is routed through the adsorption system for carbon drying.

To avoid toluene emissions during drying time, emissions from the drying recovery unit can be routed back into the installation until the activated carbon has recovered its full adsorption capacity.

[Germany 2003] [BREF STS 2007]

7.2.3 Closed-loop system

The cleaned air outlet of the adsorption system can be re-circulated into the installation to further reduce emissions to ambient air.

The system needs high capacity of the solvent recovery system to obtain low VOC concentration in re-circulated air. This can be achieved with more activated carbon and/or more frequent desorption cycles.

The system is only applicable to new presses in combination with a new solvent recovery system. Additional investment costs of closed loop recovery system are about 5 million EUR for a press with cylinders of 3 meters.

[Germany 2003] [BREF STS 2007]

Economic and cross-media impacts

More frequent desorption creates more waste water and requires more energy. Additional energy is also needed because of increased adsorption capacity. Benefits can be obtained if cooling energy is generated from waste heat, e.g. from a combined heat and power generation on site.

Workplace limit values have to be taken into account if routing air emissions from the recovery system back into the installation.

8 Summary of VOC emission reduction measures

Table 7 summarizes the various approaches to substitute or reduce VOC emissions as described in chapters 6 and 7:

Table 7: Measures for VOC substitution and VOC reduction in publication rotogravure printing

Objectives	**Description**	
VOC-free systems	VOC-free cleaners	Use of dry ice cleaning
VOC-reduced systems	Retention ink systems	Use of inks with later film forming properties
Process improvement	Increased dryer length	Longer drying time for increased toluene emission in the plant
	Storage places	Separate storage places with air extraction for cleaning rags
		Separate storage places with air extraction for waste inks
	Continuous air extraction from machines and dryers	Extraction also during stop of machines
	Continuous air extraction from machines, dryers and press room	Extraction also from areas with less toluene concentration
Abatement technologies	Efficient adsorption	Installation of sufficient adsorption capacity, efficient desorption intervals, input/output measurement
	Capturing of air emissions during drying of activated carbon	Air emissions are routed back into the installation until activated carbon has recovered its capacity
	Closed-loop system	Clean air from adsorption outlet is routed back into the installation

9 Good practice examples

A publication rotogravure printing company produces magazines, catalogues, brochures and advertising.

HOT STEAM FOR TOLUENE RECOVERY IS PRODUCED BY A GAS TURBINE

The printing house uses a gas turbine for electricity and heat production, converting part of the heat into cooling. Hot steam from the turbine is used for toluene recovery from activated carbon. When steam is produced in excess by the gas turbine, more frequent desorption of toluene from activated carbon devices is realised.

After adsorption, cleaned air is routed back into the printing room (closed-loop system).

With the closed loop system, toluene emission levels < 3 % have been achieved, resulting in specific toluene emissions of 25 – 60 mg/m^2 of printed product.

The lowest values reported in 2005 were related to more frequent desorptions realised with excess turbine steam.

[BURDA 2006]

10 Emerging techniques and substitutes under development

10.1.1 VOC-free ink systems

Tests have been undertaken with water-based inks for publication rotogravure printing, but have not been successful because the relatively high viscosity of these ink systems is not appropriate for high-speed printing.

WATER-BASED INKS HAVE NOT BEEN DEVELOPED SUCCESSFULLY

Besides quality deterioration and 30 % reduced productivity, water-based inks showed disadvantages because of increased energy need for drying, higher waste generation and more difficulties to de-ink the printed paper.

[BREF STS 2007]

10.1.2 Increased temperature in the press room

By increasing the temperature in the press room (e.g. from 40° to 90°C), more toluene evaporates from residues in the printed product. Thereby more toluene is released and recovered inside the plant and not emitted to ambient air. [BREF STS 2007]

INCREASED TEMPERATURE OF THE PRESS ROOM HAS NOT BEEN IMPLEMENTED SUCCESSFULLY IN EUROPE

With this measure toluene emissions from products were expected to be reduced by about 1 % of the total solvent input, but test applications in Europe have not achieved this level. [BREF STS 2007]

<u>Economic and cross-media impacts</u>

A significant amount of additional energy is needed to increase press room temperatures. Higher toluene emissions will need more energy for desorption but will lead to economic benefits from increased toluene recovery.

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Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive

(Directive 1999/13/EC)

Guidance 3:

Other rotogravure, flexography, rotary screen printing, and laminating or varnishing units

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses rotogravure (other than publication rotogravure), flexography, rotary screen printing, and laminating or varnishing units as well as the related cleaning of equipment, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emission Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
Printing is defined by the Directive as 'any reproduction activity of text and/or images in which, with the use of an image carrier, ink is transferred onto whatever type of surface. It includes associated varnishing, coating and laminating techniques.'
Rotogravure is defined as 'a printing activity using a cylindrical image carrier in which the printing area is below the non-printing area, using liquid inks which dry through evaporation. The recesses are filled with ink and the surplus is cleaned off the non-printing area before the surface to be printed contacts the cylinder and lifts the ink from the recesses.'
Flexography is defined as 'a printing activity using an image carrier of rubber or elastic photopolymers on which the printing areas are above the non-printing areas, using liquid inks which dry through evaporation.'
Rotary screen printing is defined as 'a web-fed printing activity in which the ink is passed onto the surface to be printed by forcing it through a porous image carrier, in which the printing area is open and the nonprinting area is sealed off, using liquid inks which dry only through evaporation. Web-fed means that the material to be printed is fed to the machine from a reel as distinct from separate sheets.'
Varnishing is defined as 'an activity by which a varnish or an adhesive coating for the purpose of later sealing the packaging material is applied to a flexible material.'
Coating is defined as 'any activity in which a single or multiple application of a continuous film of a coating is applied.'
Laminating associated to a printing activity is defined as 'the adhering together of two or more flexible materials to produce laminates.'

Other common printing techniques like sheet fed offset printing, cold set offset printing, digital printing, letter set printing or sheet fed screen printing do not fall under the scope of the SE Directive.

The following activities, covered by the SE Directive, are addressed in separate guidance documents: heatset web offset printing (guidance 1), publication rotogravure printing (guidance 2), lamination – not associated with a printing activity (guidance 15).

The SE Directive lays down the following activity specific emission limit values for rotogravure (other than publication rotogravure), flexography, rotary screen printing, and laminating or varnishing units:

Table 2: Emission limit values of the SE Directive

SE Directive – Emission limit values (ELVs) (Annex II A – activity No. 3)			
Activity	**Solvent consumption threshold [tonnes/year]**	**ELVs in waste gases [mg C/Nm^3]**	**Fugitive emission values [% of solvent input]**
Rotogravure (other than publication rotogravure), flexography, rotary screen printing (not on textile/cardboard), laminating or varnishing units	15 - 25	100	25
	> 25	100	20
Rotary screen printing on textile/cardboard	> 30	100	20

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[1] as well as for halogenated[2] VOCs that are assigned the risk phrases R40 or R68[3]. There is a general obligation to replace CMR substances – as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated VOC with R40 or R68 the emission limit values in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.

Inks and varnishes for printing should not contain carcinogenic (R45, R49) or mutagenic (R46) substances nor substances toxic to reproduction (R60, R61), due to the commitment of the European Printing Ink Association [EuPIA 2007] to exclude these substances from their products.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

1 CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)
2 Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine or iodine.
3 After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: ‘Possible risk of irreversible effects’. The new wording is: ‘Limited evidence of a carcinogenic effect’. In the ‘old’ version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: ‘Possible risk of irreversible effects’. This new risk phrase does not include carcinogenicity. The ‘new’ version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to reflect this change a final decision on which version applies can only be given by the European Court

2 Summary of VOC substitution/reduction

VOC EMISSION REDUCTION CAN BE ACHIEVED WITH IMPROVED HANDLING, WITH WATER-BASED INKS, VOC-FREE CLEANING, ENCLOSED AUTOMATIC SOLVENT BASED CLEANING, AND WITH EFFICIENT CAPTURE AND TREATMENT OF WASTE GAS

The main sources of VOC emissions from these activities are fugitive emissions from printing machines and other equipment, VOC from ink solvents remaining on the printed products and VOC in waste gas.

Substitution of solvent-based inks by water-based or radiation-curing inks is possible in case of printing on paper and - with restrictions - on plastic foils. Cross-media effects such as increased energy consumption have to be taken into account.

Regular machine cleaning can be done with VOC-free systems. The daily cleaning of parts can be done with ultrasonic water-based cleaning equipment and in closed automatic washing machines. Washing machines can also use caustic water-based systems instead of solvents. For water-based inks, water can be used for daily cleaning operations. Solvents used for manual or automatic cleaning can be subsequently recovered by distillation and re-used for cleaning.

Emissions from inks can be prevented by covering solvent-containing pots, vessels and ink reservoirs as well as by directly connecting solvent tanks with ink reservoirs. They can also be abated by using an efficient waste gas treatment system.

3 Description of the activity and related industry sector

Approximately 380 existing and new installations were reported as being registered and authorised under the SE Directive in the period 1999 – 2003 in EU-15 as carrying out “other printing” (activity 3) [Implementation 2006].[4]

Rotogravure printing and flexography are used in most countries of Europe, mainly for a great variety of packagings. In some cases flexography is used for newspaper printing and books. Substrates printed on are flexible materials (plastic foils, paper, cardboard) as well as hard materials (glass, metal, laminates of different materials, e.g. cardboard, fibreboard, plastic, metal).

Rotary screen printing is mainly used for textiles and on wall coverings (both paper and plastic substrates).

With flexography most milk cartons and multiwall bags are printed as well as about half of all flexible packaging, with the other half being printed using rotogravure. Other typical products of flexography are gift wraps, folding cartons, labels, tapes and envelopes, paper cups and plates.

Quality requirements for packaging printing vary significantly from low quality (e.g. for fertilizer packaging, carrier bags) to high quality (e.g. for food packaging, cosmetics labelling). Ink quality requirements for food packaging printing are particularly high to avoid food contamination via migration of ink substances through the package.

[German EPA 2003-1] [BREF STS 2007] [UK Guidance 2008]

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[4] No data was reported from Belgium, Italy and Sweden.

4 Technical process description

Installations consist mainly of

- Printing units (ink reservoir, printing cylinder or printing screen)
- Drying units (heated air)
- Air extraction system (with/without waste gas treatment).

4.1 Process flow and relevant associated VOC emissions

Figure 1 shows the main relevant solvent inputs and VOC outputs of packaging rotogravure and flexography printing (arrows indicate the relevance of the VOC amount). [BREF STS 2007] [Ökopol 2008]

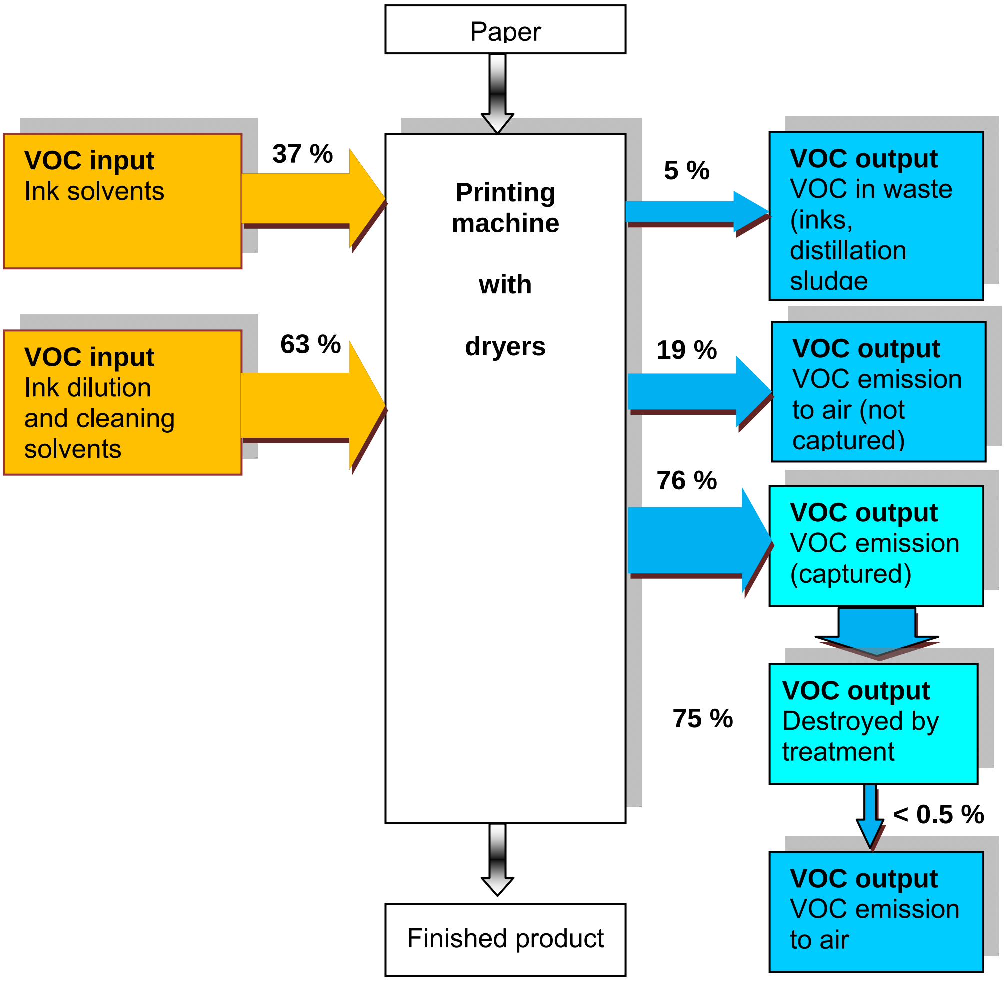


Figure 1: Main VOC input and output of packaging rotogravure and flexography printing

4.2 Process description

Table 3 shows some characteristics of the 3 main printing systems.

Table 3: Typical characteristics of different printing systems

	Packaging rotogravure	Flexography	Rotary screen printing
Image carrier	engraved cylinder	relief plate	screen
Printing cylinder material	copper/chromium	photopolymer	nickel stencil
Production speed [m/min]	250 – 300	300	40 – 100
Cylinder width [mm]	800 - 1400	600 – 1400	350 - 1100

[German EPA 2003-1] [BREF STS 2007] [Ökopol 2008]

4.2.1 Packaging rotogravure

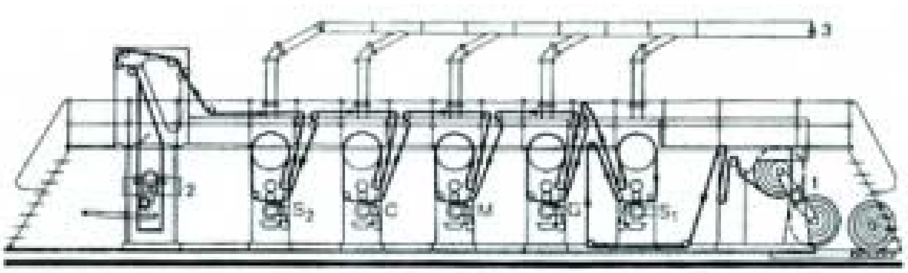
Rotogravure printing is characterized by the use of engraved cylinders made of a steel base and a copper surface. The image is engraved into the copper layer, mainly by digital laser-engraving, or, less frequently, with electromechanical engraving. To provide resistance to wear during long runs, the image is protected with a thin layer of chromium which is electroplated onto the cylinder surface.

PACKAGING ROTOGRAVURE USES ENGRAVED PRINTING CYLINDERS

During printing, the rotating cylinder is covered with ink and the surface then scraped with a ‘doctor blade’, leaving ink only in the engraved areas. The image transfer takes place when the printed substrate is pressed between the gravure cylinder and the impression roller.

The ink transfer to the substrate is regulated by variation of the depth and size of the recessed cylinder cells ('dots').

Packaging rotogravure machines can print 6 - 10 inks and varnishes on one side of the material. They use the 4 standard colours as well as job specific colours and varnishes. Machines differ by the position of the printing units: the units can be positioned on a compact central impression cylinder (satelite cylinder, see figure 3), or in series (figure 2), which also allows combining gravure printing and flexography.



[German EPA-2 2003]

Figure 2: Schematic overview of packaging printing machine in series

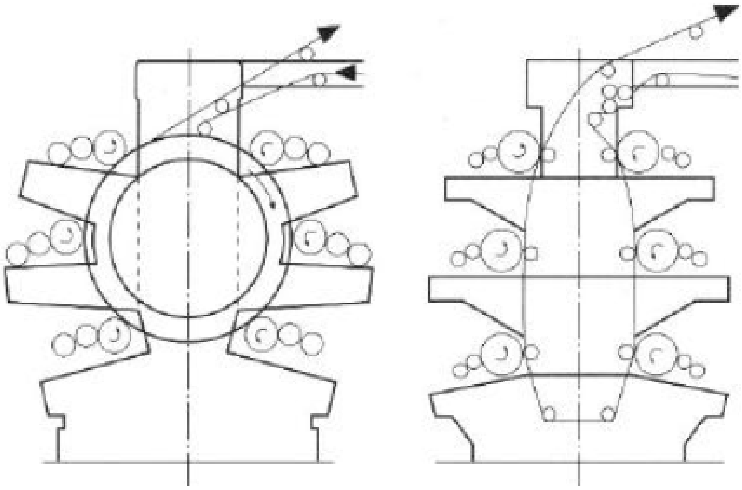
Rotogravure printing is usually a webfed process (substrates coming from a roll), except for some sheetfed presses for up to 10,000 sheets per hour, used for high quality decorative effects such as using metallic inks on metallised papers and foils.

[Mateis-2 2001] [CITEPA 2003] [UK 2004] [BREF STS 2007]

4.2.2 Flexography

Flexographic printing machines are constructed in a similar way as packaging rotogravure machines (see figures 2 and 3) and both techniques can be combined in a single machine.

FLEXOGRAPHY USES FLEXIBLE PHOTOPOLYMERS OR RUBBER MOUNTED ON THE PRINTING CYLINDERS



[German EPA-2 2003]

Figure 3: Schematic overview of packaging printing machine with two types of satellite cylinder position

Flexographic printing uses flexible plates made of photopolymer or rubber which are glued onto a metallic printing cylinder using double sided self-adhesive tape. Image areas on the plate harden when exposed to UV-light, and this "development" process produces a relief with elevated printing areas.

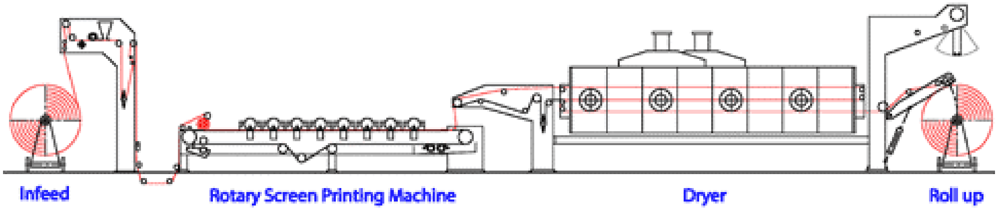
For printing, a rubber roll (‘fountain roll’) takes up ink from the reservoir and transfers it to an ‘ink-metering roll’. Excess ink on the metering roll is removed with a ‘doctor blade’ before the remaining ink is transferred to the printing cylinder. Modern ‘anilox’ metering rolls have direct ink supply from an ink reservoir using a ‘chamber doctor blade’. The printing cylinder transfers the ink from the ink-metering roll to the printed substrate. The ink transfer to the substrate is regulated by the structure and the depth of the cells on the printing roll.

ANILOX INK METERING ROLLS AVOID THE USE OF A FOUNTAIN ROLL

4.2.3 *Rotary screen printing*

ROTARY SCREEN PRINTING USES SCREENS MOUNTED ON THE PRINTING CYLINDERS

Rotary screen printing is characterized by the use of a stencil which partially covers a lightweight metal foil screen mounted on a rotating printing cylinder. The stencil is cut with a computer-controlled blade and is used to block ink from being transferred to non-image areas of the substrate. Inside the screen cylinder a squeegee is fixed, which is pressing ink through the unblocked parts of the screen and onto the substrate.



[Mitter MMB 2008]

Figure 4: Schematic overview of rotary screen printing (roll to roll)

Printed material passes under a set of cylinder screens in turn, each printing a separate colour.

The ink transfer to the substrate is regulated with an ink pump that supplies the inside of the screen cylinder.

[Maetis-1 2001] [BREF STS 2007]

4.3 Inks

Inks for rotogravure printing, flexography and screen printing can be solvent-based, water-based or radiation-curing.

For the hardening of the conventional solvent-based inks and water-based inks, a dryer is installed after each colour unit. Each ink has to dry before the substrate enters the subsequent printing unit.

Typical temperatures for ink drying are 50°C – 100°C, with blow speeds of 40 - 60 m/s [German EPA 2003-2].

Radiation-curing ink systems do not contain solvents. They use photo-initiators to start polymerisation of the binders when exposed to radiation. Inks can be cured with UV light or electron beams. For this purpose, UV lamps or vacuum tubes producing electron streams are installed in each printing unit.

[BREF STS 2007]

4.4 Cleaning

The cylinder cleaning systems for rotogravure printing, flexography and rotary screen printing may be either manual (in-situ or external to the machine) or automatic (especially in new machines).

The ink reservoir, together with tubes and pumps, has to be cleaned after each colour change. Additionally, regular machine cleaning, to remove ink splash from machine parts, is a good practice.

[German EPA 2003-2]

5 Solvent use, emissions and environmental impact

5.1 Solvents used

5.1.1 Rotogravure printing and flexography

The principal organic solvents used in rotogravure printing and flexography are ethanol and isopropyl alcohol. They are used for solvent-based ink systems, in many water-based inks, for ink dilution and for cleaning. Ethyl acetate is also frequently used as an ink solvent, sometimes mixed with ethanol. Methyl ethyl ketone is used for varnishes. Aromatic solvents are no longer used, as they are not allowed for food packaging.

ROTOGRAVURE PRINTING AND FLEXOGRAPHY USE MAINLY ETHANOL AND ISOPOPYL ALCOHOL FOR INKS AND FOR CLEANING

Tables 4 and 5 show typical solvents used for packaging printing with rotogravure printing or flexography.

Table 4: Typical VOC used for solvent-based rotogravure printing or flexography

Solvent	Vapour pressure (at 293 K) [kPa]	Field of application
Ethanol	5.9	Ink solvent, cleaning
Isopropanol	4.3	Ink solvent, cleaning
Isopropyl acetate	6.1	Viscosity adjuster
Ethyl acetate	9.2	Thinner, cleaning agent
Methyl ethyl ketone	10.5	Siccative, used in varnishes
n-Butanol	1.2	Retarder
n-Propanol	2.5	Retarder
Methoxy propanol	1.1	Retarder
Ethoxy propanol	0.65	Retarder

[BREF STS 2007] [German EPA 2003-1]

Table 5: Typical VOC used for water-based rotogravure printing or flexography

Solvent	Vapour pressure [kPa]	Field of application
Ethanol	5.9	Ink solvent, siccative, cleaning
Isopropanol	4.3	Ink solvent, cleaning
n-Propanol	2.5	Ink solvent

[BREF STS 2007] [German EPA 2003-1]

Solvent-based inks for rotogravure and flexography have a solvent content of 40 – 75 %. Machine reservoirs are generally filled with inks with a higher viscosity than needed in order to give operators the flexibilty to add solvent at the press to achieve a particular drying time. Ready-to-use solvent-based inks contain ~ 80 % solvent.

Water-based inks may contain small amounts of organic solvents. Besides allowing faster drying and better contact on plastic substrates, they act as anti-foaming agents and biocides. The total solvent content of water-based inks and varnishes is usually between 0 – 5 %. If a faster drying time is required (e.g. when printing on thin paper) the solvent content of water-based inks may be increased to 25 %.

[BREF STS 2007]

In total, European liquid ink consumption for rotogravure and flexography is about 410,000 t/year, whereof about 35 % to 40 % is water-based [Sun 2008]. The total amount of screen printing ink sold in Europe is about 18,000 t/a [Maetis-1 2001].

5.1.2 Rotary screen printing

Rotary sceen printing is employed for a great range of products and so uses a wide range of inks and solvents. Table 6 shows typical examples of the solvents used.

FOR ROTARY SCREEN PRINTING A WIDE RANGE OF SOLVENTS IS USED

Table 6: Typical organic solvents used for screen printing

Solvent	Vapour pressure (at 293 K) [kPa]	Ink system
Solvent naphtha	varying	Solvent-based
Xylene	0.7 - 0.9	Solvent-based
1-Methoxypropyl acetate	0.37	Solvent-based
White spirit	varying	Solvent-based
Benzyl alcohol	0.002	Solvent- and water-based
Diacetone alcohol	0.1	Solvent- and water-based
Glycolic acid butyl ester	0.13	Solvent- and water-based
1-methoxypropanol-2	1.15	Solvent- and water-based
Cyclohexanone	0.5	Solvent- and water-based
Dipropylene glycol	0.0029	Solvent- and water-based
Butane-2-ol	1.7	Water-based
3-methoxy-1-butanol	0.13	Water-based

[Intergraf 1999] [LASI 2007] [Ökopol 2008]

5.2 Solvent consumption and emission levels

Table 7 shows data on solvent consumption collected from a range of rotogravure printing and flexography installations.

The data show that for solvent-based systems the solvent consumption is much higher than would be expected for ready-to-use inks after dilution with thinners (~ 80 % solvent content). This is due to the use of thinners and due to the use of thinners for cleaning, due to evaporation from the ink reservoirs, and due to emissions from solvent handling operations (mixing and viscosity adjustment).

Table 7: The average solvent consumption of typical packaging printing installations when using different ink systems (related to one unit of purchased ink)

	Rotogravure		**Flexography**	
	Solvent-based [%]	Water-based [%]	Solvent-based [%]	Water-based [%]
Solvent in ink	60	5	60	5
Thinners	101	2	81	2
Cleaners	17	10	14	10
Sum of solvents	**178**	**17**	**155**	**17**

[BREF STS 2007]

Ink use for complete coverage of the printed area is ~1.5 - 2.0 g/m^2 for white, 1.0 - 1.5 g/m^2 for spot colours and 0.5 - 1.0 g/m^2 for half tone colours [BREF STS 2007].

Existing machines for rotogravure printing and flexography are generally not been fully enclosed to ease access of operators to all parts of the machine. Therefore machines may have high emissions from the cylinders and ink reservoirs - both when printing and also when the production is stopped.

The viscosity is often adjusted manually by adding solvent to the ink reservoir from an open container using a ladle. This practice facilitates the emission of VOC.

Traditionally, manual cleaning is carried out using rags wetted with solvent, leading to emissions of VOC. If solvents are used in automatic cleaning systems or recovered by distillation, emissions may occur when the doors of the equipment are opened.

If solvent-based inks are used, waste gas extraction and treatment systems are needed to achieve the emission limit values of the SE Directive.

5.3 Key environmental and health issues

In rotogravure printing, flexography and rotary screen printing, many different solvents are used for a range of processes. The most commonly used solvents are ethanol and isopropyl alcohol.

Emissions of VOC, together with NOx, are precursors of ground level ozone formation in the presence of sunlight.

Emissions of VOC to air may occur from:

- the printing process and its cleaning operations,
- the solvent recovery system,
- the printed product.

The process generates waste containing solvents that need to be disposed of in a way that emissions to air, soil and groundwater are prevented or limited.

Existing occupational workplace limits have to be taken into consideration.

6 VOC substitution

The following two sections describe potential substitutes for VOC (VOC-free systems and reduced-VOC systems). There are also descriptions of the application technologies or special conditions needed.

6.1 VOC-free systems

6.1.1 VOC-free water-based inks

Solvent-based ink and varnish systems can be substituted by water-based systems in most cases where the printed substrate is paper or cardboard. Difficulties may arise if low-weight paper has to be printed (e.g. bakery paper bags).

Modern dryers have sufficient capacity to dry not only solvent-based but also water-based inks, thus no additional investment is needed [Sun 2008].

Economic and cross-media effects

Approximately 10 % more energy is required to dry water-based inks compared to the solvent-based inks they replace [BREF STS 2007].

6.1.2 VOC-free radiation-curing inks

In some cases UV and electron-curing ink systems can replace solvent-based ink systems, particularly for new machines. Retrofitting existing machines is difficult as less pressure can be exerted between the (image carrying) printing cylinder and the impression cylinder, on the substrate to be printed.

UV and electron-curing inks are used for flexographic printing on paper, cartons and self-adhesive paper-labels, especially when a high quality result is required. Electron beam cured inks can achieve high gloss and are favoured for metal decorating applications.

If large white areas are printed, drying problems may occur when using UV-curing inks.

As it is difficult to achieve complete polymerisation of the binder monomers, small quantities of them may migrate into the package. This can cause non-compliance with food legislation. Therefore manufacturers of food packaging materials are often reluctant to apply radiation-curing inks. No such problems occur if laminates of cardboard and aluminium are used (e.g. beverage packaging).

[BREF STS 2007] [Ökopol 2008]

Economic and cross-media effects

Radiation-curing inks contain reactive acrylates, monomers and oligomers, some of which have allergenic potential.

UV curing lamps have a high energy demand and need cooling. They generate ozone and so additional air extraction is needed. Reports differ in their conclusions on whether the system needs more or less energy than conventional drying.

UV lamps contain mercury and old lamps must be disposed of with due care. Operators must adopt safe systems of work to avoid exposure to UV and electron beam radiation.

[BREF STS 2007] [Ökopol 2008]

6.1.3 VOC-free cleaning systems

VOC-free water-based cleaners can generally be used if water-based inks are applied. Cleaning needs to be undertaken before the inks have dried as otherwise organic solvents are needed for clean-up.

Provided that automatic cylinder cleaning cannot be applied, cylinders are removed from the machine, and cleaning can be carried out using water-based cleaners and ultrasonic-cleaning equipment. [IBU 2008]

Automated cleaning of parts can be carried out, using organic solvents or a caustic solution. If the latter is applied, the parts need to be rinsed with clean water before the doors can be opened to prevent exposure to the alkali.

For regular machine cleaning, CO_2 (‘dry ice’) can be used. Pellets of dry ice are blown, using pressurized air, at about 300 m/s onto the surface to be cleaned. A high degree of cleanliness is achievable and no residue is left.

Cleaning machines cost about 9,000 to 14,000 € and the dry ice about 0.6 €/kg. Dry ice consumption is about 30 - 50 kg/h. If dry ice use exceeds ~60,000 t per year it is economic to rent a pelletizing machine at a cost of about 900 €/month. [ASCO 2008]

[ICT 2006]

Figure 5: Printing machine before and after cleaning with dry ice

Economic and cross-media effects

Caustic cleaning solutions require careful handling to avoid alkali burn. They maintain an excellent cleaning power for a long time but require disposal compared with solvent-based systems that can be distilled and re-used.

When using dry ice cleaning operators must take protective measures against noise and dust. Ventilation may also be needed if the work takes place in a confined space to avoid toxic CO_2 concentrations.

6.2 VOC-reduced systems

If the complete substitution of organic solvents is impractical then changing to systems with a reduced VOC content, such as those described in this section, can decrease emissions.

6.2.1 VOC-reduced ink system

The water-based inks used instead of conventional solvent-based inks may themselves contain a small amount of organic solvents; this can be 3 – 5 % for normal substrates but can increase to 25 % for special applications e.g. for thin paper.

With these inks, simple plastic packaging materials (such as carrier bags, refuse bags, bread bags and heavy-duty bags) may be printed successfully with flexography. The use of ceramic anilox cylinders improves quality.

Recently new resins have been developed that allow flexographic printing on a wide range of plastic substrates. On polyethylene foil, at speeds up to 600 m/min, the use of water-based inks can achieve an equivalent quality as when using solvent-based inks [Value 2007].

The introduction of water-based inks onto the market for plastic substrates has been hindered by the fact that packaging printing uses numerous different plastic materials. Different water-based inks are needed for each type of plastics whereas the same solvent-based ink can be applied on all plastic materials.

For polyethylene printing in Europe, currently about 40 000 t/a of inks are used of which 6 % is water-based. [Sun 2008]

6.2.2 *VOC-reduced cleaning systems*

Cleaning of parts can be undertaken in closed automatic equipment, with distillation to recover solvents, saving both resources and reducing the environmental impact of transporting waste solvent for external distillation.

The emission peaks that occur when the automatic washing machines are opened can be avoided by systems that extract solvent-loaded air before the doors can be opened.

[DW Renzmann 2008]

Figure 6: Automatic cleaning system

Emissions can be further reduced if the automatic washing (and distillation) is connected to the waste gas treatment system.

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements and abatement techniques can be used to reduce VOC emissions in addition to VOC substitution as described in section 6. The following measures can be applied.

7.1 Process improvements

7.1.1 Improved handling

Open containers as used e.g. for the dilution of inks at the machine and for cleaning are a significant source of emissions .

Emissions can be reduced by covering solvent-containing pots, vessels and ink reservoirs as well as by direct connection of dilution solvents storage tanks with ink reservoirs.

7.1.2 Optimised extraction from the machine

Emissions from solvent-based ink systems are best reduced if the machine is enclosed as much as possible. This is easier to achieve with newer machines. Solvent-loaded air can be extracted not only from the dryers and above the printing unit but also from the bottom of the machine. This requires adaptations of the waste gas systems.

To reduce emissions, air can be extracted for later treatment from areas with high VOC concentrations like ink mixing and cleaning. If waste gases with high VOC concentrations are routed to the treatment device, reliable equipment for explosion limit control needs to be installed.

7.2 Abatement technologies / End of pipe measures

If primary measures cannot be applied, VOCs may be destroyed by thermal oxidation, biological treatment or decomposition by thermal plasma. Biological and plasma treatments are mainly used for low concentrations of VOC (< 1 gC/m^3).

Thermal oxidisation can achieve VOC reduction efficiencies of > 99.9 %. Biological treatment generally has a lower efficiency but also lower investment and operating costs.

Adsorption onto activated carbon or zeolite materials, followed by controlled desorption, may be used to concentrate a dilute effluent for subsequent treatment. Concentrated gas streams must be monitored to ensure that the carbon content never exceeds 25 – 50 % of the lower explosion limit.

Thermal oxidation can be used if concentrations are above 1 gC/m^3. Consequently, low and varying carbon concentrations may require additional fuelling with natural gas to maintain a constant flame temperature. Autothermic combustion can be achieved with total carbon concentrations of about > 2 gC/m^3.

Recuperative oxidation systems recover waste heat from the combustion, via heat exchangers, to pre-heat incoming waste gas or for process operations such as dryers, or for room heating.

Regenerative oxidation systems are more efficient than recuperative systems. The hot exhaust gas is passed through chambers containing heat retentive honeycomb-like material. When a chamber has achieved its full heat loading the exhaust gas is routed to another chamber. Cool incoming waste gas is heated by passage through the hot honeycomb-like material before it enters the combustion chamber. The regeneration of waste heat decreases the energy demand of the process significantly.

Catalytic oxidation may be used if no ‘catalyst poisons’ are present; since catalysed oxidation occurs at a relatively low temperature the energy demand is reduced.

Oxidation has also been achieved in combined heat and power plants after concentrating solvent-loaded waste gas and routing it as combustion air into the CHP plant. [HDM 2000]

8 Summary of VOC emission reduction measures

The following table summarizes the various approaches to substitute or reduce VOC emissions as described in chapters 6 and 7:

Table 8: Measures for VOC substitution and VOC reduction

Objectives	**Description**	
VOC-free systems	VOC-free water-based inks	Use of water-based inks with 0 % organic solvent content
	VOC-free radiation-curing inks	Use of UV-curing inks or inks curing with electron beams
	VOC-free cleaners	Use of water-based cleaners Use of ultrasonic cleaning Use of caustic water cleaning Use of dry ice cleaning
VOC-reduced systems	VOC-reduced ink systems	Use of water-based inks with 0 - 25 % organic solvent content
	VOC-reduced cleaning systems	Use of automatic washing machines for parts cleaning
		Connection of automatic washing systems to waste gas treatment

Objectives	Description	
Process improvement	Improved handling	Close open containers Connect dilution solvents storage tanks directly with ink reservoirs
	Optimise extraction	Enclose machines Extract from bottom of machines
Abatement technologies	Adsorption	Adsorption on activated carbon or zeolite and desorption for later treatment
	Waste gas treatment	Regenerative thermal oxidation Catalytic oxidation Thermal plasma Biological treatment Oxidation in a combined heat and power plant (CHP)

9 Good practice examples

As many installations where this activity is operated are applying waste gas treatment, the following examples focus on how such VOC abatement can be achieved in an environmentally friendly and cost-efficient way by using adsorption before oxidation or by the use of a combined heat and power plant.

9.1 Efficiency increase of waste gas treatment

A medium-sized printing company produces flexible plastic packaging with rotogravure and flexography machines.

An existing thermal oxidation system was designed for authothermal combustion with carbon input concentrations of 7 g/m^3, achieved with adsorption on activated carbon.

When the company installed additional machines, the adsorption wheels didn’t provide for sufficient capacity. Therefore a part of the waste gases had to be routed directly into the thermal oxidation, resulting in lower solvent concentrations of 3 g/m^3 and significantly increased need for additional gas firing in the waste gas treatment system.

Greater adsorption wheels were installed with an investment equivalent to 560 000 Euro for achieving less volume and higher carbon concentration, and exceeding the authothermal combustion limit of 7 g/m^3 in the oxidisation unit.

By the investment, annual gas savings in the thermal oxidisation of ~ 6000 MWh were achieved, accompanied with cost savings equivalent to 130,000 Euro per year, resulting in a pay-back period of 4.3 years.

[Amcor 2005]

9.2 Solvent waste gas oxidation use in a CHP plant

A medium-sized printing company produces packaging products using plastic and aluminium foils with rotogravure, flexography and offset machines.

About 20.000 m^3 per hour waste gas is extracted from the solvent-based rotogravure and flexography printing machines. Waste gases are passed through two adsorption wheels filled with activated carbon. After concentration of solvents, desorption with hot air of 120-140°C takes place.

Solvent-loaded air is routed to two diesel engines and used as combustion air. The engines produce electricity and heat. Heat from the engine and from the exhaust gas of the engine is used for room heating, dryers' air heating and for cooling. For the latter, an adsorption cooling system is installed.

Exhaust gases of the two engines are cleaned with soot filters and selective catalytic reduction units (SCR) for decomposition of nitrogen oxides.

An additional oil pump had to be installed to guarantee sufficient greasing of the engine before each start-up.

The system was installed in the late nineties with investment costs equivalent to 1 Mio Euro. As a result, annual energy consumption was reduced by ~ 1630 MWh, and cost savings were equivalent to 100 000 Euro per year.

[HDM 2000] [BAUM 2002] [Rahning 2008]

10 Emerging techniques and substitutes under development

No emerging techniques have been reported.

11 Information sources

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Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Guidance 4/5:

Surface cleaning

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses surface cleaning, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emission Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
Surface cleaning is defined as 'any cleaning activity, except dry cleaning, using organic solvents to remove contamination from the surface of material including degreasing. A cleaning activity consisting of more than one step before or after any other activity shall be considered as one surface cleaning activity. This activity does not refer to the cleaning of the equipment but to the cleaning of the surface of products.' The SE Directive covers installations in which this activity is taking place with an annual organic solvent consumption greater than 1 t or 2 t (depending on the used solvent (see Table 2).

Surface cleaning is a process which is applied in several industry sectors e.g. metal industry, electronic industry and typically takes place before or after another production step (e.g. before painting).

Paint stripping and dewaxing is included in the activity of 'surface cleaning' (according to the SE Directive) whereas dry cleaning is covered by a separate activity (see guidance document 11)

The SE Directive lays down the following activity specific emission limit values for surface cleaning:

THE SE DIRECTIVE APPLIES TO SURFACE CLEANING ACTIVITIES IF A SOLVENT CONSUMPTION OF 1 OR 2 TONNES (DEPENDING ON THE SOLVENTS USED) PER YEAR IS EXCEEDED

Table 2: Emission limit values of the SE Directive

SE Directive - Emission limit values (ELVs) (Annex II A – activity No. 4/5)				
Activity	**Solvent consumption threshold [tonnes/year]**	**ELVs in waste gases [mg C/Nm³]**	**Fugitive emission values [% of solvent input]**	**Total ELVs**
4. Surface cleaning using VOC with the R- phrases R45, R46, R49, R60, R61 or halogenated VOC assigned R40	1-5	20 mg/Nm³ *	15	
	> 5	20 mg/Nm³ *	10	
5. Other surface cleaning	2-10	75**	20**	
	> 10	75**	15**	

Special provisions:

* these ELVs in waste gas refer to mass of compounds in mg/Nm³, and not to total carbon.

** Installations which demonstrate to the competent authority that the average organic solvent content of all cleaning material used does **not exceed 30 % by weight** are exempt from application of these values.

Installations operating both activities 4 and 5 as defined in the Directive have to comply for each activity separately with the corresponding requirements of the SE Directive.

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[1] as well as for halogenated VOCs which are assigned the risk phrases R40 or R68[2]. There is a general obligation to replace CMR substances – as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated[3] VOC with R40/R68 the ELVs in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used. (Note that this requirement may be more stringent than the ELVs set out for activity 4 in the above table)

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

VOC REDUCTION CAN BE BEST ACHIEVED BY SUBSTITUTING VOC CONTAINING SOLVENTS WITH WATER BASED SYSTEMS OR BY ENCLOSING SURFACE CLEANING SYSTEMS

VOC containing solvents are widely used for surface cleaning and can give rise to fugitive emissions when used in an open or semi-enclosed environment with little or no fume extraction and abatement. Switching to water based systems is the most effective VOC substitution measure.

In cases where cleaning agents containing solvents with specific R-phrases are used and these cannot be replaced by less harmful substances, a sealed chamber system with integrated abatement and recycling should be used.

For solvents containing only VOCs that do not carry specific R-phrases enclosed cleaning machines or baths - with integrated abatement and recycling technologies - should be used.

Changing cleaning technology (e.g. laser cleaning, CO_2 cleaning) also provides a way of avoiding VOC emissions. Although the operational costs are comparatively low, these technologies often demand high investment costs.

Process improvements - like optimising cleaning processes to meet only the required cleanliness or the re-organisation of the production process to avoid interim cleaning steps - are also important measures to reduce VOC emission from surface cleaning activities.

[1] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

[2] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: 'Possible risk of irreversible effects'. The new wording is: 'Limited evidence of a carcinogenic effect'. In the 'old' version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: 'Possible risk of irreversible effects'. This new risk phrase does not include carcinogenicity. The 'new' version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to this change, a final decision on which version applies can only be given by the European Court

[3] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.

3 Description of the activity and related industry sectors

Surface cleaning activities are necessary in many different sectors of industry, including the electronics industry, metalworking, and engineering, ranging from manufacture of heavy machinery and vehicles down to manufacture of medical, precision and optical instruments. The choice of cleaning solvent depends on the type of cleaning process, the nature of the contaminant being removed, and the products involved.

For the period 1999 – 2003, EU 15 Member States reported approximately 2,600 installations falling under the SE Directive carrying out surface cleaning [Implementation 2006]. The total number of existing installations is very difficult to estimate because cleaning of surfaces is merely a process step carried out in numerous industrial sectors. The range of users varies from small workshops carrying out manual cleaning (and typically not covered by the SE Directive) to big industrial installations with cleaning departments.

BOTH ORGANIC SOLVENTS AND WATER BASED SYSTEMS ARE COMMONLY USED FOR SURFACE CLEANING

The substances commonly used for surface cleaning include both organic solvents (non-halogenated and halogenated hydrocarbons) and water based systems. Water based systems are widely used and have already replaced organic solvents in many cases.

Non-halogenated hydrocarbons are used in several industrial sectors for the manufacture of rubber/plastic products, glassware, pipe work, machinery, and transport equipment. There are also applications in precision / electrical engineering, electronic and precision optics and in the manufacture of printed circuit boards. The type and size of cleaning systems range from the small, open, and manually operated through to large, sealed, industrial installations. Non-halogenated solvents are also used for de-waxing cars (at distribution companies or at car dealers) and in car repair workshops.

Solvents classified as CMR substances or halogenated solvents are used to remove contamination from metals, glass, ceramics or composite surfaces such as printed circuit boards. Halogenated solvents are particularly effective for the removal of oily and fatty contaminates. They are not suitable for most rubber and plastics as these may be soluble in these solvents.

Halogenated and halogen-free solvents are used by specialist companies for the removal of paint in the automotive and aircraft industry.

4 Technical process description

4.1 Process flow and relevant associated VOC emissions

The following flow chart is a schematic overview of a typical surface cleaning process in a closed system with integrated solvent recovery (such as the type III cleaning machines described in chapter 7).

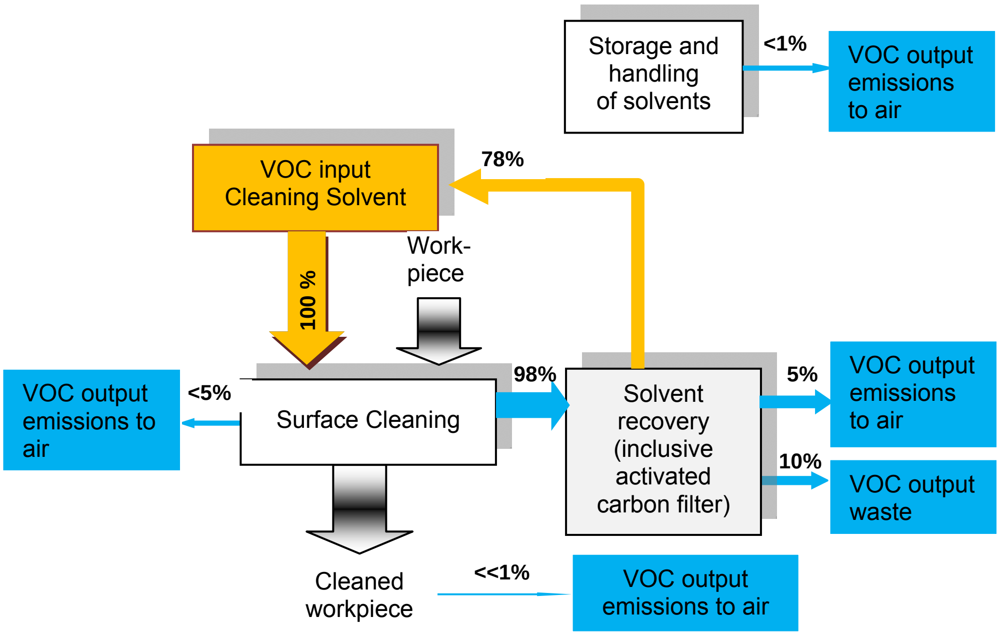

Figure 1: Typical VOC outputs from surface cleaning processes using organic solvents (closed system)

The bulk of the emissions to air arise during the cleaning process and from solvent handling and storage, but particularly when the chamber is opened to unload workpieces. Typically the VOC output to waste is recovered in a waste treatment process.

4.2 Process description

Solvent based cleaning can be differentiated into three types of processes:

- vapour phase cleaning or degreasing: solvent vapours condense on the surfaces of the product
- liquid phase cleaning (or cold cleaning): contaminants are soaked/immersed in solvent
- manual cleaning: liquid or aerosol solvents are applied using wipes, rags, brushes, etc.

The most common technologies for surface cleaning with VOCs are described below. These include the application systems for solvents used for dewaxing and paint stripping.

4.2.1 *Vapour phase cleaning: Chamber systems (with or without vacuum technology)*

Chamber systems with vacuum

INSTALLATIONS WITH VACUUM TECHNOLOGIES ARE APPLICABLE FOR CHLORINATED AND NON CHLORINATED SOLVENTS

These cleaning machines offer the highest standards of surface cleaning and emission reduction. During the cleaning operation, the emission of VOC is reduced to a minimum by the use of containment and vacuum technology (for further information on emission rates see chapter 7, Figure 5, type IV). All processes where solvent emissions might occur are enclosed in a sealed casing. During the cleaning process, which is carried out under vacuum it is not possible to open the chamber. The chamber has an integrated activated carbon filter for air cleaning and opening is controlled automatically to prevent VOC emissions. Such installations are equipped with a low temperature vacuum distillation system (for integrated solvent recycling) that separates the solvent from oils and greases for reuse. The machine is leak proof and includes safety systems to avoid emission -even in the case of mis-handling. Solvent use is restricted to designated handling area where the rate of consumption can be reduced to a minimum. The machine design is such that no exhaust air is produced and the contaminants removed are captured in sealed filters that are dried automatically.

The following figure is a schematic overview on sealed installation with a single working chamber, a closed loop drying with refrigeration and an activated carbon filter.

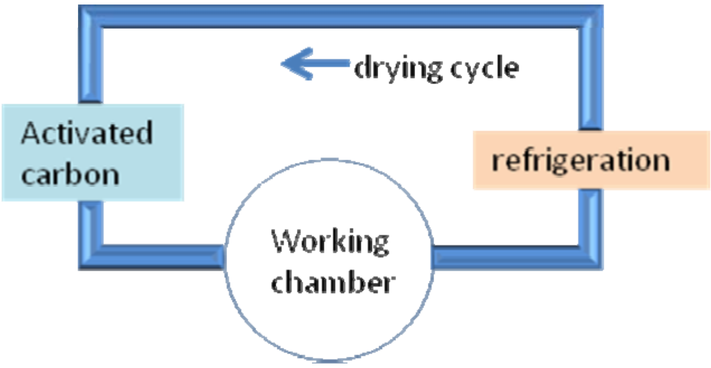

Figure 2: Schematic overview on a closed loop installation (vacuum system) [Dow 2008]

These machines can work either with chlorinated solvents or A3 class hydrocarbon solvents (flash point greater than 55°C meaning they are not flammable under vacuum conditions).

For enhanced cleaning these installations can also be equipped with ultrasonic cleaning.

These installations are available in different standard sizes (from 100 l up to 5.000 l), but customised installations are common too. [Hösel 2008], [Pero 2008]

Chamber systems without vacuum

This technique prevents direct emission of solvents by a series of interlocks in combination with a vapour extraction and/or refrigeration system. This system recycles the vapour back into the solvent sump (tank) (for further information on emission rates see chapter 7, Figure 5, type III). By contrast with the above vacuum system, this system still exhausts gas.

SEALED CHAMBER SYSTEMS WITH VACUUM REDUCE VOC EMISSIONS SIGNIFICANTLY

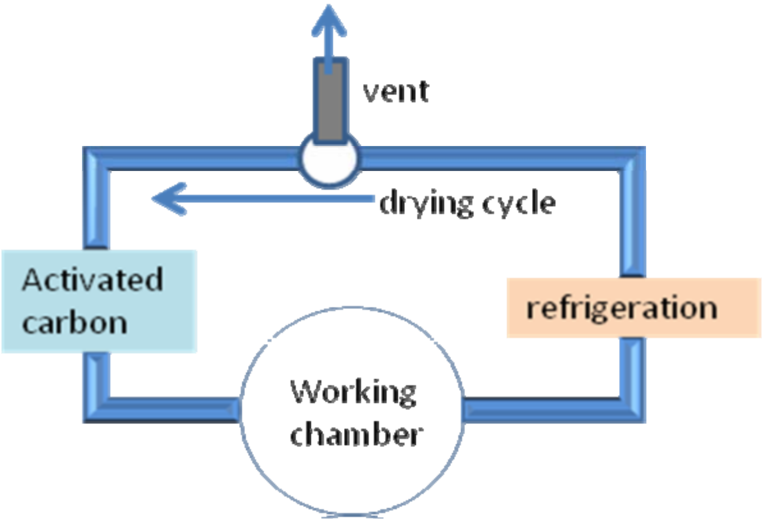

Figure 3: Schematic overview on a closed loop installation [Dow 2008]

It enables a very high degree of solvent containment and reduction of fugitive emissions. These machines can work either with chlorinated solvents or other non flammable solvents.

4.2.2 Open-top vapour systems

A typical open-top vapour degreaser has a sump containing a heater to generate solvent vapour. Parts to be cleaned are immersed in the vapour zone and solvent condenses on the work piece until it is heated up to the vapour temperature. Residual liquid solvent rapidly evaporates as the cleaned parts are slowly removed from the vapour zone. Cleaning action is often supplemented by spraying solvent onto the parts from below or by immersing them in the liquid solvent bath. Nearly all vapour degreasers are equipped with a water separator allowing the (water free) solvent to flow back into the degreaser.

To reduce VOC emissions and to protect workers open top systems should at least be enclosed to ensure the VOC emission is captured and treated (e.g. by activated carbon).

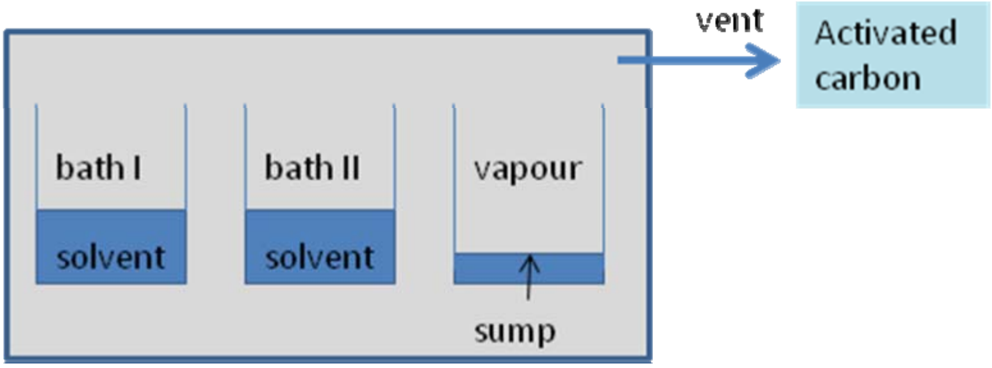

Figure 4: schematic overview on an encased open-top degreaser with activated carbon [Dow 2008]

Although open top systems using CMR and halogenated solvents (usually perchloroethylene) are still in use in some Member States these are not state of the art. In the event that these substances are the only means of achieving special cleaning requirements then sealed (in case of CMR substances) or at least enclosed systems (for halogenated substances) should be used.

4.2.3 Liquid phase cleaning: Cold cleaners

Cold cleaners are commonly used by those carrying out maintenance and manufacturing activities. They are mainly batch loaded and – compared to vapour phase cleaning - use higher-boiling point solvent degreasers. Cold cleaner operations include spraying, brushing, flushing, and immersion. In order to increase the cleaning effect dirty parts are often pre-cleaned manually by spraying before being soaked in the tank. After cleaning, the parts are either hung up to drain over the tank or placed on a separate rack. The drained solvent is then reused.

Typical cold cleaners vary widely in design, but there are two basic tank designs: a simple spray sink and a dip tank. Of these, the dip tank provides more thorough cleaning via immersion (often agitation is used to improve cleaning efficiency). VOC emissions arise from the open tank and from the cleaning process. Therefore a tightly fitting cover is often used to close the unit and prevent VOC emissions when it is not in use.

4.3 Dewaxing

A coating of 'wax' may be used to protect cars (whole vehicles) and components during transport. Dewaxing is then needed to remove the wax at vehicle distribution companies (e.g. car dealers) and sometime for vehicle assembly during the manufacturing process. These waxes are removed with solvents before further processing or vehicle sale. Typically a solvent-water mixture (e.g. kerosene) is applied by high pressure spraying at temperatures of about 80 °C, about 6-10 litre of dewaxing mixture is necessary for the average car.

DEWAXING IS MAINLY APPLIED IN THE TRANSPORT SECTOR

4.4 Paint stripping

Chemical paint stripping is typically carried out using a dipping processes or - to a lesser extent - by spraying. The operation takes place in a bath of solvent (a dip tank) at temperatures of around 80-90 °C. The choice of the stripping chemical depends on the material that has to be treated. Pure solvents are often used for light metal and non-ferrous metals; a mixture of solvents or aqueous alkaline solutions can be used for steel.

5 Solvent use, emissions and environmental impact

5.1 Solvents used

VOC with specific R-phrases

The use of CMR substances or halogenated solvents carrying risk phrase R40 is subject to specific requirements under the SE Directive (see chapter 1). Nevertheless halogenated solvents are still widely used because they have excellent cleaning properties. They have a high solvency power for a large variety of substances, low surface tension, non flammability, rapid and residue free evaporation, good recyclability and are suitable for a wide range of materials. The most commonly used halogenated VOC for surface cleaning are:

THERE IS A GENERAL OBLIGATION UNDER THE SE DIRECTIVE TO SUBSTITUTE CMR SUBSTANCES AS FAR AS POSSIBLE WITHIN THE SHORTEST TIME

- perchloroethylene (PER, perc, tetrachloroethylene), halogenated VOC (R40)
- dichloromethane (DCM, methylene chloride), halogenated VOC (R40)
- trichloroethylene (TRI, trike), CMR substance (R45)
- N-propyl bromide (nPB), CMR substance (R60)

Perchloroethylene – PER is typically used in the industrial surface cleaning of aluminium, magnesium, zinc, brass, and their alloys in closed installations. Perchloroethylene is the most commonly used halogenated solvent for vapour phase metal cleaning.

Dichloromethane – DCM is typically used for paint stripping.

Trichloroethylene – TRI has been used for vapour phase and cold cleaning. It was classified as an R45 substance in June 2001 and solvent sales in Europe show that it has already been widely replaced by other solvents - typically modified alcohols or perchloroethylene (manufacturers of closed cleaning systems have tended to prefer PER) or alternative technologies. However, finding a suitable replacement for cleaning products with a complex geometry (axle bearing) or for high-precision tools (already minor surface alterations lead to uncontrollable quality losses) has proven to be difficult.

N-propyl bromide – nPB is used for the same sectors and applications as trichloroethylene. It is mainly used to remove solder flux, wax, oil, and grease from electronics parts, metals, and other materials. The use of n-propyl bromide for surface cleaning is prohibited in Germany.

VOC without specific R-phrases

The following VOC solvents are used for surface cleaning :

A BROAD RANGE OF DIFFERENT VOC CONTAINING SOLVENTS IS USED FOR SURFACE CLEANING

- alkanes (isododecane, iso-paraffins, N-paraffins, kerosene)
- alicyclics (cyclohexane)
- alcohols (isopropanol, 1-butoxypropan-2-ol)
- polar aprotics (N-methylpyrrolidon)
- ketones (acetone, diketone)
- esters (N-butyl acetate)
- ethers (glycol ether).

N-methylpyrrolidon and higher-boiling glycol ethers are used for paint stripping, while kerosene, and iso- and n-paraffins are typically used for dewaxing.

5.2 Solvent consumption and emission levels

THE CONSUMPTION OF HALOGENATED SOLVENTS HAS DECREASED IN RECENT YEARS

The consumption of chlorinated solvents (VOCs with specific R-phrases) in Western Europe has steadily declined over recent years. Total European sales[4] of the three main chlorinated solvents - dichloromethane, perchloroethylene and trichloroethylene - decreased from 233,000 t/a to 182,000 t/a between 2003 and 2007 (these figures do not only relate to surface cleaning activities).

The falling consumption can be partly traced back to legal restrictions like the phase out of 1,1,1-trichloroethane (identified as ODS substance) and to a shift from chlorinated solvents to alternative solvents. The main reason for reduced consumption is, however, the increasing number of installations with closed systems and the improved process management. Improved emission control, an increased use of solvent recycling systems, and better management of wastes are all widely used.

Moreover the more stringent carcinogenicity classification of trichloroethylene has reduced the annual sales of the solvent by almost 60% since 2001. A further reduction of use (and emissions) of trichloroethylene is expected as the result of a voluntary agreement within the chemical industry, that after 2010 trichloroethylene will only be supplied for metal cleaning if users have totally enclosed equipment.

It is estimated that in Europe around 20 kt/year of chlorinated solvents are used for industrial surface cleaning[5]; use of non-chlorinated solvents (hydrocarbons) for metal/industrial cleaning is around 160 kt/year, which is 4% of European solvent consumption [ESIGc].

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[4] It should be noted that solvent sales reported here are those of virgin solvent sales made in the EU and do not take into account recycled solvents

[5] BiPRO estimate based on Eurochlor data

5.3 Key environmental and health issues

For surface cleaning activities a broad range of different solvents are used.

Process emissions of solvents, together with NOx emissions, are precursors of ground level ozone formation in the presence of sunlight. Existing occupational workplace limits should be taken into consideration.

Emissions of VOC to air may occur from:

- storage of the solvents

- cleaning process

Spills and leaks from storage areas may result in emissions to soil and groundwater.

The process generates waste containing solvents which need to be disposed in a way that emissions to air, soil and groundwater are prevented or limited.

VOC with specific R-phrases

The main environmental and health issues of the CMR labelled solvents result from their classification as carcinogenic, mutagenic, or toxic to reproduction.

The solvents trichloroethylene and N-propyl bromide are classified as category 2 CMR substances and there is some, limited, evidence of the carcinogenic effects of perchloroethylene and dichloromethane.

Perchloroethylene and trichloroethylene are toxic/harmful to aquatic organisms and may cause long-term adverse effects in the aquatic environment. Halogenated solvents, besides being air pollutants, are toxic to the aquatic environment.

VOC without specific R-phrases

The solvents 1-butoxypropan-2-ol, isopropanol, cyclohexane, N-methylpyrrolidon and acetone are classified as harmful and cause irritation to eyes and/or skin. Isopropanol, cyclohexane, acetone and N-butyl acetate are classified as “Vapours may cause drowsiness and dizziness”. Cyclohexane, isododecane and kerosene are harmful and may cause lung damage if swallowed. A repeated exposure to N-butyl acetate and acetone may cause skin dryness or cracking.

Some solvents are also toxic in the aquatic environment. Cyclohexane is highly toxic to aquatic organisms and may cause long-term adverse effects. Most organic solvents are highly flammable. Isopropanol, cyclohexane, acetone, isododecane are classified as high flammable, whereas N-butyl acetate is classified as flammable.

6 VOC Substitution

The following sections describe potential substitutes for VOC (using VOC-free and VOC-reduced systems). There are also descriptions of the application technologies or special conditions needed and the advantages and disadvantages compared to systems that use solvents with a high VOC content.

6.1 VOC-free systems

This section describes the ways that VOC-free products or systems can be used to replace the organic solvents currently used.

6.1.1 Substitution of VOC solvents with water based cleaning systems

Water based cleaning systems - a solution of water and detergent –are adequate for a great number of applications. Aqueous solutions of acid, alkali or neutral cleaners can be used for the industrial cleaning of some hard surfaces - metallic ones such as steel, aluminium, magnesium, copper etc., plastics, coated surfaces, glass and electronics components. Neutral (pH) cleaners are primarily used for intermediate and final surface cleaning, whereas strongly alkaline products are used to obtain very clean surfaces before surface enrichment, phosphatising or coating processes. Acidic products are used in special applications like cleaning of metals e.g. aluminium to remove metal oxides, slag's and inorganic residues from the surface.

WATER BASED CLEANING SYSTEMS MAY SUBSTITUTE FOR HALOGENATED AS WELL AS NON HALOGENATED SYSTEMS

Water-based cleaning systems can replace halogenated as well as non-halogenated solvents.

Water-based systems are now well established for a large number of industrial surface cleaning operations - some with even better cleaning results than the solvent-based systems they have replaced. The two main techniques used for water-based systems are immersion (ranging from small, ultrasonic, tanks through to multi-tank systems) and spraying/sprinkling.

Investments costs for water based installations are typically more than 50% lower than comparable solvent systems (enclosed, with air extraction). The operational costs for water based systems are highly dependent upon the choice of cleaning medium and the necessity for bath maintenance. In addition water based cleaning systems may be more energy intensive than solvent based cleaning because of the need for a drying stage. In some cases a final cleaning with deionised water may also be necessary. Water-based systems may produce more waste - the water content of the oil waste is often higher. The cleaning systems may have to be maintained/replaced more regularly to ensure constant product quality (service life from 3 weeks to 3 month) resulting in additional waste.

The efficiency of water-based cleaning can be enhanced by additional ultrasonic or megasonic cleaning systems. These systems consist of a transducer capable of generating particular sound waves. The sound waves are transmitted through the cleaning solution and create small vapour bubbles (micro-cavitation) which support the cleaning activity. Megasonic systems create smaller bubbles and so are more suitable for cleaning sensitive parts or cleaning where smaller amounts of contaminants need to be removed. It is possible to retrofit existing systems with this technology.

Another system which that improves the cleaning action is injection flood washing - where a jet is used to create vigorous turbulence within the liquid [Dürr 2008].

There are many water-based cleaning options available - for many different applications. But in all cases it is essential that water based agents are well suited to the products to be treated, can achieve the required cleanliness and are appropriate for specific process conditions being used by a company. In most cases some testing of alternative systems will be needed to find the right solution.

Biological cleaning agents

Biological cleaning agents can be effective substitutes for organic solvents used for cleaning activities at work stations.

The cleaning process is similar to other standard aqueous cleaning. Contaminants are removed from the metal surfaces by surfactants and emulsifiers and transferred to the cleaning bath. This emulsion is then fed to a separate tank. Provided the system is kept warm (typically up to 38 °C) the microorganisms in the cleaner decompose oils and grease to water and CO_2, the cleaning fluid is regenerated and its cleaning power is restored and the lifetime of the cleaner increases significantly. This water based system generates a relatively low amount of waste compared with conventional cold cleaning methods. [Kärcher 2008]

6.1.2 Carbon Dioxide Cleaning

CO_2 can be used as a solvent for the removal of oil, grease and other organic contaminants. Pellets of dry ice are blown, with pressurized air, at about 300 m/s onto the surface to be cleaned. The technique is particularly suitable for removing small amounts of organic contaminants - it is generally not suitable for the removal of rust, scale, powder varnishes, two-component paints and most inorganic compounds. A high degree of cleanliness is achievable and no residue is left. It is possible to clean electrical components and sensitive parts in situ.

Cleaning machines cost about 9,000 to 14,000 € and the dry ice about 0.6 €/kg, the machines consume about 30-50 kg dry ice/hour. If use exceeds ~60,000 t dry ice per year it becomes economic to rent a pelletizing machine at a costs of about 900 €/month. [ASCO 2008]

6.1.3 Plasma technology

Plasma technology (ion bombardment) may be used for removing thin films of organic contaminants. Two technologies are available: low pressure plasma system (LPPS) and atmospheric pressure plasma system (APPS). LPPS is especially suitable for treatment of components in batch processes while APPS can be integrated into automated systems (continuous processes). Either oxygen or argon are used as the process gas – depending on the materials to be cleaned and the composition of the contaminant.

PLASMA IS OFTEN USED IN COMBINATION WITH SURFACE ACTIVATION

Typical fields of application are the removal of grease, oxides, oil, silicones in the automotive and electronics industry, before industrial painting, or for pre-treatment before gluing or soldering. Plasma cleaning, in combination with surface activation, is often used as pre-treatment in the plastic industry to improve the bonding of water based paints. Plasma cleaning leaves no residues on the surface so there is no need for a rinsing step.

Water-based or semi-aqueous cleaning is often used for a pre-cleaning step prior to plasma treatment because plasma cleaning is only effective on thin-film contaminants (< 1µm) and is ineffective when inorganic materials are present.

The investment costs depend on the size of the installation and vary between 8,000 € and 400,000 € (for work pieces up to a diameter of 2.5 m). Installations are available from 2 liters (laboratory scale) up to 13,000 l, but customised installations are available too.

The operational costs are very low as no specific chemicals are needed (see also example in chapter 9.4). [Diener 2008]

6.1.4 UV Cleaning

Ultraviolet (UV) light and ozone can be used to remove organic contaminants from the surface of substrates such as photoresists and semiconductors. The cleaning agents are the oxygen free radicals formed when ozone and hydrogen peroxide decompose; these react with and decompose the organic contaminants. As with plasma cleaning a pre-cleaning step may be needed.

6.1.5 Laser cleaning

Laser cleaning is especially applicable for high-quality surfaces in the automotive, aviation or electronics industries. This technique employs pulsed laser radiation to remove organic protective layers and coatings either layer by layer or in their entirety. No additional cleaning chemicals are required. As well as being suitable for paints, adhesives, and other coatings, this technology can be used to remove plastic and rubber residues, and oxide layers.

The operating costs of this technology are very low but there are high investment costs.

6.1.6 Dewaxing

THE NEED OF DEWAXING WITH SOLVENTS CAN BE SIGNIFICANTLY DECREASED

In the automotive sector self-adhesive foils (PVC or PU) fixed by a water film on the surface and spray-on films (aqueous polyester-polyurethane dispersions) are steadily replacing dewaxing with organic solvents for both economic and environmental reasons [AUDI 2002], [FOLIATEC 2008], [SDK 2008].

6.1.7 Thermal paint stripping

Thermal paint stripping is applicable to all thermo-resistant materials like (stainless) steel, aluminium, etc. The process takes places in an oven at temperatures of 250-430 °C for a period of between 3 and 12 hours (depending on the material). The paint adhering to the workpiece is burned and after cooling additional treatments such as sandblasting or high-pressure water washing can be used to remove the remaining ash. This method is not suitable for plastics and wood.

VOCs are destroyed with this technique but the exhaust gases have to be treated by thermal oxidation. On the other hand, there is no waste water or sludge to be disposed of and maintenance costs are lower than for solvent based systems, while the energy consumption will be higher.

6.1.8 Laser cleaning

Laser cleaning is especially applicable for high-quality surfaces in the automotive, aviation or electronics industries. This technique employs pulsed laser radiation to remove organic protective layers and coatings either layer by layer or in their entirety. No additional cleaning chemicals are required. As well as being suitable for paints, adhesives, and other coatings, this technology can be used to remove plastic and rubber residues, and oxide layers.

The operating costs of this technology are very low but there are high investment costs.

6.2 VOC-reduced systems

If the complete substitution of organic solvents is impractical then changing to systems with a reduced VOC content, such as those described in this section, can decrease emissions.

6.2.1 Use of low VOC content products

Several low VOC content products are available on the market that might replace systems with higher solvent contents.

In addition, semi-aqueous cleaning systems are available that contain only a small amount of solvent. For example in the micro-phase cleaning system (MPC), an aqueous mixture of polar and non-polar components (at a concentration ~ 10%) is heated and agitated, the dirt removed does not bond with the active cleaning agents and can be removed by filtration. Besides reducing VOC emissions this system is reporting to have a long service life [Cleantool].

7 Other VOC emission prevention measures and abatement techniques

A complete substitution of VOC is not always possible, but in many cases additional possibilities exist to reduce VOC emission. The following measures are commonly applied to reducing VOC emissions from surface cleaning processes.

7.1 Use of closed systems

The enclosure of cleaning operations can be a highly effective way to reduce VOC emissions. Sealed chamber systems (as described in chapter 4) reduce direct solvent emissions by over 90% compared to open equipment and reduce solvent consumption by about 60-80% - depending on the solvent content of the waste transferred for external recycling [Dow 2008].

ENCLOSED HAVE SYSTEMS SIGNIFICANTLY LOWER VOC EMISSIONS

An overview of the characteristics of the different machine types (generations) is given in Table 3. The emission and consumption reductions achieved are shown in Figure 5.

Table 3: Differences between the different technologies for surface cleaning

Technology generation	Construction type	Closed loop drying with refrigeration	Solvent recycling	Vapour extraction	Activated carbon filter
Type I	Open top	No	External	No	No
Type II	Enclosed	No	External	Yes	No / Yes
Type III	Closed (sealed)	Yes	Integrated	Yes	Yes
Type IV	Closed (sealed)	Yes	Integrated	No	Yes

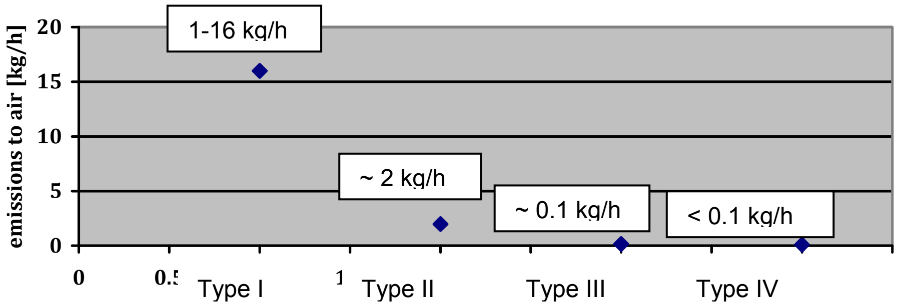

Figure 5: Development of surface cleaning technology and related air emission [Dow 2008]

In the following a short description of the above mentioned machine types is given:

Type I installations are open with no specific VOC control measures (open-top systems). The use of these installations has decreased significantly during recent years due to stricter environmental and occupational health legislation. In addition the solvent consumption – and thus the cost - is very high (see chapter 4.2.2).

Type II installations are similar to type I but are enclosed. This installation type remains widely used. Enclosed vapor degreasers incorporate both refrigerated condensation and an external carbon adsorption/desorption phase to trap and regenerate solvent.

Type III installations are closed loop systems with integrated solvent recycling. With these installations the VOC emissions resulting from the cleaning activity can be significantly reduced (~ 0.1—0.2 kg/h). For a more detailed description see also chapter 4.2.1.

Type IV installations are closed loop (sealed) systems with vacuum technology. This technology results in significant emission reduction. Closed loop operation, in combination with the vacuum technology and deep temperature condensation (< 180°C), reduces the emissions to air to a minimum of 0.001 kg/h. For a more detailed description see chapter 4.2.1). These installations have no exhaust so vapour extraction is not necessary.

7.2 Further process improvements

Use of spraying to enhance cold soaking and vapor degreasing

Spraying can enhance the cleaning efficiency of cold soaking and vapour degreasing. However emissions may increase if carried out incorrectly - low pressure spraying should be used and it should be carried out below the top of the vapour level.

Improved containment achieved by improved covers

Evaporation from cold cleaning baths can be controlled using a cover, by allowing an adequate freeboard height, and by avoiding excessive draft in the workshop.

Improved handling of solvents

Solvents should be stored in separate safety containers - one for fresh and one for used solvent. Dry-break couplings can be used to ensure leak-free transfer of solvents from containers to enclosed cleaning machines.

Generally, all containers (including those for waste) should have covers to prevent evaporative losses.

IMPROVED HANDLING AND MANAGEMENT OF SOLVENTS SIGNIFICANTLY REDUCES THE CONSUMPTION AND EMISSIONS OF VOC

Product/process design to reduce the need for cleaning

A regular re-assessment of the production process can improve manufacturing efficiency - and help to minimise VOC emissions - by identifying causes of contamination and eliminating or minimising it at the source. Typical measures to consider include:

- Tracing the source of soiling (e.g. impurities in oils) and where possible eliminating, changing or reducing the level of contamination to avoid or reduce cleaning steps
- Elimination or modification of interim cleaning processes;
- Reducing the time between cleaning and further processing;
- Pre-cleaning, e.g. manual removal of excess oil before cleaning;
- Using counter-current cleaning.

Optimized cleaning

Optimal cleaning results, with minimal VOC emissions, can only be achieved when the technology and products used are matched to the cleaning requirement. The selection should address the:

- Type of surface (e.g. metal, rubber);
- Geometry of the surface which has to be cleaned;
- Variety of parts to be cleaned;
- Required 'cleanness' of the surface;
- Type of contaminants present;
- Associated process technologies;
- Quantity of parts to be cleaned;
- Continuous or batch process.

OPTIMAL CLEANING RESULTS DEPEND ON THE SELECTED CLEANING PRODUCT AND TECHNOLOGY

Many solvent and equipment suppliers have optimised solutions for different sector applications and provide information on the Internet[6].

7.3 Abatement technologies

Where solvent capture and recovery is not a part of the cleaning installations abatement technologies may be needed to reduce VOC emissions.

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6 Activated carbon is suitable for both halogenated and non-halogenated solvents. The recovery of the solvents can either take place on site or [1] e.g. www.cleantool.org

The most common systems for surface cleaning systems are described below.

7.3.1 Activated carbon adsorption

external. On site recovery is of limited benefit to small companies as the carbon regeneration equipment is costly and experience is needed to use it properly. This is especially true for the systems for halogenated solvents.

Activated carbon is applicable for flow rates between 100 and 100,000 m³/h, with solvent concentrations of up to 50 g/m³. The recovery rate depends on, among others, the type of activated carbon used and the operating conditions. Fresh activated carbon costs about 1-1.50 €/kg, the cost for external recovery of the solvents is about 0.60 €/kg. [Donau Carbon 2008]

Compared with the investment costs for thermal oxidisers (about 150,000 €), those for activated carbon filters are significantly lower (20,000-30,000 €) but the operational costs (replacement of the activated carbon) are higher. [CTP 2008]

7.3.2 Thermal oxidation of solvent emissions

Thermal oxidation is only recommended for non-chlorinated solvents unless high temperature (> 1,100 °C) is used. Otherwise, there is a risk of generating chlorinated pollutants (e.g. dioxins) when chlorinated solvents are burned.

THE AUTO-THERMIC POINT OF REGENERATIVE THERMAL OXIDATION IS ABOVE 2-3 G VOC/NM³ IS EXCEEDED

Two types of thermal oxidiser are in common use, regenerative and recuperative. Both destroy VOCs by burning (oxidation), but the systems differ in how waste heat is recovered.

Regenerative thermal oxidation has at least two heat exchangers, these consist of beds filled with material that will allow air to pass while serving as a mass to absorb and store heat. While one bed is heated by the exhaust gas from the burner another bed releases the stored heat to the VOC containing incoming gas. In recuperative thermal oxidation the heat is transferred directly - via a heat exchanger - from the outgoing air stream to the incoming air stream.

Regenerative oxidation tends to be more efficient than recuperative thermal oxidation as it uses the recovered energy more efficiently to pre-heat incoming process air to oxidation temperatures (~ 800 °C), consequently its operating costs are significantly lower than for recuperative oxidation systems. Regenerative thermal oxidation systems (RTO) are particularly effective for process streams with relatively low solvent loadings but their operating costs are highly dependent on the efficiency of the heat exchanger.

Regenerative thermal oxidation systems are widely used because they are relatively insensitive to the composition of the solvents in the process air and the concentration.

Recuperative systems are mainly used for small flow rates - at higher rates the systems are not cost effective. They are often used in combination with catalytic oxidation systems.

Natural gas is needed to heat up thermal oxidisers to an operating temperature of 800 °C (1,100 °C in case halogenated solvents), and the process is only autothermic when the VOC concentration of the waste gas is above 2-3 g VOC/Nm^3 (for regenerative thermal oxidation). The resulting heat of the burning process, however, can be recovered and can be used for different purposes e.g. steam production.

8 Summary of VOC emission reduction measures

The following table summarizes the various approaches to substitute or reduce VOC emission as described in chapters 6 and 7:

Table 4: Measures for VOC substitution and VOC reduction in surface cleaning activities

Objective	Details
VOC-free Systems / Substitution of CMR substances	Water based cleaning systems Semi-aqueous cleaning system Biological systems Plasma cleaning technologies Carbon dioxide cleaning technologies UV cleaning technologies Laser cleaning Avoiding the need for dewaxing by using films Thermal paint stripping
VOC-reduced Systems	Using low VOC content products
Process improvements	Using closed systems Using spraying to enhance cold soaking and vapour degreasing Improving containment Improving solvents handling Reducing the need for cleaning activities Selecting the best technologies
Abatement technologies	Activated carbon Thermal oxidation (regenerative / recuperative) of solvent emissions

9 Good practice examples

9.1 Example 1: A new installation using PER as cleaning agent

An automotive industry company that cleans parts for fuel tank filler necks has recently installed a new sealed single chamber cleaning installation with a vacuum system (type IV installation, see chapter 4.2.1) at an investment cost of 240,000 €. PER is the cleaning agent used and the annual throughput of the installation is ~800 t, ~11 million stainless steel parts/year are processed, these are contaminated with stamping/drawing oils (with some chlorine and sulphur content). The consumption of solvents is significantly less than would have been needed for a conventional installation - according to the company the amount of solvent (PER) purchased to compensate for loss of solvent by emissions to air was 585 kg in the last 3 years. Compared to conventional systems this represents a VOC reduction of more than 99%. [Pero 2008]

9.2 Example 2: Process improvement (VOC without specific R-phrases)

A medium-sized automotive and electro-tool industry company has replaced a closed single chamber system with a vacuum system at an investment cost of ~ 400,000 €. The annual cleaning activity is ~2,600 t with an hourly throughput of 1.5 t. The materials to be cleaned are steel, stainless steel and aluminium, they are contaminated with emulsions or oils. With the new vacuum system the amount of solvents (hydrocarbons) purchased to compensate for losses has reduced from 6,000 l/y to 2,600 l/ year - a reduction of 57% compared to their old system. Compared to conventional systems this represents a VOC reduction of more than 99%. [Hösel 2008]

9.3 Example 3: Use of Plasma cleaning technology for degreasing and surface activation of plastic parts

Plasma cleaning technology may be used in combination with surface activation for further process steps. The VOC consumption (and emissions) are reduced to zero.

Typical operational costs for a cleaning process are as follows:

- Cleaning volume per process: 20-40 litre
- Process duration: 15-20 min
- Oxygen consumption: ~ 0.1 l/min → 1.5 l/process
- Oxygen costs: ~ 4 € per 1,000 l
- Electrical power: ~ 2.5 kWh → ~ 0.83 kWh/ process
- Maintenance: ~ 2,000 € per year

10 Emerging techniques and substitutes under development

Relatively few novel developments have been found in the literature for either new technologies, improvement of existing technologies or new/modified, non-VOC cleaning agents. However a new business model is being developed based on greater cooperation between solvent suppliers and equipment suppliers to provide an optimised solution for cleaning tasks. In this 'solvent leasing' model, payments are not based on volumes of chemical used but on the benefits achieved (e.g. number of cleaned pieces instead of kg hydrocarbons). [Chemical Leasing 2004], [Chemical Leasing 2007]

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Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Guidance 6 – Part 1:

Vehicle coating and vehicle refinishing

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses vehicle coating with an annual solvent consumption of less than 15 tonnes and vehicle refinishing and the related cleaning of equipment, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emission Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
Vehicle coating is defined by the SE Directive as 'any activity in which a single or multiple application of a continuous film of a coating is applied to vehicles as listed below: ▪ new cars, defined as vehicles of category M1 in Directive 70/156/EEC (1), and of category N1 in so far as they are coated at the same installation as M1 vehicles, ▪ truck cabins, defined as the housing for the driver, and all integrated housing for the technical equipment, of vehicles of categories N2 and N3 in Directive 70/156/EEC, ▪ vans and trucks, defined as vehicles of categories N1, N2 and N3 in Directive 70/156/EEC, but not including truck cabins, ▪ buses, defined as vehicles of categories M2 and M3 in Directive 70/156/EEC.'
Vehicle refinishing is defined by the Directive as 'any industrial or commercial coating activity and associated degreasing activities performing: ▪ the original coating of road vehicles as defined in Directive 70/156/EEC[1] or part of them with refinishing-type materials, where is carried out away from the original manufacturing line, or ▪ the coating of trailers (including semi-trailers) (Category O)'

This guidance document only addresses vehicle coating in installations with a solvent consumption between 0.5 and 15 tonnes/year.

Vehicle coating in installations exceeding this solvent consumption and other metal coating, exceeding a solvent consumption of 5 tonnes/year, are covered by the SE Directive but addressed in separate guidance documents: for vehicle coating > 15 tonnes/year see guidance no. 6 part 2, and for other metal coating see guidance no. 8.

Before 2004, the definition of vehicle refinishing given in the SE Directive also included 'coating of road vehicles[2], or parts of them, carried out as part

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1 Article 1: 'For the purposes of this Directive, "vehicle" means any motor vehicle intended for use on the road, with or without bodywork, having at least four wheels and a maximum design speed exceeding 25 km/h, and its trailers, with the exception of vehicles which run on rails and of agricultural tractors and machinery.'

2 as defined in Directive 70/156/EEC, see footnote above

of vehicle repair, conservation or decoration outside of manufacturing installations'. However, these processes have been excluded from the Directive 2004/42/EC and the products used for them are now regulated under the Paints Directive.

The SE Directive lays down the following activity specific emission limit values for vehicle coating with an annual solvent consumption of less than 15 tonnes and for vehicle refinishing:

Table 2: Emission limit values (ELVs) of the SE Directive

SE Directive - Emission limit values (ELVs) (Annex II A – activity No. 6-Part 1)			
Activity	**Solvent consumption threshold [tonnes/year]**	**ELVs in waste gases [mg C/Nm^3]**	**Fugitive emission values [% of solvent input]**
Vehicle coating	> 0,5 - 15	50 *	25
Vehicle refini-shing	> 0,5	50 *	25
Special provisions: * Compliance in accordance with Article 9 (3) should be demonstrated based on 15 minute average measurements			

The SE Directive applies to Vehicle coating and vehicle refinishing activities in installations with an annual solvent consumption of more than 0.5 tons

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[3] as well as for halogenated VOCs which are assigned the risk phrases R40 or R68[4]. There is a general obligation to replace CMR substances– as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated[5] VOC with R40 the ELVs in waste gases are 2 and 20 mg/Nm^3 respectively, and these also apply when a reduction scheme is being used.

[3] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

[4] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: 'Possible risk of irreversible effects'. The new wording is: 'Limited evidence of a carcinogenic effect'. In the 'old' version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: 'Possible risk of irreversible effects'. This new risk phrase does not include carcinogenicity. The 'new' version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to this change, a final decision on which version applies can only be given by the European Court

[5] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.

National legislation may define lower solvent consumption thresholds, stricter emission limit values or additional requirements.

2 Summary of VOC substitution/reduction

The most important sources of solvent related VOC emissions depend on the solvent content of the products used for the coating and refinishing of vehicles.

VOC emissions can be reduced by using more effective application techniques (thus reducing overspray and the total amount of solvent used).

Lower emissions may also be achieved by reducing the solvent content in the coatings and fillers (use of 'high-solids' products) or by a change of the coating system (e.g. from conventional coatings with a solvent content of about 70 % to water based products with a solvent content of about 4 - 15 %).

In some cases, VOC emissions can be totally eliminated with the substitution of solvent-based application techniques by powder coating.

VOC REDUCTION CAN BE ACHIEVED MAINLY BY MORE EFFECTIVE APPLICATION TECHNIQUES OR BY SUBSTITUTING SOLVENT-BASED COATINGS WITH WATER BASED COATING SYSTEMS OR POWDER COATINGS

3 Description of the activity and related industry sectors

In Europe there are about 500 sites, producing commercial vehicles, which have a solvent consumption not exceeding 15 t/a. [DuPont-1 2008]

Vehicle coating activities involving vans, trucks and buses where VOC consumption is between 0.5 and 15 t/a are likely to include operations for manufacture of special purpose vehicles (ambulances, fire engines, money transporters, camper vans, etc.).

If original coating of passenger cars[6] is carried out away from the original manufacturing line and refinishing-type materials are used, these coating activities are classified as vehicle refinishing (> 0.5 t/a). This is typically done to meet special customer needs e.g. for coating of a car fleet for an individual customer.

The same category of 'vehicle refinishing' applies if coating of original parts of any vehicle is carried out away from the original manufacturing line with refinishing-type materials. Examples of parts treated in this way, in installations with < 15 t/a solvent consumption, are switches and other small parts used in serial production as well as parts like buffers or rims coated in special colours.

All coating of trailers (e.g. freight trailers, animal trailers and tippers), including semi-trailers, is classified as vehicle refinishing.

Vehicle coating and refinishing processes must both deal with the following technical challenges:

- Coating of complex three-dimensional objects

[6] as defined by Directive 70/156/EEC, see footnote above

- Coating of multiple substrates (steel, cast metal, aluminium, magnesium, zinc, wood, thermoplastics, duroplastics, fibre-enforced plastics)

- Need for coating systems easy to apply under the conditions of small and medium sized enterprises (e.g. coating by both automatic and manual techniques, drying without automatic drying ovens)
- High quality is required in all stages of pre-treatment, coating application and finishing operations
- Coating systems need to perform well in a number of different ways including providing good protection from physical and chemical attack, good adhesion and elasticity, etc.
- A large range of fleet and individual colours are required both on car bodies and add-on parts

Refinishing-type coatings can meet all of these requirements. There are two important differences between vehicle refinishing-type coatings and those coatings used for serial production of vehicles.

Firstly, while serial-type coating systems have a drying temperature of about 140°C, refinishing-type coatings are (typically 2-component) paints with a drying temperature of 20 - 80°C so drying requirements are much lower.

Secondly, any colour that is required may be easily mixed on site in the case of refinishing-type coatings, whereas this is not feasible for serial-type coatings (more details are given in chapter 5.1)

4 Technical process description

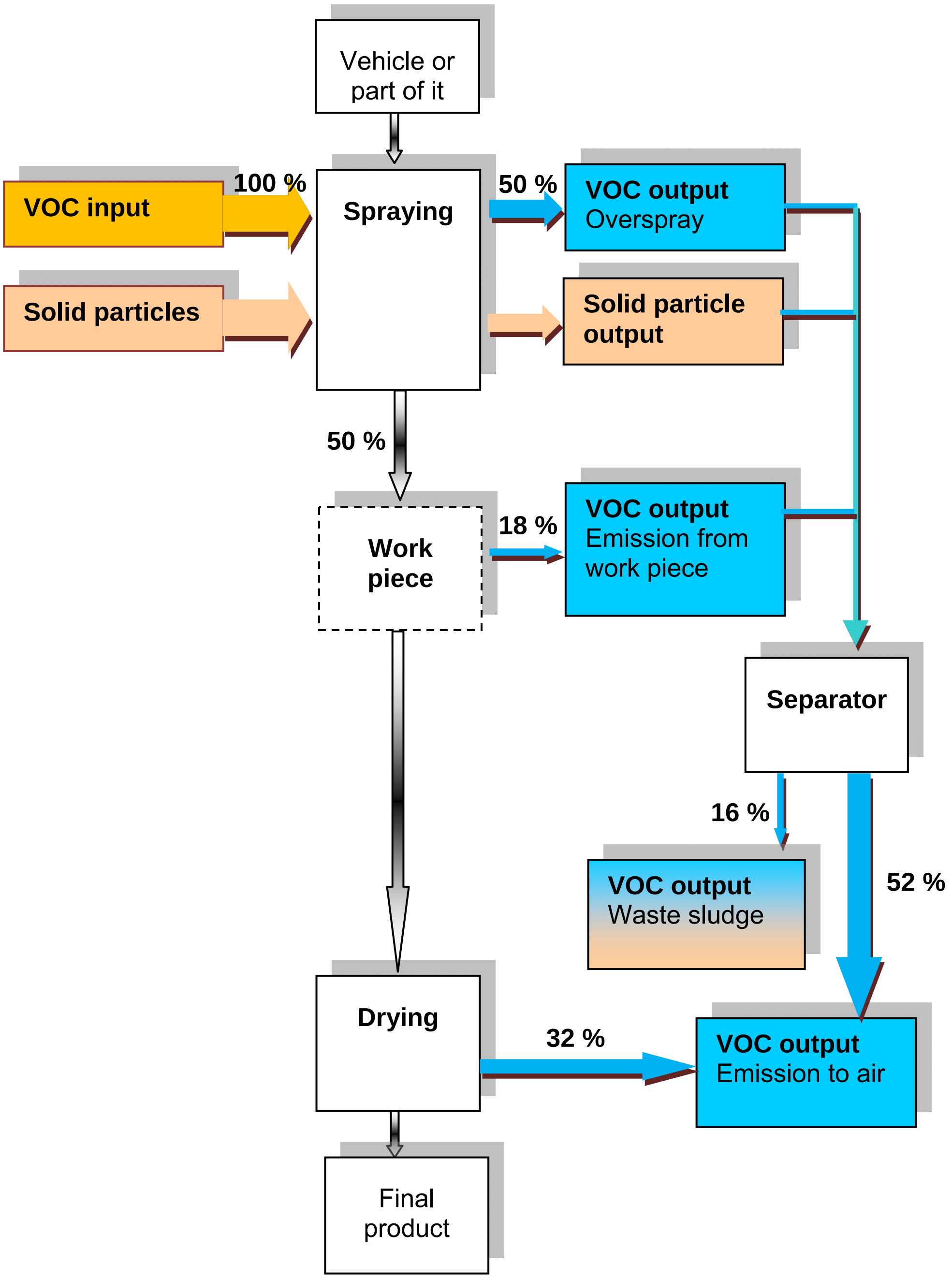
4.1 Process flow and relevant associated VOC emissions

Spraying with solvent-based coatings is the most commonly used application technique for both refinishing and small-scale vehicle coating. The following flow chart gives an overview of the typical process steps, and the VOC emissions that can occur, assuming the use of conventional spray coating techniques applying a solvent-based coating with a solid content of 50 %, and further assuming 50% overspray.

In practice, conventional spray coating may have a coating efficiency between 5% and 60%, depending on the geometry of the work piece (plane surface or lattice-like) and the skill of the sprayer.

A change of the coating efficiency (e.g. due to a change of spraying technique) or the solvent content of the coating would have a corresponding impact on the VOC flows shown in the flow chart.

TYPICAL VOC EMISSIONS OF CONVENTIONAL SPRAY COATING



Based on [DFIU 2002]

Figure 1: Exemplary VOC emissions from spray application with conventional technology

4.2 Process description

Coating processes can differ significantly due to the fact that a wide range of products are used. Typical process steps and coating application techniques are described below.

4.2.1 Degreasing

In cases where special purpose vehicles are given original coatings they (or the parts of them to be coated) are sandblasted, in most cases, and further degreasing is not necessary. The same is also true for trailer chassis. In cases of local contamination e.g. with oil from final drilling or cutting activities, these areas of the work piece would usually be cleaned manually by brushing or wiping. Degreasers used for this type of application would usually have a high VOC content, from about 50% up to 100%.

Typically, smaller vehicle parts will be pre-cleaned either with a water-based cleaning liquid using a pressure washer or with solvent containing cleaners applied by spraying. [VDL 2008]

For further details of degreasing see guidance no. 4/5 on surface cleaning.

4.2.2 Application techniques

Coating systems - and therefore the application techniques - differ depending on the products coated. In practice three main groups of coated products need to be distinguished [DuPont -1, 2008]:

Coating of special purpose vehicles: The choice of coating system depends not only on the requirements of the work piece (e.g. the corrosion resistance to be achieved) but also on the size, available equipment and core business of the paint shop or company performing the coating.

Generally, for the coating of special purpose vehicles, 1- or 2-layer-coating systems applied via **spray coating are dominant**.

Electrophoretic dipping is a major technique for applying the primer systems for the **coating of trailers**. Even small, niche, producers of specialised trailers use standard chassis pre-treated in this way. Various types of spray coating are then used for subsequent coating layers in the case of small scale or specialised trailer production, whereas for large scale production powder coatings are typically used.

In some instances, trailers are not coated at all, but are instead either galvanized or left as bare aluminium.

Coating of parts of road vehicles: Parts, including buffers, condenser grills, roof luggage rails and door handle claddings are made of a variety of materials have a wide range of work piece geometries. Nevertheless, the application techniques are usually the same: either conventional spray coating, electrostatic or electrostatic assisted spray coating or conventional dipping.

Conventional high and low pressure spraying

Coating material is ejected from the nozzle of a spray gun using compressed air. The air transports the particles of the coating material onto the surface of the work piece.

The higher the pressure of the air, the finer the particles of the coating material. Fine particles increase the quality and the smoothness of the coated surface. On the other hand, the finer the particles, the greater the ease with which they are deflected by the airflow from the coated surface and this leads to increased coating waste (overspray). Conversely, if the pressure is too low, the coated surface is of poor quality (e.g. an 'orange peel' effect is created).

The coating efficiency varies between 5 % (for lattice-like work pieces) up to 30 – 60 % (for work pieces with large and plane surfaces).

Conventional spray coating is applicable for any surface and is used in particular for topcoats because of its ability to achieve high quality finishes and special surface effects (e.g. metallic or pearl look). [DFIU 2002] [BREF STS 2007]

High volume low pressure spraying (HVLP)

For high volume low-pressure spraying (HVLP), the atomising pressure is decreased from the conventional 3 – 6 bar down to 0.7 bar. Compared to high-pressure spray coating, up to 20 % overspray can be avoided and the coating efficiency is about 40 - 80 %.

Due to the larger particles of coating material created by HVLP sprays, the quality of finish may not match that achieved with conventional, high pressure, air guns. However, improvements in HVLP gun design are such that the most modern designs are able to match the quality of finish achieved by high-pressure guns. [DFIU 2002] [BREF STS 2007]

Airless spraying

In airless spray coating, the paint is forced through very small metal nozzles (< 2 mm) with a pressure of 80 to 250 bar. The paint jet strikes the stationary air outside the nozzle and is broken up in fine particles due to the force of this impact.

The paint is delivered to the nozzle using high-pressure pumps and this prevents quick colour changes. However, a high throughput of coating is possible. Airless spray coating is cheap and fast and can be used for 1-component and 2-component paint.

Airless spray coating gives a rough finish that needs to be sanded before finer coatings can be applied. This introduces an additional process stage compared with the use of high pressure air spraying. However, optimisation of the spraying can improve finish quality to close to that achieved with HVLP guns, especially with primer coatings. Operator training is essential in order to maximise the performance of airless spraying systems.

This spraying technique may be used either manually or automatically. Material efficiency for airless spray coating is about 5 % (lattice-like work pieces) up to 40 – 75 % (large surfaces). [DFIU 2002] [BREF STS 2007]

Electrostatic spray coating

An electric field is created between the work piece and the coating material, these having opposite polarity. Coating material is atomised and sprayed; the particles are attracted to the work piece. The process halts when the film thickness is nearly equal on all surfaces and edges. Cathodic coating is the most widely used technique as anodic work pieces tend to corrode.

In general, the efficiency of electrostatic spray coating is from 95 % up to 100 %. Compared to conventional spray coating, electrostatic spray coating is more time and material efficient and easier to automate. Less waste residues are generated and spray booths require less cleaning.

For electrostatic spraying to work, the work piece has to be conductive. This limits the substrates and coatings that can use the technique (e.g. it is not possible to recoat existing coatings). In addition geometries that act as Faraday cages have to be avoided because the coating is applied to them unevenly. .

Electrostatically assisted compressed air, airless and air assisted spraying

These techniques combine paint material atomisation similar to regular compressed air or airless spraying with the electrostatic charging of paint particles

For compressed air, the material flow is up to 1000 ml/min, for airless or assisted airless techniques the material flow can be up to 3000 ml/min. The material efficiency is up to 85 %.

Compared to conventional spraying, less overspray is generated and spray booths are less polluted. Therefore, less cleaning agents are needed.

With electrostatically assisted spraying more complex geometries can be coated than with electrostatic spray coating.

[BREF STS 2007]

Conventional dipping

Work pieces are either dipped manually or transported and dipped via conveyor systems. Dipping into water-based paints might produce foam. Water-based paints are only stable over a small range of pH levels and, therefore, very sensitive to contamination that might be introduced from the pre-treatment processes.

This technique is quite cost effective and can achieve a material efficiency of up to 100%, [BREF STS 2007]

The finish quality for this coating technique is low. It is used for coating of small parts for the commercial vehicle sector. This technique is not applicable for coating of open-cell surface structures. [VDI 2008]

Electrophoretic dipping

In the process of electrophoretic dipping, a direct electric current is made to flow between the work piece and the electrodes of opposite polarity installed in a tank.

Cathodic (work piece loading) systems are commonly used, because they offer better resistance against corrosion than do anodic systems.

Electrophoretic dipping is only used with water-based coatings with a solvent content between 1 – 4 %.

Electrophoretic dipping is an efficient application technique that produces high quality coatings. However, it is a cost intensive system (investment and material costs), and requires a high level of maintenance of the paint tanks for quality assurance. [BREF STS 2007].

In the scope of this guidance, this technique is usually only used for the priming of trailers. As the work piece has to be conductive and has to be able to withstand temperatures of approx. 180°C, this technique cannot be applied for wooden trailer parts. Primer coats applied by electrophoretic dipping are usually followed by a powder coated topcoat.

Application of powder coatings

Powder coatings are applied and then melted and cured by heating the work piece at 200°-250°C [BREF STS 2007].

Powder coating – electrostatically assisted spraying: The powder particles are electrostatically charged and sprayed onto the work piece using compressed air. Spray booth and application tools can be cleaned by vacuum cleaning or by blowing with compressed air. There are no solvent emissions associated with this spraying process.

Material efficiency is about 80 – 95 %. [BREF STS 2007]

Powder sintering: The work piece is heated above the melting temperature of the powder coating before coatings are applied. As soon as the powder is in contact with the surface, sintering and merging takes place.

A high material efficiency can be achieved. [BREF STS 2007]

Powder coating is subject to similar restrictions as is electrophoretic dipping. The working piece has to be able to withstand the high temperatures used to melt and cure the powder. Therefore, this technique cannot be applied e.g. for plastic parts.

4.2.3 Drying

After the application, the coating has to dry.

In general, the refinishing-type coatings used in this activity have the ability to dry at ambient air temperatures in the workshop or outside. (see chapter 5, solvents used).

The drying time can be reduced by the use of additional drying units (ovens). Spray booths may also function as ovens.

The drying time depends on the object or substrate, the type of coating and the coating thickness, and varies from a few seconds to one hour.

For the drying of water-based coatings or a pre-drying step of wet-on-wet layer constructions, dehumidified air is used, with convection driers and an additional dehumidification step. Due to the removal of water in this manner, the drying times can be significantly reduced. [BREF STS 2007]

4.2.4 *Cleaning*

Cleaning needs to be undertaken in all application techniques: for work pieces, for work place environment, coating equipment and parts thereof.

A range of cleaning techniques can be used, from manual cleaning to automatic cleaning (e.g. for spray guns and parts), using closed systems with solvent recovery. Solvent cleaners are used (and sometimes heated for higher efficiency) as well as water. Cleaning with water is possible when water-based coating systems are used and when the cleaning is performed before paints have dried.

Cleaning needs to be effective and fast. Cleaning intensity varies according to the nature of colour changes and is also dependent on whether the contamination is semi-dry or dry.

[BREF STS 2007]

Spray booths are usually cleaned with cleaners with a low VOC content. An alternative approach is the use of a film or a strippable varnish, applied to the walls of the booth. [VDI 2008]

5 Solvent use, emissions and environmental impact

5.1 Solvents used

Coating systems for the activities covered by this guidance in most cases consist of two layers, a primer and a top-coat.

The **primer** is used for the first treatment of the metal surface, providing an anticorrosive function and helping to increase bonding of the subsequent coating.

A typical conventional primer for metal surfaces is based on polyvinylbutyral resin. These primers have a total solvent content of 55- 65 % w/w. More modern systems are either epoxy based (with a solvent content of about 40 % w/w) or polyester based (solvent content of about 20% w/w). Primers for larger-scale trailer production are applied by electrophoretic dipping, and are water-based with a solvent content of < 5%.

For most products **top-coating** is performed with a single layer system. This single layer coating has to provide both the colour/appearance and protection against chemical or other attack (sunlight, mechanical impact, etc).

The single layer coating may either be a 1-component system with a typical solvent content of about 45 - 55 % w/w or a 2-component system with solvent content of about 25-35% w/w. As an alternative, water based systems may be used with a VOC content of about 10-15% w/w.

In cases where very specific colour effects need to be achieved (e.g. on some components for passenger cars) two- or multi-layer systems are used. The two coat systems consist of a basecoat providing colour, followed by sealing with a clear topcoat. For multi-layer systems, an additional colour -coat is applied (intermediate coat). [VDI 2008]

All coatings are of the vehicle refinishing-type, drying at between 20°C – 80°C. The coatings can be produced in a wide range of colours and are mixed, often on-site, but also off-site by the coating supplier from 30 'basic' colours. This colour-flexibility is of great importance to the vehicle coating & refinishing sector, particularly for trailer coating and coating of cars for special purposes.

Solvents in conventional solvent-based coatings (solvent content > 40 % w/w) are mainly mixtures of organic hydrocarbons (xylene, toluene and white spirit), although alcohols, esters and ketones are also used. [DFIU 2003]

In high-solid coatings (solvent content < 35 % w/w) the following solvents are used: xylene, white spirit, aromatic hydrocarbon mixtures, butyl acetate, alcohols, and glycol ethers. Ketones and toluene do not play a significant role in Europe.

Water-based coatings in most cases contain organic solvents (solvent content 10-15 % w/w) as a solubiliser and to improve the properties of the wet film layer. The main solvents used are glycol ethers and alcohols. Most glycol ethers are alkyl ethers of ethylene glycol (e.g. 2-butoxyethanol) propylene glycol. The latter are used in place of the toxic ethers 2-ethoxy-ethanol and 2-methoxyethanol.

Powder coatings are VOC-free.

5.2 Solvent consumption and emission levels

General data on solvent consumption and emission levels are difficult to obtain due to the variety of vehicles and parts coated as well as the variety of application processes used. For small-scale vehicle coating less automation of processes is typical, and more difficult product geometries and sizes have to be coated. These factors both result in less efficient application and thus higher emission rates than achieved with large-scale vehicle coating.

Installations coating special purpose vehicles often need to meet individual customer requirements, and make more frequent use of metallic colours (which are applied as solvent-based coatings) than large-scale car coating installations. The higher range of colours used leads to increased cleaning requirements. [BREF STS 2007]

Conventional solvent based coatings for cabins are, typically, associated with VOC emissions of 193 – 233 g VOC/m^2, while for buses the emissions are approximately 225 g/m^2. [BREF STS 2007]

VOC emissions from conventional coating systems for aluminium rims/wheels are reported to be about 66 g/wheel; while with water-based coatings, 4 g/wheel is achieved. [BREF STS 2007]

Cleaning

Cleaning processes with organic solvents account for about 20 % of total VOC emissions from paint shops. [BREF STS 2007]

Emissions from cleaning can be reduced to < 20 g/m2 by using good practice in housekeeping, cleaning and substitution techniques. [BREF STS 2007]

5.3 Key environmental and health issues

In vehicle coating and refinishing a broad range of different solvents is used for coating materials and cleaners.

Process emissions of solvents, together with NOx emissions, are precursors of ground level ozone formation in the presence of sunlight. Existing occupational workplace limits should be taken into consideration.

Emissions of VOC to air may occur from:

- the storage of the solvents

- the process

- cleaning operations

Spills and leaks from storage areas may result in emissions to soil and groundwater.

6 VOC Substitution

The following sections describe potential substitutes for VOC (using VOC-free and VOC-reduced systems). There are also descriptions of the application technologies or special conditions needed and the advantages and disadvantages compared to systems that use solvents with a high VOC content.

6.1 VOC-free systems

This section describes the ways that VOC-free products or systems can be used to replace the organic solvents currently used.

6.1.1 Substitution by powder coating systems

Powder coatings can substitute for solvent-based coatings in many processes addressed here, provided that the work piece can be heated in order to cure the coating.

A change to powder coating requires a change to a new application technique and the need for a drying oven entailing additional costs. In addition, powder coatings are more expensive per unit weight than conventional coatings.

Conversely, each unit weight of powder coating is made up entirely of the material used to coat, unlike liquid coatings where some of the weight is solvent. Therefore, a tonne, for example, of powder coating would be able to coat a greater area than a tonne of solvent-based coating, assuming that both types of coating resulted in layers of equal thickness.

Application of powder coatings is also much more efficient. The combination of these factors usually means that the substitution to powder coatings is cost neutral. [DuPont 2008] Additional financial benefits occur where waste gas treatment systems can be avoided.

6.1.2 Substitution of VOC cleaners

Components and sub-assemblies can be degreased and cleaned in vats using water-based cleaning or degreasing techniques based on detergent systems that substitute solvent based systems.

Detergent systems can also be used for cleaning of equipment and parts when water based coating systems are used.

These systems combine detergents with alkalis and other substances, depending on the substrates and the materials to be removed. However, cleaning may take longer than with solvent-based systems.

Water based cleaning systems may also require additional heating and subsequent wastewater treatment. [BREF STS 2007]

6.2 VOC-reduced systems

If the complete substitution of organic solvents is impractical then changing to systems with a reduced VOC content, such as those described in this section, can decrease emissions.

6.2.1 Reduction of solvent content in coating systems

Often the most significant reduction in VOC emissions can be achieved by changing from conventional solvent based systems to high solid coatings or water-based systems. Total emission reductions of about 30 – 55 % can be achieved in this way. [DFIU 2000]

In the case of high-solid coatings, the higher price per unit weight for the coating is outweighed by the higher efficiency of the product (higher solid content per unit weight). [DuPont 2008]

In the case of water based systems, the change of application system requires stainless steel equipment to be used and also increases drying times. Adjusting the dryer, using heated air and increasing exchange rates, can provide the additional drying requirement. A case-by-case calculation, including energy costs, needs to be made in order to determine how costs will be affected by switching to water based coatings.

For water based coating systems for electrophoretic dipping, there are costs associated with new equipment and additional costs for additional maintenance required by this sort of application system. Here, as a rough estimate, it can be assumed that the turnover time for the coating solids in the bath volume needs to be < 1 year to achieve an economic situation. [DuPont 2008]

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements and abatement techniques can be used to reduce VOC emissions if VOC substitution as described in section 6 is not possible. The following measures are commonly applied for vehicle coating with an annual solvent consumption of less than 15 tonnes and for vehicle refinishing:

7.1 Process improvements

Because conventional spray coating is the dominant application process for this sector, process improvements to reduce VOC emissions that have been applied in other sectors can also be applied here [EPA 2005]

It is essential that spray booths are used for all spraying in order to reduce fugitive emissions.

Spray booth walls do not necessarily have to be cleaned with solvent containing cleaners but instead can be coated with a paper, film or a strippable varnish, which may then be removed and disposed from time to time (see chapter 4.2.4). Emissions from cleaning are thereby reduced.

There are enclosed containers readily available on the market that can be used for locally dispensing thinners, pre-cleaners, degreasers, etc. These can be small plunger cans that dispense small amounts of solvents onto a cloth, or containers with sealed nozzles. These containers reduce emissions from material handling.

Enclosed paint mixing equipment that reduces the release of VOC is available on the market. As refinishing-type coatings are often mixed on-site (see chapter 5.1), emissions from paint mixing are often relevant.

Spillages also lead to emissions, and failure to keep containers closed increases emissions. All containers of degreasers, pre-cleaners, cleaners and thinners should be kept closed when not in use and during handling/transport around the premises.

Lids should be tight fitting. Containers that do not seal properly, e.g. that are damaged or dented, should not be used.

7.2 Improvement of application techniques

7.2.1 General application process improvements

General measures to reduce VOC emissions by improving the application of spray coating are [according to BayLFU 2005]:

- Limiting spraying distance to the coated surface
- Keeping the spray jet vertical to the surface
- Adjusting the width of the spray jet to the work piece's width
- Applying precise contour coating
- Keeping air pressure as low as possible, but adequate for quality requirements
- Reducing the number of coating layers

7.2.2 Change to increased efficient application technique

High volume low-pressure (HVLP) spray equipment has a coating efficiency approximately 20 % better than conventional spray coating. Not only does such equipment significantly reduce emissions it also improves the finish quality and reduces paint costs - due to overspray reduction.

The typical cost of a high quality HVLP spray gun is € 400 [DFIU 2000]. These spray guns can be connected to the existing conventional pressurised air supply systems.

Typically VOC emissions can be reduced by replacing application techniques by other more efficient techniques (see table 3 below).

When changing to more efficient spray application techniques it should be remembered that operator training is likely to be necessary. Training will help operators to use spray gun types to optimum effect, thus maximising the efficiency achieved, thereby saving both emissions and money.

Improved colour mixing can reduce the amount of waste generated and help to avoid unnecessary VOC emissions. Electronic scales can improve the accuracy of batch preparation and automated data logging can be used for generating information for the solvent management plan. [EPA 2005]

Table 3: Efficiency of application techniques

Efficiency of application techniques				
Method	**Degree of efficiency [%]**	**Suitable varnish system**	**Geometry of the work piece**	**Other restrictions**
Compressed air spraying	20 – 65	1- and 2-component systems	No limitation	-
Airless	40 – 80	1- and 2-component systems	Large, simple shapes	-
Airmix	35 – 75	1- and 2-component systems	Large, simple shapes	-
HVLP	45 – 65	1- and 2-component systems	No limitation	-
Electrostatic assisted compressed air spraying	50 – 80	1- and 2-component systems	Not suitable for shapes that act as Faraday cages	Electrically conducting materials are necessary
Electrostatic assisted airless spraying	45 – 85	1- and 2-component systems	Not suitable for shapes that act as Faraday cages	Electrically conducting materials are necessary
Electrostatic assisted airmix spraying	40 – 80	1- and 2-component systems	Not suitable for shapes that act as Faraday cages	Electrically conducting materials are necessary
Flooding	85 – 95	1-component systems	Non-scooping parts	High solvent loss
Dipping	75 – 90	1-component systems	Non-scooping parts	High solvent loss
Powder with electrostatic spray technique	50 – 95	Powder	No limitation	Electrically conducting temperature resistant materials are necessary

[DFIU 2003, p.207]

7.2.3 Reduction of VOC emissions from cleaning

The following measures reduce the amount of solvents used for cleaning: [BayLFU 2005] [DFIU 2000] [BREF STS]

- No cleaning of equipment used for base coatings or coatings with low optical requirements
- Consecutive coating of same coloured work pieces
- Draining of the supply lines before cleaning, e.g. spraying until the line is empty
- Using a pig-clearing method[7] to avoid residues remaining in pipes
- Immediate cleaning of parts, leaks, spillages and working environment before coating material is dried
- Regular inspections of storage areas and working environment to ensure appropriate handling procedures are being followed
- Minimising the surface area of any solvent containing materials at the working station.
- Using systems that allow back-flow of solvents to a closed container. For example, cleaners can be pumped through a tap or sprayed onto the object in a partially enclosed work area above a storage drum. The work area allows surplus solvent to flow back through coarse filters into the drum.

Automatic washing machines can clean parts to be coated as well as coating equipment. In these machines the solvents are contained and collected for reuse. Some emissions can still occur when opening the machine to remove cleaned equipment. These emissions can be treated using a solvent recovery system. These systems can achieve up to 80 – 90 % solvent recovery. Problems may occur with 2-component clear coat materials, however, which can lead to clogging of recovery tank pipes. A typical system costs 0.4 million Euros for a single spray booth [BREF STS 2007, p. 481]

Spray gun should be cleaned in enclosed equipment and this way 80 % of the solvent emissions from cleaning can be reduced. Such systems cost between 150 and 3000 Euros – both manually operated and automated equipment are readily available on the market. [EPA 2005, BREF STS 2007]

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[7] 'Pigs' are pieces of plastic, propelled by compressed air, that scour any residual coating from pipes and force it back to the storage tank. The system is only applicable, where paints are delivered to machinery through pipes and different colours are sent through the same pipe.

7.2.4 Examples of process improvements

Windscreen wipers are usually coated with water-based coatings (often using high rotation bells) but may also be coated with powder coating. [DFIU 2002]

Radiators can be effective coated with water-based coatings using manual electrostatic spray coating - even though they have a complex geometry parts made of both metal and synthetic materials. The system can be combined with overspray recovery whereby the recovered lacquer is mixed with fresh coating material to adjust the viscosity.

The combination of water based coatings and recovery of waste material can lead to a significant VOC emission reduction. Also UV cured powder coatings are increasingly used (due to the material mix of metal and plastics and related heating sensitivity). [DFIU 2002]

Automatic electrostatic application systems, using high rotation bells, can have high coating efficiencies and are suitable for axles and chassis. HVLP spraying and water based systems can be used for manual application. [DFIU 2002]

7.3 Abatement technologies / End of pipe measures

If emission values are likely to be exceeded and primary measures cannot be applied then VOCs may be destroyed by thermal oxidation, biological treatment or decomposition by thermal plasma. Biological and plasma treatments are mainly used for low concentrations of VOC (< 1 gC/m^3).

Thermal oxidisation can achieve VOC reduction efficiencies of > 99.9 %, biological treatment generally has a lower efficiency but also lower investment and operating costs.

Adsorption onto activated carbon or zeolite materials, followed by controlled desorption, may be used to concentrate a dilute effluent for subsequent treatment. Concentrated gas streams must be monitored to ensure that the carbon content never exceeds 25 – 50 % of the lower explosion limit.

Thermal oxidation can be used if concentrations are above 1 mgC/m^3. Consequently, low and varying carbon concentrations may require additional fuelling with natural gas to maintain a constant flame temperature. Autothermic combustion can be achieved with total carbon concentrations of about > 2 g/m^3.

Recuperative oxidation systems recover waste heat from the combustion, via heat exchangers, to pre-heat incoming waste gas or for process operations such as dryers, or for room heating.

Regenerative oxidation systems are more efficient than recuperative systems. The hot exhaust gas is passed through chambers containing heat retentive honeycomb-like material. When a chamber has achieved its full heat loading the exhaust gas is routed to another chamber. Cool incoming waste gas is heated by passage through the hot honeycomb-like material before it enters the combustion chamber. The regeneration of waste heat decreases the energy demand of the process significantly.

Catalytic oxidation may be used if no ‘catalyst poisons’ are present; since catalysed oxidation occurs at a relatively low temperature the energy demand is reduced.

8 Summary of VOC emission reduction measures

The following table summarizes the various approaches to substitute or reduce VOC emissions as described in chapters 6 and 7:

Table 4: Measures for VOC substitution and VOC reduction in vehicle coating and vehicle refinishing

Objectives	**Description**	
Substitutes/ Solvent free processes	VOC Substitution by changing the application system	Use of powder coatings
	Substitution of VOC cleaners	Use of VOC-free cleaners e.g. water based cleaners for degreasing and cleaning of equipment and parts
Reduction of the solvent content	Reduction of the solvent content in coating systems	Changing from conventional coating systems to high solid and water based coating systems
Process Improvements	Improvement of application techniques	Optimising the spraying technique, reducing the number of coating layers, improving or replacing application techniques by those with a higher efficiency
	Reduction of cleaning effort	Reducing colour changes. Immediate cleaning (before drying). Minimising the use of cleaners. Emptying pipes by 'pig' systems before cleaning. Not cleaning for the application of base coats or coats with low optical requirements. Consecutive coating of coloured working pieces. Automatic washing of spray guns, parts. Coating spray booth with a film or a strippable varnish.
	General process improvements	Use spray booths for all spraying Use of enclosed paint mixing equipment Ensuring all containers with solvents are kept closed whenever possible.
Abatement Technologies	Destruction of VOC	Biological treatment, adsorption and/or thermal/catalytic oxidation.

9 Good practice examples

9.1 Coating of aluminium wheel rims

An installation coating aluminium wheel rims with conventional coating techniques used to have a VOC emission of about 66 g/wheel rim. This was reduced to 4 g/rim by changing to water based and powder-based technologies.

The conventional coating was a three-step process - a solvent free powder base coat followed by a solvent-based metallic effect base coating and a solvent-based clear top-coat. In the new system, the top-coat is powder and the metallic effect base-coat is water-based; the solvent free powder base coat remains unchanged.

The following table shows the reduction/substitution effects for each coating layer.

Table 5: Illustration of measures for VOC substitution and VOC reduction in wheel rim coating

Input of coating per coated aluminium rim				
	Conventional process		**New process**	
	Paint consumption	**Solid application**	**Paint consumption**	**Solid application**
1. Coating/basic layer				
Basic powder	80 – 100 g		80 – 100 g	
Application efficiency	98 %		98 %	
2. Metallic-basis layer				
Solvent-based wet paint	< 60 g	12.5 g (approx.)	--	--
Water-based wet paint	--	--	35 g	< 10 g
Application efficiency	50 – 60 %		80 %	
3. Coating clear coat				
Solvent-based clear coat	< 60 g	15 g	--	--
Powder	--	--	45 g	
Application efficiency	50 – 60 %		98 %	

[BREF STS 2007]

In total, paint material consumption decreased from 210 g/rim to 170 g/rim - with a constant coating thickness. Despite the use of additional powder coating, energy consumption did not increase. [DFIU 2002]

9.2 Coating of trailers

A body shop replaced its conventional coatings with high solid products. Application techniques were changed to HVLP technique and the material supply lines were shortened (from 27 m to 10 m) - thereby saving cleaning agent and effort.

The cost increase of about 15 – 20% per kilo high solid coating material is offset by the lower overall consumption of coating material.

[BayLFU 2005]

Table: 6 Measures for VOC substitution and VOC reduction in coating of trailers and superstructures

Coating of trailer and superstructures						
	Before			**Afterwards**		
Paint	**Total [kg/a]**	**VOC [%]**	**Solids [%]**	**Total [kg/a]**	**VOC [%]**	**Solids [%]**
Stopper	3622	15.5	84.5	3622	7.8	92.2
Wash primer	780	71.2	28.8	780	71.2	28.8
Primer	44	59.4	40.6	44	59.4	40.6
Filler	9255	31	69	6799	15.5	84.5
Topcoat	13910	44.5	55.5	9705	28.4	71.6
Basecoat	1406	77.2	22.8	1310	8.8	91.2
Clear coat	779	52.2	47.8	532	37	63
Hardener	9958	62.9	37.1	6922	52	48
Thinner	3932	100	0	1966	100	0
Special prod.	50	32	68	50	64	36
Cleaner	2670	100	0	1335	100	0
Total	**46406**	**53**		**33065**	**36**	

[BayLFU 2005]

9.3 Coating of brake pads

At a plant carrying out the spray coating of brake pads, a reduction of VOC consumption of about 50 % was achieved by optimizing the arrangement of the work pieces on their hangers. This led to increased application efficiency because the gaps between the discs, and overspray, were reduced.

By this simple measure the capacity of the installation was doubled and the paint consumption per brake pad decreased by more then 50%. Beside the environmental benefits the measure lead to notable economical savings.

[BayLFU 2005]

9.4 Cleaning of equipment

In a paint shop coating trailers, manual cleaning of a spraying gun consumed 480 ml of solvent cleaning agent per gun. Now, with automatic washing machines, the solvent consumption has reduced to 80 ml/gun and the used solvent is captured and recycled for reuse. Consequently the total VOC emissions from spray gun cleaning were reduced by 98%

The automatic spray gun washing machine required an investment of 2500 Euro but this investment was outweighed by a timesaving for the cleaning operation of more than 75% (from about 12 to less than 3 minutes per gun)

Figure 2: Automatic pistol washing machine

[Ökopol 2008]

10 Emerging techniques and substitutes under development

UV curing coatings are an emerging technology particularly suitable for the coating of smaller parts (this restriction is due to the size and cost of the UV curing unit). UV curing coatings may significantly improve the scratch resistance of the coated surface. [ISACOAT 2005]

Water based top coats with less than 10 % solvent content are being developed for large-scale vehicle coating and may also become more widely applicable in the future for small scale vehicle coating. [DuPont 2008]

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Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Guidance 6 – Part 2:

Vehicle coating (large series of cars, buses, vans, trucks and truck cabins)

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses vehicle coating in installations with an annual solvent consumption exceeding 15 tonnes and the related cleaning of equipment, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emission Directive (SE Directive)

SE Directive – Scope definitions (Annex I)

Vehicle coating is defined as ‘any activity in which a single or multiple application of a continuous film of a coating is applied to vehicles as listed below:

- new cars, defined as vehicles of category M1 in Directive 70/156/EEC (1), and of category N1 in so far as they are coated at the same installation as M1 vehicles,
- truck cabins, defined as the housing for the driver, and all integrated housing for the technical equipment, of vehicles of categories N2 and N3 in Directive 70/156/EEC,
- vans and trucks, defined as vehicles of categories N1, N2 and N3 in Directive 70/156/EEC, but not including truck cabins,
- buses, defined as vehicles of categories M2 and M3 in Directive 70/156/EEC.’

Vehicles as listed above are defined in Directive 70/156/EEC as follows:

- ‘vehicle’ means any motor vehicle intended for use on the road, with or without bodywork, having at least four wheels and a maximum design speed exceeding 25 km/h, and its trailers, with the exception of vehicles which run on rails and of agricultural tractors and machinery.’ (Article 1)
- Category M: Motor vehicles having at least four wheels, or having three wheels when the maximum weight exceeds 1 metric ton, and used for the carriage of passengers.
- Category M1: Vehicles used for the carriage of passengers and comprising no more than eight seats in addition to the driver's seat.
- Category M2: Vehicles used for the carriage of passengers, comprising more than eight seats in addition to the driver's seat, and having a maximum weight not exceeding 5 metric tons.
- Category M3: Vehicles used for the carriage of passengers, comprising more than eight seats in addition to the driver's seat, and having a maximum weight exceeding 5 metric tons.
- Category N: Motor vehicles having at least four wheels, or having three wheels when the maximum weight exceeds 1 metric ton, and used for the carriage of goods.
- Category N1: Vehicles used for the carriage of goods and having a maximum weight not exceeding 3 75 metric tons.
- Category N2: Vehicles used for the carriage of goods and having a maximum weight exceeding 3 75 but not exceeding 12 metric tons.
- Category N3: Vehicles used for the carriage of goods and having a maximum weight exceeding 12 metric tons. (Annex I)

THIS GUIDANCE ADDRESSES THE COATING OF NEW CARS, TRUCK CABINS, VANS AND TRUCKS AS WELL AS BUSES IF A SOLVENT CONSUMPTION OF 15 TONNES PER YEAR IS EXCEEDED

Vehicle refinishing activities and coating of trailers are addressed in a separate guidance document (see guidance 6 – part 1). This is also the case for the coating of new cars, buses, vans, trucks and truck cabins in installations with a solvent consumption ≤ 15 tonnes per year.

Different requirements under the SE Directive apply for original coating of vehicles and parts depending on whether they are coated in the original manufacturing line or away from the original manufacturing line. Please see guidance 6 – part 1 for original coating of road vehicles and the original coating of parts of them if carried out away from the original manufacturing line and carried out with refinishing-type materials.

This activity does not include the coating with metals by electrophoretic and chemical spraying techniques.

The SE Directive lays down the following emission limit values for vehicle coating in installations with an annual solvent consumption exceeding 15 tonnes per year:

Table 2: Emission limit values of the SE Directive for vehicle coating

<table>
<tr><th colspan="4">SE Directive - Emission limit values (ELVs)
(Annex II A – activity No. 6 – Part II)</th></tr>
<tr><th rowspan="2">Activity (annual solvent consumption threshold)</th><th rowspan="2">Production threshold (refers to annual production of coated item)</th><th colspan="2">Total emission limit value</th></tr>
<tr><th>New installations</th><th>Existing installations</th></tr>
<tr><td rowspan="2">Coating of new cars
(>15 t)</td><td>> 5000</td><td>45 g/m² or
1,3 kg/body +
33 g/m²</td><td>60 g/m² or
1,9 kg/body +
41 g/m²</td></tr>
<tr><td>≤ 5000
monocoque or
> 3500
chassis-built</td><td>90 g/m² or
1,5 kg/body +
70 g/m²</td><td>90 g/m² or
1,5 kg/body +
70 g/m²</td></tr>
<tr><td rowspan="2">Coating of new truck cabins
(> 15 t)</td><td>≤ 5000</td><td>65 g/m²</td><td>85 g/m²</td></tr>
<tr><td>> 5000</td><td>55 g/m²</td><td>75 g/m²</td></tr>
<tr><td rowspan="2">Coating of new vans and trucks
(>15 t)</td><td>≤ 2500</td><td>90 g/m²</td><td>120 g/m²</td></tr>
<tr><td>> 2500</td><td>70 g/m²</td><td>90 g/m²</td></tr>
<tr><td rowspan="2">Coating of new buses
(>15 t)</td><td>≤ 2000</td><td>210 g/m²</td><td>290 g/m²</td></tr>
<tr><td>> 2000</td><td>150 g/m²</td><td>225 g/m²</td></tr>
<tr><td colspan="4">The total emission limit values are expressed in terms of grams of solvent emitted in relation to the surface area of product in square metres and in kilograms of solvent emitted in relation to the number of car bodies produced.
The total emission limit value in the table below refers to all process stages carried out at the same installation from electrophoretic coating, or any other kind of coating process, through to the final wax and polish of top coating inclusive, as well as solvent used in cleaning of process equipment, including spray booths and other fixed equipment, both during and outside of production time.
The surface area of any product dealt with in the table is defined as follows:
The surface area calculated from the total electrophoretic coating area, and the surface area of any parts that might be added in successive phases of the coating process which are coated with the same coatings as those used for the product in question, or the total surface area of the product coated in the installation.
(For calculation of the surface area of the product see SE Directive, Annex II A II)</td></tr>
</table>

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[1] as well as for halogenated VOCs which are assigned the risk phrases R40 or R68[2]. There is a general obligation to replace CMR substances – as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated[3] VOC with R40 the ELVs in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

The VOC emissions from this activity depend on the coating systems being applied. The greatest reduction in VOC emissions is achieved if solvent-based coating systems can be substituted by powder systems. This is possible for primers and top coats on metal.

HIGHEST VOC REDUCTION CAN BE ACHIEVED BY APPLICATION OF POWDER BASED COATINGS

If powder application is not possible, VOC reduction can still be achieved by the substitution of solvent-based coatings with water-based systems. Water-based coatings are commonly used for electrophoretic dipping (usually containing 1 – 6 % VOC) and also widely used as primers (5 – 6 % VOC) and base coats (10 – 15 % VOC). Furthermore, water-based single-layer top coats (currently containing 11 – 15 % VOC) may be used as well as water-based clear coats (~ 15 % VOC). New top coat systems, aiming at a VOC content of < 10 % VOC, and new clear coat systems are under development.

In cases where for clear coats neither of these reduction options is applicable for quality or process reasons, the solvent content of the conventional coating systems can be reduced. High solid systems can reduce the VOC content of clear coats from ~ 50 – 60 % to ~ 35 %.

In addition the efficiency of coating application can be increased by the use of high rotation bells, or by employing electrostatic spraying.

Other measures to prevent or reduce VOC emissions include

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[1] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

[2] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: 'Possible risk of irreversible effects'. The new wording is: 'Limited evidence of a carcinogenic effect'. In the 'old' version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: 'Possible risk of irreversible effects'. This new risk phrase does not include carcinogenicity. The 'new' version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to this change, a final decision on which version applies can only be given by the European Court

[3] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.

Reduction of coating layers (e.g. substitution of primer by base coats)

- Efficient material use (reduced colour changes, cartridge systems)
- Efficient cleaning techniques (cleaner recovery, 'pig' cleaning[4])
- Appropriate solvent handling
- Substitution of VOC cleaners by VOC-free cleaners
- Concentration of VOC contained in waste gas and waste gas treatment

3 Description of the activity and related industry sectors

In 2005, 20.8 million motor vehicles were produced in Europe (including Russia). During the same year, in the EU, 1,640,769 light commercial vehicles and 549,468 heavy trucks were produced. There are about 154 car production sites, 109 van, truck and truck cabin production sites and 46 bus production sites in Europe. [BREF STS 2007]

Vehicle coatings must meet high performance requirements (particularly stringent for cars, less so for vans, trucks, buses) for:

- long-term protection against corrosion, chemical attack (e.g. bird droppings, acid rain), chipping protection, solar radiation, abrasion in car washes, etc.
- excellent optical surface properties: polish, colour depth, free of cloudiness, faultlessness,
- homogeneity and a consistency in colouring and formation of effects (such as metallic finishes, etc.).

These requirements are achieved by at least three, often four, and up to five paint layers designed to complement each other. In Europe, the following paint layer construction has come to predominate: [BREF STS 2007]

- Pre-treatment of plastics and body parts assembled from metals (e.g. steels pre-treated with phosphate for corrosion resistance)
- Pre-coat: electrophoretic dipping/cathodic electrodeposition
- Underbody protection/seam sealing
- Primer/filler coat
- Top coat: can be made up of base coat and clear coat
- Cavity conservation and, if necessary, conservation for transit.

Generally throughout Europe two-layer top coats are used for cars (rather than one-layer systems). They comprise a base coat and clear coat.

[4] 'Pigs' are plastic pieces, forced with compressed air through pipes to transport coating remains left over in pipes back to the storage tank. The system is only applicable, where paints are delivered to machinery through pipes and different colours are sent through the same pipe regularly.

Typical coating systems for vans, trucks and truck cabins, are either serial coating (with drying temperatures of about 140 °C) or 2-component paints (with drying temperature of 80 °C). Also a combination of both systems is often used.

The most commonly applied coating techniques for buses are water-based electro coats, electrostatic primers, and different types of top coat

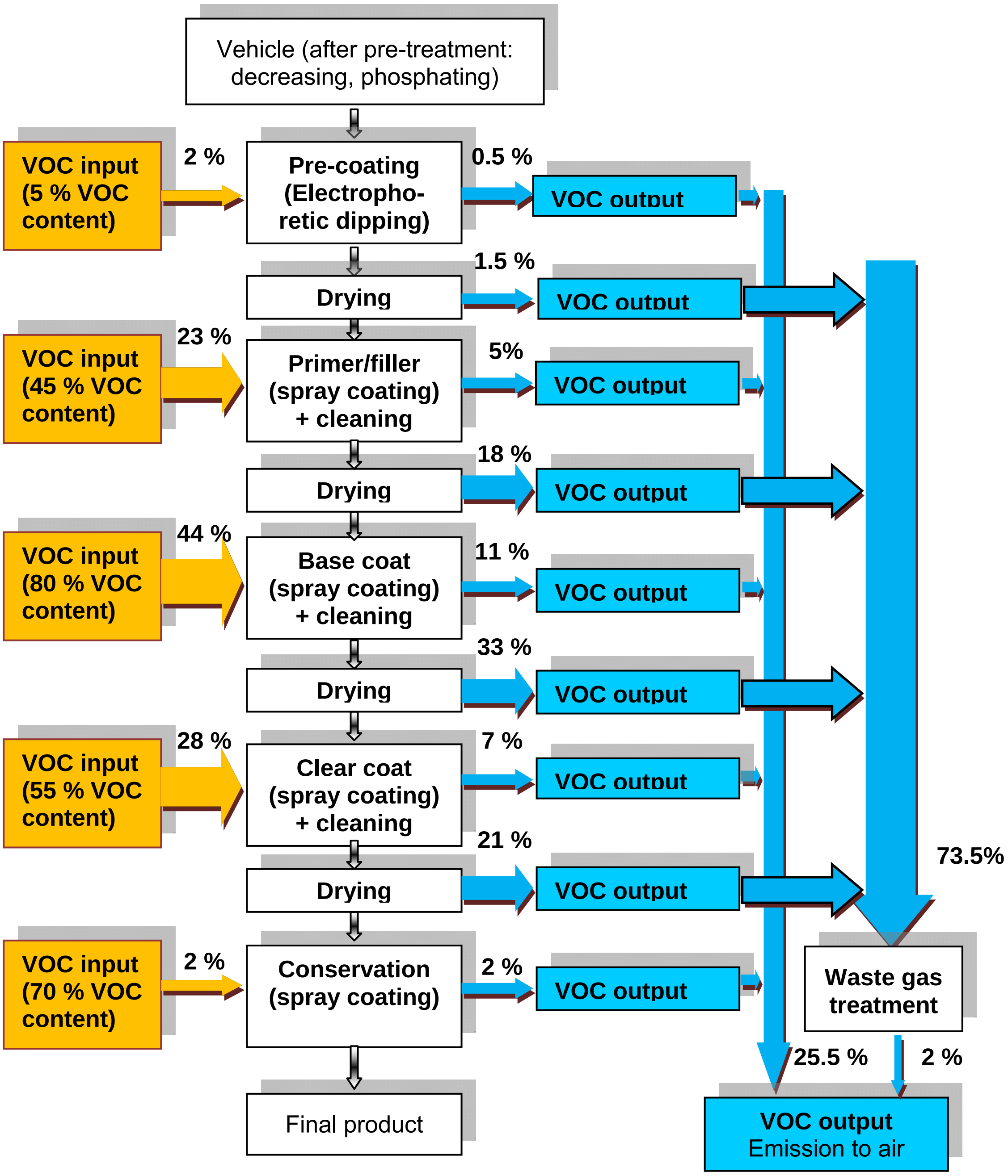
(conventional base coats and electrostatic clear coats). [BREF STS 2007]

4 Technical process description

4.1 Process flow and relevant associated VOC emissions

Coating is applied after pre-treatment (degreasing, phosphating, passivating) with at least 3 up to 5 paint and varnish layers, together with seam sealing, underbody protection and conservation for transport.

Figure 1 shows a flow chart with a schematic overview of all VOC relevant process steps and related emissions found in vehicle coating with conventional solvent-based primer and top coat systems.



based on [DuPont-2 2008]

Figure 1: Typical VOC emissions from conventional vehicle coating

4.2 Process description

4.2.1 Application techniques

In general, vehicle coating has four coating steps. The following table shows the coating products and common application techniques.

Table 3: Application techniques and coatings used for different vehicle productions

Application techniques				
	Pre-coating	**Filler**	**Top-coat (base coat)**	**Top-coat (clear coat)**
Cars Commonly	Water-based electrophoretic dipping	Water-based spray coating	Water-based/ solvent based spray coating	Solvent-based (high solid) spray-coating
Seldom used		Powder, solvent-based spray coating		Water-based, powder, powder slurry
Vans Commonly	Water-based electrophoretic dipping	Water-based/ solvent-based spray coating		Water-based/ solvent-based single-layer spray coating
Seldom used		No filler coating	Water-based/ solvent-based base coat spray coating	Water-based/ solvent-based clear coat spray coating
Truck cabins Commonly	Water-based electrophoretic dipping			Water-based top-coat spray coating
Seldom used				Solvent-based top-coat spray coating
Truck/bus chassis Commonly	Water-based spray coating	Water-based spray coating	Solvent-based spray coating	Solvent-based (high solid) spray-coating
Seldom used	Water-based electrophoretic dipping	Solvent-based spray coating	Water-based spray coating	Solvent-based single-layer spray coating
Buses Commonly	Water-based electrophoretic dipping	Water-based spray coating	Water-based/ solvent based spray coating	Solvent-based (high solid) spray-coating
Seldom used		Powder, solvent-based spray coating		Water-based, powder, powder slurry

[BREF STS 2007] [DuPont-1 2008]

Electrophoretic dipping

In the electrophoretic dipping process an electric current flowing between the immersed working piece and the electrodes of opposite polarity is used to deposit the coating. Cathodic working piece loading systems are commonly used because they offer better resistance against corrosion than do anodic systems (‘CED’ = Cathodic electrophoretic dipping).

The system is commonly used for pre-coating of cars, vans, truck cabins and pre-coated chassis (and, in few cases, for buses).

The dipping reservoir has to contain sufficient liquid for the largest possible item to be completely submerged, and have sufficient capacity to accommodate the increase in the liquid level as the object is dipped. To overcome this problem, a secondary, overflow reservoir can be used, coupled with a mixing system to ensure agitation of the coating material. [Envirowise 2003]

Electrophoretic dipping is an efficient application technique that produces high quality results but investment costs are relatively high. A high level of maintenance, particularly for the paint tanks, is needed to meet quality assurance requirements. [BREF STS 2007]

Conventional high and low pressure spraying

Conventional (non-electrophoretic) spray coating is used for top coats because of its ability to achieve high quality finishes and special surface effects (e.g. metallic or pearl look). Conventional spraying is used for inside parts of vehicles (door insides, bonnet underside) and for metallic coatings (where electrostatic application is not able to produce the desired effect).

Spray coating uses a 'gun', powered by compressed air, to atomise coating material and direct it, as a jet, onto the surface of the working piece. The higher the air pressure the finer the particles of the coating material and the better the quality and the smoothness of the coated surface. On the other hand, the finer the particles, the greater the ease with which they are deflected by the airflow from the coated surface and this leads to increased coating waste (overspray). If the pressure is too low, the surface finish is of poor quality (e.g. an ‘orange peel’ effect is created).

The material efficiency varies from 5 % (for lattice-like working pieces) up to 30 – 60 % (for working pieces with large flat surfaces). Hence, overspray depends on geometry and on the ability of workers or the programming of robots to apply the coating efficiently.

[DFIU 2002] [BREF STS 2007]

Electrostatic spray coating

Electrostatic spray coating is commonly used in the coating of cars, buses, trucks and commercial vehicles. The technique may be used either manually or automatically. It is used for all external vehicle surfaces. Its application for inside parts is difficult because of the Faraday cage effects.

Coating material is atomised and sprayed in the presence of an electric field created between the spray gun and a work piece of opposite polarity.

For compressed air systems, the material flow can be up to 1000 ml/min, while for airless or assisted airless techniques the material flow can be as high as 3000 ml/min.

The material efficiency of manual electrostatic spray coating is up to 85 %. Compared to conventional spray coating, electrostatic spray coating is more time and material efficient and easier to automate. There is less overspray so less waste residues are generated and spray booths require less cleaning.

For electrostatic spraying to work, the work piece has to be conductive. For this reason, it may be difficult to recoat over existing coatings. This limits the substrates the technique can be applied to.

Automatic spraying bells are most commonly used for electrostatic spray coating. They are suitable for small parts and tubular structures with only small depressions. Depending upon the size of the spraying bells, a maximum material flow rate of up to 600 ml/min is possible. Colour changes can be carried out within several seconds. The transfer efficiency is up to 95 %, but does depend on the process conditions and the geometry of the work piece.

[DFIU 2002] [BREF STS 2007] [DuPont-1 2008]

Electrostatic spraying with high rotation bells

This technique uses rotating bells for coating application. The technique can be used for both water-based and conventional materials.

It may be used for coating the interior of vehicles. It involves paint atomisation and, except in the case of the airless technique, is similar to conventional compressed air spraying. Hydrostatic pressure is used to atomise the coating material and the paint particles are then electrostatically charged (except when applying water-based coatings or when applied to plastic parts). [BREF STS 2007]

High volume low pressure spraying (HVLP)

This spraying technique is only used for manual repair applications at the end of the production line. The quality of coated surfaces may not match those achieved with high-pressure air guns because HVLP spray guns create larger particles of coating material.

For HVLP, the atomising pressure is reduced from the conventional 3 – 6 bar down to 0.7 bar. Compared to high-pressure spray coating, up to 20 % overspray can be avoided and the material efficiency ranges from 40 - 80 %. [BREF STS 2007]

Airless spraying

Airless spraying is used for coating bus and truck chassis. The technique may be used either manually or automatically. Airless spray coating gives a relatively rough finish that needs to be sanded before finer coatings can be applied - an additional process stage compared with high pressure air spraying. However, optimisation of the spraying can improve finish quality to close to that achieved with HVLP guns, especially with primer coatings.

In airless spray coating, paint is forced through very small metal nozzles (< 2 mm) at a pressure of 80 to 250 bar. The paint jet strikes the stationary air outside the nozzle and is broken into fine particles by the force of the impact of paint jet and air.

The paint is delivered to the nozzle using high-pressure pumps, this prevents fast colour changes but a high throughput of paint is possible. Airless spray coating is cheap and fast and can be used for 1-component and 2-component paint systems.

Operator training is essential in order to maximise the performance of airless spraying systems. The material efficiency for airless spray coating is about 5 % (for lattice-like working pieces) up to 40 – 75 % (for large surfaces). [BREF STS 2007]

Application of powder coatings

Powder coatings are automatically or manually applied and then melted and cured by heating the work piece. Powder systems are applicable to metal and plastic surfaces. They have been developed for filler and top coat applications. The use of reclaimed powder enables material re-use of up to 97 %. [BREF STS 2007] [BMW-1 2008] [PSA 2005]

Powder coating – electrostatically assisted spraying: The powder particles are electrostatically charged and sprayed onto the work piece using compressed air. Spray booth and application tools can be cleaned by vacuum cleaning or by blowing with compressed air. There are no solvent emissions associated with this coating technique. The material efficiency is about 80 – 95 %. [BREF STS 2007]

Powder sintering: The working piece is heated above the melting temperature of the powder coating before coatings are applied. As soon as the powder contacts the surface, sintering and merging takes place; a high material efficiency can be achieved. [BREF STS 2007]

Powder slurry: In this system powders are dispersed and stabilised in water. They are applied using conventional electrostatically assisted spray equipment for liquid paints.

Drying by combinations of infrared and air circulation techniques can reduce energy consumption. [BREF STS 2007]

4.2.2 Drying

Heated air circulating in a drier or oven is brought into direct contact with the object or surface to be dried. The drying time depends on the object or substrate, the type of coating and the coating thickness, and varies from a few seconds to a full hour.

Dehumidified air, or convection drier with an additional dehumidification step, is used for drying water-based coatings or as a pre-drying step of wet-on-wet layer constructions. By removing water in this manner the drying times can be significantly reduced. Dryer channels are designed in “A-form” to avoid heat losses (lifting the working piece through a channel designed like an A). [BREF STS 2007]

4.2.3 Cleaning

Cleaning is needed, whatever the coating application techniques, for the work pieces, the work place environment, the coating equipment and its parts.

A range of cleaning techniques can be used; most frequently these are automatic cleaning systems with solvent recovery (e.g. for spray guns).

Organic solvent cleaners are used (sometimes heated for higher efficiency) as well as water, the latter when water-based coating systems are used and if cleaning can be performed before coatings have dried.

Cleaning needs to be effective and fast. The cleaning intensity needed can vary according to the nature of colour changes to be made and depending on whether the contamination is semi-dry or dry. For semi-dry contaminations water-based systems (with tensides or with solvents) can be used. Solvents have to be used if the contamination has dried.

For colour changes, pipes can be pre-cleaned with ‘pigs’ for material recovery (plastic pieces pushed through pipes with compressed air) before cleaning is done with solvents or water (depending on the coating system).

[BREF STS 2007]

4.2.4 Cavity and transport conservation

Most manufacturers apply a wax protection layer for protection during transport. The wax can be solvent-based (70 % VOC) or water-based.

5 Solvent use, emissions and environmental impact

5.1 Solvents used

Organic solvents are used in the solvent-based coatings and the water-based coating used for vehicle coating, they are also used in solvent-based cleaners and in water-based cleaners.

Solvents are mainly mixtures of organic hydrocarbons (solvent naphtha, xylene, alcohols, esters and glycol ethers). Butyl acetate is a lead component in solvent-based base coats, which is also often used as cleaner. Alcohols, esters and glycol ethers are used in water-based coatings. Butyl Solvents with carcinogenic, mutagenic or reproductive toxicity are not used.

[DFIU 2003] [DuPont-1 2008]

Conventional solvent-based coatings

Conventional solvent-based coatings are classified as polycondensation- (e.g. phenol/urea/melamin resin), polymerisation- (e.g. polyesters-, acrylate resin-, alkyd resins) and polyaddition-laquers (e.g. epoxy or PU lacquers).

In high-solid coatings, the binders are based on epoxy resins, 2-component polyurethanes, polysiloxane, oxirane or alkyd resins.

Table 4 shows VOC contents of solvent-based coating systems.

Table 4: VOC content of conventional solvent-based coating systems

Primers	Base coats	Top coats	High-solid top coats	Clear coats
35 – 46 %	70 – 80 %	40 – 50 %	30 – 35 %	35 – 60 %

[BREF STS 2007] [DuPont-1 2008]

Water-based coatings

Water-based coatings are based on alkyd, polyester, acrylate, melamine and epoxy resins. They often contain organic solvents as a solubiliser and to improve the properties of the wet film layer.

Pre-coatings are generally water-based (for electrophoretic dipping). Primers, base coats and clear coats may also be solvent-based or powder systems. Table 5 shows VOC contents of water-based coatings.

Table 5: VOC content of water-based coating systems

Pre-coats	Primers	Base coats	Clear coats
1 - 6 vol.-%	5 – 10 vol.-%	10 – 15 vol.-%	15 vol.-%

[BREF STS 2007] [EGTEI 2003]

Powder coating

Powder systems are VOC-free. Powder slurries contain ~ 1 % VOC. [BREF STS 2007]

Cleaners

For solvent-based systems butyl acetate (100 % VOC) is the solvent used most frequently. [DuPont-1 2008]

Cleaners for water-based systems are either solvent-free or may contain up to 10 % solvents (mainly alcohols). [BREF STS 2007]

Transport conservation

Waxes are either solvent-free or may contain ~ 70 % solvents. [BREF STS 2007]

5.2 Solvent consumption and emission levels

Coating

High solid solvent-based systems for vehicle coating achieve VOC emissions of 43 – 72 g/m^2 for a primer/base coat/clear coat system, whereas conventional systems result in VOC emissions of 100 – 300 g/m^2. [BREF STS 2007]

According to the STS BREF, the use of Best Available Techniques (BAT) for vehicle coating is associated with the following emission values:

Table 6: VOC emission values associated with BAT in existing vehicle production

	Cars	Vans, trucks	Truck cabins	Buses
BAT associated emission values	10 – 35 g VOC/m^2	15 – 50 g VOC/m^2	10 – 55 g VOC/m^2	92 – 150 g VOC/m^2

[BREF STS 2007]

About 70 – 90 % of the total VOC emissions are emitted from the painting booths, the remaining 10 – 30 % from the drier. [BREF STS 2007]

Usually, application and drying of primer and top coat/clear coat contribute approximately 80 % of the total VOC emissions. The top coat refinishing, cleaning procedures and other sources like coating of small parts, application of underbody protection and conservation are responsible for the remaining 20 %. [BREF STS 2007]

Cleaning

If only conventional solvent-based coating systems are used, cleaners account for 15 % of the total VOC emissions from the site. If high solid systems as well as water-based primers and base coats are used cleaning with organic solvents accounts for about 20 % of total VOC emissions. It is BAT to minimise solvent emissions from cleaning to 20 g/m^2 or less. [BREF STS 2007]

5.3 Key environmental and health issues

In series coating of cars, buses, vans, trucks and truck cabins, a broad range of different solvents are used for a range of different types of processes, mainly for different coating systems and for equipment cleaning.

VOC emissions, together with NOx emissions, are precursors of ground level ozone formation in the presence of sunlight. Existing occupational workplace limits should be taken into consideration.

Emissions of VOC to air may occur from:

- the storage of the solvents,

- the process (mainly during paint application and drying),

- cleaning operations (equipment cleaning).

Spills and leaks from storage areas may result in emissions to soil and groundwater.

The process generates waste containing solvents which need to be disposed in a way that emissions to air, soil and groundwater are prevented or limited.

6 VOC Substitution

The following sections describe potential substitutes for VOC (using VOC-free and VOC-reduced systems). There are also descriptions of the application technologies or special conditions needed as well as the advantages and disadvantages compared to systems that use solvents with a high VOC content.

6.1 Powder coating systems

VOC-free powder coatings can substitute solvent-based coatings in many cases, although this is dependent on the heating of the working piece being practical and the working piece having the required surface characteristics.

Up to now only a few car producers in Europe have used the technique because powder material is more expensive and may cause quality problems. Layer thickness is greater than necessary because thin coatings are difficult to achieve yet (~ 55 - 65 µm for top coats compared with 35 – 50 µm for conventional 1-coat top coats). With powder slurries a thinner film can be achieved (~ 45 µm). [BREF STS 2007]

Initially, powder primer application in the US and in Austria (Chrysler in Graz) was considered inefficient due to material requirements and the finish quality was unsatisfactory [BREF STS 2007], but powder primer is used successfully for car coating at another site (Peugeot in Mulhouse/France) and for truck cabins without pre-coating by electrophoretic dipping (Scania in Oskarshamn/Sweden). [PSA 2005] [DuPont-1 2008]

Powder coating is also used as 1-coat top coat (Smart in Hagenau/France) and as clear coat (car coating at BMW in Dingolfing, Regensburg, Leipzig in Germany, truck chassis coating at Volvo in Gothenburg/Sweden). A parallel solvent-based clear coat line may be needed as some base coats may not be compatible with the use of the powder clear coats. [BMW-1 2008]

Powder slurry can be used as a clear coat (Daimler in Graz/Austria and Rastatt/Germany). [BREF STS 2007]

6.2 Reduction of solvent content in coating systems

The main VOC reduction possibilities, apart from changing to VOC-free powder-based systems, are to change from conventional solvent-based systems to high solid coatings, water-based systems and automatic electrostatic applications. These and other means can achieve total VOC emission reductions of about 30 – 55 %. [DFIU 2000]

High solid coatings can be used for all conventional solvent-based systems if application systems are adapted (system pressure, layer thickness).

If quality requirements allow a reduction of layers, a substantial reduction of solvent (and material) is achieved. At one site it was possible to substitute the primer by two adapted base coats that, together, have the required filler properties (‘integrated painting process’ by Mini in Oxford and VW/Seat in Martorell/Spain). [BMW-1 2008], [DuPont-1 2008]

Water-based as well as solvent-based coatings can be used on metals and plastic materials. Water-based systems cannot, however, be used with 1-coat 1-bake solid colours as they would need to be sealed with a clear coat.

Water-based primers and base coats are widely used for all types of vehicle coating.

Water-based top coats have long been used for single-layer coating of vans and driver cabins (Daimler in Düsseldorf/Germany, MAN in Munich/Germany and Steyr/Austria).

For quality reasons, in car production, water-based clear coats (with 15 % solvent content) are in use at only one site in Europe (Opel in Eisenach, Germany). [BREF STS 2007] [EGTEI 2003] Furthermore, powder slurries (water-based) are used (Daimler in Rastatt/Germany). [DuPont-1 2008]

Water-based top coats may have a poor appearance and quality due to the use of alkyd resins (also used for low quality solvent-based coatings) and poor pigment stability under UV light impact. [BREF STS 2007]

Water-based systems require stainless steel equipment and longer intermediate drying time. They require the operation of spray booths under tighter temperature and humidity controls. Drying time needs to be adjusted by heating the intermediate dryer air and by applying higher exchange rates.

Investment costs for water-based spray booths may be 10 – 20 % higher than for conventional spray booth installations. Material costs are 0 – 20 % higher compared to solvent-based coatings. Due to longer intermediate drying time the energy requirement (and related costs) for car coating with water-based systems is ~ 10 % higher than with solvent-based systems (~ 990 MJ/car instead of ~ 1100 MJ/car). [BREF STS 2007]

Switching to water-based coatings is generally combined with major plant upgrades or with new installations. In large paint shops (> 100,000 units per year) typical costs for a complete new spray booth installation are between 15 – 35 million Euro. Since 1994, most new paint shops in EU countries have been designed for water-based base coat systems.

Compared with solvent-based systems VOC reductions of 75 - 90 % are achieved with water-based systems (primers from ~ 9 to 1 g/m^2, base coats from ~ 30 to ~ 6 g/m^2 and clear coats from 13 to 3 g/m^2).

[BREF STS 2007] [DuPont-2 2008]

6.3 Substitution of VOC cleaners

VOC-free detergent systems can be used for cleaning equipment and parts when water-based coating systems are used.

The systems combine detergents with alkalis and other substances, depending on the substrates and the materials to be removed. Cleaning may take longer than with solvent-based systems.

The water-based cleaning systems may require additional heating and subsequent wastewater treatment. [BREF STS 2007]

6.4 Substitution of VOC-based conservation waxes

Solvent-based waxes can be substituted by VOC-free water-based conservation systems. [BREF STS 2007]

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements and abatement techniques can be used to reduce VOC emissions if VOC substitution as described in section 6 is not possible. The following measures are commonly applied for series coating.

7.1 Process improvements

7.1.1 Improvement of application techniques

General measures to reduce VOC emissions include:

- Reducing the number of coating layers
- Applying precise contour coating
- Adjusting the width of the spray jet to the working piece’s width
- Keeping the spray jet close to the coated surface
- Keeping the spray jet vertical to the surface
- Keeping air pressure as low as possible, but adequate for quality requirements

[BayLFU 2005]

VOC emissions can be reduced by replacing application techniques with more efficient techniques (see table 3 below).

Table 7: Efficiency of application techniques

Efficiency of application techniques				
Method	**Degree of efficiency**	**Suitable coating system**	**Geometry of the work piece**	**Other restrictions**
Dipping	75 – 90 %	1-component systems	Non-scooping parts	High solvent loss
Electrostatic assisted compressed air spraying	50 – 80 %	1- and 2-component systems	No Faraday cage	Electrically conducting materials are necessary
Compressed air spraying	20 – 65 %	1- and 2-component systems	No limitation	-
Airless	40 – 80 %	1- and 2-component systems	Big, simple	-
HVLP	45 – 65 %	1- and 2-component systems	No limitation	-
Powder with electrostatic spray technique	50 – 95 %	Powder	No limitation	Electrically conducting temperature resistant materials are necessary

[DFIU 2003]

7.1.2 Reduction of VOC emissions from cleaning

To reduce the solvents used for cleaning and thus the resulting emissions, the following measures can be applied: [BayLFU 2005] [DFIU 2000] [BREF STS]

- Using cleaning solvent as sparingly as possible
- No cleaning of equipment for base coatings or coatings with low optical requirements
- Consecutive coating of same coloured working pieces
- Use of the pig-clearing method[5] to avoid residues remaining in pipes
- Immediate cleaning of parts, leaks, spillages and working environment before coating materials dry

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[5] ‘pigs’ are plastic pieces, forced with compressed air through pipes to transport coating remains left over in pipes back to the storage tank. The system is only applicable, where paints are delivered to machinery through pipes and different colours are sent through the same pipe regularly.

- Use of systems that allow back-flow of solvents into a closed container. Cleaners are pumped through a tap or sprayed onto the object in a partially enclosed work area above the storage drum. The work area allows flow back of surplus solvents through coarse filters into the drum.

- Regular inspections of storage areas and working environment to ensure appropriate handling of cleaning solvents.

- Minimising exposure of the open surface of liquid solvent in the working station.

- Use of cartridge systems for exact dosing of coating material to avoid contamination of pipes during colour changes.

- Automatic equipment washing can be combined with re-use systems that achieve up to 80 – 90 % solvent recovery. Problems may occur with 2-component clear coat materials, which can lead to clogging of recovery tank pipes. A solvent recovery system costs 0.4 million € per spray booth. [BREF STS 2007]

7.2 Abatement technologies

If primary measures are not sufficient to meet the emission limit values or cannot be applied, VOC emissions can be destroyed by thermal oxidation.

For series coating, abatement technologies are applied to treat exhaust air from dryers after solvent-based as well as after water-based systems. Thermal oxidation is commonly used. After solvent-based clear coating it can be combined with heat recovery for pre-heating of drier air.

Thermal treatment of waste gas is also necessary when water-based primers or base coats are applied. It is less effective, as together with VOC emissions high volumes of clean air are extracted. In these cases adsorption (on zeolite) and concentration may be used to achieve VOC concentrations that do not require the use of additional natural gas to maintain the oxidising flame.

8 Summary of VOC emission reduction measures

Table 8 summarizes the VOC emission reduction measures presented in chapters 6 and 7:

Table 8: Measures for VOC substitution and VOC reduction in vehicle coating and vehicle refinishing

Objectives	Description	
Substitution/ Solvent free processes	Substitution of VOC by change of application systems	Use of powder coatings
	Substitution of VOC cleaners	Use of VOC-free cleaners e.g. water-based cleaners (with detergents) for cleaning of equipment, parts and booth
Substitution / Reduction of the solvent content	Reduction of the solvent content in coating systems	Change from conventional coating systems to high solid solvent-based systems or to water-based coating systems
Process Improvements	Improvement of application techniques	Reduction of the number of coating layers Optimisation of spraying technique (increase of automation and electrostatic applications)
	Reduction of cleaning effort	Reduction of colour changes. Immediate cleaning before drying. Recover cleaner and minimise use. Emptying of pipes by ‘pig’ systems before cleaning. No cleaning for application of base coats or coats with low optical requirements. Consecutive coating of same coloured working pieces. Use of cartridge systems for optimised material dosing.
Abatement Technologies	Concentration of VOC (before abatement)	Zeolite adsorption wheel
	Destruction of VOC	Thermal oxidation (with heat recovery)

9 Good practice examples

Application of VOC-free powder coating technology has been introduced by BMW, initially in the Dingolfing/Germany plant and later also in its plants in Leipzig/Germany and Regensburg/Germany. Before its introduction coating each car body used about 1 kg of solvent. The amount of solvent substituted, at a typical daily production of up to 1200 car bodies, is approximately 400 tonnes per year.

Robots open and close the vehicle doors automatically. Coating of the doors and the rear of the car is done by using 'line-tracking' (robot follows a specific line on the body surface). The remaining surfaces are coated by static coating machines. An electrode in the rotation atomiser electrically charges the clear-coat powder as it is sprayed – the powder particles then adhere to the grounded car-body. Later, in the dryer, the powder melts at about 145°C, becoming transparent and fusing with the coloured water-based base-coat.

The powder-coating technology used delivers both ecological advantages and a technically improved product. The automated process produces neither coating sludge nor waste water. The combination of new coating techniques and robotics guarantees high cost effectiveness. The clear-coat powder not fixed on the surface (the overspray) is collected and mixed with new powder for re-use. The new process is not only VOC-free but has also reduced the total waste of the coating installation by about 50 %.

[BMW-2 2008]

10 Emerging techniques and substitutes under development

Water-based top coats with less than 10 % solvent content (instead of less than 20 %) are under development and are expected to be employed in 2011 in the Hyundai paint shop in Ostrava/Czech Republic [Hyundai 2008].

First applications of very high solid base coats (50 – 60 % solvent content) have been realised (Ford in Genk/Belgium) [DuPont-1 2008].

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Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Guidance 7:

Coil coating

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses coil coating and the related cleaning of equipment, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emission Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
The activity 'coil coating' is defined as 'any activity where coiled steel, stainless steel, coated steel, copper alloys or aluminium strip is coated with either a film forming or laminate coating in a continuous process.' The SE Directive covers installations in which this activity is taking place with an annual organic solvent consumption greater than 25 tonnes.

The SE Directive lays down the following activity specific emission limit values for coil coating:

THE SE DIRECTIVE APPLIES TO COIL COATING IF A SOLVENT CONSUMPTION OF 25 TONNES PER YEAR IS EXCEEDED

Table 2: Emission limit values of the SE Directive

<table>
<tr><th colspan="5">SE Directive - Emission limit values (ELVs)
(Annex II A – activity No. 7)</th></tr>
<tr><th>Activity</th><th>Solvent consumption threshold [tonnes/year]</th><th>ELVs in waste gases [mg C/Nm³]</th><th>Fugitive emission values [% of solvent input]</th><th>Total ELVs</th></tr>
<tr><td>Coil coating</td><td>>25</td><td>50*</td><td>new installations: 5
existing installations:10</td><td>-</td></tr>
<tr><td colspan="5">Special provisions:
*For installations which use techniques which allow reuse of recovered solvents, the emission limit shall be 150.</td></tr>
</table>

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[1] as well as for halogenated VOCs which are assigned the risk phrases R40 or R68[2]. There is a general obligation to replace CMR substances– as far as

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[1] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

[2] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: 'Possible risk of irreversible effects'. The new wording is: 'Limited evidence of a carcinogenic effect'. In the 'old' version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: 'Possible risk of irreversible effects'. This new risk phrase does not include carcinogenicity. The 'new' version of R40 is obviously less restrictive than the old version. Untilthe SE Directive is adapted to this change, a final decision on which version applies can only be given by the European Court

possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as

CMR substances or ≥100 g/h for halogenated[3] VOC with R40/R68 the ELVs in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

In the coil coating industry VOC emissions arise from the application and the subsequent drying of solvent-based coatings. In general, there has been a trend away from solvent-based paints towards solvent reduced systems with a solvent content of 30-45%.

VOC REDUCED PAINT SYSTEMS ARE THE MOST RELEVANT VOC REDUCTION MEASURES AT PRESENT

Low VOC systems, such as high solid coatings or water-based systems, are available but the shift to these systems has been slow, either because of technical limitations or product requirements. The only VOC-free technology currently in use in coil coating is powder coating, although this is severely limited by economic and technical factors.

Where it is not possible to avoid using solvent-based systems then improved process equipment, air extraction, and end-of-pipe abatement are the most effective measures of reducing the emissions arising from the coating and drying process and the associated handling, storage and mixing of solvents.

3 Description of the activity and related industry sectors

Coil coating takes place in specialised production lines. In many cases coil coaters are part of large aluminium or steel companies [BREF STS 2007]. There are also specialised service centres or coaters of narrow strips providing customized products. The annual production volume of individual plants in the sector varies from 5 to more than 40 million m² coated product.

The main substrates which are pre-coated are either cold rolled, zinc or zinc alloy coated steel (82%) or aluminium (18%) [ECCA 2008].

In 2007 around 5,700 kilo tonnes of steel and 440 kilo tonnes of aluminium have been pre-coated in Europe[4], amounting to over 1,500 million m² of coated product [ECCA]. In total, there are 158 coil coating production lines in Europe[5] [BREF STS 2007, ECCA 2008].

CURRENTLY ONLY AROUND 5 % OF THE PRODUCTION LINES USE VOC-FREE POWDER COATINGS

Out of all the production lines, 7 use solvent-free powder coatings, the others use coatings with a varying degree of solvent content (see also Table) [ECCA 2008].

[3] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.
[4] based on latest 2007 statistics for ECCA members shipments
[5] EU 15 and Czech Republic, Hungary, Poland, Slovak Republic

Coil coated products (also named pre-coated products) are used in a wide range of applications, as Figure 1 shows:

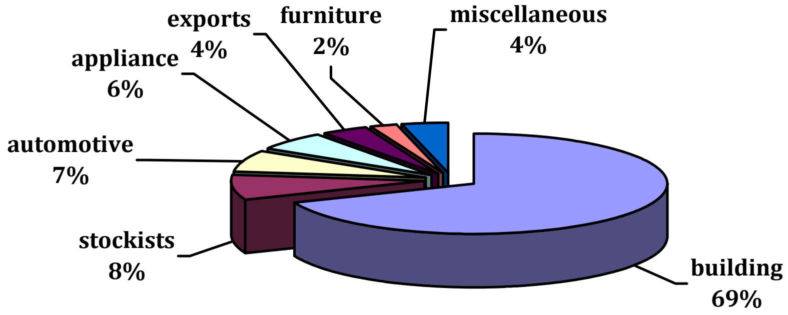

Figure 1: Application areas of pre-coated material in 2006 [source: ECCA DE]

THE BUILDING SECTOR IS THE MOST IMPORTANT APPLICATION AREA FOR COIL COATED MATERIALS

Within the building sector pre-coated metal sheets are mainly used for wall cladding (~ 75%), metal roofing and other outdoor applications (~18%) and indoor applications (~8%) [ECCA 2008, ECCA DE].

An increasing demand of pre-coated products is expected for the future.

4 Technical process description

4.1 Process flow and relevant associated VOC emissions

The following flow chart of a typical coil coating process provides an overview of possible VOC emissions. The pre-treatment, primer and coating application might take place on one or on both sides of the metal strip.

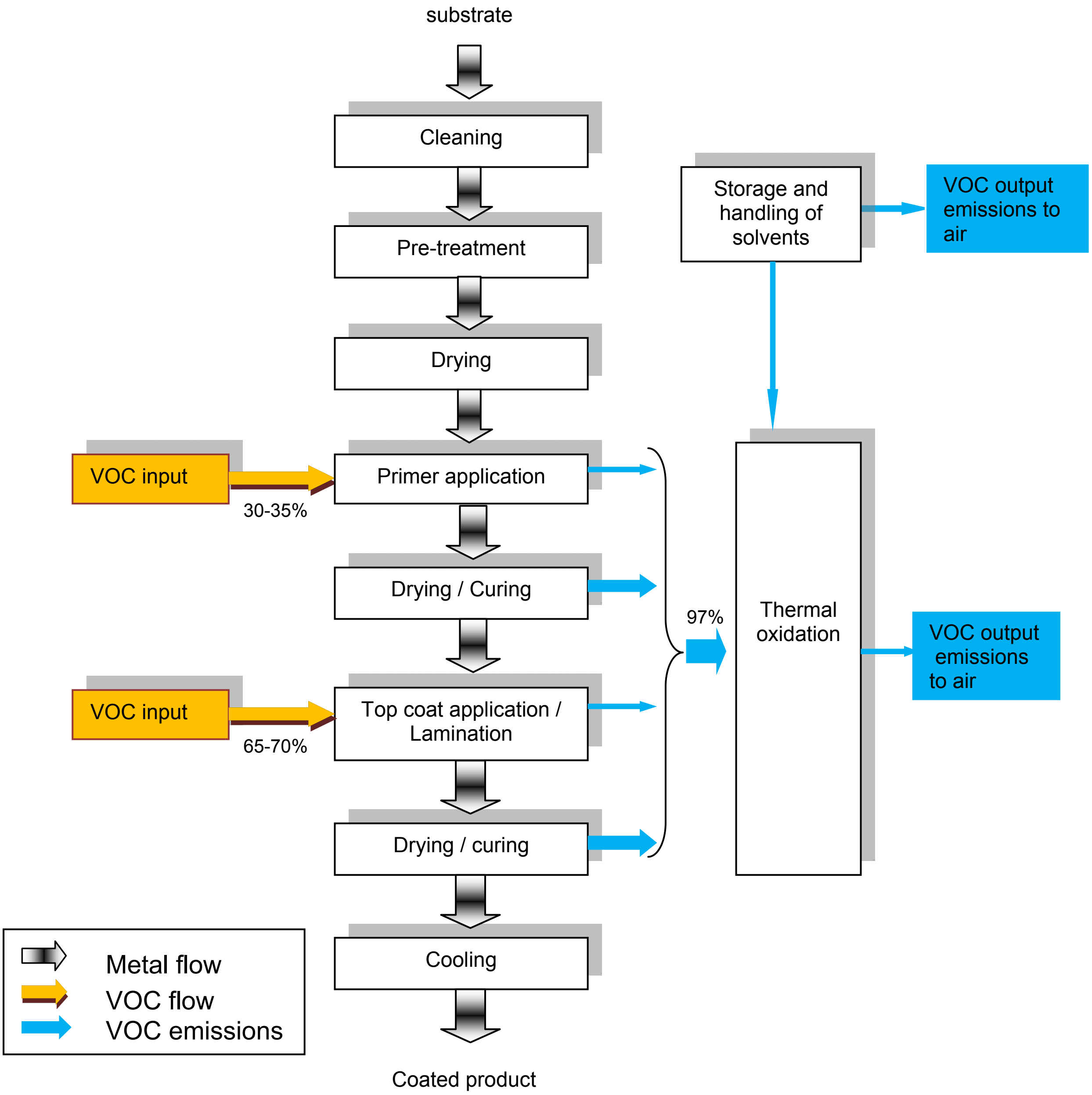

Figure 2: The possible VOC emission sources in a typical solvent based coil coating process

The drying / curing phases contribute the most to VOC emissions to air. Depending on the number of colour changes and the subsequent clean-downs of the equipment, the top-coat accounts for approximately 65-70% of the VOC emissions while 30-35% of emissions are from the primer (standard 25 µm top paint system with 5 µm primer, at the typical solvent loadings given in Table).

Around 97% of all the VOC emissions from the whole coil coating process can be captured. Fugitive VOC emissions make up the remaining 3%. [BREF STS 2007]

4.2 Process description

Coil coating is a continuous process. All production steps, from the winding of the substrate, through pre-treatment and coating application, through to the recoiling of the coated product, are carried out as a continuous sequence. Figure 33 presents an overview of a complete production line.

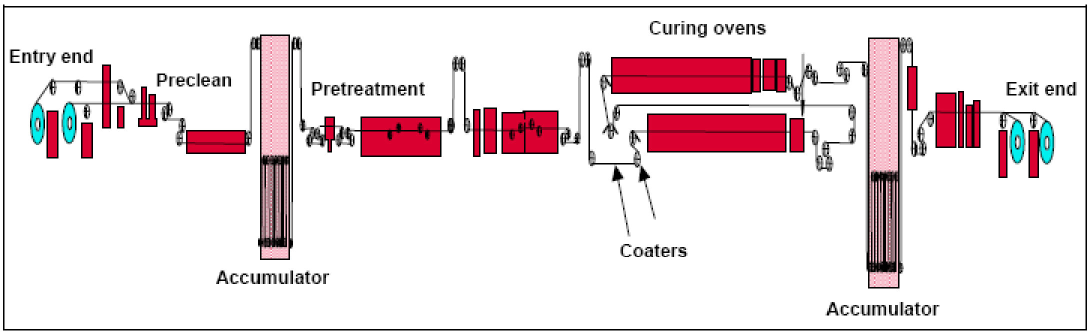

Figure 3: Schematic overview of a complete coil coating production line [ECCA 2008]

In the following the VOC relevant process steps of a typical coil coating production line are described.

Primer coat application

A primer coat is applied, by a roller coater, on one or both sides of the strip. The roller coater is adjusted to give the required primer thickness. Modern application systems are enclosed and the VOC emissions occurring are extracted and vented to the thermal oxidation unit.

PRIMERS ARE APPLIED EITHER ON ONE OR BOTH SIDES OF THE STRIP

After the primer application, the strip enters the drying oven where volatile compounds are evaporating. The metal strip is then cooled, by air or water based cooling systems or, in some instances, by both. The VOC containing air of the oven is also directed to the thermal oxidation unit.

Finishing coat (top coat) application

For the application of the finishing coat, the strip passes to a second roller coater machine. The top coat may be applied on one or on both sides.

In state-of-the-art plants, the application unit for the top coat is also enclosed and the air containing solvents is extracted and vented to the thermal oxidation unit.

After the metal strip has passed the coating area, it enters into a drying oven where the paint cures. The solvent laden exhaust gas from the oven is then passed to the thermal oxidation unit.

After the application of the top coat, the metal strip is cooled down and passed to the accumulator stack and to the recoiling unit.

Lamination

Lamination means the application of thin laminate films on an adhesive layer or special coating layer, instead of a coating. The lamination process can be carried out at the same production line as the paint coating.

IN THE LAMINATION PROCESS VOC EMISSIONS MAY RESULT FROM THE USE OF ADHESIVES OR SPECIAL BASE COATS

In case of laminate films, the adhesive or special coating required for the application can be applied with either of the roller coater heads. The thin polymer film is laid on the hot coating or adhesive layer by roll pressure, followed by a quenching and a drying step. In the lamination process, VOC emissions may result from the use of adhesives or special base coats. The; lamination film itself does not cause VOC emissions.

Cleaning activities

Organic solvents are also used for the clean-down of the equipment before a system or colour change. Generally, clean-down is much more frequent when applying the top-coat than for the primer. The cleaning of the equipment takes place in the area where off-gases are extracted, so solvent emissions are abated.

Cleaning solvents are in most cases collected and treated (usually off-site) so that they can be re-used, either as cleaning solvent again, in paint formulation or for other solvent applications. The solvent used for cleaning is generally not the same as used in the paint formulation because a very low-boiling solvent is required for cleaning while a relatively high-boiling solvent is required in paints.

4.3 Coatings used in the coil coating industry

Nearly all (> 99%) of the coatings used for coil coating are solvent based [ECCA 2008]. Powder coating systems are the only solvent-free applications commonly used in the coil coating industry. Although 7 powder coating lines exist in Europe, the overall consumption of powder coatings is marginal compared to the large amounts of solvent based products used by big production lines. Powder coating lines are typically very small with very limited capacities.

The film thicknesses that can be achieved with powder coatings are limited. It is currently not possible to achieve uniformity at less than 30 microns and so powder coating cannot be used to produce the thin films that can be achieved with conventional solvent based systems:

Solvent-based paint system (50 wt-%):	32-53 g/m² coil
Powder coating system:	60-80 g/m² coil

In addition the range of powder coatings that can meet the specific requirements of high speed coil coating production is still very limited.

Plastic laminates (representing 6% of coil-coating activities) also contain no solvent but their application is not solvent-free, since in almost every case, they require a solvent containing liquid base coat or adhesive layer for the lamination.

Table 3 below gives an overview of commonly used coil coating systems.

Table 3: Overview of coating systems typically used in the coil coating industry [BREF STS 2007, ECCA 2008]

Coating	Dry film thickness (µm)	Resin types	Solvent content (%)	Solvent types	Curing temperature (°C)
Primer					
Primers (conventional)	4-20	Epoxy/urea, Epoxy/ melamine, Polyester/melamine, Polyurethane, Acrylic	50-70	High boiling aromatics, alcohols, glycol ethers/esters, high boiling esters	210-230
Primers [42] (high build)	12-25	Polyester/melamine, Polyurethane	40-50		
Back coats					
Back coats	2-15	Polyester/melamine, Epoxy/ melamine, Epoxy/ phenolic, Alkyd/melamine	50-70	High boiling aromatics, alcohols, glycol ethers/esters,	180-250
Top coats					
Polyester	17-26	Saturated polyesters cross lined with melamine formaldehyde resins	35-55	High boiling aromatics, glycol ethers/esters, high boiling esters	210-230
SMP (silicone modified polyester)	18-25	As above except for silicone modification in the polyester resin	45-55		210-230
Polyurethane	18-30	Saturated polyesters with urethane cross-linking	30-50		220-240
PVDF PVF2	15-25	Polyvinylidene difluoride + acrylic polymer	40-65	High boiling aromatics, glycol ethers/esters, high boiling ketones	240-260
PVC plastisol	100-200	Polyvinyl chloride + plasticisers	< 10	High boiling esters, high boiling aliphatics	190-210
Water-based products (includes some primers and back coats)	1-25	Acrylic/melamine	5-15	High boiling esters, glycol ethers/esters	220-230
Non-stick bakeware coatings	12-15 (2-coat 7+7)	Polyether-sulphone PTFE	65-80	N-methlypyrrolidone, butyrolactone, high boiling aromatics	350-370
Laminate film coatings	15-120	PVC, PVF (polyvinyl fluoride), PET (polyethylene terephthalate), acrylic, polypropylene	0	None in film, but used in primer/adhesive	lamination at 180-230
Powder coating	35-100	Polyester/epoxy polyurethane	0	-	200-250

5 Solvent use, emissions and environmental impact

5.1 Solvents used

Various VOC containing products are used for coil coating (see section 4.3) and they commonly contain the solvents listed in Table 4.

SOLVENTS WITH SPECIFIC R-PHRASES ARE MOSTLY PHASED OUT IN THE COIL COATING INDUSTRY

Table 4: Overview of solvent types typically used for coil coating industry

Type of solvent	Some examples
alcohols	diacetone alcohol
glycol acetates	propylene glycol methyl ether acetate, ethyl diglycol acetate
glycols	butyl diglycol, propylene glycol monomethyl ether
high boiling esters	dibasic esters (DBE), mixtures of refined dimethyl esters of adipic, glutaric and succinic acids
ketones	isophorone
petroleum hydrocarbons	commercial aromatic fractions, xylol

Solvents with a specific R-phrase which are restricted by the SE Directive have been mostly phased out in the coil coating industry, namely those classified as R45, R46, R49, R60 and R61 or as halogenated R40. [ECCA 2008]

5.2 Solvent consumption and emission levels

In 2007 the coil coating industry consumed 200.000 tonnes of coating products. Assuming an average solvent loading of the coatings of 40-50%, the total solvent consumption from the paint used in the coil coating industry in the EU was 80 – 100 kilo tonnes in 2007.

Solvent is also used for cleaning apparatus, particularly during product changes. On some lines with frequent product changes the solvent for cleaning can amount to up to one third of the total solvent use.

Water based products and powder coatings make up less than 1% of the total products used.

An overview of the specific VOC emissions for the different systems is shown in Table 5 below.

Table 5: Specific VOC emission for different systems (average coating thickness: 55µm) [BREF STS 2007] [ECCA 2008]

Coating system	**Specific VOC emission (g/m² coated coil)**	**Abatement technique**
Solvent-based (50 wt-%)	28 – 29[1]	None
Solvent-based	<2.5	Thermal oxidation connected to oven
Powder coating	0 – 0.8[2]	None

[1] Emission levels with no further abatement of the air stream (compliance with SE Directive limit values has to be checked)
[2] VOC emissions relate to curing reactions rather than solvent use

With the installation of a thermal oxidiser the specific VOC-emissions per m² coated coil can be reduced significantly (< 2.5 g/m² coated coil), independent of the solvent content of the paint system.

Both paint and solvent consumption has increased steadily over the last years. ECCA estimates that in 2007 over 90% of installations had secondary VOC abatement technologies in place (some form of oxidiser). This could imply that although solvent use has increased (with total paint use) total VOC emissions will not necessarily have matched this. [ECCA 2008].

5.3 Key environmental and health issues

In coil coating industry a broad range of different solvents are used in the different paint systems as well as for cleaning activities.

VOC emissions, together with NOx emissions, are precursors of ground level ozone formation in the presence of sunlight. Existing occupational workplace limits should be taken into consideration.

Emissions of VOC to air may occur from:

- the storage of the solvents

- prime and top coating application

- drying processes

- cleaning operations

Spills and leaks from storage areas may result in emissions to soil and groundwater.

The process generates waste containing solvents which need to be disposed of in such a way that emissions to air, soil and groundwater are prevented or limited.

6 VOC Substitution

The following sections describe potential substitutes for VOC (using VOC-free and VOC-reduced systems). There are also descriptions of the application technologies or special conditions needed and the advantages and disadvantages compared to systems that use solvents with a high VOC content.

6.1 VOC-free systems

This section describes the ways that VOC-free products or systems can be used to replace the organic solvents currently used.

6.1.1 Powder coatings

Powder coatings are typically based on polyester resins and are 100 % VOC free. Powder coating is suitable for both steel and aluminium substrates, but it is not applicable for all end uses.

Powder coat particles are electrostatically charged either in a spray gun or in a cloud chamber and they are attracted to the earthed metal substrate. The subsequent drying or curing step is typically carried out by a combination of infrared and circulating hot air at temperatures of 180-250°C (during 1.5 to 2 minutes). For comparison, typical residence times in conventional coil-coating ovens are 15-30 seconds.

At present, powder coatings can only be applied to one side of the substrate and with only one layer. The typical layer thickness is 50 to 60 µm.

Powder coating is used for the painting of pre-formed items such as sanitary cabins, computer enclosures and for small volume and niche products. It does not generally provide the ‘heavy duty’ performance needed for coil-coated products that are subject to outdoor exposure. Powder coating of flat metal substrate is used primarily where small batch sizes and flexible colour changes are important.

No VOC emissions occur with the application of powder coatings, but odorous reaction products can occur during the curing process which might still require appropriate abatement technologies.

SLOWER LINE-SPEEDS AND RESTRICTION RELATED TO THE THICKNESS OF THE COATING ARE THE MAIN CONSTRAINTS RELATED TO POWDER COATINGS

Powder coating lines generally have a lower capacity than liquid applying coating lines because they run at a lower line speed (limited to 15 m/min). Typical capacity figures of powder coating lines are 4-8 kilo tonnes/year compared to 20-200 kilo tonnes/year of the liquid coating lines.

The production costs are higher than those of liquid coating processes due to slower line-speeds and to achieve a thin coating, (more expensive) powder is required with very small and tightly controlled particle size.

This cost penalty has prevented the widespread adoption of powder coating where traditional coil-coating can be used. It is not feasible to convert an existing liquid application production line to powder coating.

6.2 VOC-reduced systems

If the complete substitution of organic solvents is impractical then changing to systems with a reduced VOC content, such as those described in this section, can decrease emissions.

6.2.1 High solid coatings

The high solid coating systems, most typically used in coil coating processes, have a solids content of 70-95%. The most frequently used products use PVC plastisols with a solvent content of less than 10%.

THE MOST IMPORTANT HIGH SOLID PRODUCTS IN THE COIL COATING INDUSTRY ARE PVC PLASTISOLS

High solid coatings such as plastisols are typically applied with a higher film thickness (100-200 µm dry film thickness) than other solvent based paints (15-30 µm dry film thickness, average solvent content 50%). Therefore total quantity of solvent used (and so VOC emitted) per m² coated coil is often similar for both systems. For this reason, the use of high-solids coatings in the coil coating industry is generally not that effective related to the overall solvent emissions reduction.

High solid products can be applied using the same production lines as conventional solvent-based products. In general, high-solid coatings are less expensive per kg, but as they are applied at higher thickness, their application is often more expensive. They are only used if they provide the best way of achieving the required properties. A general switch from conventional products to high solid products is not possible.

Equipment maintenance costs might be higher for high solid coatings as the application places higher stress on the application rolls. The electrical energy needed to drive the coater might also be higher.

6.2.2 Reduced solvent coatings

REDUCED SOLVENT COATINGS WITH A SOLVENT CONTENT BETWEEN 30-40% ARE THE MOST PROMISING VOC REDUCED PRODUCTS FOR THE COIL COATING INDUSTRY

Reduced solvent coatings can offer a genuine reduction in the quantity of solvents used for the majority of coatings.

There are several drivers that prompted a reduction of the average solvent loading in recent years. These include reducing the cost of the solvent used, reducing the VOC emissions, and allowing faster line-speeds without increasing the solvent levels in drying ovens. However, standard paint systems still have solvent loadings in the range 30 – 40%.

Reducing the solvent loading in coatings can have an impact on paint flow and the rheology of the coating and so it must be done in a carefully controlled manner.

The operational costs of the equipment are similar to the conventional solvent-based coil coating but the costs for the coatings can be less.

6.2.3 Water based coatings

Water-based products used in the coil coating industry typically contain up to 25% of organic solvents.

Currently water based top coats are only suitable for a very limited range of end products. Water based coats are mainly applied as primer, backing or ground coating. The main difficulty is the switching between water-based and solvent-based systems. As water-based paints are not suitable for all applications, it is required to have both solvent and water products in place at the same installation.

Water-based products typically require higher energy for the drying process. In addition VOC abatement technologies are often still necessary due to the organic solvent content of the products.

Apart from the energy costs, the other operational costs of water based coatings are similar to conventional solvent based coatings. Problems might occur with corrosion in storage, pumping and application equipment. Therefore it may be necessary to replace existing equipment with stainless steel parts.

Amines are used for pH stabilisation of water based systems and some of these substances have a significant toxicity.

6.2.4 Laminate film coatings

Laminate films are solvent-free, solid polymer films that are applied to the substrate to achieve specific requirements such as stain resistance, hardness or decorative effects. Although the laminate films are solvent free, in almost all cases an adhesive or liquid coat layer is required as the basis for the film. For co-laminates (clear laminates over a liquid base coat) the base coat is often a solvent-based polyester coating. Compared to conventional solvent based products only one layer with VOC containing adhesives is required compared to at least two layers in case of conventional solvent based products with a primer and at least one layer of top coat.

The film is applied by a pressure roll onto a preheated metal strip with an appropriate base coat / adhesive (see also chapter 4.2).

LAMINATED FILMS ARE GENERALLY MORE EXPENSIVE THAN CONVENTIONAL COATING SYSTEMS

The use of laminate film coatings is generally more expensive than conventional liquid coatings and therefore they are only used as alternatives in case of very specific end use properties. Laminates are widely used in domestic appliances where their greater flexibility and toughness can allow more extreme metal forming. They are also still used extensively for applications such as external partition walls in shipbuilding. The decorative properties of laminates are often a feature of office furniture.

The cost of the film depends on factors such as thickness, colour and complexity of patterning or design. Laminate production lines also tend to have slower line-speeds than production lines for liquid coatings. In addition increased scrap levels are reported resulting in increased process costs.

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements and abatement techniques can be used to reduce VOC emissions if VOC substitution as described in section 6 is not possible. The following measures are commonly applied in the coil coating industry:

7.1 Abatement technologies / End of pipe measures

7.1.1 Thermal oxidation (recuperative / regenerative)

Two types of thermal oxidiser are in common use in the coil coating industry - regenerative and recuperative. Both destroy VOCs by burning (oxidation). Regenerative oxidation tends to be more efficient than recuperative thermal oxidation as it uses the recovered energy to pre-heat incoming process air to oxidation temperatures (~ 800 °C). Consequently its operating costs are significantly lower than for recuperative oxidation systems. However, the capital cost of a regenerative oxidiser is significantly higher than for a recuperative system and for small installations, this additional investment cannot be recouped through reduced energy costs. Regenerative thermal oxidation systems are particularly effective for process streams with low solvent loading but their operating costs depend highly on the efficiency of the heat exchanger.

REGENERATIVE AS WELL AS RECUPERATIVE THERMAL OXIDIZERS ARE IN USE IN THE COIL COATING INDUSTRY

Recuperative systems are mainly used for small flow rates. At higher rates the systems are not cost effective.

Regenerative thermal oxidation systems are widely used because they are relatively insensitive to the composition and the concentration of the solvents in the process air. Thermal oxidation systems are used for concentration rates of 1-20 g/Nm³. Thermal oxidation efficiency rates of up to 99.9% are possible.

Thermal oxidation systems use the calorific content of the effluent stream VOCs. Therefore, after a warm up phase, regenerative oxidisers can run efficiently with little or no additional fuel for the oxidation process. The minimum VOC concentration for an autothermic oxidation process is 1-2 g VOC/Nm³.

Catalytic oxidation is an alternative to thermal oxidation that is sometimes applied for coil-coating. Whether catalytic oxidation is a viable option depends on the flow rate, solvent concentration and chemical composition of the waste stream feeding it. Since catalysts are vulnerable to poisoning, catalytic oxidation should only be used if the exhaust air does not contain catalyst poisons such as sulphur, halogens, polymers or heavy metals. The consequence is that the system cannot be applied for all painting systems.

DEPENDING ON THE WASTE GAS PARAMETERS, IN SOME APPLICATIONS CATALYTIC THERMAL OXIDIZERS ARE IN USE

7.2 Process improvements

The most effective process improvement measure for emission reductions is to enclose the system and to fit seals to the entrance and the exit of the ovens/driers. VOCs arising from the coating preparation should be extracted and vented to the waste gas treatment.

8 Summary of VOC emission reduction measures

Table summarizes the various approaches to substitute or reduce VOC emissions as described in chapters 6 and 7:

Table 6: Measures for VOC substitution and VOC reduction in coil coating processes

Objectives	Description	Applicability
VOC-free Systems	Use of powder coatings	Limited applicability due to economic and performance factors
VOC-reduced Systems	Use of high solid coating systems	Only suitable for specific end-uses
	Reduced solvent coatings	Widely applicable in most cases
	Use of water-based coating systems	Limited applicability due to economic and performance factors
	Use of lamination systems	Only suitable for specific end-uses
Process Improvements	Enclosure and air extraction of coating preparation area for waste gas treatment	Applicable in all cases
Abatement Technologies	Recuperative thermal oxidation	Widely applicable but not as effective as regenerative
	Regenerative thermal oxidation	Restricted to larger installations due to capital cost
	Catalytic thermal oxidation	Restricted to installations with well defined and constant waste gas parameters and catalyst poisoning free exhaust gases

9 Good practice examples

9.1 Example 1: Use of Reduced-Solvent Polyester Paints

One major paint supplier has been working with four coil coaters to reduce the solvent content of polyester paints. Of all the paint types used, polyesters account for over 50% of top-coats and the vast majority of backing coats, so modifications to polyesters can make a very significant difference. New generations of polyester resins and careful choice of solvents have allowed solvent loadings to be reduced without having a detrimental effect on viscosity and flow properties.

The principal drivers for these developments have been to reduce total paint cost and to increase running speeds where line-speed is limited by VOC concentrations in the curing ovens. The efficiency of the abatement used on most coil coating installations means that these reductions in solvent usage have not had a significant effect on overall VOC emission rates.

The minimum permissible solvent levels in a polyester paint will depend on many factors including the colour, pigmentation, viscosity requirements and line running conditions. Reduced solvent paints will not be applicable on all lines, but across four major customers, it was found that an average reduction in solvent usage of over 6% can be achieved. The table gives more data on this.

Coating type	**Volume of paint supplied [t/a]**	**Solvent content prior to change**	**Solvent content after change**	**Solvent saved [t/a]**
Customer A	363	45%	38%	25
Customer B	168	41%	36%	8.5
Customer C	75	42%	36%	4.5
Customer D	36	45%	37%	2.5

In 2007, nearly 79,000 tonnes of polyester paint were used in the coil coating industry. Assuming that for half of this paint a reduction in solvent content could be achieved which is similar to the one illustrated here, this could lead to overall savings of over 2,000 tonnes of solvent usage per year in this sector.

[BASF 2008]

9.2 Example 2: Use of Water Reducible Epoxy Backer

The use of a water reducible backer (back coat) has been applied on aluminium substrates in at least one coil coating line in Europe. The water reducible backer (solvent content 20%) substituted solvent based coatings containing 50% solvent. In total the water reducible backer constituted approximately 5% of the site's total paint usage resulting in a total VOC reduction of 3%.

Water backers typically contain less than 20% solids and less than 20% solvent, with the remainder being water. The solvent is required to ensure that the polymer within the paint remains miscible in water.

There are numerous important limitations associated with the processing and end uses of this backer, these being, in summary:

- The coating offers no weathering resistance and no corrosion resistance so it cannot be used e.g. on steel.
- The coating is only suitable for thin film applications, where the dry film thickness required is not more than five microns. This is due to the fact that the wet film thickness requirement is approximately five times that of the dry film (based on 20% solids content) and wet film thicknesses of over 25 microns with 80% volatile material would cause processing problems on coil coating lines such as solvent boil.
- Widening the usage of water containing coatings at a line built for organic solvent coating may result in processing (equipment) problems such as flash rusting of ovens and flue liners.
- The availability of resins for water-based systems is limited.
- Only water miscible solvents are suitable for use in water containing coatings. These tend to be glycols, as opposed to aromatic hydrocarbons and esters. The glycols are more hazardous from the safety perspective and hence tend to have lower workplace exposure limits.

[ECCA 2008]

10 Emerging techniques and substitutes under development

10.1 UV/EB radiation curing

This technology uses paints that are cured with ultra violet / electron beam (UV/EB) radiation. This results in a solvent-free process with a relatively low energy penalty. Currently no commercial applications are known for coil coating. There are significant technical challenges still to overcome and radiation-cured coatings may not be suitable for all applications. Moreover, it is unlikely that existing installations would switch, due to the high capital cost of curing technology. [ECCA 2008]

10.2 Development of VOC-free or VOC reduced products

There is continuing technical progress in increasing the solids content of coil coatings.

The technical feasibility of powder coatings has been proven in major coil coating lines but its economic viability is not yet proven. It is continuously under review.

[ECCA 2008], [BASF 2008]

11 Information sources

[SE Directive 1999]
Council Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations

[BASF 2008]
BASF, UK, personal communication, 2008

[BREF STS 2007]
EU Commission: Reference Document on Best Available Techniques on Surface Treatment using organic solvents, August 2007

[DEFRA 2004]
DEFRA, Department for Environment, Food and Rural Affairs, Scottish Executive, Secretary of State's Guidance for Coil Coating, Process Guidance Note 6/13 (04)

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Coil Coating– Synopsis sheet, prepared in the framework of EGTEI, 04. Sept. 2006
http://www.citepa.org/forums/egtei/18-Synopsis-sheet-coil-coating-30-09-05.pdf

[ECCA 2008]
ECCA, European Coil Coating Association, Belgium, personal information, 2008 Mr. Graeme Peacock, http://www.eccacoil.com

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Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Guidance 8 – Part 1:

Other metal coating

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses metal coating other than for vehicle, presenting options to substitute or reduce the use of VOC and its resulting emissions. Vehicle coating and vehicle refinishing[1] are addressed in separate guidance documents: for vehicle coating of small series and for vehicle refinishing see guidance no. 6 part 1, for large series vehicle coating see guidance no. 6 part 2.

Table 1: Scope definition of the VOC Solvent Emission Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
Coating of other metal parts is defined by the SE Directive as 'any activity in which a single or multiple application of a continuous film of a coating is applied to metallic surfaces including surfaces of airplanes, ships, trains, etc.'

Emission limit values for other metal coating activities are listed in Annex II A of the SE Directive under activity no. 8, which also includes the coating of other materials like plastics, textile, fabric, film and paper. These activities are adressed in guidance document no. 8 part 2 ('other coating').

THE SE DIRECTIVE APPLIES TO "OTHER" METAL COATING IF A SOLVENT CONSUMPTION THRESHOLD OF 5 TONNES IS EXCEEDED

Table 2: Emission limit values (ELVs) of the SE Directive

SE Directive - Emission limit values (ELVs) (Annex II A – activity No. 8 – metal coating)			
Activity	**Solvent consumption threshold [tonnes/year]**	**ELVs in waste gases [mg C/Nm³]**	**Fugitive emission values [% of solvent input]**
Other metal coating	> 5 - 15	100 (1) (2)	25 (2)
	> 15	50/75 (2) (3)	20 (2)
Special provisions: (1) ELV applies to coating application and drying processes operated under contained conditions. (2) Coating activities which cannot be applied under contained conditions (such as shipbuilding, aircraft painting) may be exempted from these values, in accordance with Article 5(3)(b)[2]. (3) The first emission limit value applies to drying processes, the second to coating application processes.			

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[1] Vehicle finishing covered by the scope of the SE Directive is 'the original coating of road vehicles as defined in Directive 70/156/EEC or part of them with refinishing-type materials, where is carried out away from the original manufacturing line, or the coating of trailers including semi-trailers (Category O)'

[2] Art. 5(3)(b): 'The reduction scheme of Annex II(B) is then to be used, unless it is demonstrated to the satisfaction of the competent authority that this option is not technically and economically feasible.
In this case, the operator must demonstrate to the satisfaction of the competent authority that the best available technique is being used.'

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[3] as well as for halogenated VOCs which are assigned the risk phrases R40 or R68[4]. There is a general obligation to replace CMR substances– as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated[5] VOC with R40/R68 the ELVs in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

For ‘other metal coating’, the solvent related VOC emissions mainly depend on the coating products used and their solvent content.

VOC emissions can be reduced by using high efficiency application techniques (e.g. by reducing overspray).

Lower emissions may also be achieved by reducing the solvent content in the coatings and fillers/primers (by using ‘high-solids’ products) or by a change of the coating system (e.g. from conventional coatings with a solvent content of about 70 % to water based products with a solvent content of about 4 – 15 %).

In some cases, the substitution of solvent-based application techniques by powder coating may be possible.

VOC REDUCTION CAN BE ACHIEVED BY USING MORE EFFECTIVE APPLICATION TECHNIQUES OR BY SUBSTITUTING SOLVENT-BASED COATINGS WITH WATER BASED COATING SYSTEMS OR POWDER COATINGS

If primary measures cannot be applied then VOC emissions may be abated by efficient waste gas treatment, eventually pre-concentrating effluents with adsorption technique to achieve autothermic combustion.

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[3] CMR substances-carcinogenic(R45, R49), mutagenic(R46), or toxic to reproduction (R60,R61)

[4] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: ‘Possible risk of irreversible effects’. The new wording is: ‘Limited evidence of a carcinogenic effect’. In the ‘old’ version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: ‘Possible risk of irreversible effects’. This new risk phrase does not include carcinogenicity. The ‘new’ version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to this change, a final decision on which version applies can only be given by the European Court

[5] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.

3 Description of the activity and related industry sectors

Metal coating, other than for road vehicles, is used in all countries of Europe in a wide range of different industries. For 2004, the EU 15 Member States reported about 5000 existing and 300 new installations falling under the SE Directive[6], carrying out activities under the scope of number 8 activity of Annex II A. These figures do not only cover metal coating, as the activity also comprises activities for coating of plastics, textile, fabric, film and paper. [Implementation 2006].

In general, two types of activities can be distinguished: coating that can be applied under contained conditions (e.g. machinery, construction materials, household appliances, metal furniture) and coating that cannot be applied under those conditions (such as shipbuilding or aircraft painting).

The following sections describe examples of metal coating activities.

Coating of mechanical engineering equipment

Surfaces of machines need to have a resistance to oils, cooling agents and other liquids. Coatings therefore need to produce both a high quality surface finish and provide corrosion protection.

Typically a water-based base coat is applied first to the surface via electrostatic dipping or spray coating. This is usually followed by two top coat layers, either a 2-component coating system based on acryl, polyurethane (PUR) or epoxides as coloured base coat - followed by a clear coat, or a 2-layer colour base coat. The coatings are usually applied via spray techniques but depending on the application, casting, rolling, dipping and flooding or powder coating may be used as well.

[DFIU 2003] [EGTEI 2004]

Coating of agricultural machinery

The visual surface quality of agricultural vehicles is not as critical as that of passenger cars but its importance is increasing. Agricultural machinery is produced throughout the year but usually sold in spring. Therefore, most of the machinery needs to have an attractive coating following a period of outside-storage during both winter and summer conditions pending sale. [DuPont 2008]

The main task of the coating, nevertheless, is corrosion protection. The varnish has to sustain heavy mechanical and chemical stress. Chemical corrosion may occur due to aggressive plant residues and moisture and the coating usually cannot last the vehicle service life.

The base coating is often applied manually, via spray coating with solvent based coatings, but water-based electrophoretic dip coating is progressively displacing this technique.

The topcoat may be manually sprayed with solvent- or water-based coatings though powder coatings are increasingly being used.

In the pursuit of greater automation, manufacturers tend to apply base coat and top coats before assembly takes place. [DFIU 2003]

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[6] No data of Italy and Sweden.

Coating of special-purpose vehicles

Special-purpose vehicles[7] include town council vehicles - like street sweepers or dustcarts, vehicles for road making like asphalt-rolling or mowing and construction vehicles.

They are usually spray coated using 'serial' or 'refinishing' coatings, depending on the costumer's finishing requirements and the nature of the individual parts to be coated. [Ökopol 2008]

Coating of bikes and motorbike frames

Bicycle and motorbike coatings consist of one to three layers: a ground coat, a colour-bearing base coat and a clear topcoat. Whether a single-layer or multi-layer coating is used depends on the individual product requirements, the product size, and the equipment of coating installation.
Powder coatings are increasingly replacing the traditional solvent-based base and clear coats. Problems may be encountered, however, if the adhesive bonding of the frames weakens at temperatures of greater than 180°C, the temperature needed to fuse the powder coating. [DFIU 2003]

Coating of heating elements

For the coating of heating elements, powder coating systems are most commonly used. [DFIU 2003]

Coating of metal furniture

For the coating of metal furniture, conventional solvent-based systems, water-based systems and powder coatings are used.
Application techniques comprise spray coating (conventional/ electrostatic, manual/automatic), electrophoretic dip coating and powder coating.
Metal hospital furniture is typically coated with polyester powder coating that guarantees higher resistance to hot water and scratching as well as to disinfectants and superheated steam-sterilization.
Shelves are produced in a wide variety of colours and shapes and so conventional solvent based paint systems, water based systems and powder coating systems tend to be used.
The final coating, for standard colours, may be applied by spraying techniques or by dip coating; in some cases powder coatings can be used.

High voltage switch cabinets are usually base coated via electric dipping. Top coats are conventional 2-component systems, water-based systems or powder coatings. [DFIU 2003]

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[7] All vehicles not being road vehicles as defined by Directive 70/156/EEC

Coating of aircrafts

Coating materials on aircrafts need special permission according to international aviation rules for each type of airplane and for exterior as well as interior parts. Aircraft coating comprises two subsectors: OEM (Original Equipment Manufacturer) and MRO (Maintenance, Repair and Overhaul). Permitted coating systems for OEM may differ from those allowed for MRO. New coating systems are usually introduced first for the OEM sector and similar systems can only be used for existing airplanes after specific additional development, testing and permitting procedures for the MRO sector.
[BREF STS 2007] [Ökopol 2008]

Coating of ships

Coating systems for ships consist of one or more layers of solvent-based, low solvent or non-solvent coatings. Predominant binders are epoxy resins (usually 2-component), polyurethane, acrylates, alkyd resins and chlorinated rubber.

Layers of 200 and 1000 µm thickness are applied. A thicker layer of special top coatings is usually applied to ramps and working areas.

Coating materials are usually applied by means of airless spraying processes, which enable the processing of low solvent and non-solvent products. Roller and brush application is widely used in coating yachts. Rollers are also used for pre-delivery coating of passenger ships.

[BREF STS 2007]

4 Technical process description

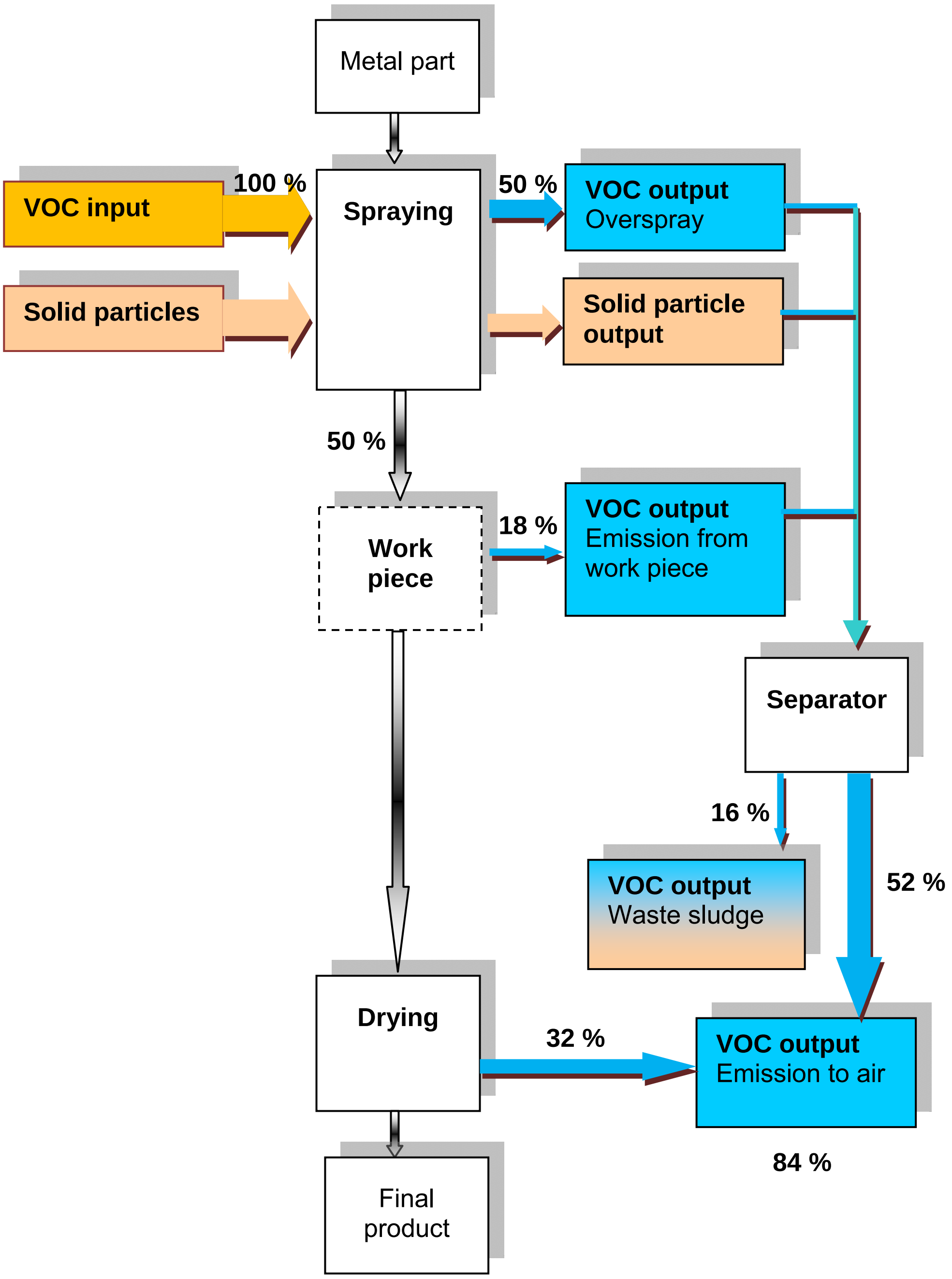
4.1 Process flow and relevant associated VOC emissions

The flow chart in Figure 1 gives an overview of the typical process steps, and the VOC emissions that can occur, assuming the use of conventional spray coating techniques with 50% overspray.

COATING EFFICIENCY HIGHLY DEPENDS ON THE GEOMETRY OF THE WORK PIECE

In practice, conventional spray coating may have a coating efficiency between 5% and 60%, depending on the geometry of the work piece (plane surface or lattice-like) and the skill of the sprayer.

A change of the coating efficiency (e.g. due to a change of spraying technique) or the solvent content of the coating would have a corresponding impact on the VOC flows shown in the chart.



Based on [DFIU 2003]

Figure 1: VOC emissions from spray application with conventional technology assuming 50% overspray

4.2 Process description

Coating processes can differ significantly due to the fact that a wide range of different products with different requirements are coated. Typical process steps and coating application techniques are described below.

4.2.1 Degreasing

In most cases where special purpose vehicles are given original coatings they (or the parts of them to be coated) are sandblasted and further degreasing is not necessary. In cases of local contamination e.g. with oil from final drilling or cutting activities, these areas of the work piece are usually cleaned manually by brushing or wiping. Degreasers used for this type of application usually have a high VOC content, from about 50 % up to 100 %.

Small metal parts are pre-cleaned either with a water-based cleaner using a pressure washer or with solvent containing cleaners applied by spraying.

For further details of degreasing see guidance document no. 4/5 (‘surface cleaning’).

4.2.2 Coating systems

Coating systems for metal coating activities in most cases consist of at least two layers, a primer and one or more top-coat layers.

The primer is used as first coating of the metal surface, having an anticorrosive function and helping to increase bonding of the subsequent coating.

A typical conventional primer for metal coating is based on polyvinylbutyral resin. These primers have a total solvent content of 55- 65 % w/w. More modern systems are either epoxy based (with a solvent content of about 40 % w/w) or polyester based (solvent content of about 20 % w/w).

In most cases top-coating is performed with a single layer system. This single layer coating has to provide both the colour/appearance and protection against chemical or other attack (sunlight, mechanical impact, etc).

The single layer top-coating may either be a 1-component system with a typical solvent content of about 45 – 55 % w/w or a 2-component system with solvent content of about 25 – 35 % w/w. As an alternative, water based systems may be used with a VOC content of about 10 – 15 % w/w.

WATER-BASED TOPCOAT SYSTEMS HAVE 10-15% VOC CONTENT COMPARED WITH 25 – 55 % IN SOLVENT-BASED TOPCOATS

In cases where specific colour effects need to be achieved two- or multi-layer systems are used. The two coat system consists of a basecoat providing colour, followed by sealing with a clear topcoat. For multi-layer systems, an additional colour-coat is applied (intermediate coat).

4.2.3 Application techniques

The application techniques used differ depending on the coated product. For efficiencies of different application systems see table 3 on page 29.

The choice of coating system depends not only on the requirements of the work piece (e.g. the corrosion resistance to be achieved) but also on the size, available equipment and core business of the paint shop or company performing the coating.

Electrophoretic dipping is a major technique for applying the primer systems. Various types of spray coating are then used for subsequent coating layers in the case of small scale production, whereas for large scale production powder coatings are typically used.

Conventional high and low pressure spraying

Coating material is ejected from the nozzle of a spray gun using compressed air. The air transports the particles of the coating material onto the surface of the work piece.

The higher the pressure of the air the finer are the particles of the coating material. Fine particles increase the quality and the smoothness of the coated surface. On the other hand, the finer the particles, the greater the ease with which they are deflected by the airflow from the coated surface leading to increased coating waste (overspray). Conversely, if the pressure is too low, the coated surface is of poor quality (e.g. an ‘orange peel’ effect is created).

The coating efficiency varies between 5 % (for lattice-like work pieces) up to 30 – 60 % (for work pieces with large and plane surfaces).

Conventional spray coating is applicable for any surface and is used in particular for topcoats because of its ability to achieve high quality finishes and special surface effects (e.g. metallic or pearl look).

[DFIU 2003] [BREF STS 2007]

High volume low pressure spraying (HVLP)

For high volume low-pressure spraying (HVLP), the atomising pressure is decreased from the conventional 3 – 6 bar down to 0.7 bar. Compared to high-pressure spray coating, up to 20 % overspray can be avoided and the coating efficiency is about 40 - 80 %.

Due to the larger particles of coating material created by HVLP sprays, the quality of the finish may not match that achieved with conventional high pressure air guns. However, improvements in HVLP gun design are such that the most modern designs are able to match the quality of finish achieved by high-pressure guns. [DFIU 2003] [BREF STS 2007]

HVLP SYSTEMS ACHIEVE HIGH MATERIAL EFFICIENCIES OF UP TO 80 %

Airless spraying

In airless spray coating, the paint is forced through very small metal nozzles (< 2 mm) with a pressure of 80 to 250 bar. The paint jet strikes the stationary air outside the nozzle and is broken up in fine particles due to the force of this impact.

The paint is delivered to the nozzle using high-pressure pumps and this prevents quick colour changes. However, a high throughput of coating is possible. Airless spray coating is cheap and fast and can be used for 1-component and 2-component paint.

Airless spray coating gives a rough finish that needs to be sanded before finer coatings can be applied. This introduces an additional process stage compared with the use of high pressure air spraying. However, optimisation of the spraying can improve finish quality to close to that achieved with HVLP guns, especially with primer coatings. Operator training is essential in order to maximise the performance of airless spraying systems.

AIRLESS SYSTEMS ARE ONLY EFFICIENT ON LARGE SURFACES

This spraying technique may be used either manually or automatically. Material efficiency for airless spray coating is about 5 % (lattice-like work pieces) up to 40 – 75 % (large surfaces). [DFIU 2003] [BREF STS 2007]

Electrostatic spray coating

An electric field is created between the work piece and the coating material, these having opposite polarity. Coating material is atomised and sprayed and the particles are attracted to the work piece. The process halts when the film thickness is nearly equal on all surfaces and edges. Cathodic coating is the most widely used technique as anodic work pieces tend to corrode.

ELECTROSTATIC SPRAY COATING CAN ACHIEVE VERY HIGH MATERIAL EFFICIENCY OF 95 – 100 %.

In general, the efficiency of electrostatic spray coating is from 95 % up to 100 %. Compared to conventional spray coating, electrostatic spray coating is more time and material efficient and easier to automate. Less waste residues are generated and spray booths require less cleaning.

For electrostatic spraying to work, the work piece has to be conductive. This limits the substrates and coatings that can use the technique (e.g. it is not possible to recoat existing coatings). In addition geometries that act as Faraday cages have to be avoided because the coating is applied to them unevenly.

Electrostatically assisted compressed air, airless and air assisted spraying

These techniques combine regular compressed air or airless spraying with the electrostatic charging of paint particles.

For compressed air, the material flow is up to 1000 ml/min, for airless or assisted airless techniques the material flow can be up to 3000 ml/min. The material efficiency is up to 85 %.

Compared to conventional spraying, less overspray is generated and spray booths are less polluted. Therefore, less cleaning agents are needed.

With electrostatically assisted spraying more complex geometries can be coated than with electrostatic spray coating.

[BREF STS 2007]

Conventional dipping

Work pieces are either dipped manually or transported and dipped via conveyor systems. Dipping into water-based paints might produce foam. Water-based paints are only stable over a small range of pH levels and, therefore, very sensitive to contamination that might be introduced from the pre-treatment processes.

DIPPING ALSO ACHIEVES VERY HIGH MATERIAL EFFICIENCY OF UP TO 100 %.

This technique is quite cost effective and can achieve a material efficiency of up to 100% [BREF STS 2007]. The finish quality is relatively low. The technique is not applicable for coating of open-cell surface structures. [VDI 2008]

Electrophoretic dipping

Electrophoretic dipping is mainly used for pre-coating. In the process, a direct electric current is made to flow between the work piece and the electrodes of opposite polarity installed in a tank.

Cathodic (work piece loading) systems are commonly used, because they offer better resistance against corrosion than do anodic systems.

Electrophoretic dipping is only used with water-based coatings having a solvent content between 1 – 4 %.

Electrophoretic dipping is an efficient application technique that produces high quality coatings. However, it is a cost intensive system (investment and material costs), and requires a high level of maintenance of the paint tanks for quality assurance. [BREF STS 2007].

The work piece has to be conductive. Primer base coats applied by electrophoretic dipping are often followed by a powder coated topcoat.

Application of powder coatings

Powder coatings achieve high efficiencies up to 100 % as overspray material can be re-used. They are applied and then melted and cured by heating the work piece at 200°-250°C [BREF STS 2007].

WITH POWDER COATING, HIGH EFFICIENCY OF UP TO 100 % IS ACHIEVED.

Powder coating – electrostatically assisted spraying: The powder particles are electrostatically charged and sprayed onto the work piece using compressed air. Spray booth and application tools can be cleaned by vacuum cleaning or by blowing with compressed air. There are no solvent emissions associated with this spraying process.

Powder sintering: The work piece is heated above the melting temperature of the powder coating before coatings are applied. As soon as the powder is in contact with the surface, sintering and merging takes place.

[BREF STS 2007]

4.2.4 Drying

After the application, the coating has to dry. The drying time can be reduced by the use of additional drying units (ovens). Spray booths may also function as ovens.

The drying time depends on the object or substrate, the type of coating and the coating thickness, and varies from a few seconds to one hour.

Dehumidified air is used for the drying of water-based coatings or a pre-drying step of wet-on-wet layers (second coating taking place before first coating has dried completely). Due to the removal of water in this manner, the drying times can be significantly reduced. [BREF STS 2007]

In contained conditions drying air can be captured and routed to treatment, eventually concentrating low VOC loaded air in activated carbon or zeolite before treatment. If drying cannot be done under contained conditions, influence of weather conditions has to be kept as low as possible (e.g.

reduction of dust sources, reduction of direct sunlight exposure during coating, if possible).

4.2.5 Cleaning

Cleaning needs to be undertaken in all application techniques: for work pieces (see also guidance document 4/5 on 'surface cleaning'), for work place environment, coating equipment and parts thereof.

A range of cleaning techniques can be used, from manual cleaning to automatic cleaning using closed systems with solvent recovery (e.g. for spray guns and parts, see figure 3). Solvent cleaners are used (and sometimes heated for higher efficiency) as well as water. Cleaning with water is possible when water-based coating systems are used and when the cleaning is performed before paints have fully dried.

Cleaning needs to be effective and fast. Cleaning intensity varies according to the nature of colour changes and is also dependent on whether the contamination is semi-dry or dry.

[BREF STS 2007]

Spray booths are usually cleaned with cleaners with a low VOC content. An alternative approach is the use of a film or a strippable varnish, applied to the walls of the booth.

[VDI 2008]

5 Solvent use, emissions and environmental impact

5.1 Solvents used

Conventional solvent-based coatings
Conventional solvent-based coatings contain about 30 - 80 vol.-% solvents. Solvents used are mainly mixtures of hydrocarbons (xylene, toluene and white spirit), although alcohols, esters and ketones are also used.
They are classified as coatings based on polycondensation (e.g. phenol/urea/melamin resin), polymerisation (e.g. polyesters, acrylate resins, alkyd resins) or polyaddition (e.g. epoxy or polyurethane resins).

[DFIU 2003]

Solvent based high-solid coatings

High-solid coatings contain < 35 % solvents.

The following solvents are used: xylene, white spirit, aromatic hydrocarbon mixtures, butyl acetate, alcohols, and glycol ethers. Ketones and toluene do not play a significant role in Europe.

Binders of high-solid coatings are based on epoxy resins, 2-component-polyurethanes, polysiloxane, oxirane or alkyd resins.
[BREF STS 2007]

Water-based coatings

The solvent content of water-based coatings is about 3 - 18 vol-%.
Water-based coatings often contain organic solvents as a solubiliser and to improve the properties of the wet film layer. Water based coatings are based on alkyd, polyester, acrylate, melamine and epoxy resins.
[BREF STS 2007]

Powder coating

Powder coatings are VOC-free. Powder coatings are typically based on acrylic resins with either an acid or an anhydride.

5.2 Solvent consumption and emission levels

At EU-25 level, VOC emissions of 544 kt from industrial paints have been estimated for 2000 from the following sectors:

- Trade coaters, general engineering, industrial equipment, original equipment, heavy engineering and aerospace industry,
- Continuous processes: furniture, rigid metal packaging and drums,
- Plastic coating: plastic and automotive components. [EGTEI, 2005]

In total, 1601 kt of paints were used, giving an average emission factor of about 340 g VOC/kg paint consumed meaning that emissions from this sector were already partly abated (unabated emission factors range between 690 and 750 g/kg of paint depending on the subsector).

[EGTEI, 2005]

Cleaning

Cleaning processes with organic solvents account for about 20 % of total VOC emissions from paint shops. [BREF STS 2007]

5.3 Key environmental and health issues

In metal coating a broad range of solvents is used for coating materials and cleaners.

VOC emissions, together with NOx emissions, are precursors of ground level ozone formation in the presence of sunlight. Existing occupational workplace limits should be taken into consideration.

Emissions of VOC to air may occur from:

- the storage of the solvents

- the process

- cleaning operations

Spills and leaks from storage areas may result in emissions to soil and groundwater.

Table 3 shows exemplary solvents of paints classified with risk phrases specifically regulated by the SE Directive.

Table 3: Exemplary solvents paints, classified with risk phrases specifically regulated by the SE Directive

Solvents	Risk Phrases
2-methoxy ethanol, CAS 109-86-4	R60, R61
2-methoxyethanol acetate, CAS 110-49-6	R60, R61
2-ethoxy ethanol, CAS 110-80-5	R60, R61
2-ethoxyethanol acetate, CAS 111-15-9	R60, R61
Trichloroethylene, CAS 127-18-4	R45
Dichloromethane (methylene chloride), CAS 75-09-2	R40

[ADEME 2003], [Ökopol 2008]

The risk classification R45 implies that the solvent may cause cancer; the classification with R60 indicates that the solvent may impair fertility, and R61 indicates that the solvent may cause harm to the unborn child. Solvents classified with R40 have a limited evidence of carcinogenic effect.

The SE Directive requires that the abovementioned solvents carrying risk phrases R60, R61 or R45 have to be substituted, if possible, because of their impact on human health. If substitution is not possible, emissions have to be minimized (see section 1).

Existing occupational workplace limits should be taken into consideration.

6 VOC Substitution

The following section describes potential substitutes for VOC (using VOC-free and VOC-reduced systems). The descriptions of the application technologies or special conditions needed and the advantages and disadvantages compared to systems that use solvents with a high VOC content.

6.1 VOC-free systems

This section describes the ways that VOC-free products or systems can be used to replace the organic solvents currently used.

6.1.1 Powder coating

Powder coatings can substitute for solvent-based or water-based coatings in many cases, but this is dependent on heating of the work piece being possible and the work piece having the required surface characteristics (see section 4.2.3 page 29). Material efficiencies of 80 – 95 % can be achieved.

The working piece has to be able to withstand the high temperatures used to melt and cure the powder.
[BREF STS 2007] [Ökopol 2008]

Cross-media effects
More energy is needed for drying of powder coatings compared to conventional solvent-based coatings.
Besides reduction of VOC emissions to zero, resulting waste amount is reduced because overspray from powder coating can be re-used.

6.1.2 Cleaning systems

Detergent systems can be used for equipment cleaning when water-based coating systems are used.
The systems combine detergents with alkalis and other substances, depending on the substrates and the materials to be removed. Cleaning with detergents may take longer than with solvent based systems.
The water based cleaning systems may require additional heating and subsequent treatment of waste water. [BREF STS 2007]

6.2 VOC-reduced systems

If the complete substitution of organic solvents is impractical then changing to systems with a reduced VOC content, such as those described in this section, can decrease emissions.

6.2.1 Reduction of solvent content in coating systems

Often the most significant reduction in VOC emissions can be achieved by changing from conventional solvent-based systems to high solid coatings or water-based systems (see section 4.2.2 on page 9). Total emission reductions of about 30 – 55 % can be achieved in this way. [DFIU 2000]

In the case of high-solid coatings, the higher price per unit weight for the coating is outweighed by the higher efficiency of the product (higher solid content per unit weight). [DuPont 2008]

Water-based systems require stainless steel equipment to be used and also increase drying times. Drying can be adjusted by installing nozzles for air turbulence during flash off, installing heating systems and increasing air exchange rates.

Prior cleaning has to be done with special care when using water-based systems for coating of large parts with non-planar geometries, to achieve surfaces completely free of dust and oil.

A case-by-case calculation, including evaluation of energy demand and costs, needs to be made in order to determine economic impacts when switching to water-based coatings.

Water-based coating systems used for electrophoretic dipping are associated with costs for the new equipment and its maintenance. Here, as a rough estimate, an economic situation can be achieved if the turnover time for the coating solids in the bath volume is < 1 year. [DuPont 2008]

Cross-media effects
More energy may be needed for drying of water-based coatings compared to conventional solvent-based coatings.
More efficient application systems produce less waste from overspray and less emissions from cleaning of the spraying booth.

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements and abatement techniques can be used to reduce VOC emissions if VOC substitution as described in section 6 is not possible. The following measures are commonly applied for ‘other metal coating’ processes:

7.1 Process improvements

7.1.1 General measures

General measures to reduce VOC emissions [BayLFU 2005]:

- Use contained conditions when ever possible
- Keeping short spraying distance to the coated surface
- Keeping the spray jet vertical to the surface
- Adjusting the width of the spray jet to the working pieces width
- Apply precise contour coating
- Keeping air pressure as low as possible, but adequate for quality requirements
- Reducing the number of coating layers

7.1.2 Efficient application

By switching from conventional application techniques to improved ones, such as HVLP spray-guns, a significant reduction of VOC emissions can be achieved by higher material efficiency respectively less overspray.
Efficient application can be achieve also by automatic mixing systems. In particular for coating of big parts (sometimes difficult to achieve under contained conditions), automatic mixing of 2-K or 3-K systems reduces the need for long pot life and therefore the need for high solvent content systems. Additionally, automatic mixing systems reduce the cleaning effort cleaning of a container - normally used for interim storage of mixed substances - is no longer necessary.
Table 4 shows efficiencies of application techniques. For a detailed description of each system see section 4.2.3 on page 29.

Table 4: Efficiency of application techniques

Method	**Degree of efficiency [%]**	**Geometry of the work piece**	**Other restrictions**
Compressed air spraying	20 – 65	No limitation	-
Airless	40 – 80	Big, simple	-
Airmix	35 – 75	Big, simple	-
HVLP	45 – 65	No limitation	-
Electrostatic assisted compressed air spraying	50 – 80	No Faraday cage	Electrically conducting materials are necessary
Electrostatic assisted airless spraying	45 – 85	No Faraday cage	Electrically conducting materials are necessary
Electrostatic assisted airmix spraying	40 – 80	No Faraday cage	Electrically conducting materials are necessary
Flooding	85 – 95	Non-scooping parts	High solvent loss
Dipping	75 – 90	Non-scooping parts	High solvent loss
Powder with electrostatic spray technique	50 – 95	No limitation	Electrically conducting temperature resistant materials are necessary

[DFIU 2003]

In general, a possibility of VOC emission reduction is the reduction of the number of coating layers. This is a decision which can only be made taking into account individual circumstances such as durability, corrosion resistance and customer specific appearance requirements.

Another possibility of VOC reduction is applying a thinner layer of the topcoat. If a layer-thickness of 50 µm (via spray coating) instead of 85 µm (via dip coating) can be achieved, the material consumption is lower (even if the efficiency is lower due to spray application). In this case the material and disposal costs are smaller, compared to dip coating. Also a better surface quality can be obtained. [DFIU 2003]

In some cases, emissions may be reduced by changing the coating layer system. For example, agricultural machinery may be coated with a two-layer system with the base coat being applied via electrophoretic dipping and the top coat by spray coating using a conventional solvent based system. Keeping the two-layer system, the top coat may be replaced by a solvent free powder coating. Alternatively, a single layer system may be used, applied via electrophoretic dipping. [DuPont 2008]

7.1.3 Reduction of cleaning effort

About 80 % of the solvent emissions from cleaning can be reduced by using closed systems for the cleaning of guns and applicators. Such systems cost between 150 and 3000 Euros. [BREF STS 2007]
Automatic washing machines are enclosed machines which can clean parts to be coated or coating equipment. The solvents are contained and collected for reuse. Automatic washing can be combined with solvent recycling by distillation that can achieve up to 80 – 90 % solvent recovery. Problems may occur with 2-component clear coat materials, which can lead to clogging of recovery tank pipes. A solvent recovery system costs about 0.4 million Euro per spray booth.

Also, the following measures can be applied:

- Using cleaning solvents as sparingly as possible
- No cleaning of equipment for base coatings or coatings with low optical requirements
- Consecutive coating of same coloured working pieces
- Draining of the supply lines before cleaning, e.g. spraying until the line is empty or use of pig-systems
- Immediate cleaning of parts, leaks, spillages and working environment before coating materials are dried
- Regular inspections of storage areas and working environment to ensure appropriate handling
- Use of the pig-clearing method[8] to avoid residues remaining in pipes
- Minimising exposure of the open surface of liquid solvent for cleaning or from solvent-based coatings in the working station.
- Use of systems that allow flow back of solvents into a closed container. Cleaners are pumped through a tap or sprayed onto the object in a partially enclosed work area above the storage drum. The work area allows flow back of surplus solvents through coarse filters into the drum.

  [BayLFU 2005] [DFIU 2000] [BREF STS 2007]

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[8] 'pigs' are plastic pieces, pressed with compressed air through pipes to transport coating remains left over in pipes back to the storage tank. The system is only applicable, where paints are delivered to machinery through pipes and different colours are sent through the same pipe regularly.

7.2 Abatement technologies / End of pipe measures

There should be VOC extraction for all potential emission sources to prevent and limit exposure of workers.

If primary measures cannot be applied then VOCs may be destroyed by thermal oxidation, biological treatment or decomposition by thermal plasma. Biological and plasma treatments are mainly used for low concentrations of VOC (< 1 gC/m^3).

Thermal oxidisation can achieve VOC reduction efficiencies of > 99.9 %, biological treatment generally has a lower efficiency but also lower investment and operating costs.

Adsorption onto activated carbon or zeolite materials, followed by controlled desorption, may be used to concentrate a dilute effluent for subsequent treatment. Concentrated gas streams must be monitored to ensure that the TOC (total organic carbon) content never exceeds 25 – 50 % of the lower explosion limit.

Thermal oxidation can be used if concentrations are above 1 gC/m^3. Low and varying carbon concentrations may require additional fuelling with natural gas to maintain a constant flame temperature. Autothermic combustion can be achieved with TOC concentrations of about > 2 g/m^3.

Recuperative oxidation systems recover waste heat from the combustion, via heat exchangers, to pre-heat incoming waste gas or for process operations such as dryers, or for room heating.

Regenerative oxidation systems are more efficient than recuperative systems. The hot exhaust gas is passed through chambers containing heat retentive honeycomb-like material. When a chamber has achieved its full heat loading the exhaust gas is routed to another chamber. Cool incoming waste gas is heated by passage through the hot honeycomb-like material before it enters the combustion chamber. The regeneration of waste heat decreases the energy demand of the process significantly.

Catalytic oxidation may be used if no ‘catalyst poisons’ are present; since catalysed oxidation occurs at a relatively low temperature the energy demand is reduced.

8 Summary of VOC emission reduction measures

Table 5 summarizes the various approaches to substitute or reduce VOC emissions as described in chapters 6 and 7:

Table 5: Measures for VOC substitution and VOC reduction in other metal coating

Objectives	**Description**	
VOC-free Systems	Substitution of VOC by change of application systems	Use of powder coatings
	Substitution of VOC cleaners	Use of VOC-free cleaners e.g. water based cleaners (with detergents) for cleaning of equipment and parts
VOC-reduced Systems	Reduction of the solvent content in coating systems	Changing from conventional coating systems to high solid and water based coating systems
Process Improvements	Improvement of application techniques	Optimise the spraying technique, reduce the number of coating layers, improve or replace application techniques by those with a higher degree of efficiency Use of automatic mixing systems.
	Reduction of cleaning effort	Reduction of colour changes. Immediate cleaning (before drying). Minimise use of cleaner. Emptying of pipes by ‘pig’ systems before cleaning. No cleaning for application of base coats or coats with low optical requirements. Consecutive coating of coloured working pieces. Automatic washing of spray guns and parts.
Abatement Technologies	Destruction of VOC	Thermal oxidation. Biological treatment.

9 Good practice examples

9.1 Water-based coating of special-purpose vehicles

A medium-sized manufacturer in Germany produces a wide range of multi-purpose vehicles (e.g. snow-ploughs and grit-spreader for winter services, vehicles for landscaping and roadside grass mowing and wheel-away platform vehicles for airport maintenance).

The vehicles are adapted to individual client requirements, including customised colour schemes.

Figure 2: Multi-purpose vehicles coated with a three-layer water-based system

Until 2006, for primers and topcoats a 2-component solvent-based system was used on-site whereas pre-coating was done by a trade coater.
Primer and topcoat application was done in 3 spray cabins which were used in series by transporting part with an overhead conveyer. Primer and topcoats were applied in separate cabins.
The company decided to use water-based systems in preference to high-solid coating systems in order to reduce the solvent emission as much as possible.
After carrying out research and consulting with a research association, cathodic dip coating technology was adopted, together with 6 spray cabins, for application of a water-based pre-coat, primer and topcoat system.
In the dip coating installation layers of ~ 20 µm thickness are applied. There are 4 drying ovens where the coating cures at a temperature of ~180°C. The dryers are interconnected to reuse heated air from neighbouring driers when doors are opened.
The dip coating uses a cascade water-supply system that minimizes fresh water demand. It produces sludge that is easier to treat than waste water and reduces environmental impacts of water treatment.
The six spraying booths are adaptations of standard automotive sector cabins, each equipped with a separate overhead conveyer to ease spray application. Both coatings can be applied in one cabin and dried in-situ.
The water-based primer is specially modified to the needs of industrial production and does not need drying time before the topcoat can be applied.
The cabins are equipped with special air nozzles that firstly produce turbulence (~ 10 min) and then dry with direct gas-heated air (~ 50 - 80 min). Flash off, drying time and temperature can be adapted to parts of different shape, size and material (metal, plastic).

The automatic mixing systems formerly used needed modification to cope with water-based system. It was possible to adapt the more recently purchased systems with stainless steel equipment but the older systems had to be replaced. The new equipment allows colour changes in less than 1 minute.

A hatch connecting the spray cabins allows using the same mixing system in two cabins by passing the tubes and pistols through the hatch. This increases productivity and reduces the cleaning effort.

Water-based cleaners can be used for the equipment in contact with the paint component but solvents have to be used for cleaning of equipment in contact with the hardener.

The investment cost for the cathodic dipping installation was 2.4 million €, and 1.2 million € for the top-coating installation.

Due to the exclusive use of water-based coatings for pre-coat, primer and top coat, VOC emissions have been reduced from 15 tonnes to less than 6 tonnes per year.

The success of the reduction was based on in-depth planning effort, valuable consultancy of the Surface Treatment Research Association and effective realisation of suppliers for cabins, overhead conveyer, mixing and application technique and in particular the coating system, selected after tendering.

[Hako-Werke 2008]

9.2 Cleaning of equipment

In a paint shop, manual cleaning of a spraying gun used to take 15 minutes and consume 500 ml of solvent cleaning agent. With the adopted automatic washing machine it takes about 3 minutes to clean the gun.
The cleaning agent is used several times, and fresh solvent is only used for final cleaning.
The solvent is recycled and reused.
[BayLFU 2005]

Figure 3: Spray gun washing machine

[Ökopol 2008]

10 Emerging techniques and substitutes under development

Water based top coats with less than 10 % water content, currently developed for large-scale vehicle coating, may also be applicable in a future to other metal coating activities.
[DuPont 2008]

11 Information sources

[SE Directive 1999]
Council Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations

[BayLFU 2005]
Vollzug der 31. BImSchV bei der Metall- und Kunststoffbeschichtung (Implementation of VOC regulation in metal and plastic coating), workshop 25. October 2005, Bayrisches Landesamt für Umwelt (Bavarian Environment Agency), Augsburg 2005.

[BREF STS 2007]
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Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive

(Directive 1999/13/EC)

Guidance 8 – Part 2:

Other coating - including plastic, textile, fabric, film and paper coating

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses coating of plastic, textile, fabric, film and paper and the related cleaning of equipment, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emission Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
The activity **'coating'** is defined as 'any activity in which a single or multiple application of a continuous film of a coating is applied'. The SE Directive covers installations in which this activity is taking place with an annual organic solvent consumption greater than 5 t.

The activity "other coating" comprises various different sectors (e.g. paper industry, textile industry) and takes place as a main process in specialised companies as well as a single production step in various enterprises.

The coating of metals and rotary screen printing on textiles is not part of this guidance document (see guidance document 8 part 1 and guidance document 3).

If the coating activity includes a step in which the same article is printed, independently by the technique used, that printing step is considered part of the coating activity and consequently included. Printing activities, however, operated as a separate activity are not covered in this document (see guidance documents 1, 2 and 3).

The SE Directive lays down the following activity specific emission limit values for *other coating*:

THE SE DIRECTIVE APPLIES TO OTHER COATING INDUSTRIES IF A SOLVENT CONSUMPTION OF 5 TONNES PER YEAR IS EXCEEDED

Table 2: Emission limit values of the SE Directive

SE Directive - Emission limit values (ELVs)
(Annex II A – activity No. 8)

Activity	Solvent consumption threshold [tonnes/year]	ELVs in waste gases [mg C/Nm^3]	Fugitive emission values [% of solvent input]	Total ELVs
Other coating, including metal, plastic, textile, fabric, film and paper coating	5-15	100(1), (4)	25(4)	
	>15	50/75(2),(3)(4)	20(4)	

(1) Emission limit value applies to coating application and drying processes operated under contained conditions.

(2) The first emission limit value applies to drying processes, the second to coating application processes.

(3) For textile coating installations which use techniques which allow reuse of recovered solvents, the emission limit applied to coating application and drying processes taken together shall be 150.

(4) Coating activities which cannot be applied under contained conditions (such as shipbuilding, aircraft painting) may be exempted from these values, in accordance with Article 5(3)(b).

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[1] as well as for halogenated VOCs which are assigned the risk phrases R40 or R68[2] There is a general obligation to replace CMR substances – as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated[3] VOC with R40/R68 the ELVs in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

This activity covers the coating of plastic, textile, fabric, film and paper. Various different industry sectors carry out the process, using many different technologies and coatings. Solvent-free or low-solvent alternatives like water-based (e.g. primers and base coat from the automotive industry) or hot melt coatings (e.g. food industry) are already available for many applications. In the case that performance or quality requirements demand solvent based products often also VOC reduced products such as high solid coatings are available.

WATER-BASED COATINGS, HOT MELTS, UV AND EB CURING COATINGS ARE TYPICALLY USED SOLVENT BASED COATING SUBSTITUTIONS.

Radiation curing coatings (UV or electron beam (EB) curing) are important VOC-free or low solvent products, mainly applied for foil/film coating.

Abatement technologies such as activated carbon or regenerative/recuperative thermal oxidation are commonly used when VOC-substitution or reduction are not available or not applied.

3 Description of the activity and related industry sectors

This activity covers coating processes with organic solvents on various different substrates - like plastic, textile, fabric, film and paper.

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[1] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

[2] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: ‘Possible risk of irreversible effects’. The new wording is: ‘Limited evidence of a carcinogenic effect’. In the ‘old’ version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: ‘Possible risk of irreversible effects’. This new risk phrase does not include carcinogenicity. The ‘new’ version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to this change, a final decision on which version applies can only be given by the European Court

[3] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.

Consequently this guidance document is suitable for use with a wide range of different sectors and in particular for those described below.

EU 15 Member States reported about 5000 existing and 300 new installations in 2004, carrying out activities under the scope of number 8 of Annex II A, which comprises activities for coating of metal, plastics, textile, fabric, film and paper [Implementation 2006].

3.1 Paper coating

WATER-BASED COATINGS ARE MAINLY USED IN THE PAPER COATING INDUSTRY

Paper coating is applied to improve gloss, colour, printing detail or the brilliance of the paper. Coatings can be applied on-machine (i.e. the coating is an integral part of the paper machine), or off-machine. [IFC 2007]

Many products in the paper industry are coated with solvent free or low solvent coatings with negligible emissions – like in the plastic extrusion coating process (see section 0).

Almost all paper coatings are water-based products, which may contain small amounts of VOCs. The required solid content is 30-50 % for air knives applications and 50-70% for other applications. [BREF PPI]

Coated paper is mainly used for art paper, machine coated paper, light weight coated (LWC, 45-80 g/m²) paper, folding box and chromoboard. [BREF PPI 2001]

The paper coating carried out in the furniture industry uses mainly water borne products with a solvent content of less than 5 %, but also UV or EB curing coatings with a solvent content of less than 0.5 %. [BASF-2 2008].

Wallpaper manufacturer partly uses paper basis which are coated with PVC coatings and pre-pasting. Printing techniques as gravure, flexography and screen printing and embossing are typically applied for the final wall paper design.

The general trend is to use non- or low VOC products and thus many installations fall below the consumption threshold value of the SE Directive. If the threshold value is exceeded VOC are generally abated using thermal oxidation.

3.2 Plastic coating

UV CURING COATINGS ARE A GROWING TECHNOLOGY IN THE PLASTIC COATING INDUSTRY

The vast majority of the paint used for plastic coating is applied by the automotive industry (~75 %). In particular exterior parts as bumpers and frontends are coated to achieve the same decoration/colour as the rest of the car. The other 25 % are mainly used for coatings in the electronic industry, e.g. for TV's, Hi-Fi's and computer housings. [BREF STS 2007]

In 99% of the cases the plastic itself has the required physical and decorative properties. Coating of plastic is generally used for outside applications. [pro-K 2008]

The major reason for coating plastic is to add value and special effects to the plastic component but also to achieve a required touch/feel and/or water resistance. Water-based and solvent-based resins, energy curable resins and powder coating resins are typically used. The choice of resin is influenced by the nature of the substrate, the application method and the functional requirement. [Cytec 2008]

Powder coating of temperature sensitive substrates, including plastics, can be achieved by the application of UV curable powders. In this case the powder is made to flow with a brief IR heating followed by a UV light treatment.

The use of UV-curing technology is increasing due to improved performance characteristics of existing UV-resins and the development of new UV-binders. These developments have enabled better quality coating results for plastic substrates such as polyethylene (PE), polypropylene (PP), acrylonitrile butadiene styrene (ABS) and polymethylmethacrylate (PMMA). The advantages of UV-curing technology are the rapid curing, no or very low VOC content and high performance properties as scratch and stain resistance. [CYTEC 2008]

3.3 Foil/Film coating

Typical applications of foil coating include decorative furniture foils, food packaging films and agricultural films. Foils produced for furniture are predominately prepared using UV-curable and electro-beam curable paints. Apart from these radiation-curing products acid curable waterborne systems are also commonly used to finish foils.

FILMS ARE TYPICALLY COATED BECAUSE OF DECORATIVE, ANTI FOGGING AND ANTISTATIC REASONS

In general foil coatings are applied as water or solvent-based solutions with additives (e.g. glycol mono oleate, sorbitan esters, ethoxylated alcohols) - depending on the physical properties of the surface. This has the advantage that the required finish is achieved immediately and materials use is minimised. Another possibility to influence the property of a foil surface is to add specific additives to the foil formulation.

Coating on films/foils can serve different purposes such as:

- Anti fogging: preventing condensation of water vapour on a plastic film.
- Antistatic: preventing foils to become statically charged. [WEKO]

Anti fogging coating:

Anti fogging coatings are used for food packaging and agricultural films. The coatings are applied by spraying or dipping.

Antistatic coating

Antistatic coatings are applied, by spray or immersion, to prevent the build up of a static charge on polymer surfaces that might have a negative impact during the production process, forming operations and/or during the service life of the final product.

3.4 Textile coating

Textiles production uses numerous production steps to achieve the properties and functionalities demanded of the final product. Textile coating has long been part of the manufacturing process for cloth for 'day to day' use. More recently other sectors are becoming more important - such as the manufacture of clothes with more specialised functional requirement (e.g. for the medical sector) and for the fabrics needed to meet the

WATER COATING IS THE MAJOR APPLICATION IN THE TEXTILE COATING INDUSTRY technical requirements of architectural, automotive and environmental applications. [TEGEWA 2008]

The use of organic solvents for coating activities in the textile industry has decreased steadily; In Germany, it was reported that hardly any solvent-based product is used anymore. In Europe coatings are predominantly water-based with a small amount of solvents, which act as biocides. The solvent content commonly is between 0.1 to 2%. [TEGEWA 2008], [BASF-3 2008]

Since the implementation of the SE Directive, the demand for water-based products has increased significantly [BASF-3 2008]. Companies ask their suppliers to provide VOC-free or low-solvent products in order to remain below the threshold limits of the SE Directive.

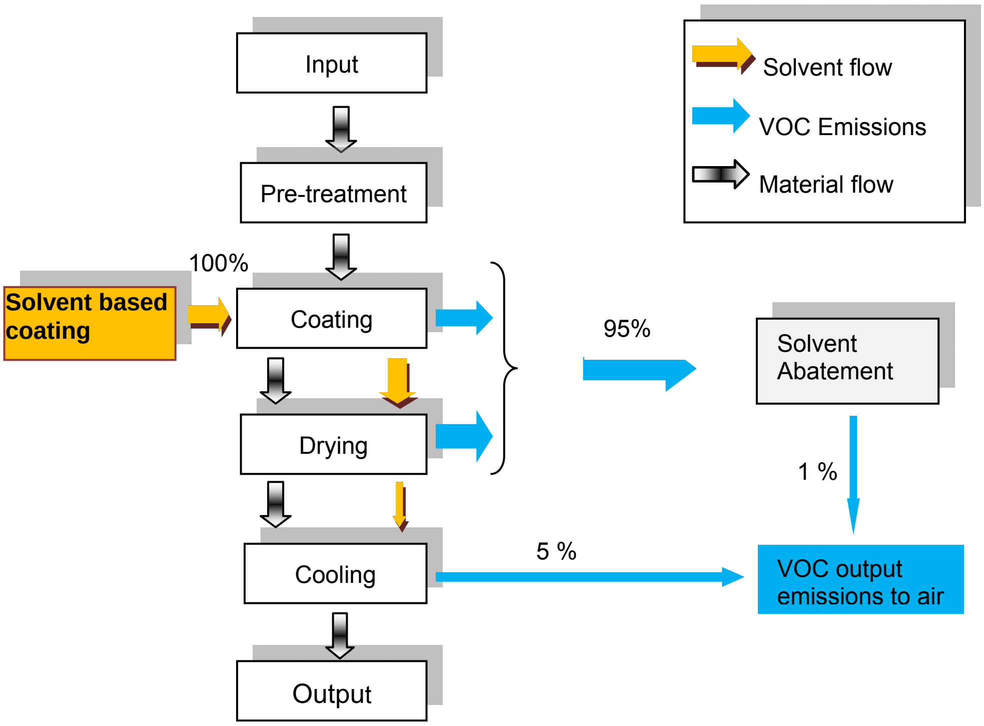
Printing is one remaining activity where solvents are still in use; as thickeners and rotary printing is the most important printing technology in the textile industry. This activity is not addressed by this guidance document (see guidance document 3).

In Europe, for the year 2008, the production of textile floorings was estimated to be 950,000,000 m². Less than 2% of this used solvent-based coatings [TFI 2008] . The only process where VOC emissions may occur is the back coating of carpets (floorings) based on non-polymerised monomers - typically aqueous latex dispersions are used. The average solvent content of the aqueous systems is about 0.02 %. This resulted in total emission of 53.2 t of VOC from the carpet industry in Europe.

4 Technical process description

4.1 Process flow and relevant associated VOC emissions

The flow chart in Figure illustrates the typical process steps of coating applications. The VOC emission from a process step depends on the application technology used and the coating system. VOC emissions predominantly occur during the coating and drying process:



VOC EMISSION OCCUR DURING THE COATING, DRYING AND COOLING STEP

Figure 1: Possible VOC emission sources in coating processes using solvent-based paints or varnishes

4.2 Process description

4.2.1 Coating of plastic

The coating technology used depends on the substrate and the intended use of the finished product. In many cases two or more layers, formed of different types of coatings, may be used:

- Primer
- Base coat
- Clear coat (top coat)

Plastic coatings that are wet paints are typically applied by high pressure or air assisted spraying. High-volume low-pressure (HVLP) paint application can increase the coating efficiency from 20-40 % up to 25-50 %. Where possible, the application is carried out robotically to ensure a consistent layer thickness.

Electrostatic application techniques can be used to form multilayer superstructures.

Plastic is heat sensitive and in general temperatures of 80 °C should not be exceeded for the drying step. In some cases a heat up zone of up to 135 °C with a hold zone of 110 °C can be used.

Plastic coating of automotive parts is often carried out in booth. The most typical abatement technique in this industry is thermal oxidation. The use of an adsorption wheel may increase the efficiency of the thermal oxidation.

4.2.2 Coating of paper, film and foils

Coating units for large flat areas, such as paper and film, typically consist of an unwinder, a coater station or stations, a drying section and a reel. The application of the coating is carried out with roller, air knife, size press, blade, nozzles or bar coating systems to ensure a consistent thickness. Approximately 70 % of all the solvent used is emitted from the coating lines with most coming from the first zone of the drying oven. The other 30 % are emitted from the solvent transfer, storage, and mixing operations. Typical abatement technologies in this industry are thermal oxidation and active carbon filters. [EPA Paper coating 1981] [BREF PPI 2001]

4.2.3 Application technologies

Coating application techniques vary widely but generally can be categorised in the following three groups:

- Brush/roller application
- Dipping
- Spraying

In general spraying techniques are the most commonly used.

The number of coatings and subsequent drying steps depend on the required surface finish.

Complex coating units are often used for the coating of films. The coating can either be rolled or sprayed, within a closed chamber, onto the surface.

Primer

Primer is often applied to prepare the surface for the next coating step. The primer may also act as a protection layer for the substrate e.g. against UV radiation. Coloured primers might be applied in conjunction with thin base coat films. Furthermore primers can be applied to provide a conductive layer on non-conductive substrates to enable electrostatic coating. Primers are often solvent-based products.

PRIMER AND BASE COAT CAN BE SOLVENT FREE BUT THE TOP COAT IS OFTEN SOLVENT BASED

Base coat

Base coats typically provide colour and aesthetic effect, and they are available as solvent-based, water-based and high solid products.

Water-based primer and base coat present no particular problem for the automotive industry provided that they have totally dry before the application of the solvent based top-coat.

Clear coat (Top coat)

Clear coats are used as protective and/or decorative final layers. Often clear coats give a special effect to the base coat (e.g. more saturated colour, brilliance etc.) but they may also have to resist potential external impacts (e.g. abrasion).

Clear coat commonly are solvent–based. The use of water-based primer and base coat is - for the automotive industry- no problem but they have to be totally dried before the application of the solvent based topcoat.

Special layers:

Adhesion promoter

So-called "adhesion promoters" are used for plastic parts as a pre-treatment before electrostatic coating. They consist of chlorinated polyolefin (CPO) and conductive resins that allow the subsequent electrostatic coating of plastic surfaces. Adhesion promoters are available as solventbased and water-based systems. [Du Pont 2008]

Electrocoat

Electrocoating can only be applied onto conductive substrates or surfaces. The main functions of an electro coat are the creation of a smooth surface for further coating layers and the increase of corrosion resistance. Electrocoats are suitable for the coating of complex shapes and areas that are not in direct line of sight.

Table 3 gives an overview of the efficiency of the different application technologies. These technologies are applicable for all types of coats (primer, base coat, top coats), [BREF STS 2007], [Twinning 2004]:

APPLICATION EFFICIENCY VARIES GREATLY DEPENDING ON THE APPLICATION TECHNIQUE

Table 3: Achievable application efficiency factors for different coating application systems used

Application technique	Application efficiency [%][4]	Remarks
Brush painting	95-100	Reduced uniformity of painted surface compared with other application techniques.
Plastic extrusion	95-100	Application of a molten thermoplastic sheet that is extruded from a slotted die at temperatures of up to 315 °C
Spraying, conventional (High pressure compressed air)	30-60	High volume of overspray depending on geometry of painted workpiece. For most applications, efficiency is in the range of 30–45%.
Spraying HVLP (High Volume, Low Pressure)	40-75	Application of low viscosity paint systems.
Hot spraying	40-60	Application of paints with a high solid content, also applicable for hot wax

Application technique	Application efficiency [%][4]	Remarks
		spraying
Airless spray application	40-75	Bundling of spray-beam, therefore higher efficiency compared to conventional spraying
Air assisted airless technique	35-50	Bundling of spray-beam, therefore higher efficiency compared to conventional spraying
Spraying, electrostatically assisted wet lacquer	50-70	Electrical conductivity is required (minimum dampness of 8% or a conductive primer needed), can be used with any of the spraying techniques mentioned above.
Spraying, electrostatically assisted powder	80-95	Electrical conductivity required.
Curtain coating	95	Limited by workpiece geometry
Rolling, flooding	95	Limited by workpiece geometry; reduced uniformity of painted surface (rolling)
Vacumat technique	95	Only applicable for narrow parts and edges, water-based paints and UV cured materials with a high solids content, also the workpiece geometry has to be considered
Dipping/flooding	95-100	Limited by workpiece geometry

5 Solvent use, emissions and environmental impact

5.1 Solvents used

The coatings considered under this activity are based on a broad variety of different solvents:

- alkanes (isododecane, iso-paraffins, N-paraffins, kerosene)
- formaldehyde contained in urea or melamine formaldehyde (UF/MF)
- alcohols (methanol, ethanol, isopropyl alcohol)
- phenols (toluene, xylene)
- ketones (acetone, methyl-ethyl-ketone)

Toluene, xylene and methyl-ethyl-ketone are the most important solvents.

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[4] Based on applicable paint input in process, not on solid paint on surface

5.2 Solvent consumption and emission levels

This guidance document covers a wide range of different sectors. An estimation of solvent consumption and emission levels is therefore not possible. Most of the solvent-based paints are applied by spraying and so have a high potential to emit VOC to air.

5.3 Key environmental and health issues

Process emissions of VOC, together with NO_x emissions, are precursors of ground level ozone formation in the presence of sunlight. Existing occupational workplace limits should be taken into consideration.
Emissions of VOC to air may occur from:

- - the coating process
- - the drying process

Spills and leaks from storage areas may result in emissions to soil and groundwater.

Processes may generate waste containing solvents that need to be disposed in a way that emissions to air, soil and groundwater are prevented or limited.

Toluene is one of the most important solvents used for the paint systems of this group of industries; it is classified as irritating to skin, and as harmful - with a danger of serious damage to health by prolonged exposure through inhalation. Formaldehyde is less commonly used but is of special interest as it is classified as a CMR substance category 3 (R40, limited evidence of a carcinogenic effect).

6 VOC Substitution

The following chapter describes potential substitutes for VOC (using low-VOC and VOC-free systems) and any associated application technologies and/or special conditions needed for their use. It also lists the advantages and disadvantages compared to systems that use solvents with a high VOC content.

6.1 VOC-free systems

This section describes the ways that VOC-free products or systems can be used to replace the organic solvents currently used.

6.1.1 Plastic extrusion coating

A TYPICAL APPLICATION FOR PLASTIC EXTRUSION COATING IS THE COATING OF PAPER FOR THE FOOD INDUSTRY

Plastic extrusion coating is a type of hot melt coating. A thermoplastic sheet is extruded from a slotted die at temperatures of up to 315 °C. The substrate and the molten plastic coat are united by pressure between a rubber roll and a chill roll, which solidifies the plastic. This process can be used to improve the characteristics of paper by coating it with polyethylene to make it more resistant to water, grease and humidity. It improves protection against light making it useful for packaging applications. Many products, such as the polyethylene-coated milk cartons, are coated with solvent-free extrusion coatings. Other applications are pharmaceutical bags, protective caps and pouring lids.

6.2 VOC-reduced systems

If the complete substitution of organic solvents is impractical then changing to systems with a reduced VOC content, such as those described in this section, can decrease emissions.

6.2.1 Low VOC systems

VOC emissions from coating processes may be reduced by lowering the VOC content of paints, by increasing the efficiency of the coating process, (see also chapter 4.2) or by a combination of these approaches. Low VOC systems are:

- Water-based paints: < 20% VOC
- High solids paints: 25 – 40 % VOC
- Radiation curing paints: < 5 % VOC

Water-based paints

The problems encountered when changing from solvent-based coatings to water-based coatings often relate to the longer drying times required, which may increase costs and lead to higher dust adhesion from the surroundings onto the surface of the wet material. Poor drying can lead to formation of a skin, encapsulating water, and a surface texture of low quality.

These disadvantages can often be avoided by using dehumified air for water based lacquer drier. In that case the drying process uses dehumidified air instead of heat. Air at about 60 °C is transported to a heat exchanger, as the air is cooled water vapour condenses. The cooled air is re-heated by the heat exchanger before it is passed to the drying chamber. This closed cycle minimises energy consumption. Typical advantages compared to high temperature heating are:

- Low energy consumption
- Low crack formation
- Very little exhaust gases due to a closed air circle
- Faster drying time (~25-30 %)
- No need for cooling area of substrate
- Retrofitting possible
- Relatively low investment costs
- Little place requirement

WATER BASED SYSTEMS CAN BE APPLIED WITH THE SAME EQUIPMENT AS SOLVENT-BORN PRODUCTS.

Typically, when switching from solvent-based systems to water-based systems, no major changes in the production are necessary.

In the automotive industry water-based primers, and based coats are applied e.g. for the coating of bumpers. The top coat still has to be solvent-based to fulfil the required quality criteria. When using of water-based primers and base coats, a drying phase has to be applied after each coating process.

Many parts of the painting and drying equipment used with solvent borne paints are made of carbon steel. Water-based paints (and amines, which are often a component in such paints, would cause increased corrosion of these parts. Therefore corrosion resistant materials are required for the coating and curing process equipment.

Reactive coatings

Reactive coatings are products that cure via chemical reaction (usually polymerisation). During the formation of the new compounds the 'reactant' VOC becomes part of the coating and stays with the substrate as residual VOC. VOC emissions may, arise from residual monomers but these are negligible. Reactive coatings are applied by spraying. They can be used for, among other things, door or floor coverings and decorative furniture foils.

Radiation curing paints (pre-polymer coatings)

UV CURING COATINGS STILL CONTAIN 0.5 – 5% SOLVENTS

UV or EB (electron beam) coatings contain ’reactive solvents’ that are chemically incorporated into the paint layer during the curing process. Completely VOC-free paints are rarely used for coating. 0,5 - 5% of the UV curing paint is solvent, 1-5% is a photoinitiator and the rest are monomers and additives.

Radiation curing coatings have no or very low solvent content. As no drying ovens are necessary the energy consumption is significantly lower compared to solvent-based or water-based products. The curing only takes place when the coating is exposed to the proper type of UV or EB radiation. Thus cleaning of the equipment is easier as the coating does not cure in case of downtimes.

Switching to radiation curing requires investment in new application equipment as the coatings behave differently than solvent-borne coatings. Also the drying unit needs to be changed. In addition the coatings are more expensive than solvent-based systems.

One major disadvantage of radiation-cured coatings is that they have the potential to cause irritation and/or allergic reactions on skin contact; the level of irritation may further increase if there is also skin contact with cleaning agents.

In the automotive industry (e.g. exterior parts) EB or UV curing is not yet used as the quality is not sufficient. But researches are ongoing. For the cosmetic industry currently the first VOC-free products are in use.

Radiation curing is particularly suited to spraying flat materials and for producing thin coatings.

High solid coatings

High solid products reduce the amount of solvents by increasing the solid content. The typical solid content is between 60 to 80 %. High solid products are available for a variety of different applications as e.g, automotive parts.

Electrostatic coating

Electrostatic coating relies on the conductivity of the paint and the object to be painted to increase the efficiency of painting. According to the IFF [IFF Projekt Nr.: BW D 20007] the electrical resistance should be below 10^9 Ω on any area to be painted and the conductivity of the paint should be above 1 µS. Furthermore between grounding and the point of paint application a wet film of paint is needed. Waterborne paints fulfil these criteria and solvent-based paints can be modified (e.g. by using organic ammonia compounds) to do so.

In case of nonconductive substrates there are two options for achieving the level of conductivity needed:

ELECTROSTATIC COATING IS ALSO POSSIBLE FOR NONCONDUCTIVE SUBSTRATES, BY INCREASING THE MOISTER CONTENT OR BY APPLYING A CONDUCTIVE PRIMER

- Increasing moisture content to more than 8% (however this is too high to be acceptable for many applications)
- Use of a conductive primer, applied by using conventional spraying

Other approaches are under development but have not yet been used at industrial scale.

Electrostatic coating can be used with all available spraying techniques (e.g. compressed air, airless) including high-speed rotational bells.

In addition to the technical constraints mentioned above there are safety issues that must be resolved for each type of equipment (e.g. danger of electrical accidents for operator).

Electrostatic coatings may be applied using either air or airless spray equipment. The transfer efficiency can be increased from the 20-30 % achieved using conventional coatings to 50 to 60%. It is often used for complicated geometrical shapes with surfaces that cannot be reached by other techniques.

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements and abatement techniques can be used to reduce VOC emissions when VOC substitution, as described in section 6, is not possible. The following measures are commonly applied for other coating process:

7.1 Abatement technologies / End of pipe measures

Due to the diversity of processes and the different types and amounts of VOC emissions arising abatement techniques remain important means of reducing VOC emissions from coating processes. The selection of suitable abatement measures strongly depends on process parameters such as flow rate and VOC concentration (and their variation).

In many cases a combination of different abatement measures - although costly - offers the best solution. For VOC capture and recovery condensation, absorption and adsorption offer the best opportunities whilst oxidation techniques destroy the VOCs.

7.1.1 Refrigerated condenser

A refrigerated condenser works best on emission streams containing high concentrations of VOC emissions. The emission stream is cooled to below the dew point of the solvent. The solvent condenses and can be recovered and reused. The air stream leaving the condenser will still contain some solvent but if this is re-cycled in a closed loop system. The overall solvent emission is reduced to a large degree. Care is needed, if the system is working with ambient air then the concentration of VOC should not be more than about 5 % of the lower explosion limit (LEL). If inert gases are used (i.e. N_2) then concentrations up to 50% LEL can be tolerated. A higher loading reduces the drying time and the length of the drier. A disadvantage of using inert gases is that, after equipment down time or outage, the whole system has to be purged until the oxygen is removed.

7.1.2 Adsorption wheel

ADSORPTION WHEELS ARE USED TO INCREASE THE VOC CONCENTRATION IN THE AIR AND THEREFORE MAKING THERMAL OXIDATION MORE ECONOMICAL

Particularly in case of plastic coating in booth high volumes of exhaust air with relatively low VOC content occur. To increase the VOC concentration an adsorption wheel can be used.

High amounts of air with low VOC content are passed through the major section of the rotating adsorption wheel that is filled with activated carbon. The VOC are captured on the surface of the carbon. At a separated segment a small amount of hot air is used to remove the VOC from the surface of the activated carbon. The VOC loaded air is then passed to the thermal oxidation. Due to the higher concentration the natural gas consumption is reduced and the thermal oxidation can be operated economically.

7.1.3 *Thermal oxidation (Regenerative /recuperative)*

Thermal oxidation is a commonly used VOC abatement technique for this industry.

Three types of thermal oxidisers are in use: regenerative, recuperative and catalytic oxidation. All destroy VOCs in the waste gas stream by burning (i.e oxidation), but they differ in how waste heat is recovered and in their level of efficiency.

Regenerative thermal oxidation has at least two (often three) heat exchangers; these consist of beds filled with material that allow air to pass while absorbing and storing heat. While the exhaust gas from the burner heats one bed another is releasing its stored heat to the VOC laden incoming gas. In recuperative thermal oxidation the heat is transferred directly, via a heat exchanger, from the outgoing air stream to the incoming air stream.

Regenerative oxidation tends to be more efficient than recuperative thermal oxidation as it uses the recovered energy more efficiently to pre-heat incoming process air to oxidation temperatures (~ 800 °C); consequently its operating costs are significantly lower than for recuperative oxidation systems. Regenerative thermal oxidation systems (RTO) are particularly effective for process streams with relatively low solvent loadings, but their operating costs are highly dependent on the efficiency of the heat exchanger.

Regenerative thermal oxidation systems are widely used because they are relatively insensitive to the composition of the solvents in the process air and their concentration.

Recuperative systems are mainly used for small flow rates - at higher rates the systems are not cost effective. They are often used in combination with catalytic oxidation systems.

THE AUTO-THERMIC POINT OF REGENERATIVE THERMAL OXIDATION IS ABOVE 2-3 G VOC/NM³

Catalytic systems are single-bed units. The catalyst is supported on ceramic tiles. Waste air is blown or sucked through the pre-heated bed and the temperature is maintained by the oxidation of VOC provided the system is above the auto-thermal operation limit (approximately 2 g/m³). These systems operate at low temperatures (350 – 500 °C) therefore the emission of NO_x is significant lower. Dust and catalyst poisons (e.g. sulphur-compounds) must be avoided but these are not usually present in coating processes.

Natural gas is needed to heat up thermal oxidisers to an operating temperature of 800 - 850 °C (400 °C for catalytic oxidation), and the process is only autothermic when the VOC concentration of the waste gas is above 2-3 g VOC/Nm³ (regenerative systems). The resulting heat can be recovered and can be used for different purposes.

Regenerative and catalytic systems are widely used for solvent-based coating processes because the load of VOC is high and relatively constant (mainly controlled by the drying unit of the lamination equipment).

Operational costs are highly dependent on the average concentration of VOC in the waste gas and the operation time of the plant as well as on the type and cost of fuel needed for the operation – so it is difficult to determine a 'typical' cost.

Usually the waste air stream is a mixture of the extracts from the drying unit of the coating equipment and room ventilation and has a VOC concentration well above auto-thermal operation limits. Thermal oil heat transfer systems are often used to recover heat energy for heating drying units [Mondi 2008].

7.2 Process improvements

Fugitive VOC emissions may arise from solvent storage and handling. The most commonly used measures to reduce them involve process improvements to collect vapours escaping from application systems, drying areas, storage and handling areas etc. in local exhaust ventilation hoods for subsequent treatment or abatement.

PROCESS IMPROVEMENTS CAN HELP TO REDUCE VOC EMISSIONS FROM THE APPLICATION PROCESS

A wide range of best practice and process improvements is available. The following list gives some examples:

- Increased efficiency from optimised application technologies
- Collection of VOCs from different, distributed, sources using local exhaust ventilation hoods, for subsequent abatement of point and fugitive emissions
- Back venting to the delivery tanks during bulk storage tank filling
- Improved exhaust air collection systems
- Using closed or covered application systems
- Using closed containers for the transport and intermediate storage of solvents

8 Summary of VOC emission reduction measures

The following table summarizes the various approaches to substitute or reduce VOC emission as described in chapters 6 and 7:

Table 4: Measures for VOC substitution and VOC reduction for coating activities

Objectives	**Description**	**Applicability**
VOC-free Systems	Plastic extrusion coating	Typically applied in the coating of paper for the food industry
VOC-reduced Systems	Water-based paints	Water-based paints still contain up to 20% VOC; they are mainly used as primers and base coats.
	Reactive coatings Radiation curing paints	Currently only applied in the cosmetic industry at an industrial scale.
	High solid paints	High solid products are available for many different applications
Process Improvements	Dehumidified air for water-based paint driers	Applicable for all water-based systems.
	Use of application technologies with increased efficiency (e.g. electrostatic coating)	Applicability depends on the electrical resistance and the conductivity of the surface.
	Use of an adsorption wheel to increase the efficiency of the thermal oxidation	Particularly applicable in case of high volumes of exhaust air with relatively low VOC content
Abatement Technologies	Refrigerated condenser	Particularly applicable in case emission streams containing high concentrations of VOC emission
	Recuperative thermal oxidation	Widely applicable but not as effective as regenerative
	Regenerative thermal oxidation	Restricted to larger installations due to capital cost

9 Good practice examples

9.1 Example 1: Change from solvent-based system to water-based systems

The company has three production lines for lacquering plastic parts such as plastic bumpers for the automotive industry. The newest production line was developed for water-based paints.

The second production line (18 years old) was converted from solvent based paint to water based paints. This led to a complete change of the lacquering equipment due to the different behavior of the water based paints (e.g. different viscosity). The costs for the reconstruction of the production line with a capacity of about 2.000 parts per day were 3-4 million €. The water based paints have a solvent content of about 12-18 %. Due to the change the amount of solvent used has decreased by about 75 %.

The third production line is a conventional production line for the use of solvent-based paints.

Although water based paints have the disadvantage that the process parameters have to be controlled more accurately and the energy consumption is higher the company plans a complete shift of the third production line to water based paints.

The complete shift to water based paints is due to the requirements of the costumers. The customers asked for specified colours that are often only available as water based paints.

Although experience exists for the installation of a new production line using water based paints as well as for refitting an existing line, it is not yet clear which option will be chosen for the third line. The main reason is that in case of water based painting a drying step is needed after the application of the base coat. The need for this drying chamber in the middle of the process line and the required space is a problem when retrofitting.

[Peguform 2008]

9.2 Example 2: Drying of water based coatings by dehumidified air

This case study shows an application, using a drier using dehumidified air, for drying water-based coatings that avoids crack formation.

The implementation of such a system in a coating company reduced the drying time of the coated articles from 30 to 15 minutes at 60 °C. The drying areas could be reduced by about 50 %. [JOT 2001]

Examples of typical prices for a dehumidified air water based lacquer coating drier are listed in Table 5:

Table 5: Prices and nominal capacity for dehumidified air drying of water based coatings

Water displacement [kg/h]	Price [€]	Nominal capacity [kW]
4	~ 25,000	~ 4.3
10	~ 40,000	~ 11
20	~ 60,000	~ 24

[Harter 2008]

9.3 Example 3: Plastic extrusion coating

This case demonstrates the retrofitting of a coating machine from a solvent based coating to a plastic extrusion coating.

Typical substrates for this plastic extrusion coating machine are:

- fabrics used for textiles, tarpaulins, sun awnings and big bags
- paper for food packaging and snacks
- flexible components such conveyor belts, drive belts, automotive door panels and protective clothing

Parameters of this machine are given in Table 5.

Table 6: Parameters for a plastic extrusion machine

Coating thickness	30-50 g/m²
Line speed	< 150 m/min
Finished product width	Max. 1600 mm
Extrusion capacity	230 kg/h
Power (installed capacity)	700 kVA

The advantages of mechanised plastic extrusion coating compared to solvent based coating with a doctor knife technique are the possibility of a thicker coating, multilayer coating within one station, no drying area and being nearly completely waste free (except some cut-off).

The disadvantages are the need for large batch sizes to compensate for slow start-up and poor product quality at the beginning of a new batch. Another disadvantage is the extra space needed alongside the machine for the extruder; an overall width of about 13 meters is needed for a coating a 2 meters broad film. Retrofitting costs start at about 2 million €.

[Reifenhäuser 2008]

10 Emerging techniques and substitutes under development

Several techniques have been under permanent development, or transferred to various industries as improved water-based systems, very high solids paints and powder coating. These R&D activities, which are especially driven by the big paint producers, often involve developing non-thermal drying or curing by UV or other radiation.

10.1 Coating of plastic – Use of powder coatings

Powder coating is a virtually VOC free process. The coatings are applied by electrostatic spraying, fluidized bed, electrostatic fluidized bed and flame spraying techniques.

Electrostatic spraying and the electrostatic fluidized bed application methods can only be applied if the substrate is conductive or if the surface is made conductive by a pre-treatment step.

Electrostatic spraying, fluidized bed, and electrostatic fluidized bed application methods are only appropriate for work pieces that resist temperatures up to 200°C.

The flame spray method can be used for powder coating non-conductive substrates such as plastic, wood or rubber. This method is also applicable for large none-transportable structures.

Conversion to powder coatings often requires investment in new application equipment. Powder coating is used, predominately, for metals but can also be applied for other (pre-treated) materials, including plastics. [BASF-1 2008]

The use of powder coatings is still limited despite recent technical developments. Typical difficulties and restrictions are:

- Very thin coatings are difficult to apply without leaving pinholes
- Uniform thickness is difficult to achieve
- Powder storage and handling requires special climatic control
- Sharp corners are difficult to coat
- Conversion from liquid coating is expensive

[PPC 2008]

The capital costs of a typical powder coating installation are about 25 % less than of a comparable conventional solvent-based installation but still about 10 % more than of a waterborne or high solid installation.

Powder coatings (material) cost about 20 % less than solvent-based or waterborne coatings.

The costs, per coated area, of powder systems are around 30% less than those of solvent based systems.

Powder coating is seen as an interesting VOC- free alternative but further research is needed to achieve the required quality standards and to cover the whole product range.

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Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Guidance 9:

Winding wire coating

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses winding wire coating, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emission Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
The activity "winding wire coating" is defined as ‘any coating activity of metallic conductors used for winding the coils in transformers and motors etc.’. The SE Directive covers installations in which this activity is taking place with an annual organic solvent consumption greater than 5 tonnes.

Winding wire coating is a surface treatment basically involving the application of an electrical insulation layer (enamel) onto the surface of a copper or aluminium wire. The surface also needs a well-defined lubricant layer to ensure good coiling performance and smooth laying of the wire.

The SE Directive lays down the following activity specific emission limit values for winding wire coating:

THE SE DIRECTIVE APPLIES TO WINDING WIRE COATING IF A SOLVENT CONSUMPTION OF 5 TONNES PER YEAR IS EXCEEDED

Table 2: Emission limit values of the SE Directive

SE Directive - Emission limit values (ELVs) (Annex II A – activity No. 9)				
Activity	**Solvent consumption threshold [tonnes/year]**	**ELVs in waste gases [mg C/Nm³]**	**Fugitive emission values (% of solvent input)**	**Total ELVs [g/kg]**
Winding wire coating	> 5			10* 5**
* for installations where average diameters of wire ≤ 0,1 mm ** for all other installations				

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[1] as well as for halogenated VOCs which are assigned the risk phrases R40 or

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[1] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

R68[2]. There is a general obligation to replace CMR substances – as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated[3] VOC with R40/R68 the ELVs in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

Solvents are often used both in the coating of winding wire itself and for the application of the lubricant film.

Solvent free lubricants are available and are used in commercial applications but their use is still very limited for fine wires and they do not always meet high quality requirements.

High solid enamel coatings, with a solid content between 30-45%, are commonly used in the winding wire industry. Typical VOC emission values for the total process (enamelling and lubrication) are close to 5 g/kg product for wires with a diameter above 0.10 mm, and 10 g VOC/kg product for wires with a diameter below 0.10 mm. In case of solvent free lubrication the total VOC emissions can be reduced by about 60 %.

Catalytic oxidation, with an efficiency of at least 97 %, is the most commonly used measure for abating emissions arising from the coating of winding wire.

3 Description of the activity and related industry sectors

Winding wire is required for the coils of motors, transformers and other electromagnetic equipment used for energy transformations - electrical to electrical, electrical to mechanical and mechanical to electrical.

The European winding wire industry comprises about 40 installations in 14 countries and employs nearly 4600 workers. The majority of enterprises are small and medium sized (SME) [FVKiD 2008]. In 2004 EU 15 Member States reported about 400 existing installations [Implementation 2006].

Winding wires are produced as round or rectangular wires in various dimensions, but they are generally grouped as shown in Table 33.

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[2] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: 'Possible risk of irreversible effects'. The new wording is: 'Limited evidence of a carcinogenic effect'. In the 'old' version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: 'Possible risk of irreversible effects'. This new risk phrase does not include carcinogenicity. The 'new' version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to this change, a final decision on which version applies can only be given by the European Court

[3] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.

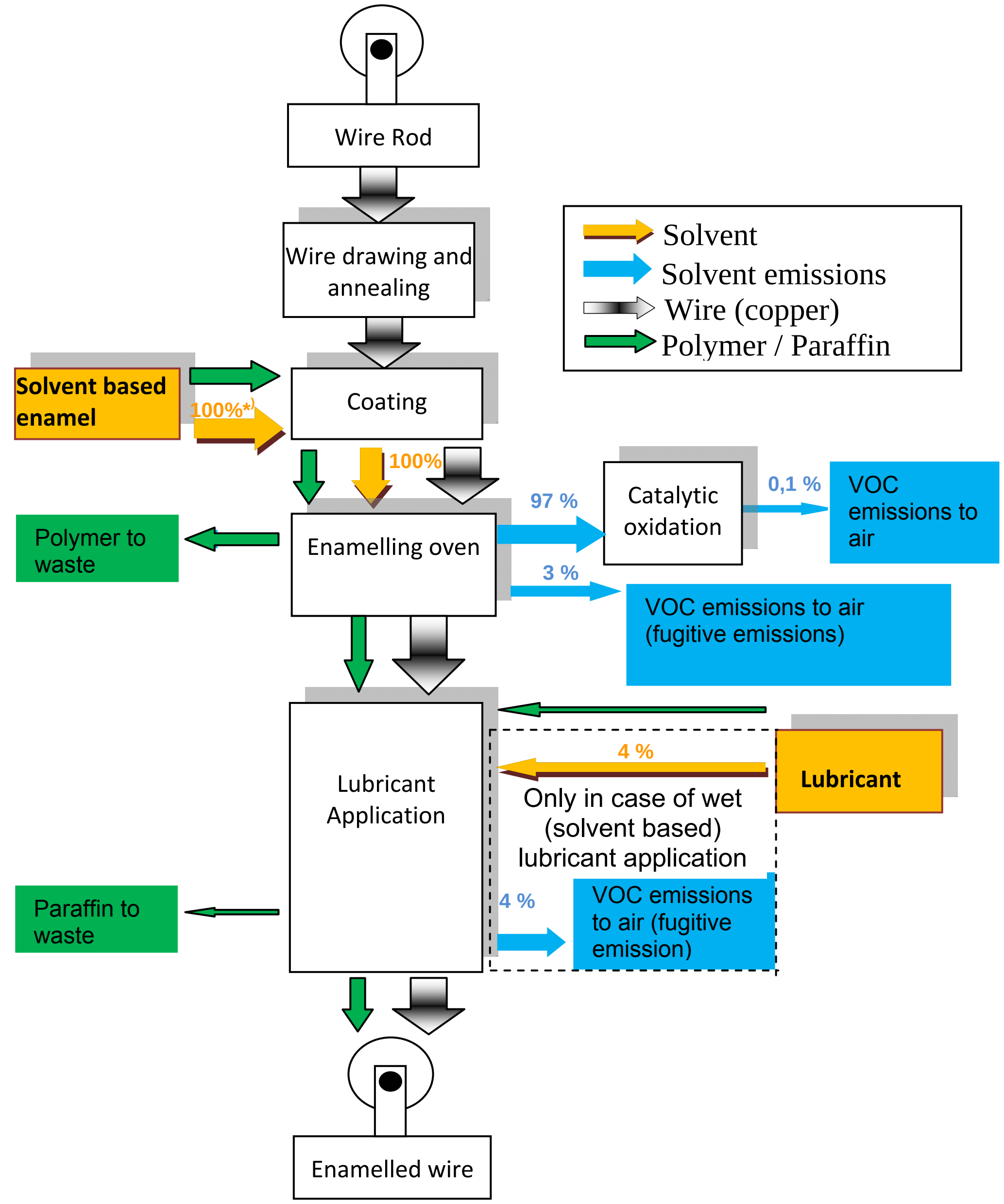
Table 3: Overview of the different winding wire types [BREF STS 2007]

Wire type	Above (mm)	Up to and including (mm)
Ultrafine wires	-	0.040
Fine wires	0.040	0.10
Medium wires	0.10	1.0
Thick wires	1.0	6.0

4 Technical process description

4.1 Process flow and relevant associated VOC emissions

The VOC emissions arising depend, among others, on the technology used by each single machine, the wire diameter and the quality of product required. Figure 1 illustrates the main process steps of the coating and wet lubrication of round wires. The production of rectangular wires includes the same process steps apart from lubrication application. In case of rectangular wires no lubrication takes place.



EMISSION FROM THE LUBRICANT APPLICATION IS CONSIDERED TO BE THE MAJOR FUGITIVE EMISSION

*) The amount of solvent which is coated onto the winding wire is the base for the calculation of the other materials in weight %.

Figure 1: VOC relevant flow chart for possible VOC emissions from winding wire coating

4.2 Process description

Two different types of winding wires are produced: round and rectangular winding wires. From a VOC emission point of view the major difference is that only round wires are lubricated as these have to slide next to each other in order to receive a dense winding.

In the production of round winding wires there are two stages where solvents may be used: coating and lubrication. The coating process uses liquid enamel which is a polymer dissolved in an appropriate solvent. The lubricant application adds wax to the surface of the enamelled wire which is often dissolved in a solvent.

During the coating process the winding wire is passed through a coating bath or coating impregnated felt. By repeating this process layers with different properties can be applied successively on the surface of the winding wire.

There are two different ways for applying lubricant onto the wire, solvent free application systems and the traditional solvent based process. The solvent based lubricant application is the major source of fugitive VOC emissions.

Solvent based coating bath with dies

Wires are usually coated by passing them through a bath of enamel having a solvent concentration of 50 to 80%, depending on the product. The higher the quality requirements and the finer the wire the higher the solvent content has to be. For each layer the surplus enamel is removed by passing the wire through a die. Coating layers are between 1 and 10 µm thick. Each layer of the coating is dried and cured in the enamelling chamber where the solvent is evaporated. Typically 5 to 10 layers are applied onto the surface of the winding wire.

SOLVENT BASED COATINGS CONTAIN ABOUT 50 TO 80 % SOLVENT

Solvent based coating with dosed coating supply and felt application

Another way of applying the coating is to pull the wire pulled through a felt impregnated with a solvent based coating. This technology is typically used for fine winding wires due to the gentle application. The felt has to be treated as waste afterwards.

Lubrication of the winding wire

Solvent based lubricant application is also called wet lubrication. In this process the wire is pulled through a felt that is soaked with a solvent based lubricant, containing about 98 –99 % w/w solvent and 1 % w/w of paraffin. The felt cannot be recycled and has to be treated as waste.

SOLVENT BASED LUBRICATES CONTAIN ABOUT 98 TO 99 % SOLVENT

The lubricant layer is necessary for the coil winding operation. Too little or too much lubricant makes the winding wire sticky and prevents close coiling. The lubricant film is nearly mono-molecular with about 30 – 60 mg/m^2 of lubricant applied for medium or thick wires and 5 – 10 mg/m^2 of lubricant applied for fine wires with a diameter below 0.10 mm.

The solvent based lubricant cannot be dried in the enamelling oven as the wax would burn off at such high temperatures. Therefore drying takes place at room temperature in a non encapsulated area (required drying distance ~ 10 m). Extraction and subsequent incineration of these large quantities of air with low VOC concentrations (50 – 100 ppm) and temperature would be very inefficient and energy-consuming. The solvent from the lubricant accounts for about 60 % of the fugitive emissions from the process as a whole.

Lubrication can also be performed by solvent free lubricants. Molten, solvent-free, lubricant is applied to the wire surface using for example a wetted felt or a lubricant soaked filament.

5 Solvent use, emissions and environmental impact

5.1 Solvents used

Typical solvents for enamels (coatings) are n-methyl-pyrrolidone (NMP), naphtha and other aromatics e.g. cresols (cresylic acid) with xylol as a diluent. These solvents all have very low evaporation rates. The creosol isomers for example have an evaporation rate which is 40 to 100 times lower than butyl acetate.

Cresol and n-methyl-pyrrolidone are very strong solvents and typically used to dissolve high molecular weight polymers, which are necessary to achieve high temperature resistant coatings. Propylene carbonate, which has a lower toxicity potential, might be used as an alternative for cresol. [BASF 2004] [CHEMOX 2005]

For lubricants white spirit is a commonly used solvent.

Currently, in Europe, halogenated VOCs are not used in the production of winding wires [FViD 2008].

5.2 Solvent consumption and emission levels

In 2000 the production of enamelled wires in Europe (EU 15) was 390 kt with a total consumption of organic solvents of about 25 kt, which gives an average solvent consumption of 0.065 t per tonne winding wire. About 97% of the VOCs are abated by catalytic oxidation, and about 3 % are emitted.

The high costs of the solvents used are an incentive for industry to reduce the solvent consumption. The production of winding wire in Europe increased by a total factor of 2.6 between 1970 and 2000, while over the same period the solvent consumption increased by a factor of 2.25, resulting in an overall reduction of the specific solvent consumption (tonne solvent/tonne product) of about 13 %. [EGTEI 2005]

EUROPE PRODUCES 390 000 T ENAMELED WIRES WITH A SOLVENT CONSUMPTION OF 0,065 T PER TONNE WINDING WIRE

The quantity of solvents used for coating and lubricating depends very strongly on the winding wire diameter. Thin wires usually require more solvents to be used [per kg of product] for two reasons. The first one is that thin wires have a higher surface to volume ratio and therefore more coating material is required per kg of copper. The second reason is that fine and ultrafine wires are very fragile and cannot withstand strong traction forces. The lower the solvent content of the lubricants/coatings, the higher the friction resistance and the greater the tendency of the wire to break.

Many lubricants contain a mixture of VOCs with a total content of 98 to 99.9 %, the remaining 0.1-2% is the paraffin (wax) or mineral oil, which is the actual lubricant.

There are different coating product types in the winding wire industry. These differ in their average solvent content. Coatings for solderable round wires have an average solvent content between 65 and 80 %, high temperature and bonding round wires about 55 to 75 % and rectangular about 60 to 80 %. The shares of each category in the overall production are shown in Figure 2.

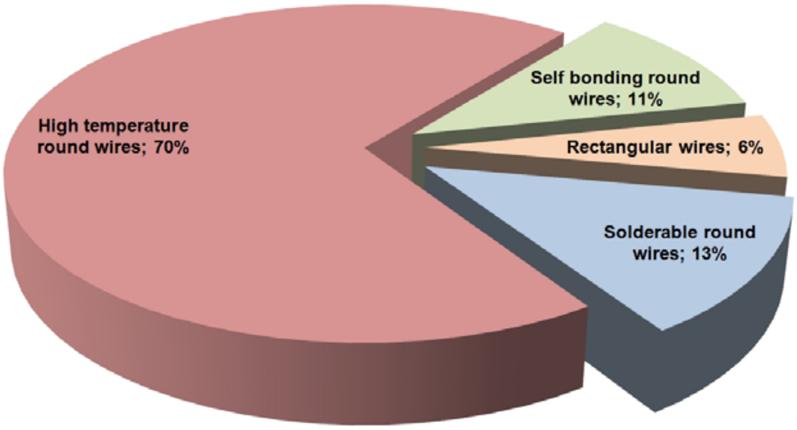


Figure 2: Breakdown of the different winding wire products [BREF STS 2007]

5.3 Key environmental and health issues

VOC emissions, together with NO_x emissions, are precursors of ground level ozone formation in the presence of sunlight. Existing occupational workplace limits should be taken into consideration.

Emissions of VOC to air may occur from:

- the storage of the solvents
- the drying processes

Spills and leaks from storage areas may result in emissions to soil and groundwater.

The process generates waste containing solvents which need to be disposed in a way that emissions to air, soil and groundwater are prevented or limited.

Cresol is toxic by ingestion, inhalation and in contact with skin. It is a severe skin and eye irritant and may cause skin burns or discolouration. Chronic exposure may lead to kidney or liver damage. It has the risk phrases: R23, R24, R25 and R34.

N-methyl-pyrrolidone is irritating to the eye and skin and has the risk phrases R36 and R38.

6 VOC Substitution

The following sections describe potential substitutes for VOC (using VOC-free and VOC-reduced systems). There are also descriptions of the application technologies or special conditions needed and the advantages and disadvantages compared to systems that use solvents with a high VOC content.

6.1 VOC-free systems

The lubricating process, with its high solvent content wax solution, is the major source of VOC emissions and is therefore an important process step when it comes to the reduction of VOC emissions.

6.1.1 Solvent-free lubricants

There are two possible ways to apply lubricants without using VOC containing solvents. One way is by using a lubricant wetted felt. The felt encloses the wire which is pulled through. This applies molten lubricant onto the wire surface. Another way is to use a lubricant impregnated filament, from which the wax melts due to the residual heat of the wire and the frictional heat. The filament is looped 2-3 times around the enamelled wire and moved into the same direction using a lower velocity than the wire.

The lubricant has to fulfil specified requirements, ensuring an appropriate constant thickness and evenness of the lubricant film which can be achieved in a higher quality, if the lubricant is diluted in a solvent (typically VOCs). Especially fine wires (less than 0.15 mm) are vulnerable to break due to the higher friction during the solvent-free lubrication application step. Parameters as wire speed, temperature and traction have to be permanently monitored and automatically adjusted by a control device to avoid quality problems and the breaking of the wire.

6.1.2 Solvent-free coating

At the moment no solvent free coating are applied.

6.2 VOC-reduced systems

If the complete substitution of organic solvents is impractical then changing to systems with a reduced VOC content, such as those described in this section, can reduce emissions.

6.2.1 High solid enamel coating

"HIGH SOLID" ENAMEL COATINGS CONTAIN LESS THAN 70 % OF SOLVENTS

During the last 20 years the solids content of coatings has generally increased from 30 to about 45 %. In case of wire sizes finer than 0.10 mm the solid content of coatings increased from 20 to about 30 %. These are considered as 'high solid' coatings in the winding wire industry. Progress in reducing the use of the solvents to save cost has been offset by the experience that increasing the solid content tends to lead to inferior quality levels of insulation films. It is also more complicated to achieve the right thickness of each layer of the insulation.

All plants in the EU are currently applying coatings with a solids content of at least 30 % for winding wires < 0.2 mm.

[BREF STS 2007] [FVKiD 2008]

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements and abatement techniques can be used to reduce VOC emissions if VOC substitution as described in section 6 is not possible. The following measures are commonly applied for the winding wire coating process:

7.1 Process improvements

Around 40% of the fugitive VOC emissions from winding wire coating may arise from solvent storage and handling. The most commonly used measures to reduce fugitive emissions involve process improvements to collect vapours escaping from application systems, drying areas, storage and handling areas etc. in local exhaust ventilation hoods for subsequent treatment or abatement.

PROCESS IMPROVEMENTS REDUCE FUGITIVE EMISSIONS

A wide range of process improvements are possible which aim at containing and/or collecting VOC emissions. The following list is not exhaustive:

- Increased efficiency from optimised application technologies
- Using closed or covered application systems
- Using closed containers for the transport and intermediate storage of solvents
- Implementing leak prevention systems
- Optimisation of process parameters
- Effective production and maintenance scheduling

7.2 Catalytic oxidation

Due to the fact that currently no VOC-free coatings are available an adequate abatement technology is of major importance. Catalytic oxidation is the commonly used technology in the winding wire industry.

The advantage of the catalytic oxidation (e.g. by using a metal oxide, precious metals as catalyst) compared to conventional thermal oxidation is that it takes place at lower temperatures and thus energy consumption is lower. For the use of the catalytic oxidation, the waste gases which are incinerated need to fulfil the following conditions:

- well-defined solvent content and composition
- low flow rates

- free from catalyst poisons (e.g. heavy metals).

Catalytic oxidation can take place at temperatures as low as 280-350 °C. In the winding wire industry, the catalyst is operated at 500 to 700 °C, for a better oxidation of the used solvents and to achieve a VOC removal efficiency of at least 97 %.

Typically achieved emission levels for the total process (enamelling and lubrication) are less than 5 g VOC/kg product for wires with a diameter above 0.10 mm, and 10 g VOC/kg product for wires with a diameter below 0.10 mm.

Up to 50 % of the energy required for the enamelling process can be supplied from the catalytic oxidation system.

[BREF STS 2007] [FVKiD 2008]

8 Summary of VOC emission reduction measures

The following table summarizes the VOC emission reduction measures discussed in chapters 6 and 7:

Table 4: Measures for VOC substitution and VOC reduction in winding wire coating

Objectives	**Description**	**Applicability**
VOC-free systems	Solvent free lubricants	Not applicable in all cases especially problematic for thin wires problematic
VOC-reduced systems	High solid coating	Not applicable in all cases especially problematic for thin wires problematic
Process Improvements	Good housekeeping Proper handling of solvents	applicable in all cases and state of the art
Abatement Technologies	Catalytic oxidation	applicable in all cases and state of the art

9 Good practice examples

There are only 2 enamelling machine suppliers in Europe, both of them supplying similar technologies, so in most installations machinery is 'comparable' and emission levels are similar.

Due to the general use of catalytic oxidation and increased solvent free lubricant application systems (when technically possible), the main solvent emission reductions have been the result of operational and process improvements.

It is not possible to propose a more detailed general approach for reducing emissions further because of the diversity of the quality requirements of individual customers.

10 Emerging techniques and substitutes under development

10.1 Self lubricating enamels

Generally, the lubricity of enamelled varnishes used for self-lubricating enamelled wires is improved by adding small amount of lubricant (e.g. polyolefin system or fatty-acid-ester systems). Therefore a separate lubrication step would be no longer necessary as the coating system itself already contains a special wax lubricant and thus acts as well as a lubricant.

The currently available self-lubricating coating still needs an additional application of an external lubricant to reach the some properties as conventional coatings. With the currently available products the winding is less efficient and slower and the filling factor is reduced.

Today this solution is only successful when the lubricant is not allowed e.g. due to fire protection reasons in some types of cooling compressors, where customers then have to accept lower winding performances. But it is currently tested for a wider range of other applications. A practical system may be available within the next five years.

This technology is not applicable to flat wire manufacturing.

There is a zero cost impact expected as the enamel cost is higher but the cost of the solvent-based lubricant is eliminated.

A practical system may be available within the next five years.

[BREF STS 2007] [FVKiD 2008]

10.2 Water based enamel coating

Water-based enamel coatings are available but they still contain at least 15 % solvent in order to maintain the surface performance of the coating. In addition, tests demonstrating that coating with such low levels of solvents can meet the IEC standard series 60317 and 60851 (isolation specific thermal product criteria for winding wires) are still not available. The use of water-based systems requires higher energy consumption to ensure a longer, and hotter, drying zone. Furthermore the installations have to be equipped with stainless steel pipes.

WATER BASED ENAMEL COATINGS ARE NOT SOLVENT

There are no data available at the moment about winding wire factories using this type of material. [FVKiD 2008]

10.3 UV curing enamel

The UV curing enamel is applied onto the surface of the winding wire. Whereas in the case of the solvent based coatings curing takes place due to the evaporation of the solvent the curing of the UV curing coatings is performed with UV-light, which is provided with from special UV lights.

This technique is VOC free and might become an alternative to conventional solvent based enamel coatings. However, considerable problems currently exist in achieving the correct thickness required by the winding wire industry. Additionally any blisters resulting from this process will compromise the electrical performance. The UV curing enamels have a non pleasant odour and workers might be allergic to them. Furthermore the used acrylates cannot fulfil the required temperature resistance.

The method/process has not been used in practice yet. There is currently some on-going development activity, and one pilot plant has been set up. [Nexans 2004]

[BREF STS 2007] [FVKiD 2008]

10.4 Hot melt enamel coating

Different types of material can be used as bonding enamels: thermoplastics and thermosets. Thermoplastics (Hot melts) are polymers which are liquid at higher temperature. At elevated temperature (>100 °C) the hot melt is applied with dies onto the winding wire as a liquid. The hot melt cures when the winding wire is cooled.

This technique is nearly solvent free, except for some alcoholic substances in the coating. The thermosetting material is applied, with dies, onto the surface of the wire but requires new machinery.

The application of the hot melts requires resin circulating pumps running at temperatures of about 80 to 100 °C.

Tests, especially with wire diameters >0.355 mm, have yet failed to produce a product that can meet the minimum requirements regarding adherence and flexibility, heat-shock, cut-through, thermal resistance, resistance to abrasion and centricity of insulation film. Given the high solids content, which produces fewer insulation layers, it has not yet been possible to achieve film thicknesses with the required precision.

Due to the lack of performance, high costs, and technological and safety aspects, this alternative is not yet proven as suitable.

[BREF STS 2007] [FVKiD 2008]

11 Information sources

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Umweltbundesamt Berlin, Integrierter Umweltschutz bei bestimmten industriellen Tätigkeiten (Integrated environment protection for defined industrial activities), October 2002

Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Guidance 10:

Coating of wooden surfaces

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses coating of wooden surfaces, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emissions Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
The activity 'Coating of wooden surfaces' is defined as 'any activity in which a single or multiple application of a continuous film of a coating is applied to wooden surfaces'. The SE Directive covers installations in which this activity is taking place with an annual organic solvent consumption greater than 15 t

If the coating activity includes a step in which the same article is printed by whatever technique used, that printing step is considered part of the coating activity. However, printing activities operated as a separate activity are not included, but may be covered by the Directive if the printing activity falls within the scope thereof. This activity does not cover impregnation of wood (see guidance document 12).

The SE Directive lays down the following activity specific emission limit values for coating of wooden surfaces:

THE SE DIRECTIVE APPLIES TO COATING OF WOODEN SURFACES IF A SOLVENT CONSUMPTION OF 15 TONNES PER YEAR IS EXCEEDED

Table 2: Emission limit values of the SE Directive

Activity	**Solvent consumption threshold [tonnes/year]**	**ELVs in waste gases [mg C/Nm³]**	**Fugitive emission values [% of solvent input]**
Coating of wooden surfaces	15—25	100*	25
	> 25	50/75 **	20
Special provisions * Emission limit applies to coating application and drying processes operated under contained conditions. **The first value applies to drying processes, the second to coating application processes			

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[1] as well as for halogenated VOCs that are assigned the risk phrases R40 or R68[2]. There is a general obligation to replace CMR substances– as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated[3] VOC with R40 the ELVs in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

The most important sources of solvent related VOC emissions depend on the process and products used and the subsequent drying process of the coated workpiece.

Techniques to reduce or substitute VOC are:

VOC REDUCTION CAN BE ACHIEVED MAINLY BY LOW VOC PAINTS, INCREASED PAINTING EFFICIENCY AND ABATEMENT TECHNOLOGY

- Use of low-VOC paints
- Improved painting efficiency in the coating process
- Use of abatement technology (especially thermal oxidation)

Other reduction options (e.g. powder coating) have a limited applicability in specific areas.

The operator, as part of implementing an effective VOC reduction strategy based on substitution (low VOC paints), must also optimise equipment performance and any influential non-painting process steps (such as surface preparation by grinding and wood drying) that influence the painting.

To optimise the coating process (and minimise emissions) all involved process-steps and the properties of wood have to fit together. Changes in the coating process (e.g. usage of water-borne paints) leads usually to changes in the application technology, grinding technology, different air filters etc.

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[1] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

[2] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: ‘Possible risk of irreversible effects’. The new wording is: ‘Limited evidence of a carcinogenic effect’. In the ‘old’ version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: ‘Possible risk of irreversible effects’. This new risk phrase does not include carcinogenicity. The ‘new’ version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to this change, a final decision on which version applies can only be given by the European Court

[3] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.

3 Description of the activity and related industry sectors

Wood coatings are an important sector within the coating industry. Wood coating activities include products for domestic and office furniture, window frames, doors, flooring, decking and other construction materials, fencing materials, toys, and components for vehicles etc. In general the basic reason for coating a wood substrate or object is to provide either an aesthetic or protective layer (or both).

Coatings can protect wood against damage by UV radiation, dampness and excessive temperature variations, as well as providing resistance to chemical attack and mechanical abrasion.

There is considerable variation in the properties of wooden substrates that require coating, since these encompass a wide variety of natural wood, as well as products made from wood particles (chipboards, oriented strand board, and fibreboards).

There are many different products produced where the coating of wooden surfaces is part of the production process. Therefore, only general statements can be made regarding VOC reduction options and site-specific factors need to be considered for each individual plant.

EU 15 Member States reported about 500 existing and 40 new installations in 2004, carrying out activities under the scope of activity 10 of Annex II A. [Implementation 2006].

4 Technical process description

4.1 Process flow and relevant associated VOC emissions

Pre-treatment, suitable for the type of wood and the coating process to be used, is an essential part of the finishing processes.

Wood coatings range widely in their VOC content and so emissions during coating can vary significantly. Water-borne products or VOC free products (e.g. powder coatings) as well as solvent-borne products are used. Individual sites (producing the same product) may use a combination of solvent free, low VOC, and solvent-based products.

Figure 1 gives an overview of typical process steps for the coating of wooden surfaces with related VOC emissions

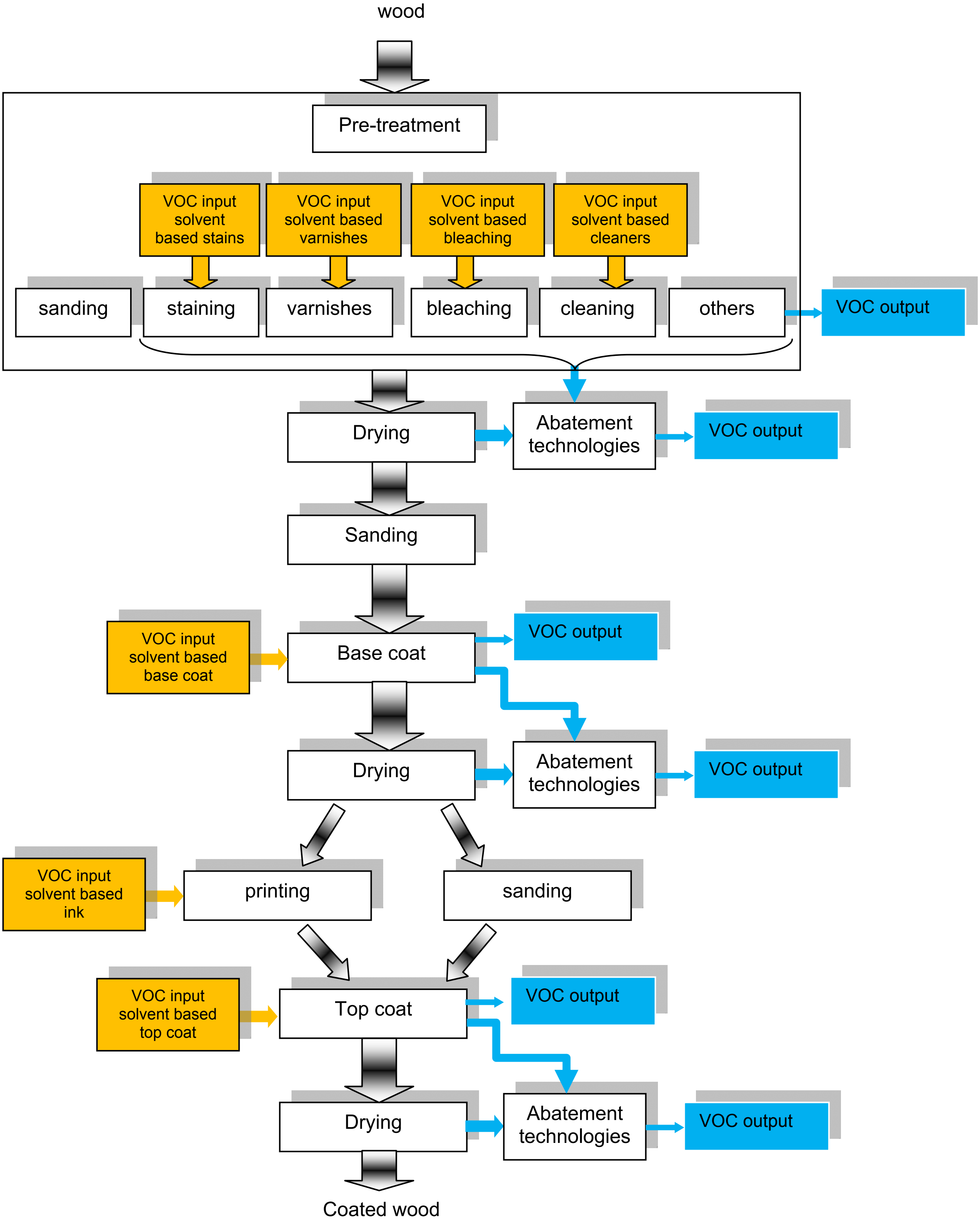

Figure 1: Main VOC input and output of coating processes of wooden surfaces

The major VOC emissions arise during the application and drying process of solvent-based coatings. Minor VOC emissions occur from mixing processes (for example of 2-component paints), cleaning of tools and equipment, storage of paints, wastes and other VOC-containing products used in the coating process but they can be minimised by 'good housekeeping practices' [BREF STS 2007, p 403 ff].

4.2 Application systems

The following systems are in use for the application of pre-treatments, base coats and topcoats [SE Directive 1999], [BREF STS 2007], [Twinning 2004]:

Table 3: Achievable application efficiency factors for different application systems

Application technique	**Efficiency factor [%]**[4]	**Remarks**
Brush painting	95-100	Reduced uniformity of painted surface compared with other application techniques.
Spraying, conventional (High pressure compressed air)	30-60	High volume of overspray depending on geometry of painted workpiece. For most applications, efficiency is in the range of 30–45%.
Spraying HVLP (High Volume, Low Pressure)	40-75	Application of low viscosity wood stains, increasing use also for other paint systems.
Hot spraying	40-60	Application of paints with a high solid content, also applicable for hot wax spraying
Airless spray application	40-75	Bundling of spray-beam, therefore higher efficiency compared to conventional spraying
Air assisted airless technique	35-50	Bundling of spray-beam, therefore higher efficiency compared to conventional spraying
Spraying, electrostatically assisted wet lacquer	50-70	Electrical conductivity is required (minimum dampness of 8% or a conductive primer needed), can be used with any of the spraying techniques mentioned above.
Spraying, electrostatically assisted powder	80-95	Electrical conductivity required, Currently, only applicable for the coating of MDF[5] (only a few applications)
Curtain coating	95	Limited by workpiece's geometry
Rolling, flooding	95	Limited by workpiece's geometry; Reduced uniformity of painted surface (rolling)
Vacumat technique	95	Only applicable for narrow parts and edges, water-based paints and UV cured materials with a high solids content, also the workpiece's geometry has to be considered
Dipping/flooding	95-100	Limited by workpiece's geometry

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[4] Based on applicable paint input in process, not on solid paint on surface

[5] Medium density fibreboard

4.3 Coatings

4.3.1 *Pre-treatment*

Pre – treatment is either done to improve the appearance of the wood or to prepare it for painting. The following products are in use for the pre-treatment of wooden surfaces:

- Stains and varnishes: For some applications this is the only coating step. These coatings fulfil protective (weather resistance) and aesthetic (colour) functions. Stains and varnishes can be divided into film producing (> 5µm) and non-film producing (< 5µm) products. Penetration below the surface of the wood is an important feature of these coatings.
- Bleaching: in general (waterborne) inorganic chemicals are used.
- Cleaning: Solvents are required to remove resin–residues. Water-based cleaning is seldom used because it would raise the water content of the wood and, for most applications, this should be below 10%.

Typical VOC contents of pre-treatment products are shown in the table below:

Table 4: Typical VOC contents of pre-treatment materials (source: [Twinning 2004] and own research)

Type	Remarks/ Main content	% VOC
Varnishes, stains Alkyd resin solvent based	Mainly transparent coatings to enhance wood properties	Up to 70%
Varnishes, stains Alkyd resin waterborne	Usability depending on kind of wood. Some (e.g. oak) tend to swell and/or to produce upright fibres more than others and this can prevent the use of waterborne glazes and stains	Up to 10%

6.1.2 *Base coat & Topcoat*

According to [SE Directive 1999]. [BREF STS 2007], [Twinning 2004] the following paints are used for coating of wooden surfaces:

Table 5: Typical VOC contents of paints

Type	% VOC	Type
Nitro cellulose paint (NC)	70 - 75	Solvent based
Acid curing paints	1C: 65–75 2C: 30 - 60	Solvent based
Polyurethane paints	pigmented: 35 – 60 clear coat: 65 – 70	Solvent based
Unsaturated polyester paints (UP)	12 - 15	Solvent based
Acrylic paints solvent based **conventional** **UV-curing**	65 – 75 up to 40	Solvent based
Acrylic paints water based	2 - 10	Water based
Powder coating	0	Solvent free
100% UV paints	0	Solvent free

5 Solvent use, emissions and environmental impact

5.1 Solvents used

The following VOC relevant products (containing organic solvents as defined in the SE Directive) are currently used for the coating of wooden surfaces:

- Pre-treatment agents
- Paints
- Inks

A wide range of different solvents is used in these products. Typical examples are white spirit, ethyl acetate, and xylene.

Solvent consumption and emission levels

Table 6: Typical solvent consumption for selected applied technology [BREF STS 2007 p. 360]

Application	**VOC-emissions [g/m²]**
High-pressure (‘conventional’) spraying using paint containing 65% solvents	80 – 100
High-efficient coating technology (e.g. rolling, flooding, electrostatic-airless spraying) using paint containing 65% solvents	40 – 60
High-efficient coating technology (e.g. rolling, flooding, electrostatic-airless spraying) using paint containing 20% solvents	10 – 20
High-efficient coating technology (e.g. rolling, flooding, electrostatic-airless spraying) using paint containing 5% solvents	2 – 5

Table 6 gives some approximate solvent consumption figures for a range of paint types and application methods. Because of the huge variety of objects painted, and the differing reasons for doing the coating, the stated ranges may not cover all existing processes.

Approximately 15% of industrial paints used in Germany in 2000 were used for coating wooden surfaces (this figure excludes industrial use of decorative paints) [Markt 99]. Austrian figures for 2006 and 2007[6] indicate a similar picture. The total volume of paints used for coating wooden surfaces in the EU-27 is estimated at approximately 400 kt.

Most companies using solvent-based paints use more than 15 t of solvents per year (SE Directive threshold). Approximately 480 installations that carried out coating of wood in EU 15 [Implementation 2006] were registered and authorised under the Directive in the period from 1999 – 2003.]. The total number of existing installations is unknown and would be difficult to estimate because some coating of wooden surfaces may be carried out as a part of many, various, industrial processes.

Fugitive emissions are significant in many plants using solvent-borne coatings, particularly if stack emissions are already treated with abatement systems. In these cases, fugitive emissions will constitute the bulk (90-95%) of emissions - based on (unpublished) solvent balances prepared by Bipro.

5.2 Key environmental and health issues

Process emissions of solvents, together with NOx emissions, are precursors of ground level ozone formation in the presence of sunlight. Existing occupational workplace limits should be taken into consideration.
Emissions of VOC to air may occur from:

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[6] Source: statistics of the industrial association of paint producers, not published.

- the storage of the solvents
- the coating processes
- drying processes

Contaminated water, produced by separating overspray from the waste air in a certain type of application cabinets, should be disposed as hazardous waste.

Spills and leaks from storage areas may result in emissions to soil and groundwater.

The process generates waste containing solvents which need to be disposed in a way that emissions to air, soil and groundwater are prevented or limited.

6 VOC Substitution

The following chapter describes potential substitutes for VOC (using low-VOC and VOC-free systems) and any associated application technologies and/or special conditions needed for their use, it also lists the advantages and disadvantages compared to systems that use solvents with a high VOC content.

6.1 VOC-free systems

This section describes the ways that VOC-free products or systems can be used to replace the organic solvents currently used.

6.1.2 Powder coatings

The usage of powder coatings for wooden surfaces at an industrial scale is limited to coating of MDF[7]. Research is ongoing but no example of coating for other wood types was found. The use of powder coatings requires investment in new application technology, and there are coating performance issues that may create barriers to the use of this technology.

6.2 VOC-reduced systems

If the complete substitution of organic solvents is impractical then changing to systems with a reduced VOC content, such as those described in this section, can decrease emissions.

VOC emissions from coating processes may be reduced by lowering the VOC content of paints, by increasing the efficiency of the coating process, or by a combination of these approaches. Low VOC systems are:

- Waterborne paints: 5 – 15% VOC
- High solids: 25 – 40 % VOC

- UV curing paints: 2 -5 % VOC

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[7] Medium Density Fibreboard

UV-curing coatings employ 'reactive solvents' that are chemically incorporated into the paint layer during the curing process. Completely VOC-free paints are rarely used for wood coating.

There are some obstacles to the use of all of these coating types:

a) Generic:

- Investment in different application technology - the coatings behave differently to solvent-borne coatings and this usually necessitates changes to application equipment.
- Changes to and/or investment in additional exhaust and drying technology - extraction and drying processes often have to be modified or replaced when using waterborne paints or high solids. In the case of UV-curing the drying process needs to be completely changed.

b) Specific:

- Potential adverse impacts on substrate properties (e.g. swelling of wood or production of upright fibres with water-borne coatings). These problems can sometimes be overcome by applying an initial coating using solvent-borne paints. The seriousness of the adverse impact of water-borne paints varies between different types of wood, and optimising any prior grinding stage can also reduce the impact.
- Corrosion of painting/drying equipment. Many parts of painting and drying equipment for solvent borne paints are made of carbon steel. Water-borne paints (in the presence of amines, which are often a component in such paints) cause increased corrosion of these parts.

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements, and abatement techniques exist to reduce VOC emissions when the substitution of VOC, using the systems described in section 6, is not possible. The following measures are commonly applied for the coating of wooden surfaces:

7.1 Electrostatic coating

Electrostatic coating relies upon the use of conductivity of the paint and the object to be painted to increase the efficiency of painting. According to an IFF project [IFF Projekt Nr.: BW D 20007] the electrical resistance should be below $10^9\ \Omega$ on any area to be painted and the conductivity of the paint should be above 1 µS. Furthermore between grounding and the point of paint application, a wet film of paint is needed. Waterborne paints fulfil these criteria. Solvent-based paints can be modified (e.g. by using organic ammonia compounds).

With wooden substrates, there are a number of options for achieving the level

Of conductivity needed.

- Increasing moisture content to greater than 8% (however this is too high to be acceptable for many applications)
- Use of a conductive primer, applied using conventional spraying
- Use of conductive aggregates (like carbon black or ammonium phosphate) in the manufacture of the MDF.

Other approaches are under development but have not yet been used at industrial scale.

Electrostatic coating can be used with all available spraying techniques (e.g. compressed air, airless). Electrostatic coating using high-speed rotational bells is also possible and has been described in [IFF Projekt Nr.: BW D 20007]. An example of the use of this technology is described in section 9.1.

The maximum emission reduction which can be achieved by the implementation of electrostatic coating using water based paints compared to conventional coating (without end-of pipe treatment) can be estimated by the figures shown in table 6 (up to 98 g/m²).

In addition to the technical constraints mentioned previously, there are safety issues that must be resolved for each type of equipment (e.g. danger of electrical accidents for operator).

7.2 Improvement of waste air collection system

Leakage from waste air collection systems can lead to fugitive emissions of between 0.5 and 1.5% of the transported volume.

Therefore the installation of tightly fitting components and regular maintenance can lead to significant reduction of fugitive emissions.

7.3 Abatement technologies /End of pipe measures

Solvent and waterborne paints and other products for the coating of wooden surfaces contain a mixture of different solvents and therefore recovery and re-use of the solvents is not practical. This means that abatement based on recovery e.g. adsorption, condensation, is not economic compared with destruction techniques. However, adsorption can be used as a means for concentrating waste gas streams prior to destruction.

7.3.1 Waste air with high VOC concentration

The main abatement technologies for waste air with high[8] VOC concentrations are compared in the following table:

Table 7: Comparison of abatement technologies [BREF CWW 2003]

	Thermal oxidation[9]	**Regenerative/ recuperative thermal oxidation**	**Catalytic thermal oxidation**
Treatment temperature	800 – 1 000°C	800 – 1000°C	300 – 500°C
Typical air volume (Nm³/h)	> 2 000 – 10 000	> 10 000 – 86 000	> 10 000 – 86 000
VOC concentration needed for auto - thermal operation	> 2g/m³	> 2g/m³	>2g/m³
Max. VOC concentration	25 % LEL[10]	25 % LEL	25 % LEL
Natural gas volume needed for start up	3-5 kWh/ 1 000 Nm³	5-8 kWh/ 1 000 Nm³	1-2 kWh/ 1 000 Nm³
Weight of equipment	> 5t	> 20 t	> 10 t
Limitations on waste gas composition	Not specific	Dust < 1 mg/m³	Dust < 1 mg/m³, no catalyst poison (e.g. organic S- or N-compounds.)
Typical clean gas specification (mg/m³):			
VOC	< 20	< 20	< 20
NOx	< 100	< 100	< 50
CO	< 100	< 100	< 50
Investment (€/1 000 m³) based on max. size mentioned above	20 000	15 000	17 000

8 most of time above auto thermal threshold
9 non-regenerative/recuperative and non-catalytic
10 LEL = Lower Explosion Limit

Operational costs are highly dependent on the average concentration of VOC in the waste gas and the operation time of the plant (range from 1 shift 5 days per week to 24 hours per days 7 days a week) as well as on the type and cost of fuel needed for the operation – therefore typical costs are difficult to be determined.

With the above described technologies VOC reduction potentials > 99% are possible.

7.3.2 *Waste air with medium to low VOC concentration*

For large waste air volumes containing concentrations of less than 1 g/m³ absorption (using zeolite) can be used to concentrate the VOC. Continuous desorption is then used to generate a smaller and more concentrated, volume of (waste -) air and this air is then treated with one of the technologies mentioned in the previous section(most likely thermal oxidation). Investment costs are approximately € 20 000/1 000 m³.

7.4 Process improvements and operational measures

‘Good housekeeping’ can be used to minimise VOC-emissions from mixing processes (for example of 2-component paints), cleaning of tools and equipment, storage of paints, wastes and other VOC-containing products used in the coating process.

The VOC content of the air extracted from painting and drying operations may be a minor part of the total process arising; a significant proportion of the fugitive VOC emission arise from operations that are not directly involved with painting or drying, these include the waste air collection system (ventilators, flaps, folded spiral seam pipes and their connections etc.).

8 Summary of VOC emission reduction measures

The following table summarizes the VOC emission reduction measures discussed in chapters 6 and 7:

Table 8: Measures for VOC substitution and VOC reduction in coating of wooden surfaces

Objectives	**Description**
VOC-free Systems	Use of powder coating Use of VOC-free UV cured coatings
VOC-reduced Systems	Use of - UV-cured coatings (low VOC) - Waterborne coatings - High solids coatings (25 – 40% VOC)
Process Improvements	Improved painting efficiency (e.g. use of electrostatic painting) Optimisation of waste air collection system Good housekeeping (reduction of fugitive emissions)
Abatement Technologies	Absorption (to increasing VOC concentration in the waste air before thermal oxidation) Thermal oxidation (regenerative or recuperative) Catalytic oxidation

9 Good practice examples

9.1 Example 1: Replacing solvent-borne polyurethane paint by water-borne paint

The example shows the effects in term of VOC emissions reduction of replacing solvent-borne polyurethane paint by water-borne paint and introducing an electrostatic support to enable the automated painting of kitchen furniture (door fronts) with high quality requirements. All data are based on [IFF Project Nr. BW D 2007].

a) Technical data

Object being coated: Doors for kitchen furniture

Original process:

- First layer: basecoat 2-component polyurethane paint (airless automated equipment)
- Grinding
- Second layer: 2-component polyurethane texture finish (airless automated equipment).
- Third layer: 2-component polyurethane clear coat (airless automated equipment).

Modifications and results:

The second layer is replaced by the application of a water-borne textured finish, applied using high rotation bells. During testing, some minor modifications to the painting equipment were necessary:

- The carrying units (made of plastic) have to be replaced with metal parts
- paint used for the first layer was modified in order to achieve a conductivity of 10^9 Ω.

No changes were made regarding grinding. The solid content of the waterborne paint was 45%.

As an option (option 1) for further optimisation, the painted objects were wetted using a conductive waterborne solution before application of the second layer.

The key process parameters of the 3 process types are shown in Table 9:

Table 9: Example 1: Comparison of key figures before and after optimisation

Parameter	1) Original process	2) Waterborne paint	3) as 2) plus wetting (option 1)
Efficiency [%]	43 – 45	57 – 62	68 – 71
Paint consumption [g/ piece]	140 – 145	Appr. 83	Appr. 75
Paint on painted piece (solvent/water) [g/ piece]	Appr. 60	Appr. 51	Appr. 52
Paint on painted piece (solids) [g/ piece]	23 – 24	Appr. 24	Appr. 25
Emitted solvent [g/ piece]	70	4,3	3,8
Painting time [sec]	27	20	20

The results show that solvent emissions were substantially reduced by use of the waterborne coating, but that the dry film on painted pieces was essentially the same in all three cases.

Minor problems occurred and were solved during the test, none of them continued to be a problem. The availability of the equipment was > 97%. There was no need to change cleaning routines.

b) Economic data

Costs for the use of the waterborne coating as described above (without option 1) have been calculated as follows:

Investment: € 150 000 (2/3 on equipment, 1/3 on development, education of operators, and maintainance)

Savings:

1) Waste

The original process created waste (used paint) that represented a cost of € 117 per tonne. This number is based on an efficiency of 50% and a solid content of 50% plus 10% coagulation agent which equates to 0.28 t solid waste and a solid content of 60% of the waste).

Savings using waterborne paint as described above: 45% (€ 53/t)

2) Usage of paint

Increasing the efficiency (from 45% to 60%) leads to savings of 25% of the paint. Based on an average price of € 8/kg for both kinds of paints savings of appr. € 2 000 can be achieved.

Return on investment:
A reasonable volume of 75 tonnes of paints per year for a medium size plant

leads to a ROI of approximately 1 year.

c) VOC-reduction

The usage of 75 t of solvent borne paint (appr. 550 000 pieces painted) leads to emissions of ~ 37 500 kg VOC.

Painting the same number of pieces with waterborne paint reduces the VOC emissions down to 2 300 kg

9.2 Example 2: Substituting solvent based paints by water based paints

The second example describes the changes made in late 2007 in a company producing custom made furniture and the resulted reduction of VOC emissions by substituting solvent based paints by water based ones. All data provided by the company are based on the results of the first 6 months of 2008

a) Technical data

Object coated: Various furniture parts.

Parts with simple geometry are painted using automatic painting equipment (airless spraying), complex parts are painted by operators using airless spraying in a spray booth.

Substrate: MDF[64], 18 different kinds of wood.

Original process:

- First layer: 2-component polyurethane base-coat

- Grinding

- Second layer: predominantly 2-component polyurethane (with some production using high gloss special products)

Solid content of paint: 60%
Painting efficiency: 47%
Paint consumption: approximately 760 g/m²

Modifications and results:

The original automatic painting equipment has been replaced by a new one, air condition has been installed to provide constant temperature and humidity.

2/3 of the solvent borne paint has been replaced with water borne UV-curing paint (basecoat and topcoat).

All drying equipment for the automatic painted parts was replaced.

The cleaning agent has been replaced to meet the needs of the water-based paint and the cleaning of the belt carrying the parts to be painted was optimised to reduce the volume of cleaning agent. Nevertheless VOC´s are still needed to clean dry and half-dry residues of water borne paint.

Grinding has been modified (to use another type of grinding material).

The total capacity has been increased by 10%.

Table 10: Example 2: Comparison of key figures before and after change

Parameter	1) Original process	2) Waterborne paint
Area painted automatically [m²/year]	85 000	180 000
Area painted by hand [m²/year]	120 000	45 000
Total paint consumption [kg/year]	70 000	60 000
Thereof solvent borne paint	70 000	12 000
Thinner consumption [kg/year]	5 800	2 000
Total consumption of cleaning agent (VOC) [kg/year]	25 000	10 000
Efficiency [%]	47	48
Paint consumption [g/ m²]	760	520
Paint on painted piece (solvent/water) [g/ piece]	360	250
Emitted solvent for automated paint application [g/m²]	300	30

b) Economic data

Total investment: € 500 000 (without internal manpower).

Table 11: Example2: Changes in operational costs

Parameter	Additional costs (€/year)	Savings (€/year)
Grinding	+ 5 000	
Paint		- 3 000
Cleaning agent		-10 000
Waste		- 3 000

What we can observe in this case it that higher costs/kg of paint and cleaning agent are overcompensated by less volume consumed. Some significant increase in operational costs can be observed, even if it is not possible to quantify them precisely:

Manpower for grinding: + 30%

Energy consumption (electricity): +30%

Dust filters: +35%

Therefore a reasonable return on investment can only be achieved by the increased capacity.

c) VOC-reduction

Total emissions were reduced by 2/3 from approximately 60 t per year to 20 t per year despite the increase of painted surface of 10%.

d) Specific remarks

The planning process and tests required about one year. Leading operators were involved from the very beginning.

The new painting process has required modifications to the air conditioning and the grinding processes. Also the changed properties of the overspray dust caused problems and a significant increase in the consumption of dust filters.

Conclusion:

The example shows that for an investment of € 500 000 a reduction of 40 t VOC/year (= € 1 250 per t) was achievable. Marginal savings in operational cost (appr. minus € 10 000 per year) and an increase in capacity of 10 % were other economical effects. Apart from technical obstacles convincing and training of the operators were the major issues which were overcome by involving them into the process of change right from the beginning.

9.3 Example 3: Results of an overview study on furniture producing companies

The example shows the aggregated results of 41 furniture producing companies in the UK trying to reduce their VOC-emissions. All data is based on [BFM 2001]. Though the data is almost ten years old, the branch-specific experience is still interesting and actual for many companies.

The report of this study can be found at the following website: http://www.bfmenvironment.co.uk/

It lead to more or less the same conclusions as the individual case studies:

1) Substitution of paints is always related to changes in the main process (spraying).
2) Besides paints, cleaning agents are very important VOC-sources. Emissions can be reduced by either substitution or usage of closed cleaning equipment (e.g. for tools) and good housekeeping to avoid fugitive emissions.
3) Investments to reduce the VOC-input and emissions can be cost-neutral or even create savings if the grade of automation is high.

10 Emerging techniques and substitutes under development

Paints and coating technologies for wood surfaces are continuously being improved. The main focus has been on improving the efficiency of the painting process – particularly the consumption of paint (per m² or piece). The emerging techniques for improving coating efficiency provide benefits both in terms of lower costs for paint input, reduced emissions and less waste.

Three main areas:

- Technology improvements:
  Typical examples are automation (painting robots capable of following complex structures like in the car-industry), optimisation of layer thickness, electrostatic media (see below).
- Electrostatic spraying or high rotation bells:
  Materials and pre-painting operations are being refined to extend the applicability of electrostatic techniques (see section 0).
- Powder painting
  Powder painting, currently is only used for coating of MDF, research is aimed at improvements to layer thickness achievable, melting temperatures and film quality.

11 Information sources

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European Commission, DG Environment, Analyses of the reports submitted by

Member States on the implementation of Directive 1999/13/EC, ENTEC UK Limited, 2006.

[Markt 99]
Der deutsche Markt für Farben und Lacke 1999 [German market for paints and varnishes], Chem Research GmbH

[Rippert]
Franzgrote, engineering, (2008 June 24) telephone interview
Company: Rippert, supplier of painting equipment

[SE Directive 1999]
Council Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations

[Twinning 2004]
Best available technique for coating of wood - Twinning Project CZ 2002/IB/EN/01 Implementation of the Environmental Acquis at Regional Level – Follow up seminar for surface treatment using solvents in the Czech Republic – September 2004

[Venjakob]
Nüsser sen., managing director, (2008, June 25) telephone interview,
Company: Venjakob, supplier of painting equipment

Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Guidance 11:

Dry cleaning

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses dry cleaning, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emission Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
The activity ‘dry cleaning’ is defined as ‘any industrial or commercial activity using VOCs in an installation to clean garments, furnishing and similar consumer goods with the exception of the manual removal of stains and spots in the textile and clothing industry’. The SE Directive covers all installations in which this activity is taking place independent of the annual organic solvent consumption.

Dry cleaning takes place in the commercial sector as well as on an industrial scale in specialised companies.

Table 2 shows the emission limit values set out in the SE Directive for dry cleaning. The Directive does not set a solvent consumption threshold for this activity. It only contains a total emission limit value and no separate ELVs for waste gases and fugitive emissions.

THE SE DIRECTIVE APPLIES TO ALL DRY CLEANING ACTIVITIES, INDEPENDENT OF THE ANNUAL CONSUMPTION OF ORGANIC SOLVENTS

Table 2: Emission limit values of the SE Directive

SE Directive - Emission limit values (ELVs) (Annex II A – activity No. 11)				
Activity	**Solvent consumption threshold [tonnes/year]**	**ELVs in waste gases [mg C/Nm³]**	**Fugitive emission values (% of solvent input)**	**Total ELVs**
Dry cleaning				20 g/kg (1) (2)
Special provisions:[1] (1) The total ELV is expressed in mass of solvent emitted per kilogram of product cleaned and dried. (2) The emission limit in Article 5(8)[2] does not apply for this sector.				

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

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[1] A particular exemption applies for Greece concerning installations in remote areas or on islands.

[2] Article 5(8): For discharges of halogenated VOCs which are assigned the risk phrase R40, where the mass flow of the sum of the compounds causing the labeling R40 is greater than, or equal to 100 g/h, an emission limit value of 20 mg/Nm³ shall be complied with. The emission limit value refers to the mass sum of the individual compounds.

Specific requirements apply for VOCs classified as CMR substances[3] as well as for halogenated[4] VOCs which are assigned the risk phrases R40 or R68[5]. The discharge of such VOCs shall be controlled as emissions from an installation under contained conditions as far as technically and economically feasible to safeguard public health and the environment. For CMR substances, there is a general obligation to replace them– as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for such substances the ELV in waste gases is 20 mg/Nm³, and it also applies when a reduction scheme is being used. The emission limit value for halogenated VOCs which are assigned the risk phrase R40/R68 set out in article 5(8) of the SE Directive does not apply for this sector.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

VOC FREE DRY CLEANING OPTIONS ARE: WET CLEANING, LIQUID SILICONE AND LIQUID CO_2

There are a number of VOC-free dry cleaning options, including wet cleaning, and liquid CO_2. None of them, however, have quite the same stain-removing power of the most commonly used solvent, perchloroethylene (Perc), and they can be more expensive.

Closed machines, equipped with a condenser with refrigerated cooling coils and an activated carbon filter to recover the solvent, have lower consumptions of Perc and emissions are typically less than 10 g/kg.

The use of sealed units for the collection of distillation residues reduces VOC emissions even further.

Good operating practice is important in dealing with the sludge (closed containers).

3 Description of the activity and related industry sectors

DESPITE INCREASED USE OF SUBSTITUTES PERC IS STILL WIDELY USED FOR DRY CLEANING

There are approximately 58,000 dry cleaning installations in the EU (27) [TSA 2009], 60 to 90 % of the European textile care companies still use Perc but it is expected that the proportion in professional cleaning will decrease. [CINET 2006]

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[3] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

[4] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.

[5] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: 'Possible risk of irreversible effects'. The new wording is: 'Limited evidence of a carcinogenic effect'. In the 'old' version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: 'Possible risk of irreversible effects'. This new risk phrase does not include carcinogenicity. The 'new' version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to this change, a final decision on which version applies can only be given by the European Court

4 Technical process description

4.1 Process flow and relevant associated VOC emissions

The following flow chart provides an overview of possible VOC emissions from a typical modern perc dry cleaning machine fitted with a condenser and an activated carbon filter system:

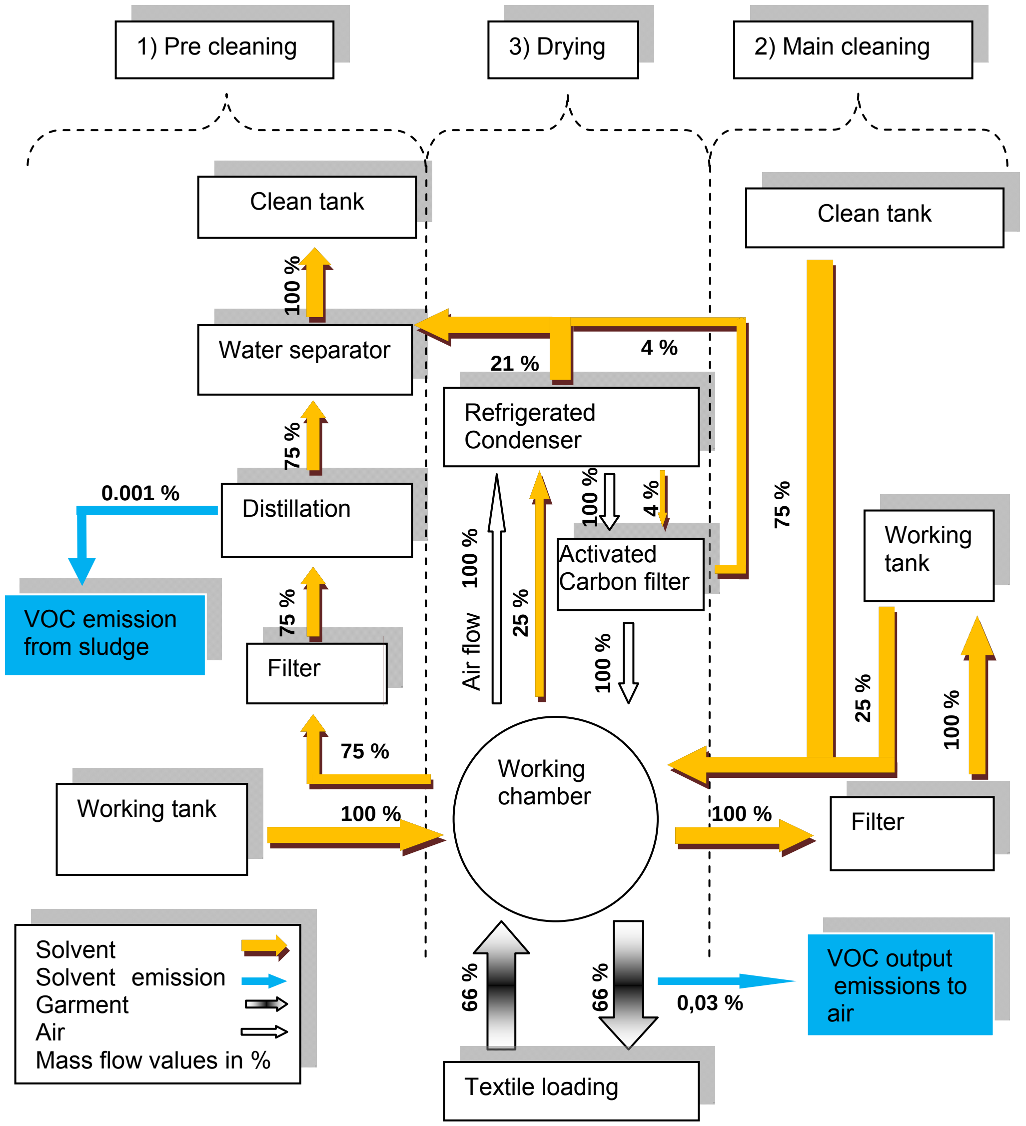

Figure 1: Possible VOC emission sources in dry cleaning

When using modern dry-to-dry machines, equipped with a refrigerated condenser and an activated carbon filter, most of the emission occurs when the working chamber is recharged. The chamber is about 20 times the volume of the load which means a volume of 1 m^3 for a machine with 50 kg garments per cycle. Typically the VOC concentration in the chamber air after completion of the cleaning and drying cycles is less than 2 g/m^3. If it is assumed that all of these VOC are emitted when garments are removed, then these emissions are less than 0.04 g/kg. Emissions can also arise from the distillation residue, which can contain from 10 – 15 % Perc. The residues should be collected and treated by suitably qualified waste disposal companies. [Multimatic] In intervals of 2 weeks to 6 months, about

100 l of sludge has to be disposed of and treated by a specialist company. The time interval varies according to a variety of factors, e.g. the kind of garments cleaned, the degree of contamination and the rate of utilisation of the machine.

4.2 Process description (Perc Dry cleaning machines)

DRY-TO-DRY CLEANING COMBINES CLEANING AND DRYING IN ONE MACHINE

Dry cleaning machines typically range in capacity from 10 to 50 kg of garments per cleaning cycle. The garments are placed in a perforated steel drum that rotates about 38 times a minute. Modern machines, so called 'dry-to-dry' machines, are able to both clean and dry, eliminating the need to transfer wet garments from a cleaning machine to a drying machine. The introduction of dry-to-dry machines makes possible the recovery of nearly all of the Perc used during cleaning.

The cleaning cycle consists of two steps:

The first step is a pre-cleaning cycle where the majority of dirt is removed. The solvent for this step comes from a working tank. If the Perc becomes heavily contaminated during this cycle, it is subsequently distilled to recover clean solvent. This is then recovered and stored in a tank for reuse, while the sludge is collected as waste. If the Perc is not heavily contaminated it is stored in a working tank

The second step removes any remaining dirt. The perc is taken from the clean tank and working tank. After a dip level is reached Perc is continuously pumped from the drum over a filter back into the drum. At the end of the second cycle the Perc is filtered and stored in a working tank.

During the drying process, warm air is circulated through the garments, and the residual solvent vaporizes and is extracted from the working chamber. The solvent-laden air is passed through a refrigerated condenser, where the Perc and water are recovered using refrigerated cooling coils. Because Perc and water are immiscible and separate into two phases, water can be removed relatively simply and the Perc recycled. [Miele]

5 Solvent use, emissions and environmental impact

5.1 Solvents used

The following solvents are currently used for dry cleaning:

Perchloroethylene ($Cl_2C=CCl_2$ or Perc)

Perc is the solvent most commonly used by the dry cleaning industry (~85%) [Live Science]. It is a non-flammable VOC, capable of dissolving oil based stains and, with detergents, of dissolving non-oil based stains.

Hydrocarbons

Some non-halogenated hydrocarbons (DF-2000^{TM}Fluid, EcoSolv$^{®}$Dry Cleaning Fluid, Pure Dry®, Shell Sol 240 HT, Stoddard Solvent) [ATCM

2005], which have good cleaning properties and are less harmful than Perc, are also used. However, they are flammable and require the use of fire prevention measures. Hydrocarbon-machines require vacuum-distillation systems and can typically not be operated with Perc. [Multimatic]

Liquid silicone

A liquid silicone product, decamethylcyclopentasiloxan is a VOC solvent[6] which degrades within days to the natural components: silica, water and carbon dioxide. It does not have any Risk/Safety phrases but is under review in some countries as it might be harmful to the environment.

Others

Besides the VOC solvents mentioned above, the following substances, which are VOC free, can also be used:

- Water
- CO_2

A detailed description of these cleaning agents is given in chapter 6.

The share of the different cleaning techniques can vary significantly from one country to another. The estimated intervals are shown in the following table:

Table 3: Application for different cleaning techniques in different countries of Europe

Solvent	**Amount [%]**
Perc	60 - 98
Hydrocarbon	1 - 40
Wet cleaning	1 - 30

The use of Liquid Silicone and CO_2 is still very little but a growing technique. [CINET 2006]

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[6] There is no international consensus on whether this product should be considered as VOC or not (e.g. in the U.S. it is not regarded as a VOC) [TSA 2009].

5.2 Solvent consumption and emission levels

For the pre-cleaning process, the weight ratio of Perc to garments is about 3:1 - which means that 150 kg of Perc would be used in a cleaning machine with a garment load of 50 kg. In the main cleaning process, the ratio is 5 : 1, and 250 kg of Perc would be used. The solvent consumption of Perc is about 1 ml/kg garments, where hydrocarbons are used the consumption is about 2,8 ml hydrocarbon/ kg garments.

Cleaning machines with the closed sludge-removal system and activated carbon systems emit about 10 g Perc per kg garments, but may be less with good practice, re-usage and maintenance.

5.3 Key environmental and health issues

Process emissions of solvents, together with NO_x emissions, are precursors of ground level ozone formation in the presence of sunlight. Existing occupational workplace limits should be taken into consideration.

Emissions of VOC to air may occur from:

- the process
- the recharging from the drum

Spills and leaks from storage areas may result in emissions to soil and groundwater.

The process generates waste containing solvents which need to be disposed in a way that emissions to air, soil and groundwater are prevented or limited.

Perc is classified as a category 3 carcinogen substance - which means that it could cause cancer. It is toxic/harmful to aquatic organisms and may cause long-term adverse effects in the aquatic environment. Halogenated solvents, resulting from inappropriate use and storage, are common pollutants in groundwater. Additionally, the non-halogenated hydrocarbons used in dry cleaning can be flammable.

6 VOC Substitution

In the following chapters potential substitutes for VOC and their associated technologies are presented. This includes application conditions as well as advantages and disadvantages compared to VOC systems.

6.1 VOC-free systems

This section describes the ways that VOC-free products or systems can be used to replace the organic solvents currently used.

6.1.1 Wet cleaning

In wet cleaning, water based solutions containing various detergents are used as the solvent. These systems are completely VOC free, but cause discharges of contaminated water.

The approach differs from that of household washing in the detergents used, the size of the machine, and the mechanical treatment of the textiles. The detergents mainly consist of tensides (alkylbenzene sulfonates) to remove oil based stains. The effectiveness of the cleaning is dependent on the experience of the cleaning staff.

WET CLEANING NEEDS DETERGENTS TO REMOVE OIL BASED STAINS

Wet cleaning is highly effective for water-soluble stains such as blood or wine, and removes these stains better than Perc. The technique is less suitable for garments that have layers of different materials (e.g. suits). Another disadvantage of wet cleaning, in comparison to dry cleaning, is that creases are removed during the washing; therefore the finishing process is more extensive, which increases the cost of the cleaning.

Nevertheless, from an economic point of view, at least 35 % of garments are suitable for wet cleaning.

A typical wet cleaning washing cycle takes about 21 minutes (but the garments are only pre dried and the finishing of each garment of the load takes time [3-5 min]), while dry cleaning takes about 45 to 50 minutes. [Miele]

6.1.2 Liquid CO_2 cleaning

Liquid carbon dioxide (CO_2) may be used as a solvent. CO_2, which can exist as a liquid at room temperature if kept at a high pressure in a closed system, has a gas-like consistency and a low surface tension. It functions as a very effective cleaning agent when combined with detergents to remove dirt from garments. Liquid CO_2 is effective on most materials and can remove a wide range of stains and dirt. It is non-flammable and completely VOC free. CO_2 is also used for fire and water damage restoration because of its effectiveness in removing toxic residues, soot and associated odours of fire.

CO_2 CAN BE USED AS A CLEANING FLUID, EVEN AT ROOM TEMPERATURE, IF USED AT A HIGH PRESSURE. IT IS NON-FLAMMABLE AND VOC FREE

Since liquid CO_2 technology operates at room temperature, any stains that remain on a garment after the washing cycle have not been heat-set - as they might have been with traditional dry cleaning systems; consequently post-wash spot removal is very effective. Liquid CO_2 has good colour retention performance characteristics that equals or exceeds those for Perc dry cleaning for a wide variety of coloured fabrics.

However, this technique is less suitable for garments made from triacetate and acetate fabrics, especially if yellow dispersive dyes have been used.

The process takes place in a high-pressure vessel at about 30 to 40 bar hence the machines are relatively costly (60,000-90,000 €).

As there is no drying cycle, CO_2 systems typically have a total cleaning cycle of 30 minutes or less, which is significantly shorter than the cycle for cleaning in Perc. It is necessary to install an alarm because of oxygen displacement in case of leakage.

The only emission from this system is CO_2. [EPA 2007]

6.2 Substitution of substances with specific R-phrases

The following alternatives are available for substances with specific R-Phrases (e.g. liquid silicone). Although these alternatives do not always result in reduced total VOC emissions, they are preferable because they reduce health risks.

6.2.1 Liquid silicone cleaning

A liquid silicone product, decamethylcyclopentasiloxan, known under the trade name GreenEarth® is a VOC solvent used in the cleaning industry (by about 1,7% of companies worldwide in 2008) [MFG Consulting]. The product degrades within days to the natural components: silica, water and carbon dioxide. By contrast with hydrocarbon solvents, it does not cause skin irritation or lead to groundwater contamination. Toxicology studies report varying findings, ranging from completely harmless to the observation of small but statistically significant increases in uterine cancer for rats as a result of very high exposure of liquid silicone. [CINET 2008]

A PERC MACHINE CAN BE CONVERTED INTO A LIQUID SILICONE CLEANING MACHINE BUT IT IS NOT RECOMMENDED

The effectiveness of liquid silicone products in removing stains is less than that of Perc but comparable to water-soluble products. A 1 % concentration, by volume, of detergent is automatically injected with each load to ensure good stain removal.

While, in principle it is possible to convert a cleaning machine using Perc to a GreenEarth® machine, there may be technical and commercial difficulties to overcome. The operating costs are higher compared to dry cleaning.

The duration of the washing cycle is 53 - 58 minutes, which is some 10 minutes longer than for dry cleaning [Green Earth ® 2002]

6.2.2 Hydrocarbon based systems

'Hydrocarbons' used for dry cleaning are a mixture of different (non-halogenated) components - typically n- and iso-paraffins. Some of the hydrocarbons are flammable and therefore corresponding safety measures have to be taken into consideration. The major difference between cleaning machines operating with hydrocarbons and those using Perc is that the former use vacuum distillation for solvent recovery. Some, but not all, Perc cleaning machines can be converted to use hydrocarbons and in general a hydrocarbon machine is about 40 % more costly. The cleaning strength is close to Perc but drying of garment requires more energy especially for thick garments. An advantage of hydrocarbons is their lack of an unpleasant 'dry cleaning' smell. The washing cycles are about the same but the cleaning does not completely match the quality achieved when Perc is used [Multimatic]. Hydrocarbons are not under suspicion of being carcinogenic, in contrast to Perc. [CINET 2006] [Neighborhood Cleaners]

HYDROCARBON DO NOT HAVE THE EXCELLENT CLEANING QUALITY OF PERC BUT THEY ARE NOT CATEGORIZED AS CARCINOGENIC

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements and abatement techniques can be used to reduce VOC emissions if VOC substitution as described in section 6 is not possible. The following measures are commonly applied for Dry cleaning process:

7.1 Sealed distillation unit and drum

Sealed distillation units can be used to avoid any emissions during the removal of the distillation residues. These systems provide an alternative to manual removal of residues. In the sealed distillation unit the residue is pumped directly into the safety can. The sealed drum prevents emission during the washing cycle. When used in combination with a Perc monitoring device, preventing premature chamber opening, emissions due to operator procedures can be prevented. The combination of a condenser and an activated carbon filter can reduce the emissions during the garment exchange step by over 80 %. [Multimatic]

7.2 Activated carbon recovery

Activated carbon recovery is the most effective technique currently used to reduce emissions from Perc (or hydrocarbon) cleaning machines. If an activated carbon recovery system is installed the refrigerated condenser can be designed smaller.

CONCENTRATIONS OF LESS THAN 2 G/M³ CAN BE ACHIEVED WITH ACTIVATED CARBON FILTERS

During the washing cycle, Perc is circulated in a sealed system, but when the garments are removed, the system is opened and Perc vapour may be emitted. The concentration of Perc in the working chamber of a machine not equipped with an activated filter, is about 10 to 14 g/m³. Machines incorporating an activated carbon filter re-circulate the air in the working chamber through the carbon filter until a pre-set (low) threshold concentration of Perc is reached - hence a measuring device is necessary;

concentrations of << 2 g/m³ [BÖWE] can be reached using this technique. The capital cost of an activated carbon filter system, which automatically regenerates itself is about 6,000 to 7,000 € for a 10 kg load machine and about 22,000 € for a 70 kg load machine. It is useful, for operational reasons, to install two active carbon filters so that one can work while the other is being automatically regenerated, thereby reducing downtime. [Multimatic]

7.3 Condensation

Refrigerant cooled condensers are used to recover solvent from both Perc and hydrocarbon cleaning machines. During the cleaning process, and before the drum is opened to remove the garments, warm, solvent-laden air flows through the condenser. The condenser reduces the air temperature, causing most of the solvent to condense and to be removed from the air stream. Refrigerated cooled condensers are about 60 % more efficient than water cooled condensers - reducing the concentration from about 1,100 ppm down to 450 ppm [OSHA 2005].

8 Summary of VOC emission reduction measures

The following table summarizes the VOC emission prevention and reduction measures discussed in chapters 6 and 7:

Table 4: Measures for VOC substitution and VOC reduction in dry cleaning

Objectives	**Description**
VOC-free Systems	Wet cleaning Liquid CO_2 cleaning
Substitution of CMR substances	Hydrocarbon based systems Liquid silicone cleaning
Process Improvements	Sealed units
Abatement Technologies	Activated carbon filter Condensation – refrigerated cooling

9 Good practice examples

9.1 Liquid silicone cleaning

The investment cost for a 10 kg load cleaning machine with a drying function is about 19,000 €. Licenses are also required, and cost ~1600 € / year according to the distributor.

The whole cleaning machine with the working and storage tanks contains about 200 litres of solvent. The solvent costs about 4 €/litre but consumption is less than that of a similarly sized Perc cleaning machine. Within 6 to 8 weeks about 110 litres of residue accrue, the disposal costs are about 100 €. [Green Earth Cleaning]

9.2 Liquid CO_2 cleaning

The investment costs of liquid CO2 cleaning machines, according to an American producer, are about 60,000 €. This is high compared to other techniques because of the need to work at high pressure. A Perc dry cleaning machine costs about half and a hydrocarbon-cleaning machine about two thirds of this price. As the CO_2 process does not need a drying period the washing cycle is about half that of Perc-based cleaning. Theoretically one CO_2 cleaning machine can do the work of two Perc cleaning machines. The operational costs are about 0.90 € per kg garments which is within the range of Perc and hydrocarbon dry cleaning. During the washing of a 30 kg load about 5 kg CO_2 are vented to air and about 98 % are recycled.

Conversion from a Perc machine to a CO_2 cleaning machine is not possible as completely different working processes are involved. [EPA 2007]

9.3 Perc cleaning

VOC emissions from dry to dry machines with water-cooled condensers can be further enhanced by retrofitting a refrigerated condenser at a cost of less than 5,000 €. Further reductions can be achieved with activated carbon filters (~ 6,000 € for a filter system containing 100 kg activated carbon) and the use of a sealed distillation unit - which pumps the residue from the distillation automatically into a safety can. To avoid the opening of the machine before a Perc concentration of 300 ppm is reached, the door can be equipped with a safety interlock. The refrigerated condenser reduces emission by about 60 % and with the activated carbon filter the final emission is reduced by about 90 % [OSHA 2005] [Corbett]

Depending on the size of a Perc cleaning machine, the capital cost can vary between about 25,000 and 40,000 €.

10 Emerging techniques and substitutes under development

In the last 20 years many new technologies have evolved to replace the use of Perc. A technology that will be ready for the market in 2009 is the virtually waterless washing machine.

Virtually waterless washing machine

This machine uses 98 % less water (about 100 ml per kg of garments) and energy than a conventional washing machine. The process is based on the use of plastic granules (or chips) that are tumbled with the clothes to remove stains. It is reported that this process can remove virtually all types of everyday stains as effectively as existing processes whilst leaving clothes just as fresh as normal washing. In addition clothes emerge from the process almost dry, reducing the need for tumble-driers. It is too early to specify costs but it is expected that the machine will not be more expensive than conventional dry-cleaning machines. Savings in energy use are expected but not proven yet. [LEEDS 2008] [Xeros 2008]

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Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Guidance 12:

Wood impregnation

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses wood impregnation, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emissions Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
The activity 'wood impregnation' is defined as giving a loading of preservative in timber. The SE Directive covers installations in which this activity is taking place with an annual organic solvent consumption greater than 25 t

The preservation of wood takes place either in specialised companies or as a production step in sawmills or other wood processing industries, e.g. window production.

This activity does not cover the surface coating of timber with paints, varnishes or lacquer. Although these applications include a protective function, the main purpose of these activities is of decorative nature (coating of wooden surfaces guidance document 10).

The SE Directive lays down the following activity specific legal provisions for wood impregnation:

Table 2: Emission limit values of the SE Directive

SE Directive - Emission limit values (ELVs) (Annex II A – activity No. 12)				
Activity	**Solvent consumption threshold [tonnes/year]**	**ELVs in waste gases [mg C/Nm³]**	**Fugitive emission values [% of solvent input]**	**Total ELVs [kg/m³]**
Wood impregnation	>25	100*	45	11
Special provisions: * does not apply for creosote.				

THE SE DIRECTIVE APPLIES TO WOOD IMPREGNATION IF A SOLVENT CONSUMPTION OF 25 TONNES PER YEAR IS EXCEEDED

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[1] as well as for halogenated VOCs which are assigned the risk phrases R40 or

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[1] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

R68[2]. There is a general obligation to replace CMR substances– as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated[3] VOC with R40/R68 the ELVs in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

Resistance to both decay[4] and insect attack is enhanced by application of preservatives (by low or high pressure processes) or by modification of wood using physical or non-biocidal chemical processes.

The most important sources of solvent related VOC emissions arising during wood impregnation will vary according to the process, products used and the subsequent drying process of the wood.

VOC emissions may be reduced by substituting solvent-based preservatives with water-based products or by switching to other wood modification processes (e.g. thermal treatment).

VOC REDUCTION CAN BE ACHIEVED MAINLY BY SUBSTITUTING SOLVENT-BASED PRESERVATIVES WITH WATER-BASED PRODUCTS OR LOW VOC CONTAINING PRODUCTS (IN CASE OF CREOSOTE)

VOC emissions from the impregnation of wood with creosote can also be reduced by using water-based preservatives or by using a creosote formulation with a low VOC content (EN 13991 Grade C[5]).

Timber impregnated at high pressure with water-based preservatives has a similar resistance to decay to that of some creosote impregnated timber. Wood treated at high pressure is more resistant than wood treated at low pressure. Since wood treated with solvent-based preservatives may not be as durable as creosote treated wood the use of water-based preservatives at a low pressure treatment may be a suitable alternative.

Enclosed vacuum preservation systems, with solvent recovery, are effective techniques to reduce emissions at process level.

3 Description of the activity and related industry sectors

In Europe, around 11.5 million m³ of wood is treated with preservatives each year [BREF STS 2007], the quantity of pressure-impregnated wood is estimated to be around 6.5 million m³ [WEI 2008]. Pressure-treated wood is mainly used for outdoor applications where timber is exposed to weathering and attack by pests e.g. fencing and fence posts, playground equipment,

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[2] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: ‘Possible risk of irreversible effects’. The new wording is: ‘Limited evidence of a carcinogenic effect’. In the ‘old’ version mutagenity (cat 3) was included. This mutagenic effect is now

[3] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.

[4] a term used to describe fungal attack

[5] (formerly known as WEI creosote type C)

carports, decking, constructional timber, joinery, telegraph poles, electricity distribution and transmission poles, jetties, railway sleepers.

The sector is characterised by a relatively large number of small plants with a solvent consumption of less than 25 t/y [BREF STS 2007] which are therefore not covered by the SE Directive. In Europe approximately 250 companies have a production capacity of more than 75 m³ per day [WEI 2008].

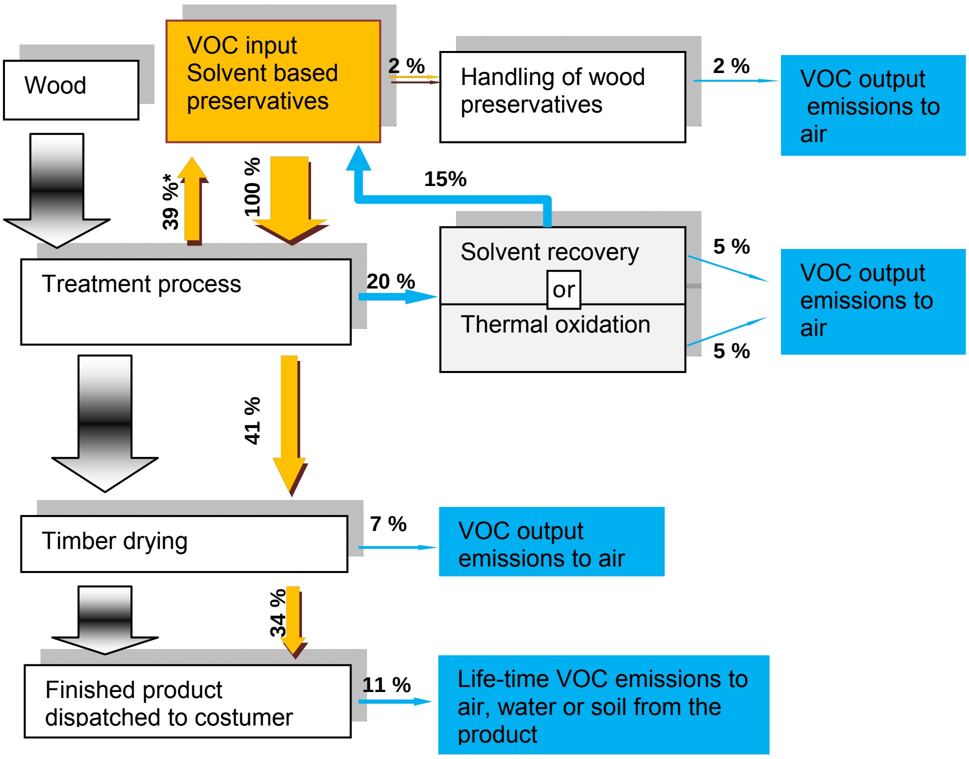
CURRENTLY 3 TYPES OF WOOD PRESERVATIVE PRODUCTS ARE MAINLY USED

The amount and type of preservative used depends on the type of wood being treated, the use that the wood will ultimately be put to, and the treatment process used by the installation. Preservatives can be applied using vacuum processes, pressure processes, by dipping/immersion [see part 4 of this document for details]. Currently three main types of wood preservation products are used: water-based, solvent based and oil based (creosote) products, and these are described in part 5 of this guidance document.

4 Technical process description

4.1 Process flow and relevant associated VOC emissions

The following flow chart illustrates the process steps for wood impregnation using solvent-based products and shows where VOC emissions can occur. The flow chart also gives an indication of how much solvent is emitted from each process or remains in products. In the case of creosote the flow chart looks similar but solvent recovery is not possible.



* The flow chart shows the input of VOC preservative and the 39 % excess, not taken up by the wood, which is pumped back into the storage tank

Figure 1: Typical VOC inputs and outputs in wood impregnation processes using solvent-based preservatives

Approximately one third of the solvent that remains in the wood after drying at the wood preservation plant will evaporate over time, but the other two thirds will stay in the wood over its working life.

4.2 Process description

Techniques for the impregnation of wood include the use of vacuum and pressure processes for long-term protection for wood intended for outdoor use. Dipping, spraying or brushing, on the other hand, are used mainly for temporary or short-term protection or for wood that will be used for indoor applications.

Double vacuum impregnation (vacuum low pressure impregnation)

DOUBLE VACUUM IMPREGNATION IS APPROPRIATE FOR WATER AND SOLVENT BASED PRESERVATIVES

High efficiency double vacuum impregnation is a state of the art technique for applying solvent-based and water-based preservatives to “finished” products where dimensional stability is important (e.g. window frames, doors, balconies and garden furniture).

In the double vacuum process, impregnation takes place in a treatment chamber that is first evacuated and then, after flooding it with preservative, pressurised to increase the penetration of preservative into the wood. The chamber is then drained before a final vacuum stage is applied to remove excess preservative from the surface layer of the wood, the timber is then left to dry in the open air. In case of solvent based products about 15-25 % of the solvent remains in the wood [BREF STS 2007] after the drying process. In order to reduce the consumption and emission of VOC, these installations are typically equipped with a solvent recovery system or with thermal oxidation units for treatment of emissions.

High pressure process (Vacuum/Pressure impregnation)

HIGH PRESSURE IMPREGNATION IS APPROPRIATE FOR THE APPLICATION OF CREOSOTE OR WATERBORNE SYSTEMS

This technique is used for both water-based preservatives and creosote. A cylinder is filled with the preservative solution and pressure is applied to it (up to 14 bars). After a period, the preservative is drained from the vessel and, typically, a final vacuum is applied to extract excess wood preservative from the timber. The application efficiency of the vacuum process approaches 100 %. In case of creosote impregnation this type of installation is typically equipped with either a solvent recovery system or a thermal oxidiser for treatment of emissions.

Dipping / immersion

Dipping involves immersing timber in a tank of solvent-based, creosote or water-based preservatives. Dipping is more efficient than brushing, spraying or deluging. Where solvent-based preservatives are used, plants are usually enclosed in order to minimise solvent consumption and, therefore, emissions.

5 Solvent use, emissions and environmental impact

5.1 Solvents used

The following VOC relevant preservative products (containing organic solvents as defined in the SE Directive) are currently used for wood impregnation:

Solvent based preservatives

Solvent based products contain approximately 5 % of active ingredient (insecticides, fungicides or water repellents) and 95 % organic solvent. Approximately 20 kg are needed for the impregnation of 1 m^3 of wood.

SOLVENT BASED PRODUCTS ARE APPLIED WHEN DIMENSION STABILITY IS REQUIRED

Nowadays the so called LOSP – light organic solvent preservatives – are used. In these products, organic solvents such as white spirit or other petroleum based hydrocarbons are used as solvents to carry the active ingredients (e.g. fungicides, insecticides, water repellents) into the wood. White spirit consists mainly (>80 %) of C_9-C_{11} hydrocarbons (aliphatics, alicyclics and aromatics), the remainder is largely C_7-C_8 and C_{12} hydrocarbons.

LOSP can be applied in the double vacuum impregnation process and in the immersion/dipping processes. They are used for finishing wooden components in their final machined shape and form, as LOSP does not cause swelling or distortion of the timber products. Solvent based preservatives are used by the construction industry for specific activities when precise dimensions and long lasting protection are required.

Creosote

The use of creosote for wood impregnation is restricted to wood for outdoor applications with special requirements (ground contact) e.g. posts, poles, fencing or sleepers (Directive 76/769/EEC)[6]. Between 40 and 150 kg of creosote is needed for the impregnation of 1 m^3 wood.

CREOSOTE IMPREGNATION IS USED FOR OUTDOOR APPLICATIONS WITH SPECIAL REQUIREMENTS

Creosotes are distillate fractions consisting of a multitude of chemical compounds. They are differentiated into three types (type A – C, according to [EN 13991]) with different vapour pressures. According to the SE Directive, the fraction of creosote which exceeds the value of 0.01 kPa vapour pressure at 293.15 K shall be considered as a VOC. The VOCs are the low boiling fraction of the creosote.

Creosote use is restricted - due to its classification as Carc. Cat. 2[7] substance because of its benzo[a]pyrene content. According to Directive 2001/90/EC[8] ,if the product contains less than 0.005 % (by mass) of

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[6] In some EU Member States the use of creosote is more restricted, or even completely banned (type A-C).

[7] Category 2 carcinogens

[8] Commission Directive 2001/90/EC of 26 October 2001 adapting to technical progress for the seventh time Annex I to Council Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations (creosote)

benzo[a]pyrene and less than 3 % (by mass) water extractable phenols, it may be used, but only in industrial installations or by professionals.Therefore Type A creosote, which can now contain 0.005 to 0.05 % and formerly contained up to 0.1 % benzo[a]pyrene, is banned in the EU.

Type B creosote is currently the most widely used oil based product with an average VOC content of 20 % and less than 0.005 % benzo[a]pyrene.

Type C creosote, with a much reduced VOC content (~2%), and a content of less than 0.005 % benzo[a]pyrene has a high viscosity and high crystallisation temperature. Therefore it is necessary that the storage and impregnation system is heated. The advantages are the lack of odour and reduced tendency for the wood to sweat. [Rütgers 2007]

Creosote is an effective preservative; it has a very low solubility in water and so is highly resistant to leaching. It is normally not corrosive to metals, it protects timber against splitting and weathering, it has a high electrical resistance and it is available in several grades to suit different applications [EGTEI 2004].

Creosote is typically applied in closed, vacuum/pressure impregnation, processes and, to a minor extent, it is also used in non-pressure processes.

5.2 Solvent consumption and emission levels

WATER-BASED PRODUCTS ARE THE MOST WIDELY USED PRESERVATIVE PRODUCTS FOR PRESSURE TREATMENT OF WOOD

The use of solvent based products declined significantly with the implementation of the SE Directive [WEI 2008]. They have been widely substituted by water-based products or by wood modification treatment systems and this trend is on-going.

Pressure systems (including double vacuum impregnation and the high pressure process) account for more than 50% of the whole impregnation sector, the estimated distribution of preservative used is shown below:

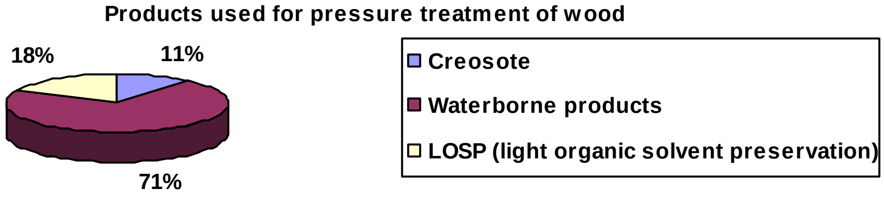

Figure 2: Preservation product types used for pressure treatment of Wood (Western Europe) [WEI 2008]

The total consumption of creosote as a preservative is declining overall due to increased regulation and because of the availability of non-wooden products e.g. the use of concrete ties for new railway-lines. However, in the case of poles, an increased use of creosote has been reported because the potential substitutes (water-based CCA-products) cause higher disposal costs due to the heavy metal compounds which require special waste treatment. [TeliaSonera 2005].

5.3 Key environmental and health issues

Process emissions of solvents, together with NO_x emissions, are precursors of ground level ozone formation in the presence of sunlight.

Emissions of VOC to air may occur from:

- the storage of the solvents

- the impregnation process

- the drying process

Spills and leaks from storage areas may result in emissions to soil and groundwater.

Creosote is toxic and classified as Carc. Cat. 2. As a consequence of its potential health impact creosote is also classified as a R45 substance that ‘may cause cancer’. Since emissions arise from its handling and storage occupational workplace limits should be taken into consideration.

Water based preservatives that contain ammoniacal copper quaternary compounds (ACQ) or copper azole (Cuaz) are considered to be less toxic.

6 VOC Substitution

The following sections describe potential substitutes for VOC (using VOC-free and VOC-reduced systems). There are also descriptions of the application technologies or special conditions needed and the advantages and disadvantages compared to systems that use solvents with a high VOC content.

6.1 VOC-free systems

This section describes the ways that VOC-free products or systems can be used to replace the organic solvents currently used.

6.1.1 Water-based systems

Typically *water-based preservatives* are copper azole (CuAz) and other copper-based systems (where copper acts as a fungicide component). Quaternary ammonium, hydrogen fluoride, fluorosilicate, or boron based compounds are also used. In case of hydrogen fluoride and fluorosilicate based preservatives, it has to be born in mind that on the one hand the VOC´s are reduced but on the other hand these substances are toxic and environmentally critical.

Before September 2006 water based copper chromium arsenic (CCA) products also have been used as preservatives. Since September 2006 CCA is no longer authorised for use in the EU as biocide (according to Directive 98/8/EC[9]).

WATER-BASED PRODUCTS CAN BE APPLIED BY HIGH OR LOW PRESSURE PROCESSES DEPENDING ON THE FINAL USE

Water-based preservatives differ from each other in their activity spectra, their leaching resistance, their application process (high or low pressure process) and therefore their suitability for the intended final use of the treated wood. The application of water-based systems is carried out either by high or low-pressure processes (see part 4 for descriptions). Water-based, low pressure processes mainly substitute solvent based preservative systems while water-based high-pressure processes are suitable to substitute creosote. Water-based treatments can be used instead of creosote for some end-uses up to 30 year life expectancy (and longer with case-by-case approval of the preservative manufacturer). Examples are medium-life fencing, cladding of agricultural buildings, some horticultural uses [WPA 2009]

The process of impregnation of solvent based and water-based preservatives is very similar with no significant economic differences. Water-based preservatives have the advantage that they can be also used in open impregnation systems, e.g. in dipping installations. However, the substitution with water-based preservatives is not always possible due to the swelling of the wood, which must be avoided when treating certain finished products. In addition, timber treatments with higher levels of copper (ACQ and CuAz) are more corrosive.

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[9] Directive 98/8/EC of the European Parliament and of the Council of 16 February 1998 concerning the placing of biocidal products on the market

Water-based solvents are also used instead of white spirit to emulsify LOSPs (water-based micro emulsion). While the VOC emissions are significantly reduced, such a substitution may cause a swelling of the timber from 0.5 up to 6 % - depending on the wood.

Water-based treatment is approximately 3 times less expensive than comparable solvent based processes. Recent increases of oil prices are the key factor causing this difference. Because water-based and solvent based treatments use the same or similar active substances and the same type of timber treatment plant the major difference is the formulation of the active substances. [ARCH 2008]

Water-based micro emulsions such as azoles or quaternary ammonium compounds can replace solvent-based products. They are applied either by dipping or in vacuum processes. These water-based products contain 1% solvent. [EGTEI 2005]

WITH THE USE OF WATER-BASED PRODUCTS VOC EMISSIONS REDUCTION UP TO 100% IS POSSIBLE

Water-based micro emulsions systems generally require a high dosage of preservative which results in an increase of the moisture content of the timber having an effect on the dimensional stability of the timber and may also require the timber to be re-dried prior to use.

Switching from solvent-based preservatives to water-based systems can achieve a VOC reduction approaching 100 %, or, for water-based micro emulsions systems, a reduction of 99 %.

6.1.2 Non-solvent systems (thermal treatment of wood, platonising)

The thermal treatment is based on the pressure impregnation technology but requires no chemicals or inert gases. As such, it is a completely solvent free process. This treatment is applicable to all types of wood (dry or fresh), and it is especially suitable for European wood. The thermally treated wood can be used for both outdoor (not for ground contact) and indoor applications.

FOR THE THERMAL TREATMENT OF WOOD NO CHEMICALS ARE REQUIRED

The process consists of steam treating the wood in an autoclave at a temperature of 140-210 °C and a pressure of 14-20 bar. The process modifies the cell structure of the wood, thus reducing its water absorption capacity. Additionally the dimension stability is improved and the wood becomes more durable. The wood is preserved throughout its cross section whereas in the case of impregnation, this can only be achieved for wood of small dimension. The process is already used at industrial scale but there is work on progress to improve product quality. It seems that the durability and preservation resulting from this process, if applied properly, are similar to creosote impregnated wood. [Thermowood 2008]

Another method of wood modification would be the use of hydrothermal technology. The process consists of five steps:

- Pre-drying stage
- Hydro-thermolysis stage. The wood is heated to 150 – 180°C in an aqueous environment. The cellulose remains intact, and the wood keeps therefore its good mechanical properties.
- Drying stage. The wood is reconditioned to a dry environment in a conventional industrial wood kiln

- Curing stage. The wood is heated to 150-190 °C under dry conditions.
- Conditioning stage. The moister content of the wood is elevated to a level which is necessary for manufacturing.

The process and future developments are available as a license. [Plato 2002] [Plato 2006] [CEN/TS 2007]

During the thermal treatment of wood, there is no need for any chemicals. Another environmental benefit is that the waste from thermally treated wood can be more easily reused as a solid fuel. Due to loss of water from the wood during treatment, the total weight loss is about 50 %, and so transport costs decrease as well. [Corbat 2006]

There are some disadvantages of the process. Energy consumption is increased due to the higher temperatures and longer treatment times compared with other treatments. The heat treatment may also affect the product quality. It results in a loss of the wood's elasticity and solidity and as a consequence, its mechanical strength. In addition, a darkening of the wood occurs. In some cases a change of shape may result from it. Finally, choice of the correct temperature curve for each wood requires skill and experience.

The investment cost for thermal treatment installations is nearly double that of water-based systems. The process is generally more expensive than other preservation techniques, there is no cost of preservative but the process take 2 to 5 times longer.

6.1.3 Acetylisation of wood

The hydroxyl groups of the wood absorb and release water which is the main reason for swelling and shrinking of the wood. It is assumed that the digestion of the wood by enzymes is initiated at the free hydroxyl groups.

In the acetylisation step hydroxyl groups are changed to acetyl groups which results in higher dimensional stability and a higher durability.

For the acetylation the wood is loaded into a reactor. Acetic acid is reacted to acetic anhydride, which is pumped into the wood loaden reactor. The wood treatment takes place at a certain temperature, pressure and time, in which the hydroxyl groups are replaced to form the acetylated wood. In this reaction acetic acid is formed again and reused. After the reaction is finished the wood can be discharged from the reactor.

With the acetylisation of the wood the following properties are possible:

- Dimensional stability
- High durability
- Mould and insect resistance
- Good machinability
- Non toxic
- UV resistant

The process and future developments are available as a license. [Accoya 2008]

6.2 VOC-reduced systems

If the complete substitution of organic solvents is impractical then changing to systems with a reduced VOC content, such as those described in this section, can decrease emissions.

6.2.1 Use of Type C Creosote

Creosote is only allowed[10] for outdoor products like sleepers, poles (electric power transmission and telecommunications) and fences. The use of creosote treated wood inside buildings, in toys, playgrounds, garden furniture or outdoor facilities where there is a risk of frequent skin contact is not allowed.

Currently type B creosote is the most widely used in Europe but is rapidly being replaced by Type C due to environmental legislative pressure. In the last 10 years, the substitution of type B creosote by type C has been significant, even for heavy-duty purposes such as railway sleepers or poles. Railway sleepers treated with Type B creosote emit approximately 5 kg VOC over 25 years - about one third of the preservative in the wood; the use of type C creosote reduces the emissions by 90 % over this period. Furthermore the product has less of the typical "impregnation odour" and a reduced tendency to sweat. No negative effects related to the product quality have been reported.

BY USING CREOSOTE TYPE C VOC REDUCTION OF MORE THAN 90% IS POSSIBLE

This shift, however, results in higher costs for operators. On the one hand, the product itself is more expensive (~25 %) and, on the other, process equipment has to be modified. Due to the higher crystallisation properties of creosote C, the storage tanks and the supply pipes have to be heated. A higher temperature is also necessary during the impregnation process itself to reduce the viscosity of the preservative and to guarantee its fast and efficient penetration into the wood. This results in higher energy consumption and costs.

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[10] According to directive 76/769/EEC

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements and abatement techniques can be used to reduce VOC emissions if VOC substitution as described in section 6 is not possible. The following measures are commonly applied for wood impregnation process:

7.1 Process improvements

The most important measure related to emission reductions by process improvement is the use of closed systems (double vacuum or high pressure impregnation). Due to the final vacuum step excess solvent can be removed before the wood is stored for a week to dry. In the vacuum step about 10 % of the impregnation fluid is extracted while another 10 % evaporates during the drying process.

7.2 Abatement technologies / End of pipe measures

Exhaust gases can be treated to reduce VOC emissions using either carbon filters to adsorb and then recover VOCs, or by thermal oxidation, in which case the VOCs are thermally decomposed. By using abatement technology, emissions of VOC can be reduced by about 95 - 99 %. [CTP 2008]

In case of thermal oxidation natural gas is needed to heat up the furnace to its operating temperature of 800 °C. Thermal oxidation does need any extra heating with natural gas if the VOC concentration of the waste gas is above the autothermal point (2-3 g VOC/Nm^3). The resulting heat of the burning process, however, can be recovered and can be used for different purposes within the facility as for example heating of the creosote Type C.

In case of activated carbon filters, the carbon has to be regenerated every 3-6 months depending on, among others, the type of activated carbon, amount of activated carbon in the filter, required emission level and operating conditions. The activated carbon costs about 1–1.50 €/kg, the cost for external recovery of the solvent is about 0.60 €/kg.

8 Summary of VOC emission reduction measures

The following table summarizes the various approaches to substitute or reduce VOC emission as described in chapters 6 and 7:

Table 3: Measures for VOC substitution and VOC reduction in wood impregnation

Objectives	**Description**	
	Solvent-based preservatives	**Creosote**
VOC-free Systems; **Substitution of CMR substances**	Water-based preservatives Thermal treatment Acetylisation	Water-based preservatives Thermal treatment Acetylisation
VOC-reduced Systems		Use of type C creosote (instead of type B)
Process Improvements	Application by double vacuum impregnation system Enclosing of the process wherever possible and extraction and treatment of emissions Use of final vacuum stage to remove excess solvent or carrier Use solvents with lower ozone-forming potentials Drain surplus pesticide in contained areas Solvent recovery and recycling system	Use of final vacuum stage to remove excess solvents Closed cooling system Safe handling of the creosote
Abatement Technologies	Thermal oxidation Activated carbon filter	Thermal oxidation

9 Good practice examples

9.1 Use of EN 13991 Grade C

This company produces about 10,000 m³ of type C impregnated wood per year. The duration of the impregnation is about 10.5 hours with a batch size of 45 m³. The working pressure is 8-10 bar and vacuum under 0.1 bar.

The changes necessary for conversion from type B to C were small because the heating system was already integrated. Additional isolations and heating elements – especially located close to valves - had to be installed resulting in costs in the range of 80,000 – 100,000 €. In order to avoid unnecessary energy costs from heating, storage amounts were kept as small as possible by good inventory management.

The exhaust gases are cleaned with a carbon filter. Regeneration of the contaminated carbon is outsourced.

When substituting type B with type C special care was taken to ensure use of correctly dimensioned vacuum pumps. Since a pressure of less than 0.1 bar has to be reached once the impregnation is finished to remove the excess creosote from the wood. Some additional measures have been necessary to avoid problems due to crystallisation of creosote components plugging the system. All parts of the system have to be heated (20 °C above the crystallisation temperature) and isolated. During machine downtime all pipes have to be emptied.

9.2 Thermal treatment of wood

In a typical thermal treatment installation wood is treated during 48 hours, The majority of the time is used for the heating and cooling and not the holding process with a maximum temperature of about 200 °C. At the beginning of the process a vacuum is applied in the chamber to remove the oxygen. During the following heating process applying steam to the wood the pressure reaches a value of 20-25 bar.

Investment costs for thermal treatment equipment are typically between 500,000 and 1,000,000 € for a batch size of 50 m³ or more, the operational costs are about 50-100 €/m^3.

During the whole process the timber is only treated with vacuum, pressure and heat and is never in contact with any kind of solvent or water. Therefore the emissions of VOCs are minimal. According to the information of the company the thermally treated wood shall be useable for any kind of application (even for wood with ground contact).

For thermal treatment special knowledge about the heating program, especially in the heating and cooling slope, is crucial. Only with the proper process parameters are good preservative properties and negligible loss of mechanical strength possible.

9.3 Water-based preservatives

In a typical new installation wood is treated in a 18 m^3 reactor with a charge capacity of 14 m^3 wood. The impregnation cycle takes 4 hours and can therefore be repeated 6 times a day due to a 24 hour shift work. With 250 working days a yearly production of about 20,000 m³ can be achieved. Depending on the intended application the raw material costs are between 10 and 30 €/m^3, energy costs are negligible and water costs are 0.5 – 1.5 €/m^3. The investment costs for this plant are about 250,000 €. Depending on the preservative type, the impregnation costs can vary between 20 and 40 €/m^3.

10 Emerging techniques and substitutes under development

The current trend in the development of wood preservatives is to use biocide combinations which include both inorganic-organic and organic-organic binary mixtures.

New preservative systems

New water-based systems

Zinc-based systems are very attractive because of zinc's low cost, long history of use as a wood preservative, and ability to be formulated in a colourless form. The relatively low use of this system is due to its lower efficacy compared with VOC containing products and the high costs of registering new wood preservatives.

Aluminium-/iron/boron/zirconium-based systems are described in literature and various patents as wood preservatives. With the exception of the use of zirconium in Japan [Goliath], there is limited published information on their use, and most of the systems are still at the research stage.

Metal-free systems

- **Micro-emulsions** are organic biocides, sparingly soluble in water, suspended in water as micro-emulsions. It is possible, in future, that blends of different organic biocides may be formulated, as micro-emulsions, to specifically target the various organisms that wood may be exposed to when used outdoors. At the moment they are too expensive for large-scale use and further research is necessary in order to bring them to the market.

New Treatment technologies

Supercritical CO_2 as carrier medium for biocides (Denmark, Supertrae A/S)

Supercritical carbon dioxide ($scCO_2$) is being used as a 100 % VOC free solvent in a wood preservation plant in Denmark, and research is currently being undertaken related to the viability of $scCO_2$ use in Australia. For different woods e.g. spruce good results can already be achieved, but the costs are unclear at the moment[11].

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[11] University of Copenhagen http://www.bfafh.de/inst4/45/ppt/8supercr.pdf

Natural protection system

Plant alkaloids extracted from the Neem tree, salicylic acid, and wood vinegar, as well as bacterial metabolites and cysts are of interest. Hiba and cypress pine oil preservatives are being sold commercially in Japan and Australia. The widespread use of such products on an industrial scale is limited by cost and the availability of the source materials. Therefore establishment of large-scale plantations or integrated biomass processing technology, that produces the active biocide as a by–product would be necessary. [Evans 2003]

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Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Guidance 13:

Leather coating

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses leather coating activities and the related cleaning of equipment, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emission Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
Coating of leather is defined by the SE Directive as ‘any activity in which a single or multiple application of a continuous film of a coating is applied to leather.’

Coating of non-natural leather may be covered by other activities under the SE Directive which are addressed by other guidance documents: for coating of plastics and fabric see guidance 8 part 2.

Leather surface cleaning (e.g. sheepskin degreasing) using VOC solvents may also be covered by the SE Directive (see guidance documents 4/5). Finishing activities of footwear using VOC may be covered by the SE Directive under ‘footwear manufacture’ (see guidance document 14).

The SE Directive lays down the following activity specific emission limit values for leather coating:

THE SE DIRECTIVE APPLIES TO LEATHER COATING IF A SOLVENT CONSUMPTION OF 10 TONS PER YEAR IS EXCEEDED

Table 2: Emission limit values of the SE Directive

SE Directive - Emission limit values (ELVs) (Annex II A – activity No. 13)				
Activity	**Solvent consumption threshold [tonnes/year]**	**ELVs in waste gases [mg C/Nm³]**	**Fugitive emission values [% of solvent input]**	**Total ELVs [g/m^2]**
For leather coating activities in furnishing and particular leather used as small consumer goods like bags, belts, wallets, etc.	>10			150
Other coating of leather	> 10 – 25			85
	> 25			75
Special provisions: Emission limits are expressed in grams of solvent emitted per m^2 of product produced.				

As the total VOC emission limit value refers to square meters of product produced, the annual leather production (in terms of surface of each of the two product groups mentioned above) has to be documented accordingly.

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[1] as well as for halogenated VOCs which are assigned the risk phrases R40 or R68[2]. There is a general obligation to replace CMR substances– as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated[3] VOC with R40/R68 the ELVs in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

The largest VOC emissions result from the application of solvent-based coatings. Less significant VOC emissions may result from water-based coatings and from cleaning of equipment.

Switching to water-based coating systems is the most effective VOC substitution measure. These can produce top quality results for a wide range of product requirements and have already replaced many solvent-based systems.

Water-based (alkaline) cleaning systems can generally clean equipment that has been used to apply water-based coatings, reducing further the emissions.

Water based systems may, nevertheless, emit VOC because they often contain some organic solvent to dissolve binders (0 - 15 % VOC, with ethyl

[1] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

[2] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: ‘Possible risk of irreversible effects’. The new wording is: ‘Limited evidence of a carcinogenic effect’. In the ‘old’ version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: ‘Possible risk of irreversible effects’. This new risk phrase does not include carcinogenicity. The ‘new’ version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to this change, a final decision on which version applies can only be given by the European Court

[3] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.

acetate as a typical solvent). Similarly the cross-linking agents[4] of acrylic binders contain 20 - 50 % of organic solvents. The proportion of cross-linking agent used can range between 2 - 13 wt-%[5], resulting in an effective VOC content of the coating material of between 1 - 7 % [Ökopol 2008]. Organic solvents are also used to adjust viscosity before spraying (e.g. methoxypropanol, isopropanol).

FOR SOME TOP COAT SYSTEMS, WATER-BASED COATINGS ARE STILL UNDER DEVELOPMENT.

Emissions may be reduced even below the emission limit values of the SE Directive (see table 2) provided that only water-based systems are used.

For product groups requiring a high gloss effect, such as handbags and fashion products it is difficult to replace solvent-based top-coats and, if production levels are high, primary and/or secondary abatement measures may be required to reduce VOC emissions. Water-based systems for these product groups are, however, under development.

VOC EMISSION REDUCTION FROM SOLVENT-BASED SYSTEMS CAN BE ACHIEVED BY USING APPLICATION TECHNIQUES WITH LOW VOC CONSUMPTION.

A further reduction of VOC emissions can be obtained by reducing solvent consumption using application techniques that reduce the thickness of coatings and thereby minimise material loss. Spray coating can achieve a thinner finish than roller or curtain coating. The VOC emission reduction achieved with spray coating is greatest when high-solid coatings and airless spray equipment are used - with optical detection of the product to be sprayed.

Appropriate handling and dosing of organic solvents (both for coating and for cleaning) can lead to a further reduction in solvent consumption.

Where primary measures are not sufficient to reduce the VOC emissions below the limit values, waste gas treatment systems may be necessary: biofilters and activated carbon filters are often used in the leather coating industry.

3 Description of the activity and related industry sectors

FINISHING MAY CONSIST OF UP TO FOUR COATS.

Leather coating is a process which is included within the ‘finishing’ stage of treatment at a tannery. When finishing, tanneries use a combination of processes including conditioning, staking, buffing, coating, milling, plating and embossing, in order to prepare leather for sale to the manufacturers of leather goods.

The objective of the finishing processes is to improve the appearance and properties of the leather. Depending on the intended purpose and the desired colour fastness properties, leather is finished with up to three or four coats: base-coat, intermediate coat, top-coat, and in some cases an additional coat for a special surface texture.

A wide range of leather products is made - these include shoes, furniture, automotive upholstery, clothing, bags, purses and belts.

The most important user of EU leather production is the footwear industry (50 %). The clothing industry takes about 20 %, leather for furniture and automotive upholstery about 17 %, and small leather goods compose about 13 % of the production. [BREF TAN 2003]

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4 Cross-linking agents promote or regulate the bonding between polymer chains to create a more rigid structure.

5 wt.-%: abbreviation for “weight percent”

In the EU-15, approximately 3000 companies produce 25 % of the world's leather, manufacturing around 74 000 tonnes of heavy leather and 240 Mio m^2 of light leather. With 2 400 companies, Italy is the most important European producer of leather - accounting (in EU-15) for 65 % of production; Spain has ~ 255 companies, Greece ~ 150, France ~ 113, Portugal ~ 100, UK ~ 55, and Germany ~ 37. [BREF TAN 2003]

The sector is dominated by small and medium sized enterprises: 90 % of the companies employ less than 20 employees, 8.5 % employ 21 - 100 people. About 30 companies (1%) in EU-15 employ 101 - 200 people and no more than 10 companies more than 200 people. [BREF TAN 2003]

In 2006, 12 Member States of EU-15 reported an estimated number of 32 leather coating installations falling into the scope of the SE Directive (missing data of Belgium, Italy and Sweden). [Implementation 2006]

4 Technical process description

The type of coating materials used has a key influence on the magnitude of VOC emissions; both conventional solvent-based systems and water-based systems are commonly used.

4.1 Process flow and relevant associated VOC emissions

Figure 1 gives a schematic overview of the process steps and possible VOC emissions from conventional solvent-based spray coating.

TYPICAL VOC EMISSIONS FROM CONVENTIONAL SPRAY COATING

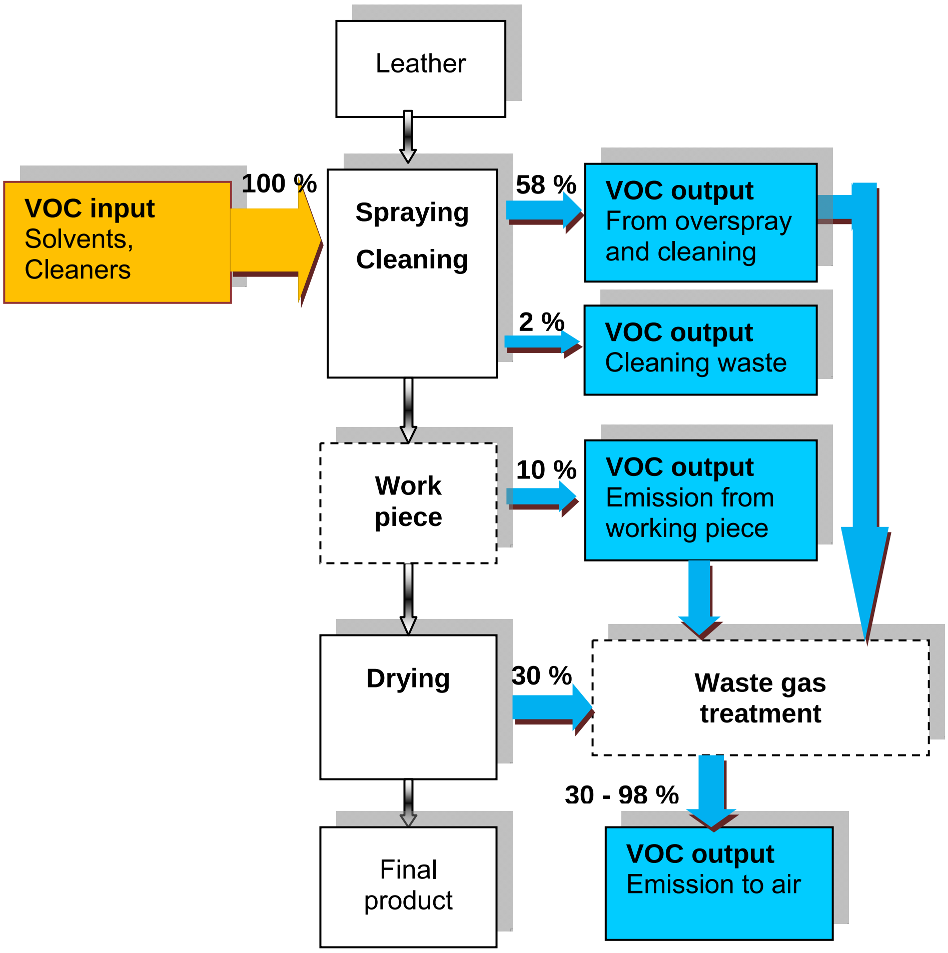

Figure 1: Typical VOC emissions from conventional solvent-based spray coating

THE SECTOR IS DOMINATED BY SMALL AND MEDIUM SIZED ENTERPRISES

4.2 Application systems

The finishing materials used depend on the properties that the customer requires the leather to have. These may include protective coatings to preserve leather (and its colour) when it is subject to wet-rubbing and wet-flexing, to maintain a particular look, or to keep an attractive fashion effect or texture.

ROLLER COATING, CURTAIN COATING AND SPRAY COATING ARE MOST COMMONLY APPLIED SYSTEMS

The industry uses a wide range of application techniques to achieve the desired finish. Roller coating, curtain coating and spray coating are the most commonly used coating systems; other techniques are foam coating, padding, brushing and transfer coating (transfer of a foil previously treated with adhesive).

PADDING IS A MANUAL PROCESS, ALL OTHER TECHNIQUES CAN BE USED OR MANUALLY OR AUTOMATICALLY

Padding is a manual process but all the other techniques can be applied either manually or automatically. Automatic techniques are only used by the biggest tanneries because of the investment cost; these range from ~80,000 – 100,000 Euros for ~125 hides per hour. [BREF TAN 2003]

Curtain and roller coating are currently more effective (10 % waste) than spray coating (40 – 60 % waste) whereas the latter allows about double the throughput per hour. [BREF TAN 2003]

[CARLESSI 2008]

Figure 2: Automatic spray coating machine

Table 3 shows the different coating techniques with their characteristics and alternatives.

Table 3: Leather coating techniques and their implications

	Padding/ brushing	Spray coating	Roller coating	Curtain coating	Transfer coating	Foam coating
Method	The finishing material is padded or brushed onto the leathers surface	The finishing material is sprayed upon the surface with pressurised air	Roller coating applies the finishing mix to the surface using rollers	The leather passes through a curtain of finishing material	Coating from a continuous foil/film	A thick film of foam is applied onto the surface
Practice	Usually applied manually with a brush or a sponge	Generally computer based in spray cabinets. HVLP spray guns and airless spray guns.	Similar to a printing process	The liquid film forms a surface coating	Transfer of an adhesive pre-impregnated film onto the leather	The micro foam system allows the application of a 100-400 g/m² coat onto the surface.
Application range i.a.	Small leather goods with special look and effects	Thin and plain top coats	Especially (not exclusively) for coating large pieces of leather. Used for car seats, upholstery and shoe leather. May be used for special surface effects.	For heavy finish leathers only.	For upgrading poor quality leather and splits. Also for special surface effects.	For buffed and impregnated leather. Useful when thick surfaces are required. Often applied on car seats and upholstery.
VOC	VOC based lacquers and finishing mixtures	Mainly VOC-free or low VOC content mixtures (3% - 8%)	VOC-free or low VOC content mixtures (2% - 8%).	Finishes with a high VOC content (80 – 90 %)	VOC free	
Alternative	None when these methods are required to create a special look	Depending on the requirements: Roller coating	Depending on the requirements: Curtain coating	Can be compared to roller coating. Can NOT be used as a substitute for spray coating	None	None. Used to apply a much thicker coat than roller and curtain coating.
Waste		Overspray - may be reduced by using computer based spray coating, which improves spraying efficiency up to 75% (from 30%)	Very precise coating. Therefore almost no waste such as overspray. The coat is heavier than applied through spray coating.		Due to the different shapes and size of the hides the wastage of films can be up to 30%	
Cross media effects			Cross-linking agents: isocyanides			Considerable energy savings due to low water content
Clea-		Varies:	Varies: water			

	Padding/ brushing	Spray coating	Roller coating	Curtain coating	Transfer coating	Foam coating
ning		water up to high VOC content mixtures.	up to high VOC content mixtures.			

[BREF TAN 2003], [Ökopol 2008]

5 Solvent use, emissions and environmental impact

5.1 Solvent use

The basic components of leather coatings are binders, lacquers, colouring agents, solvents (organic substances, water) and additives (surface active substances, waxes, oils, cross-linking agents for water-based systems and other chemicals).

Various resin types can be used as binders e.g. acrylics, butadienes, polyurethanes and vinyl acetates. Solvent based resins are used for special effect coatings and to achieve particular requirements (for example, to preserve the appearance of leather which is subject to wet-rubbing and wet-flexing or to increase the permeability of the leather). The most commonly used binders are water-based resins (purchased as powder or dissolved in sodium hydroxide and other chemicals).

Lacquers may consist of nitrocellulose dissolved in organic solvents or polyurethane in water-based systems. Colouring agents are organic and inorganic pigments, dissolved in the particular coating systems (water or solvent-based).

The main solvents are water and organic hydrocarbons; these are used as carriers to create suspensions or dispersions of binders.

CONVENTIONAL SOLVENT-BASED COATINGS CONTAIN 80 – 90 % VOC

Conventional solvent-based systems contain between 80 – 90 % VOC while reduced organic solvent systems (e.g. water dilatable lacquer emulsions) contain ~40 % VOC.

WATER BASED COATINGS CONTAIN 0 - 15 % VOC

Water based systems can contain 0 - 15 % organic solvents (e.g. ethyl acetate) but most commonly used water-based lacquers contain 5 – 8 % VOC.

Organic solvents are also used to adjust viscosity (e.g. methoxypropanol, isopropanol) and for equipment cleaning (using similar solvents as those used for dispersion and viscosity adjustment).

WATER BASED COATINGS OFTEN CONTAIN CROSS-LINKING AGENTS WITH 20 – 50 % VOC CONTENT

Organic solvents can be found in surface-active substances and cross-linking agents (both organic substances). Cross-linking agents usually contain 20 -50 % VOC.

Examples of cross-linking agents are [BREF STS 2003, p. 43f, 87, 94]:

- Poly-isocyanides, carbodiimides for polyurethane base- and top-coats
- Poly-aziridines for base-coats and top-coats
- Epoxies for top-coats
- Formaldehyde for casein and protein finishes

- Ethylene-imine-based[6] cross-linking agents for top-finishes
- Metal oxides for butadiene finishes for splits[7].

Table 4 shows some of the organic solvents used for leather coating.

Table 4: Examples of organic solvents used for leather coating

Hydro-carbons	**Ketones**	**Alcohols**	**Esters**	**Glycol Ethers**
Xylene	Acetone	Methanol	Isopropyl acetate	2-Ethoxy-ethanol
Toluene	Methyl ethyl ketone	Ethanol	n-Butyl acetate	2-Butoxy-ethanol
	Methyl iso-butyl ketone	n-Propanol	Ethyl acetate	2-Ethoxyethyl acetate
	Cyclo-hexanone	Isopropanol	n-Propyl acetate	2-Butoxyethyl acetate
	Di-iso butyl ketone	n-Butanol	n-Amyl acetate	1-Methoxy-2-Propanol
		Di-acetone alcohol		1-Methoxy-2-Propyl acetate

[BREF STS 2003, p. 36]

5.2 Solvent consumption and emission levels

The quantity of coating material applied can range from 0.2 g/m² up to 400 g/m². [BREF TAN 2003, page "iii"]

In Austria, as the result of an increasing application of water-based technologies, VOC-free top coats and use of roller coating, every tannery can achieve emission levels $\leq$ 35 mg VOC per square meter of produced leather. [BREF TAN 2003, pages 38/39]

VOC CONSUMPTION DEPENDS ON THE TYPE OF PRODUCT PRODUCED

The VOC consumption and any associated emissions depend on the type of product produced and the extent to which it is possible to substitute water-based coating systems for solvent-based systems. For additional VOC reduction, some producers have installed waste gas treatment systems (biofilters).

Table 5 shows illustrative data on solvent consumption and emission levels of three production lines using predominantly water-based systems. Two of the producers do not fall under the SE Directive because they have a solvent consumption of less than 10 tonnes per year.

Small amounts of solvent-based coatings are still used. The figures of the third producer show a high total VOC emission per m^2 of product, for those products where solvent-based systems were applied.

[6] Ethylene-imine is toxic and carcinogenic

[7] Splits are pieces of leather obtained by splitting the hides and skins horizontally

Table 5: Examples of VOC consumption and emission levels of leather coating

Type of products	Annual production of coated leather	Annual VOC consumption	VOC emission per m² product
Car leather, furnishing	> 2,000,000 m²/a	> 10 t	7.5 g/m²
Furnishing	> 500,000 m²/a	< 1 t	0.9 g/m² (related to total production)
	Thereof coated with solvent-based system: ~ 100,000 m²/a		4.5 g/m² (on products coated with solvent-based systems)
Car leather, shoe leather, furnishing	> 2,500,000 m²/a	< 1 t	~0.25 g/m²
	Thereof coated with solvent-based system: ~ 3000 m²/a		222 g/m²

[Ökopol 2008]

5.3 Key environmental and health issues

In leather coating activities a broad range of different solvents is used, mainly when applying coating systems containing organic substances and when cleaning equipment.

Process emissions of solvents, together with NOx emissions, are precursors of ground level ozone formation in the presence of sunlight. Existing occupational workplace limits should be taken into consideration.

Emissions of VOC to air may occur from:

- the storage of the solvents
- the process
- cleaning operations

Spills and leaks from storage areas may result in emissions to soil and groundwater.

In leather coating toluene may be used as solvent of coatings. It is classified with the risk phrase R40, providing limited evidence of carcinogenic effect. In cases where the mass flow is $\geq$ 100 g/h, the SE Directive sets specific emission limit values (see section 1).

6 VOC substitution

The following sections describe potential substitutes for VOC (using VOC-free and VOC-reduced systems). There are also descriptions of the application technologies or special conditions needed and the advantages and disadvantages compared to systems that use solvents with a high VOC content.

In general, substitution of VOC emissions from leather coating activities can be achieved by:

- Substitution of solvent-based coatings by VOC-free water-based coating systems
- Use of VOC-free cleaners

6.1 VOC-free systems

This section describes the ways that VOC-free products or systems can be used to replace the organic solvents currently used.

6.1.1 Substitution of solvent-based coatings by VOC-free water-based coating systems

For tanneries, the 2003 BREF document defined the following as best available techniques (BAT) for leather finishing when organic solvents are used [BREF TAN 2003, p. 168]:

- Substitution with water-based finishing systems.
  Exception: if very high standards of topcoat resistance to wet-rubbing, wet-flexing and permeability for perspiration are required.
- Substitution with low-organic solvent-based finishing systems.
- Use of systems with low content of aromatic organic solvents.

VOC-free water-based coatings are available for a wide range of products and customer requirements. They can be applied to most leather products.

It should be noted, however, that some water-based substitutes for solvent-based systems may not be able to achieve fully equivalent properties of topcoat resistance to wet-rubbing, wet-flexing and permeability for perspiration, UV resistance, and colour conservation e.g. for upholstery for automotive and furniture.

SUBSTITUTION MAY NOT BE POSSIBLE IF HIGH RESISTANCE IS NEEDED

Similarly, special effect lacquers for fashion articles are often only produced as solvent-based systems (e.g. for shoes, bags, clothing etc - mainly produced in southern Europe).

Organic solvents reduce the surface tension of water thus giving the finish improved flow properties. In contrast, VOC-free coatings have poor flow properties; consequently droplets may form on the leather.

Coating systems have been developed to improve these characteristics (polyurethane dispersions and acrylic emulsions as well as hybrid acrylic polyurethane polymers).

There are water-based products on the market that do not contain cross-linking agents but are self-linking and consequently do not cause VOC emissions.

6.1.2 Use of VOC-free cleaning agents

Dry ice (CO_2) can be used for routine machine cleaning. If water-based systems are used VOC-free cleaning agents can be applied.

6.2 VOC-reduced systems

If the complete substitution of organic solvents is impractical then changing to systems with a reduced VOC content, such as those described in this section, can decrease emissions.

6.2.2 Substitution of solvent-based systems and reduction of VOC content of coating systems

For some lacquers, it may be possible to substitute conventional products (80 – 90 % solvent content) with VOC-reduced systems that contain ~40 % organic solvents (water dilatable). Water-based coating systems are able to meet most product requirements.

The solvent in water based systems is partly added to control the viscosity of the coating (0 - 15 % organic solvents is added for this purpose) and is partly present as a result of being used in the cross-linking agents that are added to the water-based coatings. Different types of cross-linking agent are available and the VOC content ranges from 20 to 50 % VOC reductions can be achieved by using products with lower VOC content.

Cross-media effects

When using low-organic solvent systems and water-based systems, the toxicity of the cross-linking agents used in the coating polymers needed to achieve acceptable leather characteristics can present workplace safety problems. Safety data sheets and national regulations need to be taken into consideration.

CROSS-LINKING AGENTS OF WATER-BASED COATINGS MAY BE HARMFUL TO HUMAN HEALTH.

A further cross-media effect is the higher energy consumption for drying water-based top-coats. [BREF TAN 2003, page 95]

7 Other VOC emission prevention measures and abatement techniques

Preventative measures, process improvements and abatement techniques can be used to reduce VOC emissions if VOC substitution as described in section 6 is not possible. The following measures can be applied for leather coating:

- Improved solvent handling when preparing coatings
- Reduction of VOC emissions from cleaning of coating equipment (improved solvent handling)
- Increased coating efficiency (by reducing overspray)
- Installation of abatement systems

7.1 Process improvement

To minimize costs and to save resources, coating layers should be as thin as possible while still meeting product requirements; improving the efficiency of the coating application also reduces VOC emissions.

The following coating techniques can be selected to reduce overspray (exception: conventional spray coating has to be used if very thin coatings e.g. on aniline and aniline-type leather have to be applied) [BREF TAN 2003, p. 170]:

- Roller coating
- Curtain coating
- HVLP spraying
- Airless spraying

SEVERAL PROCESSES CAN HELP IMPROVING COATING EFFICIENCY, WHICH LEADS TO LESS VOC EMISSIONS

7.2 Waste gas abatement

Achieving the VOC total emission values required by the SE Directive may be difficult if solvent-based systems cannot be avoided.

In these cases untreated organic solvent emissions from the finishing process may vary between 800 and 3,500 mg/m³. Approximately 50 % of VOC emissions arise from spray-finishing machines, and the remaining 50 percent from dryers. [World Bank 2007]

In such cases, waste gas abatement is likely to be required. Depending on the VOC concentration in waste gases, thermal oxidisation, adsorption and treatment with biofilters may be used. [World Bank 2007]

In the case of biofilters, VOC reduction efficiencies of 50 – 65 % have been reported from the leather industry. [Ökopol 2008]

8 Summary of VOC emission reduction measures

The following table summarizes the various approaches to reduce VOC emissions that are described in chapters 6 and 7:

Table 6: Measures for VOC substitution and VOC reduction in leather coating

Objectives	**Description**	
VOC-free Systems	Substitution of solvent-based coating systems	Use of VOC-free water-based coating systems with VOC-free cross-linking agents or with self-linking substances
	Substitution of solvent-based cleaners	Use of water-based cleaners
VOC-reduced Systems	Reduction of the VOC content in coating systems	Use of solvent-based systems with reduced VOC content
		Use of water-based systems with low content of organic solvents
Process Improvements	Use of more efficient application techniques	Roller coating Curtain coating HVLP spraying Airless spraying
	Reduction of VOC emissions from cleaning	Improved handling (in particular when storing, barrel pumping, mixing)
Abatement Technologies	VOC destruction	Thermal oxidation Biofilters
	VOC adsorption for later destruction or recovery	Activated carbon

9 Practical examples

9.1 Swedish case

A Swedish producer of leather for upholstery and automotive applications has abandoned its traditional solvent-based systems in favour of exclusively water-based coatings. Since these have a VOC component the water effluent from the overspray water curtain is treated with a mechanical biological treatment system.

The VOC content of the water-based coating systems is continuously assessed to identify further opportunities to reduce the VOC content.

Prior to these VOC reduction initiatives, the VOC emission was about 180 g/m^2 of finished product, after their introduction emissions reduced to 6 – 10 g/m^2.

[ELMO 2008]

9.2 Italian case

An Italian company specializing in the production of cattle-hide leather for upholstery and automobile products has introduced a finishing plant with a substantially improved spraying system and has achieved a significant reduction in its VOC emissions.

The coating machine consists of a spray booth, fed by conveyor belt, and equipped with three innovative oscillating spray bars - these are transverse to the feed direction. Each spray bar has 100 airbrush spray guns in line, equipped with micro pressure nozzles. Each oscillating bar has double circuits for the coatings, special conduits for compressed air, and electric valves to control the nozzles.

The bars can easily be dismantled into 5 pieces that can be cleaned, automatically, in an hermetically sealed tank.

[SICA 2008]

Figure 3: Conveyor belt spraying booth and oscillating bars with spray gun nozzles

The plant is equipped with an optical detector bar at the input side of the booth that transmits command signals to the three spray bars. Depending on the feed rate, a process controller calculates the time necessary for the hide to reach the three bars. This allows openings at the input side of only 2 cm which reduces VOC emissions to the workplace.

The system uses an atomization pressure 30 times less than that of traditional guns and 10 times less than HVLP spray guns.

The use of reduced pressure and 'fixed' guns reduces overspray - the spray efficiency reaches 94 - 96 % compared to 15 - 35 % in conventional rotary spray gun booths. Overall the use of coating material and related VOC emissions is reduced by up to 35 %.

Additional benefits are a higher particle scrubbing efficiency compared with common particle scrubbers that operate at a high air flowrate and seldom exceed 90 % efficiency. The booth can operate without a water curtain on the side walls, saving water and pump energy as well as reducing waste. The system is significantly less noisy too; this is due to the lower airflow for particle scrubbing, reduced air pressure for atomization and the elimination of the spray pistol carousel.

The system achieves a uniform spraying quality that otherwise would be difficult to obtain. The low pressure and almost vertical spray direction allows the use of natural dyes. The technique allows the conveyor speed to be increased by 40 %.

[SICA 2008]

10 Emerging techniques

Electrostatic spraying

In the Reference document on best available techniques for the tanning of hides and skins [BREF TAN 2003], electrostatic spraying is referred to as an emerging technique for leather coating.

Electrostatic spraying technique is applicable, but only if both the coating material and the coated object can be electrically charged. As leather is not a conductor of electricity, this can only be achieved if the leather is sprayed while in contact with a piece of metal of the same shape; since hides are of different shapes and sizes this is a difficult condition to meet cost effectively.

[FILK 2008]

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Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Guidance 14:

Footwear manufacture

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses footwear manufacturing and the related cleaning of equipment, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emission Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
The activity "footwear manufacture" is defined as “any activity producing complete footwear or parts thereof”. The SE Directive covers installations in which this activity is taking place with an annual organic solvent consumption greater than 5 tonnes.

Not addressed in this guidance is the coating of the leather away from the footwear manufacturing site. For ‘coating of leather’ activities see guidance 13.
The SE Directive lays down the following activity specific emission limit values for footwear manufacturing. It only contains a total emission limit value and no separate ELVs for waste gases and fugitive emissions.

Table 2: Emission limit values of the SE Directive

<table>
<tr><th colspan="5">SE Directive - Emission limit values (ELVs)
(Annex II A – activity No. 14)</th></tr>
<tr><th>Activity</th><th>Solvent consumption threshold [tonnes/year]</th><th>ELVs in waste gases [mg C/Nm³]</th><th>Fugitive emission values [% of solvent input]</th><th>Total ELVs [g per pair]</th></tr>
<tr><td>Footwear manufacture</td><td>> 5</td><td>--</td><td>--</td><td>25</td></tr>
<tr><td colspan="5">Special provisions:
Total emission limit values are expressed in grams of solvent emitted per pair of complete footwear produced.</td></tr>
</table>

THE SE DIRECTIVE APPLIES TO FOOTWEAR MANUFACTURE IF A SOLVENT CONSUMPTION OF 5 TONNES PER YEAR IS EXCEEDED

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[1]as well as for halogenated VOCs which are assigned the risk phrases R40 or R68[2]. There is a general obligation to replace CMR substances– as far as

[1] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

[2] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: ‘Possible risk of irreversible effects’. The new wording is: ‘Limited evidence of a carcinogenic effect’. In the ‘old’ version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: ‘Possible risk of irreversible effects’. This new risk phrase does not include carcinogenicity. The ‘new’ version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to this change, a final decision on which version applies can only be given by the European Court

possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated[3] VOC with R40/R68 the ELVs in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.
National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

The use of solvent-based adhesives is the most important source of solvent related VOC emissions during footwear manufacture.

VOC EMISSION REDUCTION CAN BE ACHIEVED BY SUBSTITUTING VOC BASED ADHESIVES BY VOC-FREE PRODUCTS, BY PROCESS IMPROVENTS AND BY APPLYING WASTE GAS CLEANING.

The substitution of solvent-based adhesives by hot melts or water-based adhesives offers the greatest potential for reducing emissions. The applicability of these solvent-free systems depends on the type of footwear, on the used materials and the performance expected of the adhesive.

Process changes can avoid the need for adhesives altogether. Injection moulding may be used instead of gluing sole parts. However, this technique is applicable to a limited market segment only - shoes with a planar sole form and uniform colour (mainly applicable for fashionable, high production volume footwear).

Improving the handling of solvent and adhesives, upgrading equipment and changes to adhesive application techniques can result in further VOC emission reductions.

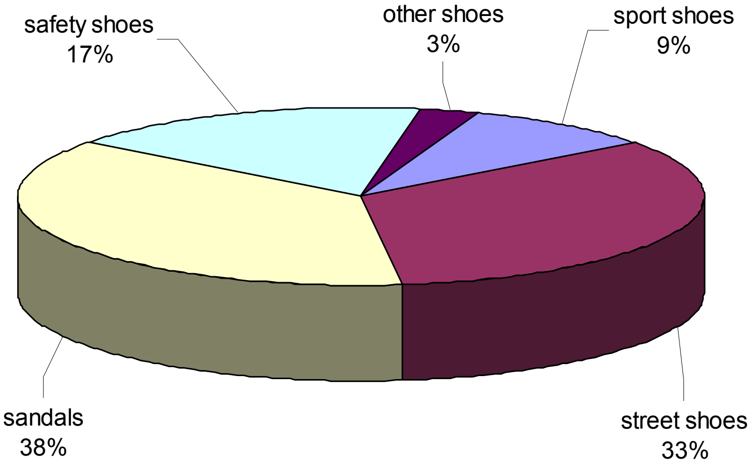
Substitution of solvent-based adhesives is more difficult for the manufacture of heavy duty footwear such as heavy work/safety boots or walking/alpine boots. Installations producing these types of footwear are less likely to be able to meet the SE Directive emission limit values without the use of waste gas cleaning systems such as thermal oxidisation, bio-filtration or adsorption.

3 Description of the activity and related industry sectors

The footwear-manufacturing sector consists of small and middle-sized enterprises. The market is characterised by strong segmentation and small scale production, with the exception of a few large producers, mainly of sports shoes (3 large producers).

Most production is small scale (handcraft) [DFIU 2002]. If the solvent consumption threshold of the SE Directive is exceeded, meeting the emission limit values can have a significant business impact [Scherer 2005].

[3] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.



[HDS-1 2008]
Figure 1: Market breakdown for shoe production (Germany 2007)

Approximately 53 installations were registered and authorised under the SE Directive in the period from 1999 – 2003 in EU-15 as carrying out footwear manufacture [Implementation 2006].[4]
Total production in EU 27 in 2006 was around 637 millions of pairs of shoes [CEC 2008].

4 Technical process description

A typical street shoe consists of 50-150 parts: soles, heel seats, toe puffs and heel stiffeners etc. These are manufactured separately by component suppliers and they consist of different materials, e.g. textiles, plastics and leather. These materials differ in their technological features (such as bonding properties). [DFIU 2002]

The manufacturing process varies according to the type of shoe manufactured (e.g. children shoes, trekking boots, men and women fashion street shoes or sport shoes).

In the **upper department** (see figure 2), the components of the shoe upper and the linings are attached together. The quality requirements for the connection of the individual parts differ, due to the varying shape of the parts and their function. The individual parts of the shoe upper may have to be flexible or static, the appearance of the part may be important, or it may need to possess high tensile strength. Adhesives have to be applied to seams (overlap areas) – these may vary in size, therefore influencing the magnitude of adhesive use.

Therefore, varying techniques and adhesive systems are used in this department. Generally, the parts are joined via bonding and then stitched together. Only about 10 % of adhesives used in the upper department are solvent-based. The remaining adhesives are either dispersions (70 %) or hot-melt (10%). [DFIU 2002]

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[4] Additionally, Portugal has given general data with percentages for each activity, resulting in 370 installations carrying out footwear manufacturing. Italy did not report data.

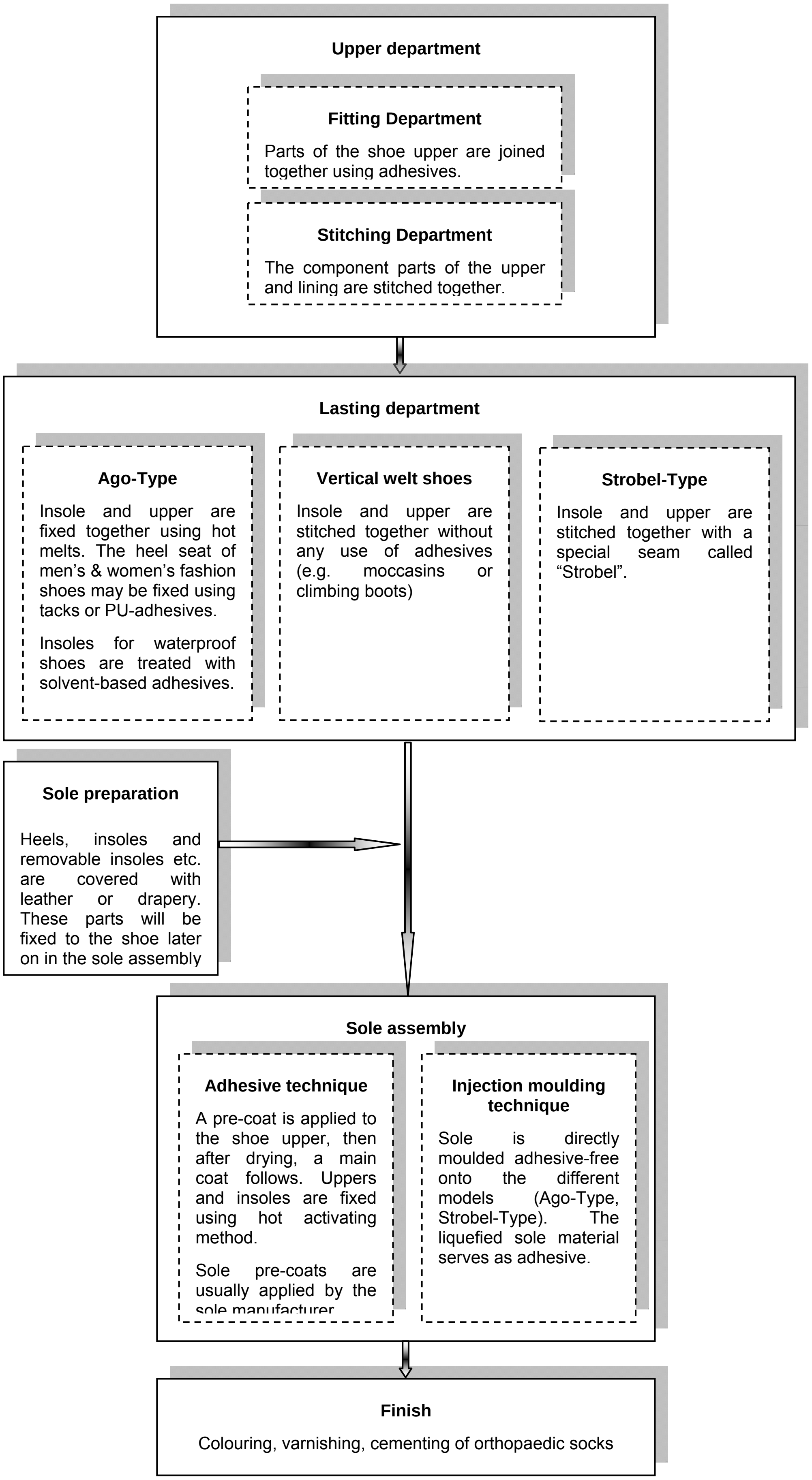


Figure 2: Process steps of footwear production [DFIU 2002]

In the **lasting department**, insole and shoe upper are joined together. Shoes of the Ago-Type (the most common type) are bonded using hot melt adhesives, whereas Vertical-Welt shoes and Strobel-Type shoes are stitched (see Figure 2) with no adhesive being required. Dispersions are also used in the lasting department, the quantities of hot melt and dispersion adhesives being about equal.

Small quantities of solvent-based adhesives are used in case of waterproofed Ago-Type shoes in order to seal the gap between the insole and the sole.

Heels, orthopaedic socks, insole and removable insole etc are covered with leather or drapery in the **sole preparation department**. These parts are prepared to be fixed later in the sole assembly department (see figure 2). The bonding is occasionally done using dispersions or hot melts, however, for bonding of curved parts (which are typical), solvent-based adhesives have to be used.

As well as adhesives, a ‘halogenizer’ has to be used (solvent-based surface treatment to roughen the material) to pre-treat soles in order to ensure a strong adhesion of the adhesive layer to the sole.

In the sole **assembly department**, the sole is connected to the insole and the shoe upper (see figure 2). This can be affected using either the adhesive technique or the injection moulding technique.

The adhesive technique involves pre-treating the shoe upper with a 2-component adhesive pre-coat. This pre-coat soaks into the leather and serves to harden the fibres. After evaporation of the solvents, the main-coat layer is applied. The sole is usually already pre-treated by the sole-manufacturer and -supplier. The bonding of shoe upper and sole takes place via the hot activating method: when the previously coated materials are warmed, the adhesives bond together.

Solvent-based adhesives provide better grease-resistance and higher tensile strength compared to dispersions, and are therefore the only adhesives used in sole assembly. Typically, polyurethane and neoprene adhesives are used.

Injection moulding involves the direct moulding of the sole onto the shoe upper and the insole. This technique is adhesive-free; the liquefied sole-material serves as a bonding material as it cools and hardens. Some solvent may be required for cleaning of the sole moulding, however.

In the **finishing department**, colouring, brilliant varnishing and cementing of orthopaedic socks into the shoe are done (see figure 2). In general, dispersions are used (water-based colours and varnishes, latex adhesives). For sandals the sole is joined with solvent containing adhesives. Colouring and varnishing material can also contain solvents.
[DFIU 2002]

4.1 Process flow and relevant associated VOC emissions

The following flow charts show that the production processes of different kind of shoes differ significantly and this is reflected in the solvent consumption and in the VOC output. This is due to the different safety and aesthetic requirements of the shoes and the different materials used.

For **fashion shoes** (see figure 3) many different materials are combined within the shoe, and the materials used may not lend themselves to gluing and bonding (being combinations of wood, synthetics, plastic, cork, etc.). This is especially the case for women's fashion shoes. Furthermore, the shape of the sole may be very curved, compared to street shoes, which demands special bonding properties (e.g. high initial bonding ability). This technical problem is most easily solved by the use of solvent containing adhesives.

Thus, the process of sole assembly (joining the “fashion materials”) generates the highest solvent emissions of the process (> 40 %). The finishing of the shoes - colouring, brilliant varnishing, etc - also generates high emissions (~ 20 % of the total, see figure 3).

Substitution of solvent-based adhesives may still be possible but solutions need to be individually tailored to specific problems and it is not possible to apply generic solutions.

Heavy boots (e.g. for fire brigades) and alpine boots have to be of very high quality, durability and safety (see figure 4).

Therefore, the bonding properties of the materials have to be excellent and the materials are first halogenized to increase their bonding capability. This process generates about 11 % of the VOC emissions, which is high compared to fashion shoes, where this step is typically about 1 % of the total.

Water-based adhesives are difficult to use because halogenizers evolve hydrochloric acid which will react with the adhesives’ water content and will reduce the bonding properties. For this reason, solvent-based adhesives are used.

Heavy boots are made waterproof by sealing the materials with solvent containing adhesives. Therefore, preparing and pre-coating the uppers also generates an exceptional high emission (about 30 %).

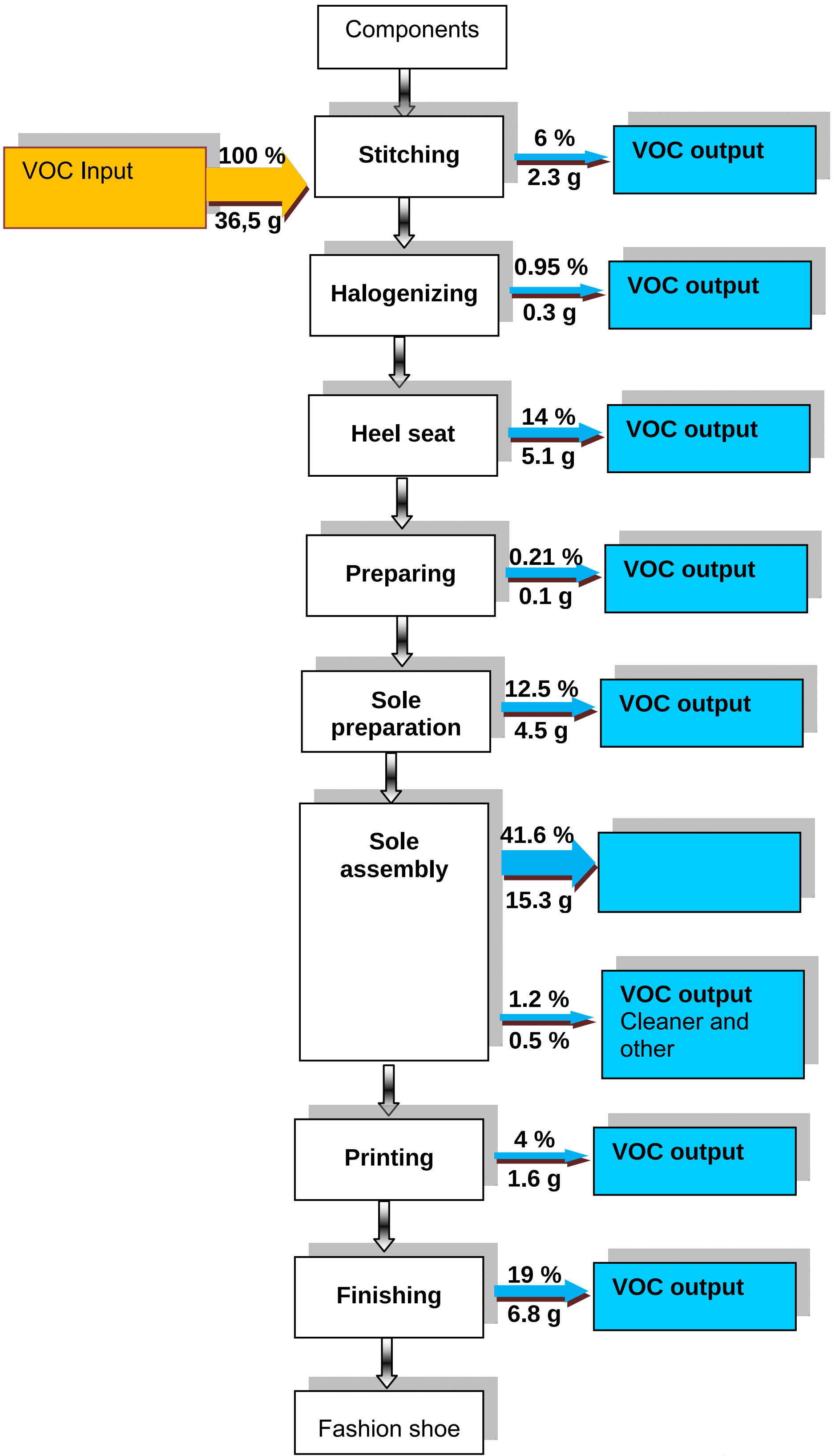
The soles of **children shoes** (figure 5) are injection moulded (see figure 2) and so the emissions are low. There is, nevertheless, a small emission from this process step (0.4 % compared to about 41 % of fashion shoes and 24 % of heavy boots) generated when cleaning the mould.

Since injection moulding is only possible for flat soles this technique is only applicable for a small range of shoes produced in high volume (e.g. for “sneakers" but not for most of women's fashion shoes).

Otherwise, the finishing of children shoes generates almost 54 % of the VOC emissions of this process. This is due to finishing with fashion colours. [Scherer 2005]

This flow chart shows typical VOC consumption for fashion shoe production.

OVERVIEW ON THE PROCESS STEPS OF FOOTWEAR MANUFACTURE (FASHION SHOES)

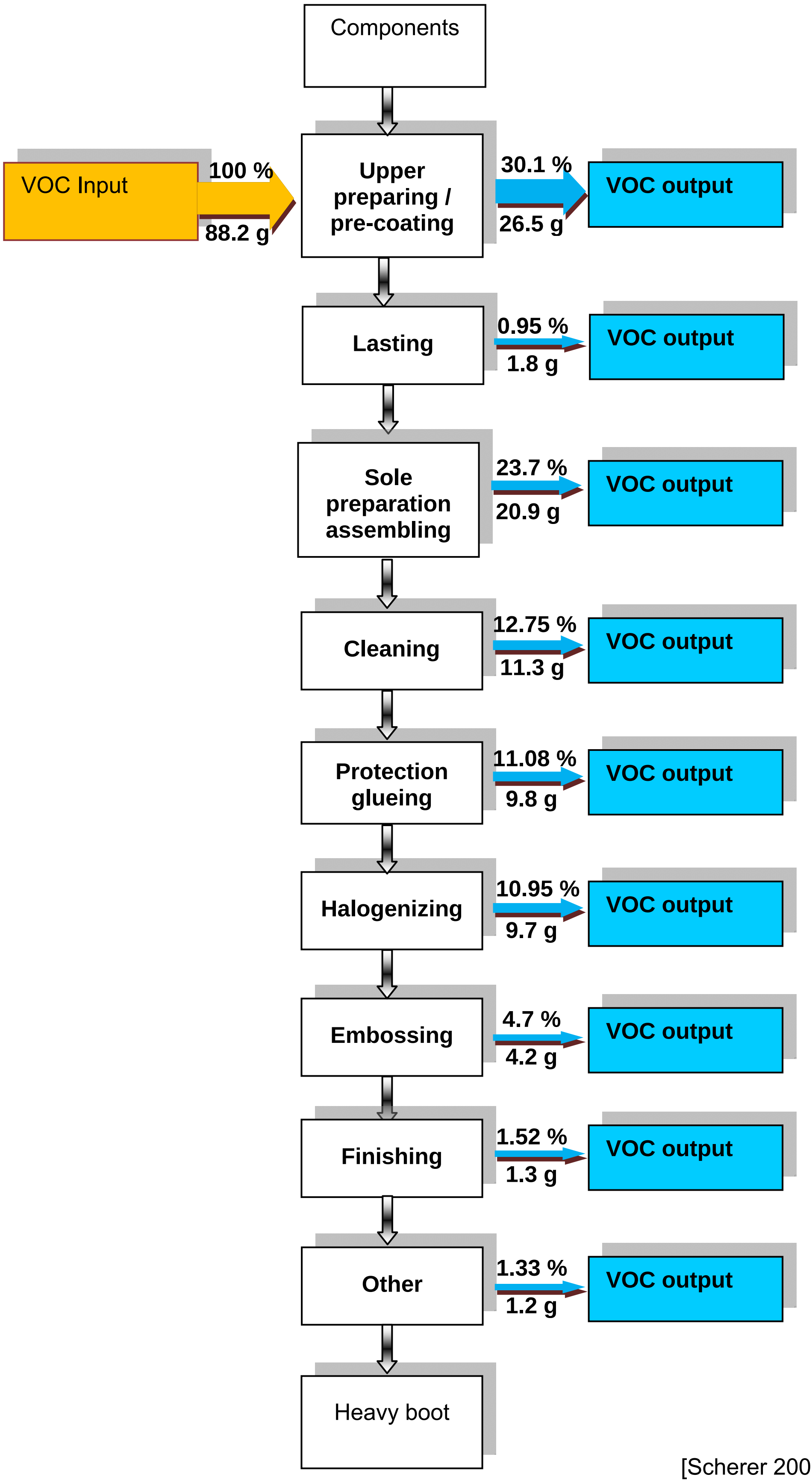


[Scherer 2005]

Figure 3: Typical solvent consumption in footwear manufacture of fashion shoes

This chart shows typical solvent consumption for heavy boot production.

OVERVIEW ON THE PROCESS STEPS OF FOOTWEAR MANUFACTURE (HEAVY BOOTS)

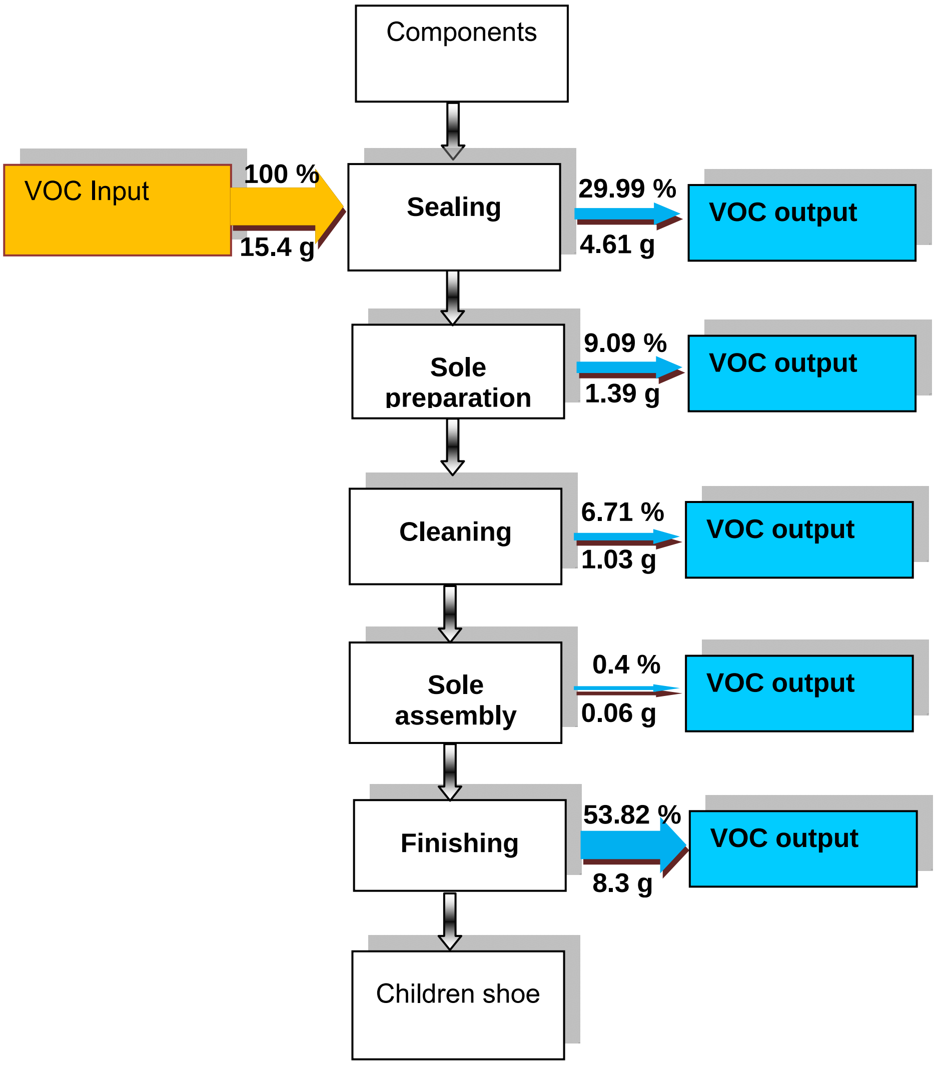


[Scherer 2005]

Figure 4: Typical solvent consumption in footwear manufacture of heavy boots

This chart shows typical solvent consumption for children’s shoe production.

OVERVIEW ON THE PROCESS STEPS OF FOOTWEAR MANUFACTURE (CHILDREN SHOES)



[Scherer 2005]

Figure 5: Typical solvent consumption in footwear manufacture of children shoes

5 Solvent use, emissions and environmental impact

5.1 Solvents used

A market evaluation at European adhesive producers shows the following adhesive types offered for footwear manufacture in general and for sole bonding in specific:

Table 3: Evaluation of adhesives offered for shoe production/for sole bonding

	Number	**Share**	**Number for sole bonding**	**Share**
Solvent-based adhesives	151	55,1 %	74	79,6 %
Water-based adhesives	61	22,3 %	15	16 %
Hot melts	61	22,3 %	4	4,3 %
Tapes	1	0,3 %	0	0 %
Examined amount	274	100 %	93	100 %

[Scherer 2005]

The high proportion of solvent-based adhesives used is due to the fact that these adhesives offer a high bonding strength immediately from application – this is important since often the materials being bonded are under tension. Once hardened, adhesive bonds have to resist high levels of mechanical stress and must not be sensitive to water. Often, only solvent-based adhesives meet these requirements. Table 4 shows adhesives frequently used in the footwear industry. [DFIU 2002]

Table 4: Adhesives used in the footwear manufacturing industry

Solvent-based adhesives	**Water-based adhesives (latex adhesives)**	**Hot melt**
Polyurethane, neoprene	Polyurethane, natural and synthetic rubber	Polyester, polyamide, ethylene vinyl acetate (EVA)

[DFIU 2002]

The solvent content of **solvent-based adhesives** varies in the range of 70 to 80 %. Solvents used in polyurethane systems include acetone, butanone, MEK, and ethyl acetate. Solvents used for neoprene adhesives can include hexane, cyclohexane, heptane, ketones, and ethyl acetate. [EGTEI 2003] [Wakol 2008]

The high solvent content in these adhesives provides the useful function of ensuring good penetration of the adhesive into the leather fibres.

Water-based adhesives are mainly based on polyurethane, natural or synthetic rubber with water as dispersing agent. These adhesives are also known as 'latex adhesives' or 'dispersions'. Most water-based adhesives are VOC-free, with the exception of a few products containing up to 2 % VOC. [DFIU 2002]

Hot melts are solvent-free systems, based on polyester, polyamide and vinyl acetate. The choice of this adhesive type depends on the process and the temperature sensitiveness of the materials being bonded.

Halogenizers may be used to ensure that materials (for example, some rubbers and textiles) exhibit good bonding characteristics. Halogenizers consist of up to ~ 100 % VOC.

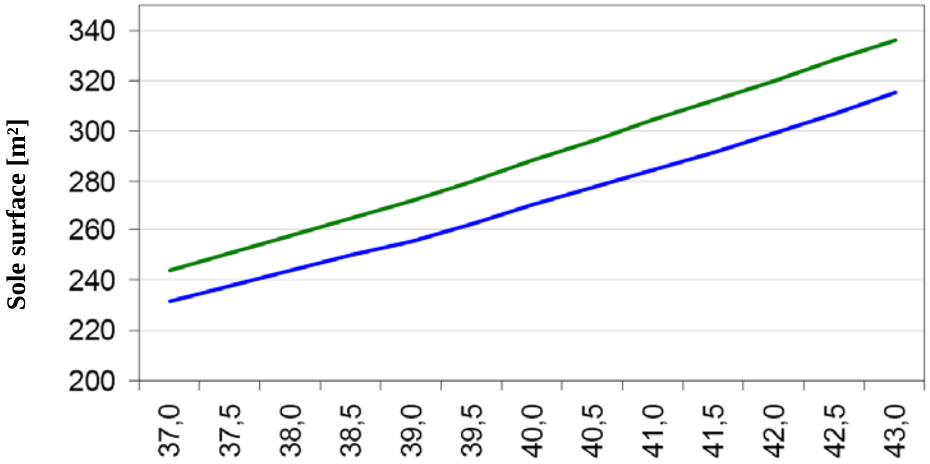
Finishing materials (colouring and varnishing material) may contain solvents.

5.2 Solvent consumption and emission levels

Adhesives, finishing products and cleaners contribute to the VOC emissions. VOC emissions may also arise from primers, separating agents, printing inks or finishing pastes. [Scherer 2005]

For mid-size shoe production, between 20 and 60 g solvent-based adhesives is applied per shoe. Solvent-based polyurethane adhesives contain about 70 – 80 % solvent. Hence about 14 – 48 g solvent is used per pair. This results in a solvent consumption of about 14 – 48 t/a in larger installations (~ 1 Mio pairs of shoes per year). [DFIU 2002], [EGTEI 2003] For shoe production using injection moulding, about 10 g solvent per pair is used. [EGTEI 2003]

The size of a shoe significantly affects the quantity of adhesive required. Figure 6 shows, that a medium sized men's shoe (size 43) has nearly 50 % more surface than a medium sized women's shoe (size 37), hence will need about 50 % more adhesive. Therefore, a manufacturer producing exclusively men's shoes will have a higher average solvent consumption per pair compared with a footwear manufacturer producing the same volume of unisex fashion shoes. [EWEN 2007]



[EWEN 2007]

Figure 6: Surface where adhesive is applied in relation to shoe size of two different types of soles

The type of sole lasting also affects the adhesive consumption because either adhesive is required for coating of the entire surface or is only applied on the frame of the sole. [EWEN 2007]

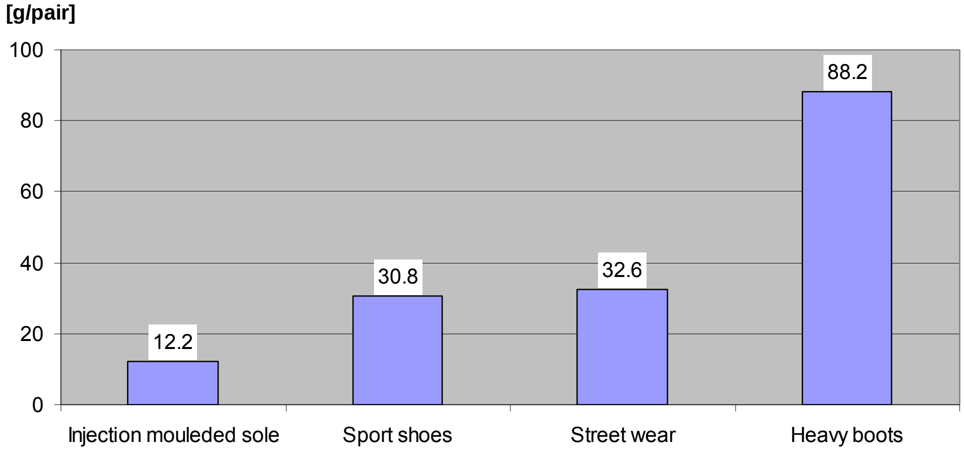
[EWEN 2007]

Figure 7: Different types of soles: [A] Sole of rubber and phylone (alpine climbing boot), [B] rubber walking sole (safety shoe), [C] rubber frame sole with steel inlay (safety boot), [D] rubber sole (street walking shoe)

Figure 7 shows different types of soles. These different sole shapes and properties require different assembly techniques and thus lead to differences in solvent consumption.

The flow charts in chapter 4 (figures 3 – 5) show, that e.g. preparation and assembly for soles for a safety shoe/heavy boot (B in figure 7) will require a solvent consumption of about 23.7 % of the total solvent used for this type of footwear (this is equal to 20.9 g of solvent per pair). On the other hand, sole assembly for children’s shoes with an injection moulded sole will use around 0.4 % of the total solvent required for that type of shoe, equal to a mass of 0.06 g per pair.

The total VOC consumption for footwear is around 25 g/pair on average, but this varies depending on the type of footwear being produced. Fashion shoes and sport shoes have a solvent consumption of 32 g/pair. For heavy boot manufacturing, solvent consumption values of 46 – 160 g/pair are typical, depending upon the nature of the boot. The smallest solvent consumption occurs for the manufacturing of footwear with injection-moulded soles - about 12 g/pair. [Scherer 2005]



[Scherer 2005]

Figure 8: VOC consumption of different types of shoes

The variation in solvent consumption depends upon the volume of adhesive used, but also upon the use of halogenizers (98 % solvent content) or other treatments like pre-coating or main-coating, which is necessary for heavy-duty alpine boots, but not for street shoes or sports shoes. [EWEN 2007]

5.3 Key environmental and health issues

For leather coating a broad range of different solvents is used for a wide range of different processes e.g. halogenizers for pre-treatment and adhesives for gluing overlap areas, joining insole, shoe upper and sole.

Process emissions of solvents, together with NOx emissions, are precursors of ground level ozone formation in the presence of sunlight. Existing occupational workplace limits should be taken into consideration.

Emissions of VOC to air may occur from:

- - the storage of the solvents
- - the process
- - cleaning operations

Spills and leaks from storage areas may result in emissions to soil and groundwater.

6 VOC Substitution

The following sections describe potential substitutes for VOC (using VOC-free and VOC-reduced systems). There are also descriptions of the application technologies or special conditions needed and the advantages and disadvantages compared to systems that use solvents with a high VOC content. Table 5 gives a general overview.

Table 5: Overview on possibilities of VOC substitution in all production steps

Process step	**VOC Solvent emissions substitution**
Preparing and cutting	Printing with solvent-free printing systems
Lasting	Use of hot melt adhesives
Upper precoating	Water-based precoating
Sole precoating	Using water-based coatings
Sole main coating	Using water-based coatings
Finishing	Using water-based or paste with low volatile solvents

[Scherer 2005]

6.1 VOC-free systems

This section describes the ways that VOC-free products or systems can be employed to replace the organic solvents currently used.

6.1.1 Substitution of halogenizers containing solvents

For materials that require pre-treatment with halogenizers, solvent-free 2-component systems have been developed to substitute commonly used halogenizers with up to ~ 100 % VOC.

Solvent-free halogenizers suffer from the disadvantage that they have to be used within one working day. Furthermore, solvent-free halogenizers are very reactive and, during use, the chlorine content evaporates rapidly, which makes it necessary to work next to extraction hoods. Solvent-free halogenizers achieve good results under laboratory conditions, however practical application requires testing and optimisation for each individual process. [Wakol 2008]

6.1.2 General substitution of solvent-based adhesives

Alternatives to solvent-based adhesives are available for some but not all process steps or for all kinds of shoes. Solvent-based systems are still necessary for the bonding of heavily greased leather parts or for footwear that has to fulfil special requirements, such as for alpine boots or specialist footwear such as boots for fire fighters.

If synthetic materials with poor bonding characteristics are used for bottom filling of soles, it is not yet possible to substitute solvent-based adhesives. [Scherer 2005]

The collar and upper cushions can be fixed with self-adhesive coatings. Other bonding (e.g. overlap areas, sandals) may still need the application of solvent-based adhesives.

Most solvent-based adhesives are used for bonding of soles and shoe uppers. As an alternative, soles and insoles can be fixed with VOC-free water-based adhesives or hot melt adhesives.

Instead of solvent-based adhesives, water-based adhesives or hot melts can generally be applied to internal, concealed parts of the shoe (e.g. heel seats, insoles or orthopaedic socks). This is not possible however for strongly curved surfaces in which case solvent-based polyurethane adhesives need to be used.

For lightly greased leather, solvent-free water-based precoats are available.

6.1.3 Applicability of hot melt adhesives

The general applicability of hot melt adhesives depends on the process and the temperature sensitiveness of the materials being bonded.

In the ‘lasting department’ polyester and polyamide based hot melts can be used, although for sealing waterproof shoes solvent-based polyurethane adhesives have to be used.

For the bonding of reinforcing materials such as toecaps, solvent-free alternatives are available in the form of hot melt coated reinforcing materials.

For splicing of soles, reactive hot melts can be used, in particular for planar soles, e.g. gym shoes, for the bonding of shoe upper and sole. For this sole type, hot melts can be applied economically using rollers.

Water-based adhesives can also be used for fixing of orthopaedic socks.
[DFIU 2002] [Scherer 2005]

6.1.4 Applicability of water-based adhesives

Water-based adhesives are more difficult to handle than solvent-based systems. Thicker coats need to be applied and this results in longer drying times being required. This is true even where forced drying in ovens or tunnels is employed. [DFIU 2002]

During bonding of soles and other curved material, an immediate bonding ability is necessary to stand the tensile strength of the materials. Water-based adhesives have a lower initial strength (slower hardening) and a poorer surface penetration than solvent-based adhesives and this makes them less suitable for such process steps. [DFIU 2002]

While water-based adhesives have a lower initial strength, after drying their final strength is generally higher than that achieved with solvent-based adhesives.

The disadvantages of water-based adhesive can be overcome to some extent by ensuring very precise application of the adhesive. In spite of their disadvantages, water-based adhesive with binders of polyurethane or neoprene have been successfully used as the main adhesives by some large-scale manufacturers of sports shoes. [DFIU 2002]

6.2 VOC-reduced systems

If the complete substitution of organic solvents is impractical then changing to systems with a reduced VOC content, such as those described in this section, can decrease emissions.

Instead of solvent-based adhesives (~ 70 % VOC), high solid adhesives (~ 40 % VOC) may be used. The suitability of high solids adhesives, however, does need to be established through testing for each individual process. It depends on the materials used, the kind of shoe manufactured and the type of manufacturing process used. [EWEN 2007]

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements and abatement techniques can be used to reduce VOC emissions if VOC substitution as described in section 6 is not possible. The following measures are commonly applied for footwear manufacturing process:

7.1 Process improvements

7.1.1 Sole assembly

In sole assembly, a pre-coat and a main coat layer of polyurethane adhesive usually has to be applied. However, in certain cases (for certain shoe types) options exist for dispensing with the need for adhesives, either by stitching or injection moulding.

Stitching: Sole and insole can be sewn up manually. This application is limited to certain types of shoes (e.g. for moccasins). It may not be possible for the final lasting of the insole but can often at least substitute the first step of bonding. The parts may be co-located correctly by stitching, thereby reducing the amount of solvents needed for the final lasting quality.
Injection moulding: With the injection moulding technique, the sole can be directly moulded onto the shoe without adhesives. The hot and liquefied sole material bonds with the rest of the shoe as it dries. Solvents are only used for cleaning (compare section 5.2 and figure 8).

Because of the high operating costs, injection moulding is best suited for larger scale production in cases where there is limited variation in sole shapes and colours. The system is mainly used for the manufacturing of sports and children’s shoes. [DFIU 2002]

Where injection moulding is used, finishing is the main source of VOC emissions (see chapter 4.1 and figure 5). However, emissions can be further reduced by the use of low-solvent finishing products. [Scherer 2005]

7.1.2 Alternatives for halogenizer pre-treatment

As mentioned in chapter 6.1.3, some materials need to be treated in order to improve their bonding ability. Various alternatives to conventional halogenizing can be used. No general recommendations can be given, as the best option for different materials can only be determined through experiment. Apart from substituting the solvent in halogenizers, there are only few other techniques, which can be applied successfully:

Plasma technology pre-treatment: An interelectrode high voltage discharge takes place. The discharge is channelled to the leather surface where plasma (ionised air) is created. Radicals are produced, which react with the material surface, thereby increasing the bonding ability. Ozone and nitrogen oxides are produced during the treatment, and have to be treated. [EWEN 2007]

UV-treatment: The material is irradiated with UV-light, which causes molecular disruption in the surface layer of the material. This changes the quality of the surface and increases its bonding ability. During tests by a sports shoe manufacturer using rubber materials, about 65 – 70 % of the solvents used during the halogenizing process-step could be eliminated using this technique. The remainder was required to clean the soles from separating agent which is used in the moulding of soles. [EWEN 2007]

7.1.3 General process improvements

Apart from the use of adhesives, VOC emissions may also arise from primers, separating agents, printing inks or finishing pastes.
Improved material handling and good housekeeping measures can further lower emissions. The table below shows example measures.

Table 6: Overview of possibilities of VOC reduction in all production steps

Process step	**Solvent emissions prevention or reduction measures through process improvements**
Overall measures	Minimise evaporation by closing containers of solvents (e.g. cleaners) wherever possible.
Upper production	Choosing materials that can be used with water-based or hot melts adhesives
Sole preparation	Choice of sole material taking account of the need for washing/cleaning or halogenation

[Scherer 2005]

7.2 Abatement techniques

As a result of the low concentration of VOC in typical exhaust gases, thermal oxidisation is expensive (due to significant consumption of support fuel) and often not very efficient. For large-scale production of footwear, biofiltration will be less expensive than thermal oxidation, so it is potentially applicable. [DFIU 2002]

However, the efficiency of biofiltration depends upon the biodegradability of the VOCs being treated. Table 7 indicates the level of biodegradability of various solvents used in the sector.

Table 7: Biodegradability of solvents used in footwear manufacture

High biodegradability	**Medium biodegradability**	**Low biodegradability**
Toluene Xylene Methanol Butanol Formaldehyde	Acetone Styrene Benzene Phenol Hexane Methylethylketone	Dioxane Trichlorethene Tetrachlorethene

[Scherer 2005]

Adsorption can be considered as a method for pre-concentration of emissions before further treatment, e.g. oxidation systems (thermal, catalytic, plasma or UV oxidisation).

The investment costs and annual (operating) costs vary from one abatement system to another.

Table 8 shows exemplary costs of different abatement systems evaluated by an alpine boot production site for treatment of 35000 m^3/h (wet, at 20°C, 1013 mbar) with mean VOC concentrations of 250 mgC/m^3, guaranteeing emission values below 50 mgC/m^3.

Table 8: Cost appraisal for alpine boot producer (orientation price offers)

Company	**Technique**	**Invest [€]**	**Annual operating costs [€ / a]**	**Costs per pair/shoe [Ct / pair]**
Supplier 1	Biofilter *	153,000	41,652	12
Supplier 2	Scrubber / biofilter	265,000	51,037	15
Supplier 3	Low-temperature plasma	280,000	63,882	19
Supplier 4	Biotrickling	325,000	64,993	19
Supplier 5	Adsorption / catalytic oxidation	350,000	66,891	20
Supplier 6	UV-Treatment with catalyst	324,000	79,058	23
Supplier 7	Adsorption / Thermal oxidation	600,000	104,834	31
Supplier 8	Regenerative thermal oxidation	333,500	108,890	32
Supplier 9	Regenerative thermal oxidation	450,000	137,275	40
* Evaluated as not being able to guarantee emission values < 50 mg/m^3.				

[EWEN 2007]

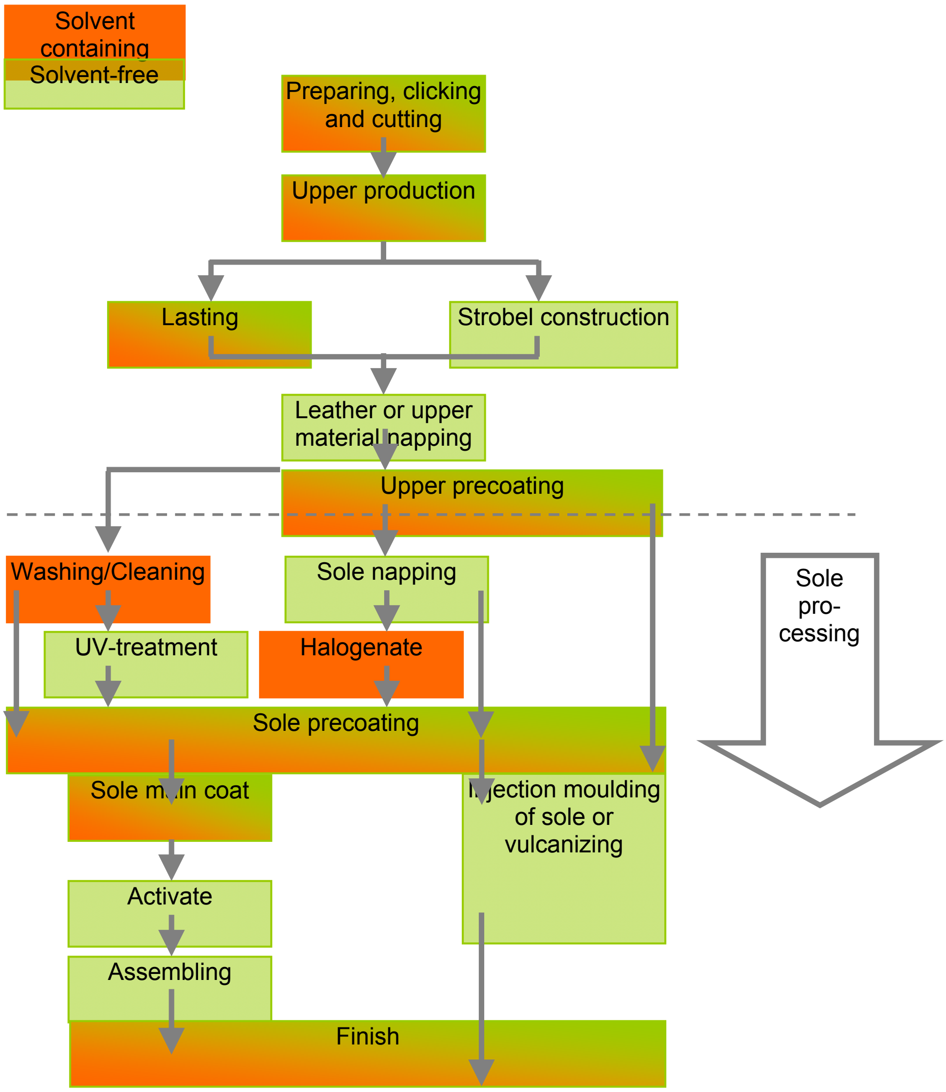
8 Summary of VOC emission reduction measures

The following table summarizes the various approaches to substitute or reduce VOC emissions as described in chapters 6 and 7:

Table 9: Measures for VOC substitution and VOC reduction in footwear manufacturing

Objectives	Description	
VOC-free Systems	Water-based adhesives	Bonding of sole and shoe upper Precoating of lightly greased leather
	Hot melt adhesives	Bonding of sole and shoe upper Bonding of internal components Lasting Bonding of reinforcing materials Splicing of soles
	Solvent-free printing	
	Water-based coating and finishing	Sole precoating Sole main coating Finishing
	Halogenizing	Use of solvent-free halogenizers
VOC-reduced Systems	Use of low solvent finishing pastes	Finishing
Process Improvements	Improved material handling and good housekeeping	Closure of containers of volatile materials wherever possible
	Halogenizing	Plasma-treatment UV-treatment
	Adhesive-free sole assembly	Stitching Injection moulding
Abatement Technologies	Adsorption	Generally as a pre-concentration stage before further treatment
	VOC destruction	Biofiltration Thermal oxidation Catalytic oxidation Plasma oxidation UV-oxidation

Figure 9 shows the potential for reducing the solvent use during footwear manufacture, according to a study on VOC reduction potential. Those process stages highlighted in red tend to require solvent-based materials whilst the process stages coloured green can either be converted to VOC-free techniques or are VOC-free by nature. The remaining process stages, highlighted in a mixture of red and green, are areas where a combination of solvent and non-solvent processing can be undertaken. [Scherer 2005]



[Scherer 2005]

Figure 9: Indication of potential VOC emissions (red) from each process steps

9 Good practice examples

9.1 Ladies shoes manufacturer in Romania

A company in Romania produces ladies footwear. Between 1998 and 2007 the company achieved a significant VOC reduction as well as substitution of substances classified as carcinogenic, mutagenic and reproduction toxic (CMR) by less noxious substances such as ethyl acetate and 4-methyl-m-phenylen 2-isocyanate.

VOC emissions from solvent-based coatings and adhesives were reduced by introducing the use of high-solid products (50 – 75 % VOC) and water-based or reactive products (based on natural and epoxide resins).

Further VOC emission reduction of 65 % was achieved by installing a waste gas scrubber. VOC emissions are reduced from 38 to 13 mgC/m^3.

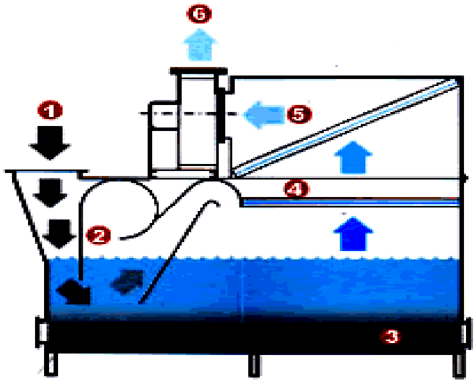


Figure 10: Scheme of the waste gas treatment

The waste gas is introduced (1) into the system that contains water for adsorption and particle separation (3). In a patented "maze" (2) high turbulence is created to increase adsorption. Before the clean air outlet (6), the gases pass a drop filter (4) and an additional particle filter (5).

[Romania 2008]

9.2 Sports and utility footwear manufacturing in Bulgaria

A company in Bulgaria produces approximately 2,200,000 pairs of quality sports and utility footwear per year at four production sites.

In 2001 about two times as much adhesive, solvent, and cleaning products was used per shoe produced compared to similar manufacturers in the EU. Approximately 60 tons of VOCs per year were being released from three of four production sites.

An assessment was conducted in 2001 regarding production and product quality issues, VOC emissions, and the handling of hazardous materials. Alternatives to reduce VOC emissions were developed and implemented. Several hundred employees were trained on how to improve procedures regarding the handling of hazardous materials.

At the end of the project, VOC emissions were reduced by 14 % with additional reductions anticipated. At one of the sites, implementation of the proposed program reduces the use of solvents by 50 % and the consumption of cleaning agents by 20 %. In 2007 the company expected to use the same quantity of adhesives and solvents per pair of shoes as EU manufacturers.

Due to the reduced consumption of adhesives and solvents, the company generates savings in raw material purchases.

[Valeo 2002]

10 Emerging techniques and substitutes under development

An emerging technique is the use of VOC-free adhesive tapes during sole bonding. These can be used for temporary bonding of small parts.

Further new developments include one-component cross-linking thermo-active water-based adhesives. These VOC-free adhesives have improved handling characteristics compared with other water-based adhesives and may therefore lead to increased substitution of solvent-based systems. [Scherer 2005]

10.1 Alpine boots

Alpine boots have to meet the highest requirements for safety and toughness. To meet those requirements, significantly more adhesives have to be used for the bonding of the sole. At the current time, there are no suitable alternatives.

Rubber bandages and uppers do not have such tough safety requirements but are responsible for approximately 17 % of solvent consumption from manufacture of alpine boots [EWEN 2007]. Therefore water-based dispersions have been tested for this process. Standard tests under laboratory conditions did not reveal significant differences in performance from the use of solvent-based or water-based adhesives. Initial testing at larger scale confirmed the laboratory findings.

Further reductions may be possible through the optimization of the halogenizing process or the replacement of halogenizing by other surface treatment methods [EWEN 2007]

10.2 Application techniques

At the moment, application techniques are undergoing testing, which could further reduce VOC emissions. These include dosing stations for adhesives, to avoid overdosing and the unnecessary emissions that result. Furthermore, low pressure spray application of solvent containing paints (finishing) is being tested.

The development of reduced-solvent cleaning agents is expected.

[EWEN 2007]

11 Information sources

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Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Guidance 15:

Wood and plastic lamination

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses wood lamination, plastic lamination, combined wood and plastic lamination and the related cleaning of equipment, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emissions Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
The activity 'wood and plastic lamination' is defined as 'any activity to adhere together wood and/or plastic to produce laminated products.' The SE Directive covers installations in which this activity is taking place with an annual organic solvent consumption greater than 5 t.

Wood and plastic lamination takes place either in specialised companies or as a production step in sawmills or other wood processing industries, e.g. parquet production.

This activity does not cover:

- ⇨ Any activity to adhere together aluminium and plastics to produce laminated products;
- ⇨ Any lamination associated with printing activities that adhere together two or more flexible material (covered in activity No. 3)
- ⇨ Adhesive coating covered in activity No. 16 (i.e. use of adhesives for other purposes than producing wood and/or plastic laminates).

The SE Directive lays down the following activity specific emission limit values for wood and plastic lamination:

Table 2: Emission limit values of the SE Directive

SE Directive - Emission limit values (ELVs) (Annex II A – activity No. 15)				
Activity	**Solvent consumption threshold [tonnes/year]**	**ELVs in waste gases [mg C/Nm³]**	**Fugitive emission values [% of solvent input]**	**Total ELVs [g/m²]**
Wood and plastic lamination	>5			30

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[1] as well as for halogenated VOCs which are assigned the risk phrases R40 or R68[2] .There is a general obligation to replace CMR substances– as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated[3] VOC with R40/R68 the ELVs in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

Water based or solvent-free adhesives are state of the art for lamination processes. However, some exceptions exist due to chemical and thermal stability of the bond.

If solvent based adhesives have to be used the thermal treatment of waste air and the minimisation of fugitive emissions can lead to emission levels, almost comparable with those achieved when using water based adhesives.

3 Description of the activity and related industry sectors

The activity is performed in different branches of industry. Main branches are:

a) flexible packaging

b) wood processing (production of laminates for parquet flooring, furniture etc.)

The restriction to wood and/or plastic lamination and the exception that lamination processes together with printing processes are not covered reduces the industrial activities covered by this activity of the Directive. Neither the lamination of aluminium or paper foils with plastic nor the production of fibre reinforced plastics (FRP - using reactive solvents like styrene [UP resin group 2006]) are covered by this activity.

The production of parquet flooring or laminates for furniture is not using

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[1] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

[2] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: ‘Possible risk of irreversible effects’. The new wording is: ‘Limited evidence of a carcinogenic effect’. In the ‘old’ version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: ‘Possible risk of irreversible effects’. This new risk phrase does not include carcinogenicity. The ‘new’ version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to this change, a final decision on which version applies can only be given by the European Court

[3] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.

solvent based adhesives. Most common are hot melt – adhesives, resins and high pressure applications. [Marutzky 2007] [EPLF 2008] [Pfleiderer 2008].

Therefore only the lamination of plastics is described in this guidance document.

Approximately 380 installations were registered and authorised under the Directive in the period from 1999 – 2003 as carrying carried out wood and plastic lamination in EU 15 [Implementation 2006].

4 Technical process description

4.1 Process flow and relevant associated VOC emissions

The flow chart of Figure 1 shows the process steps of plastic lamination applying solvent-based adhesives and provides an overview on possible VOC emissions.

OVERVIEW ON THE PROCESS STEPS OF PLASTIC LAMINATION WITH SOLVENT-BASED ADHESIVES

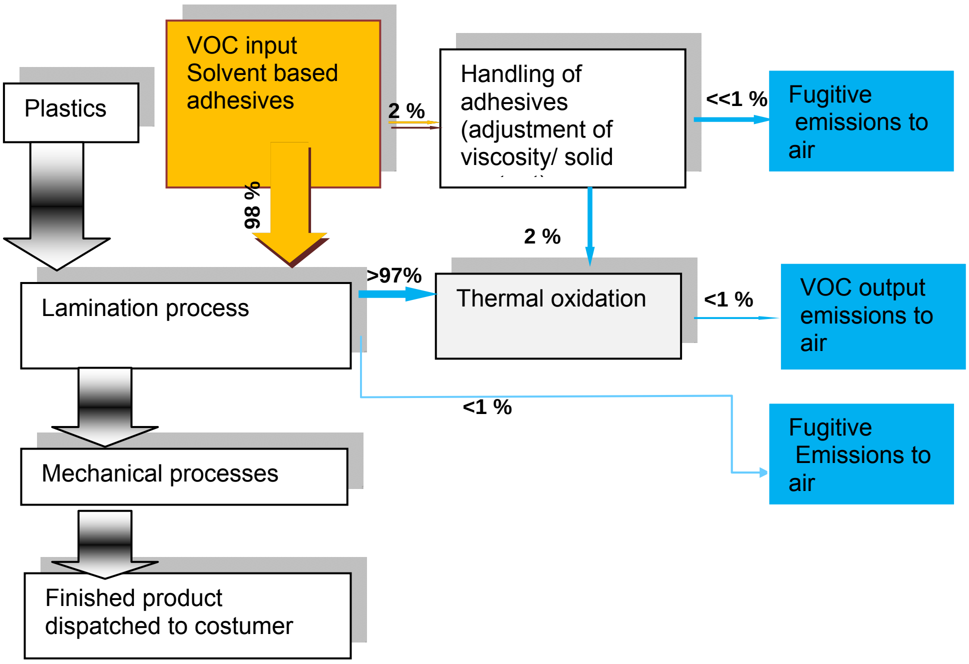

Figure 1: Possible VOC emission sources in plastic - lamination processes using solvent-based adhesives

Emissions to air during the lamination process itself (including fugitive emissions) and the subsequent thermal oxidation (depending on the efficiency) are the most relevant emissions sources related to lamination using solvent based adhesives. Preparation of the adhesive - adding solvent to adjust the viscosity – is considered a minor but still relevant source.

4.2 Application systems

Solvent based adhesives for plastic lamination are usually polyurethane – systems dissolved in ethyl acetate. The solvent content of the adhesive delivered by the producer is within the range of 30 - 50% and it is increased to 60 – 70% by adding solvent [Mondi 2008].

The application of the adhesive takes place on one of the two surfaces which are pressed together continuously at speeds of 120 – 180 m/min. The drying process is done in the same equipment, using warm air at about 60 – 70 °C. Dryers are controlled to keep the solvent content of the airflow at about 20 - 25% of the Lower Explosion Limit (LEL) in order to minimise the energy consumption of the process.

If – as in most cases – only ethyl acetate is used, the above mentioned figures equal to 15 – 19 g/m³ of solvent.

5 Solvent use, emissions and environmental impact

5.1 Solvents used

The most important solvent for lamination of plastics is ethyl acetate (> 90%). Methyl-ethyl ketone or acetone are other possible components [Henkel 2006] [Novacote].

5.2 Solvent consumption and emission levels

Depending on the plastics used and the needed properties the solvent consumption varies from 4 – 8 g/m². Assuming an average lamination speed of 160 m/min and a broadness of 1 m of the foils, the consumption of VOC is then 40 to 80 kg/h.

The air flow from the drying unit depends on the size of the lamination equipment. For the example described above a range of 4.000 – 6.000 Nm³/h is normally used.

The total volume of waste air, including exhausting of the operating area, depends on the size and number of lamination equipments.

5.3 Key environmental and health issues

VOC emissions to air typically arise from process areas. VOC emissions to air together with NO_x emissions are precursors of ground level ozone formation in the presence of sunlight.

Spills and leaks from storage areas may lead to emissions to air as well and have the potential to contaminate also soil and/or groundwater.

Ethyl acetate is irritating to eyes and repeated exposure may cause skin dryness or cracking (R36, R66) in addition vapours may cause drowsiness and dizziness (R67). [BIA GESTIS 2008].

The substance is low hazardous to water organisms [BIA GESTIS 2008].

6 VOC Substitution

The following sections describe potential substitutes for VOC (using VOC-free and VOC-reduced systems). There are also descriptions of the application technologies or special conditions needed. Furthermore the advantages and disadvantages are compared to systems that use solvents with a high VOC content.

6.1 VOC-free systems

This section describes the ways that VOC-free products or systems can be used to replace the organic solvents currently used.

6.1.1 Use of VOC-free products

The first solvent free adhesives introduced were polyurethane based products, but the first generation of these products needed application temperatures of 90 – 100°C [Flexo] and had problems with bubbles (caused by CO_2 produced by the reaction) and sometimes cloudy appearance of the film. The second generation overcame these problems but high amounts of residual free isocyanates (and diffusion of these) and low initial bond strength created new problems. The third generation with a very low (but still questionable for some applications esp. food packaging) free isocyanate content needed application temperatures of 50°C to 70°C and required up to 24 hours before further processing.

A relatively new technology for laminating plastics is the use of solvent free epoxy-based adhesives. If these systems are used, the laminated foils have to be stored for a couple of days at higher temperatures (35 – 45 °C)

Technical limitations are on the one hand the difficulty to achieve thermal stability (e.g. for the sterilisation of the final product) and on the other hand the lower chemical resistance as described for water based systems.

6.2 VOC-reduced systems

VOC-reduced systems are not common in plants using solvent based products because these plants are either equipped with thermal oxidation units since their start-up or they fulfil the requirements of the legislation and there is little incentive for a change.

6.2.1 Water based systems

Water based adhesives are polyurethane based (dispersions). These adhesives can be used for laminating a huge variety of plastics. [Mondi 2008] For less stringent applications acrylic emulsions might be applicable, too [Flexo].

The limitations of water based systems are related to the final usage of the flexible packaging. Main obstacles are:

a) sterilisation: the adhesives can not handle high temperatures for a long time

b) chemical resistance: diffusion of certain chemicals (acids, alkaline, certain flavours) can cause serious damages to water based adhesives

c) adhesion properties (acrylic emulsions)

Water based adhesives are usually cheaper than solvent based ones and contain less than 2% VOC [Mondi 2008].

The energy consumption is higher due to the thermo-dynamical properties of water compared to solvents (enthalpy of evaporation for water is more than twice that of solvents).

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements and abatement techniques can be used to reduce VOC emissions when VOC substitution, as described in section 6, is not possible. The following measures are commonly applied for other coating process:

7.1 Abatement technologies / End of pipe measures

Thermal oxidation is commonly applied as VOC abatement technique for plastic lamination processes.

Three types of thermal oxidisers are in use: regenerative, recuperative and catalytic oxidation. All destroy VOCs by burning (oxidation) the waste gas stream, but they differ in how waste heat is recovered and in their level of efficiency.

Regenerative thermal oxidation has at least two (often three) heat exchangers; these consist of beds filled with material that allow air to pass while absorbing and storing heat. While one bed is heated by the exhaust gas from the burner another bed gives up its stored heat to the VOC laden incoming gas. In recuperative thermal oxidation the heat is transferred directly - via a heat exchanger - from the outgoing air stream to the incoming air stream.

Regenerative oxidation tends to be more efficient than recuperative thermal oxidation as it uses the recovered energy more efficiently to pre-heat incoming process air to oxidation temperatures (~ 800 °C); consequently its operating costs are significantly lower than for recuperative oxidation systems. Regenerative thermal oxidation systems (RTO) are particularly effective for process streams with relatively low solvent loadings but their operating costs are highly dependent on the efficiency of the heat exchanger.

THE AUTO-THERMIC POINT OF REGENERATIVE THERMAL OXIDATION IS ABOVE 2-3 G VOC/NM³

Regenerative thermal oxidation systems are widely used because they are relatively insensitive to the composition of the solvents in the process air and the concentration.

Recuperative systems are mainly used for small flow rates - at higher rates the systems are not cost effective. They are often used in combination with catalytic oxidation systems.

Catalytic systems are single-bed units. The catalyst is based on ceramic tiles. Waste air is blown or sucked through the pre-heated bed and the temperature is maintained by the oxidation process of VOC above the auto-thermal operation limit (approximately 2 g/m³). These systems operate at much lower temperatures (350 – 500 °C) therefore the emission of NO_x is significant lower. Dust and catalyst poisons (e.g. sulphur-compounds) must be avoided but these are usually no problem in the lamination process.

Natural gas is needed to heat up thermal oxidisers to an operating temperature of 800 - 850 °C (400 °C for catalytic oxidation), and the process is only autothermic when the VOC concentration of the waste gas is above 2-3 g VOC/Nm³. The resulting heat can be recovered and can be used for different purposes e.g. thermal oil to be used in the drying unit of the lamination equipment.

Regenerative and catalytic systems are widely used for solvent-based lamination processes because the load of VOC is high and relatively constant (mainly controlled by the drying unit of the lamination equipment).

Operational costs are highly dependent on the average concentration of VOC in the waste gas and the operation time of the plant as well as on the type and cost of fuel needed for the operation. Therefore, typical costs are difficult to be determined.

Usually the waste air stream is a mix from the drying unit of the lamination equipment and the room ventilation containing VOC concentration well above auto-thermal operation limits. The recapture of heat energy by thermal oil heat transfer systems for the drying unit is often used [Mondi 2008].

7.2 Process improvements

Typical measures to reduce fugitive and process emissions of the lamination process are:

a) enclosure of the lamination equipment and thermal oxidation of the exhausted air from the enclosure

b) Efficient ventilation around the lamination equipment in addition to the ventilation system of the equipment itself. Automatic doors and closed windows reduce fugitive emissions effectively.

c) Enclosed in-line equipment for adding solvent to the adhesive for adjustment of solid content and viscosity before application (prevention of solvent losses to air and either diffuse or other emissions)

d) Preventive maintenance during regular downtime of the plant for the treatment unit to provide an operational availability of more than 99% during the year

e) Good housekeeping for adhesives, solvents and solvent-containing waste. These are mostly simple measures like preventing open cans or drums containing solvent (or solvent containing products or waste like residues and cleaning rags), installation of solvent-storage tanks with vapour return pipes

Implementing these measures result in total emission values less than 5% of the solvent input can be achieved.

8 Summary of VOC emission reduction measures

The following table summarizes the various approaches to substitute or reduce VOC emissions as described in chapters 6 and 7:

Table 3: Measures for VOC substitution and VOC reduction in plastic lamination

Objectives	**Description**	
VOC-free Systems	Epoxy-based adhesives	Tempered storage needed
VOC-reduced Systems	Water based polyurethane adhesives	Less than 2% of solvent
Process Improvements	Encapsulation of lamination and preparation of adhesive Good housekeeping	Applicable for most installations
Abatement Technologies	Recuperative thermal oxidation	Widely applicable but not as effective as regenerative
	Regenerative thermal oxidation	Restricted to larger installations due to capital cost
	Catalytic oxidation	Only applicable for well defined waste air composition

9 Good practice examples

No good practice examples available.

10 Emerging techniques and substitutes under development

A strong and growing demand for innovation in the area of water based and solvent free systems for lamination exists because these systems are cheaper than solvent based adhesives. Therefore adhesive producing industry tries continuously to improve the thermal and chemical resistance of water based and solvent free adhesives. As a result the product range and market share of these VOC-free products increases steadily.

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[BREF STS 2007]
EU Commission: Reference Document on Best Available Techniques on Surface Treatment using organic solvents, August 2007

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[SE Directive 1999]
Council Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations

[UP resin group 2006]
Technical Bulletin of UP Resin Group, CEFIC May 2006

Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Guidance 16:

Adhesive Coating

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses adhesive coating presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emissions Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
The activity "adhesive coating" is defined as 'any activity in which an adhesive is applied to a surface, with the exception of adhesive coating and laminating associated with printing activities'. The SE Directive covers installations in which this activity is taking place with an annual organic solvent consumption greater than 5 t.

Adhesive coating is a process step in many different industry sectors, e.g. automotive, paper, construction, leather or footwear industry. This activity does not cover the following:

- Laminating of wood and plastic (see guidance document 15)
- Adhesive coating and laminating which is associated with printing (see guidance document 3)
- Adhesive application in footwear manufacture (see guidance document 14)

The SE Directive lays down the following activity specific emission limit values for adhesive coating:

The SE Directive applies to adhesive coating if a solvent consumption of 5 tonnes per year is exceeded

Table 2: Emission limit values of the SE Directive

SE Directive - Emission limit values (ELVs) (Annex II A – activity No. 16)			
Activity	**Solvent consumption threshold [tonnes/year]**	**ELVs in waste gases [mg C/Nm³]**	**Fugitive emission values (% of solvent input)**
Adhesive Coating	5—15	50*	25
	> 15	50	20
Special provisions: * If techniques are used which allow reuse of recovered solvent, the emission limit value in waste gases shall be 150 mg C/Nm³			

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[1] as well as for halogenated VOCs which are assigned the risk phrases R40 or

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[1] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

R68[2]. There is a general obligation to replace CMR substances– as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥ 100 g/h for halogenated[3] VOC with R40 the ELVs in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

Substitution and reduction measures have to be evaluated on a case-by-case basis. There is no single solution for reducing emissions due to the diversity of processes and products involved in this activity.

THERE IS A TREND AWAYFROM SOLVENT BASED ADHESIVES TOWARD SOLVENT FREE OR SOLVENT REDUCED

Significant VOC emissions arise from the application and the subsequent drying of solvent-based adhesives. In general, there has been a trend away from solvent-based adhesives to solvent free (e.g. hot melts) or solvent reduced systems. Many applications that formerly used solvent-based adhesives have already been converted to waterborne systems.

For some applications, however, the shift has been partial due to technical limitations or product requirements. One sector where solvent-based systems are still widely used is the manufacture of adhesive tapes; here the substitution of solvent-based systems has only been possible for lower quality products.

Where it is not possible to avoid using solvent-based systems then improved production equipment, air extraction, and end-of-pipe abatement technology are the most effective measures to reduce emissions arising from the coating and drying process and the corresponding handling, storage and mixing of solvents.

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[2] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: ‘Possible risk of irreversible effects’. The new wording is: ‘Limited evidence of a carcinogenic effect’. In the ‘old’ version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: ‘Possible risk of irreversible effects’. This new risk phrase does not include carcinogenicity. The ‘new’ version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to this change, a final decision on which version applies can only be given by the European Court

[3] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.

3 Description of the activity and related industry sectors

In 2004 it was reported that the SE Directive applied to around 300 installations that carry out adhesive coating in EU 15 [Implementation 2006].

ADHESIVE COATINGS ARE USED IN VARIOUS DIFFERENT SECTORS

Adhesive coating takes place in many different industry sectors as part of the production. Products and applications for the do-it-yourself sector are not covered by the SE Directive.

Adhesives are widely used for the packaging of products in different industries as e.g. in the food, pharmaceutical, cosmetic, technical, industry. However, the adhesive systems most widely used in these sectors are solvent free or contain very low proportions of solvent (1 - 2 %). In the food industry for example hot melts are typically used and starch based adhesives are used for the production of corrugated paper.

Adhesive tapes have a wide range of functions and applications, including surface protection, electrical insulation, thermal insulation, HVAC[4]-sealing, medical applications, etc. The adhesive tape industry is a major user of solvent-based adhesives.

In the automobile sector the use of adhesives has become more important as a result of the need to reduce the weight of vehicles and because of the excellent properties of adhesive bonding compared to that of other connecting options (e.g. mechanical fixings). Modern cars contain between 15-18 kg of adhesives used [Klebstoffe], variously, for coating of insulation materials, assembly bonding of car interiors and exteriors, seating manufacture, etc. Solvent-based systems are only used to a limited extent because the automobile industry has stringent sector indoor emissions specific provisions concerning maximum allowed emissions from (e.g. VOC emission or fogging tests[5]). Hot melts are often used as an adhesion technique for this industrial sector. The application is typically performed pointwise and not as a continuous film and is therefore not covered by the SE Directive.

In the wood and furniture industry adhesives are important for solid wood bonding, typical applications include window frames, finger-jointing, construction of staircases, windows, and doors, etc. but also for the manufacture of upholstered furniture. Solvent-based systems are often used for the bonding of foams (e.g. mattress manufacture) but the major adhesion is done with starch based adhesives.

Moreover, adhesive coating processes are used for many other applications e.g. bookbinding, filter production, textile industry.

In the textile industry starch based adhesive with no or low VOC content products are commonly used and therefore emissions from this sector are insignificant.

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[4] HVAC: heating- , ventilation- and air-conditioning systems

[5] There are a lot of sector specific engineer standards in the automobile industry, e.g. for the measuring of emissions in the interior of a car eg. DIN 75201-B, DIN EN 14288-B, ISO 6452-B. The automobile industry has many (sometimes individual) different certifications which ask for these measurements.

4 Technical process description

4.1 Process flow and relevant associated VOC emissions

Considering the broad range of applications and user requirements it is not surprising that the process flow, and the associated VOC emissions, vary significantly depending on the application system and area of use.

The manufacture of adhesive tapes is a particularly important example of the use of solvent-based adhesives. Adhesive tapes can be either single or double-sided.

The following figure illustrates the structure of a typical double-sided adhesive tape:

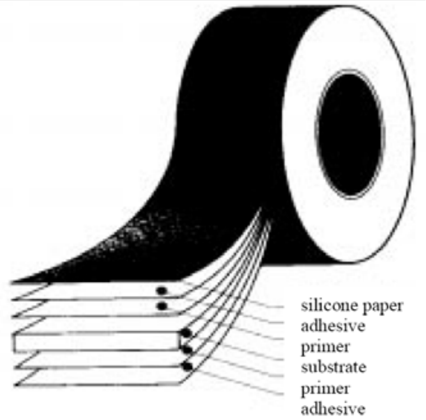

Figure 1: Structure of a double sided adhesive tape [DFIU 2002]

Primers are adhesion promoters which can contain up to 98 % solvents. They are necessary to guarantee a proper connection to substrates such as e.g. glass. The solvent of the primer accounts for less than 1 % of the overall solvent content of the adhesive.

Without the primer the solvent content of the adhesive has to be increased which would result in a higher total solvent consumption. A possible reduction could be in the regulation of the primer film thickness or a shift to less harmful solvents as from heptanes to isopropanols.

Several coating steps might be necessary - depending on the structure of the adhesive tape. The following flow chart provides a simplified overview of the process and illustrates the main steps of coating and the related VOC emissions:

The main VOC emission occur during the drying step the major VOC amount in the air is liquefied with a condenser and after the activated carbon filter only 1% of the solvent input ends up as Emission. Some diffuse emissions exist at the coating and cooling step during the production of the adhesive tape and during its lifetime. The weight of the substrate is only 10 % of the solvent based adhesive with which it is coated

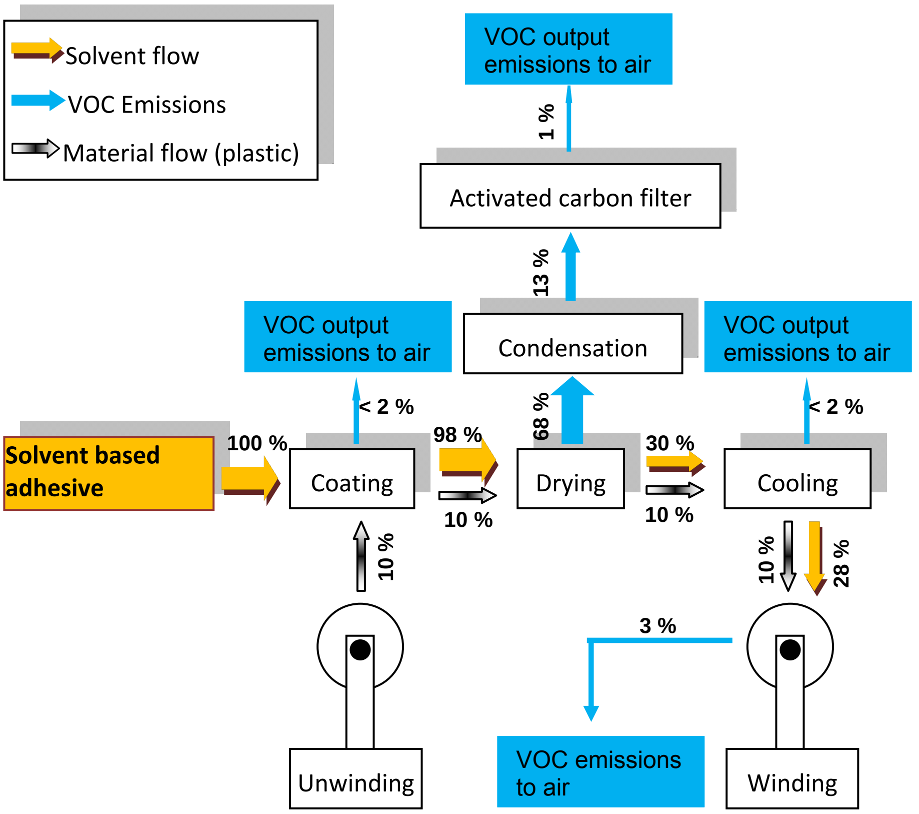

Figure 2: Possible VOC emission sources from adhesive tape coating

DRYING IS THE MAJOR SOURCE OF VOC EMISSIONS IN THE PRODUCTION OF ADHESIVE TAPES

4.2 Process description

As a consequence of the wide range of application, the techniques used also differ - ranging from manual coating through to automated coating in big industrial installations. The process characteristics depend on the type of adhesive and the surface and geometry of the substrate to be coated.

Typical coating methods for solvent-based adhesives include spraying, brushing, and notched scrapers (manual methods) and roller coating and flow guns – which can be automated. Manual methods are time-consuming and rarely used in industrial applications.

Primers are used for the pre-treatment of certain surfaces to improve the bonding properties of the adhesive. Conventional primers contain around 95 - 98 % of solvents e.g. butanol. Prior to 2000 primers based on dichloromethane were also used.

PRIMERS MAY CONTAIN SOLVENTS, BUT DICHLOROMETHANE BASED PRIMERS ARE NO LONGER IN USE

Adhesive sprays are widely used for household applications, but there are also industrial scale spraying techniques, often used in the furniture industry, but rarely in the tape manufacturing process.

Flow guns are typically used for automotive or industrial sealant and adhesive applications. They deliver a high flow rate and give precise control of highly viscous materials.

The tape industry typically uses the roller coat system. The coating material is carried via a coating roller to the surface of the tape. After the coating the adhesive is dried, cooled and wound onto a reel.

Drying time is a critical functional parameter for most adhesives, as is staying power. An adhesive that dries too quickly, before pieces can be fitted properly, is a problem - as is an adhesive that takes too long to dry. Adhesives, typically, are made with solvent blends that allow optimal performance for each application, from home use to high-speed manufacturing.

4.3 Adhesives

A broad variety of adhesives are marketed to meet a range of application requirements. There is no standard classification of adhesives. They may be classified according to their basic raw materials (e.g. polyurethane, epoxy, polyacrylate adhesives), the application (e.g. hot melt, contact adhesives), the use (paper, wood adhesives) or the type of solvents.

Adhesives tend to be classified according to their composition and/or mode of use:

1. solvent-based adhesives;
2. high solid adhesives
3. waterborne adhesives (emulsion); (see section 6.1.1.)
4. hot melt (100% solids) adhesives; (see section 6.1.2.)
5. UV curing adhesives (see section 6.1.3.)

THERE ARE NOT YET SUBSTITUTES FOR SOLVENT BORNE ADHESIVES FOR ALL APPLICATIONS

Organic solvents are used to support the application as well as the drying of the adhesive bonding.

Solvent borne adhesive

The proportion of solvent in a conventional solvent-based adhesive is between 60 and 75 wt%.

Solvent-based adhesives have the advantage that the polymers can flow freely before curing – enabling a very high adhesive strength that cannot yet be matched, in some applications, by substitutes.

Common types of solvent borne adhesives are pressure-sensitive, non pressure-sensitive and contact adhesive applications. The pressure-sensitive applications are mainly used for tapes and labels (PSTL)[6], the non-pressure sensitive ones are typically mastics and sealant. Contact adhesives are used for footwear and construction assembly.

High solid adhesives

High solid adhesives contain up to 60 % solids and, depending on their composition, they can contain up to 40 % organic solvents. High solid adhesives are still considered to be solvent-borne adhesives.

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[6] Pressure sensitive tapes and labels

5 Solvent use, emissions and environmental impact

5.1 Solvents used

Solvent-based adhesives typically contain a mixture of solvents, often aliphatic and/or aromatic hydrocarbons, e.g. toluene (the most commonly used), xylene, hexane, heptane, octane, naphta, methylen chloride, methyl ethyl ketone, n-butyl acetate, mineral spirits and their mixtures.

5.2 Solvent consumption and emission levels

In Europe, around 50 % of the solvent based adhesives are used for adhesive tape production, the other 50 % are shared among the other applications such as automotive, furniture, footwear, lamination, disposables [EGTEI 2005]. For the adhesive tape industry, the water borne, solvent borne and hot melt technologies had the following shares in 2005:

Table 4: overview of different technology in the adhesive tape industry [AFERA 2006]

Adhesive technology	**Share [%]**
Solvent borne technology	45
Hot Melt technology	39
Water borne technology	16

It is estimated that the use of solvent borne technology will decrease by about 3 % a year. Between 1989 and 2001 the share of the tape industry using hot-melt coating grew by ~ 17 % per year. Between 2001 and 2003 the growth rate was only 6% and from 2004 to 2005 even – 6 %. The proportion of water borne technologies, in the same time period, had an annual growth rate of ~ 19 % and was about 0 % in the following years [Exxon Mobil] [AFERA 2006].

VOC emissions from the use of adhesives can vary significantly from country to country. Emissions from the adhesive industry in 2000 have been about 257.6 kt NMVOC representing about 2.4 % of total NMVOC emissions. [EGTEI 2005] In 2003 about 6,100 million m^2 of solvent based adhesive tape were produced. [AFERA 2006] [EGTEI 2005]

5.3 Key environmental and health issues

In adhesive coating a broad range of different solvents are used.

Process emissions of solvents, together with NO_x emissions, are precursors of ground level ozone formation in the presence of sunlight. Existing occupational workplace limits should be taken into consideration.

Emissions of VOC to air may occur from:

- the storage of the solvents

- the coating

- the curing and drying of the coating

Spills and leaks from storage areas may result in emissions to soil and groundwater.

Toluene is the most important solvent used for adhesive coatings. Amongst others it is classified as irritating to skin, harmful with danger of serious damage to health by prolonged exposure through inhalation.

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6 VOC Substitution

The following chapter describes potential substitutes for VOC (using low-VOC and VOC-free systems) and any associated application technologies and/or special conditions needed for their use, it also lists the advantages and disadvantages compared to systems that use solvents with a high VOC content.

6.1 VOC-free systems

This section describes the ways that VOC-free products or systems can be used to replace the organic solvents currently used.

WATERBORNE ADHESIVES HAVE LOWER PERFORMANCE THAN SOLVENT BASED ADHESIVES

6.1.1 Waterborne coating

Waterborne polymers alone are not sufficient to impart optimum adhesion to the adhesive, and tackifier resins are necessary to improve adhesion to different materials. In many cases the same elastomers and tackifiers can be used as those used in solvent based systems.

Water based adhesives raw materials are available in dry and wet form. Adhesive in dry form has about 65 % less volume and 75 % less weight than solvent-based adhesive – consequently transport costs are relatively low. The disadvantage of transporting it in dry form is that it has to be formulated on-site - which requires large water resistant mixing tanks with non-corrosive piping, fittings and stainless steel mixers and pumps. This increases the capital cost of operation. Ready mixed waterborne adhesives have roughly the same volume and weight as the solvent-based adhesive and transport costs are similar.

WATERBORNE ADHESIVES ARE NON-FLAMMABLE AND EASIER TO HANDLE THAN SOLVENT BASED ADHESIVES

Water-borne adhesives are not as widely applicable as solvent based adhesives due to their lower performance; for instance they have a more restricted operational temperature range.

Investment costs for waterborne adhesive applications are estimated to be ~ 8% lower than for conventional solvent-borne systems. The higher costs for solvent based systems result from the need for explosion-proof electrical equipment and emission control systems and waste disposal charges.

The operating costs for both water borne and solvent based systems are about the same - apart from the lower energy costs due the missing abatement technologies for water based systems.

Water-borne adhesives can be completely solvent free but they often contain about 0.5% solvent as a softener to keep the glued joint flexible. They suffer from mould growth and should be stored above freezing point (multiple freeze-thaw cycles should be avoided). [Klebstoffe1]

Compared to solvent-based adhesives, the most important difference is their lower price - approximately 15-20 % that of conventional products. The amounts of solids in both adhesives are about the same.

6.1.2 Hot melt coating

HOT MELTS: OPERATIONAL COSTS ARE LOW BECAUSE NO DRYING OR VOC EMISSION ABATEMENT ARE NECESSARY

Hot melts are solid at room temperature, and must be heated to 100 – 250 °C before being used. In practice, the liquid hot melt is applied to a substrate and the parts to be glued are brought together promptly. Hot melts bond efficiently on cooling and solidifying, the working time ranges from a few seconds to several minutes.

Hot melts are available in sheet foil, granular material, pillows or block form. The adhesive is then processed with a melting appliance and custom made nozzles.

Hot melt adhesives are 100 % solvent free. They cannot be used over the same wide temperature ranges as the solvent based adhesives and do not have the same high quality. Therefore hot melt adhesive are only suitable for the lower quality range of packing and masking tapes and cannot substitute the solvent-based adhesives entirely.

A major advantage of hot melts is that almost any substrate can be bonded. They are around 80 % less expensive per dry kg than solvent based adhesives and the corresponding equipment costs are 50-70 % lower – because there is no need either for driers or abatement technology. Advantageous product properties of hot melt adhesives compared to solvent-based systems include low odour, good solubility and excellent heat stability.

A disadvantage of the technology is the necessity for heating equipment and the associated energy costs, the extra energy needed depends on the size of the production side. For small applications this starts with a capacity need of ~ 2 kW.

Due to the lack of an energy intensive dryer and abatement technology the overall energy consumption of hot melt coating is about 33% less compared to solvent based coating. [BREF STS 2007]

Hot melts are useful in the manufacturing of adhesive tapes for the lower quality range of packaging and masking tapes as well as for double-sided tapes.

6.1.3 UV curing adhesive

Most UV curing adhesives are completely solvent free but for some applications UV curing adhesives can still contain solvents to reduce viscosity. They consist of two compounds: one is the adhesive resin itself and the second is the photo-initiator. Once the photo-initiator is exposed to ultra violet light it undergoes a chemical reaction and produces by-products causing the adhesive to harden. Heating is not required. UV curing adhesives can be used with a wide range of materials as ceramic, composite materials, concrete, fabric, glass, metal, paper, plastic rubber or wool.

UV curing adhesives have a high cohesiveness and high adhesion strength but are difficult to use if materials to be combined are not UV light transparent. UV light can be exposed to the edge of a connection and the reaction can progress through the full volume of adhesive, but this may take hours or days. Other options include delayed curing products that can be activated by UV light to initiate the curing before the pieces to be joined are positioned.

The advantages of UV curing adhesives include: easy use, process consistency and flexibility, reduced environmental impact and the availability of high performance materials. There is a wide variety of UV curing adhesives available enabling a broad range of applications.

UV CURING ADHESIVES ARE SOLVENT FREE AND WORK BEST WITH UV TRANSPARENT MATERIALS

In general UV curing adhesives cannot be used to cure through opaque materials. Some UV curing adhesives (particular epoxy adhesives), however, only need an initial UV beam to start the reaction. Once the curing reaction started, a catalyst - included in the coating - promotes the further curing of the adhesive. Therefore opaque materials can be glued together if only a part is exposed to UV light - even so the curing time can take hours or days. The process is known as 'shadow' curing.

Epoxy adhesives, with additives, can have electric and thermal conductivity.

Acrylic adhesives have the property of curing only where exposed to UV light offering the possibility of selective curing.

This technology is becoming more widely adopted by industry due to the degrease of the high-capital equipment costs and the use of better but more expensive formulated systems.

Developments to increase the quality of glued surfaces of different materials are ongoing.

6.1.4 Use of VOC free primers

Primers are used for the pre-treatment of the surface. Products are now available containing only solvents with a very low vapour pressure, and thus not qualified as VOC. VOC free primers are often used in combination with reaction adhesive.

6.2 VOC-reduced systems

If the complete substitution of organic solvents is impractical then changing to systems with a reduced VOC content, such as those described in this section, can decrease emissions.

6.2.1 Use of high solid products

HIGH SOLID PRODUCTS STILL CONTAIN A LOW SHARE OF VOCS

High-solid adhesives are often used for bonding foams as, for example, in the manufacture of mattresses. Although water based systems are available for some applications, a full substitution of VOCs is not possible for technical reasons. The adhesives are applied to surfaces that are to be combined under pressure and which must bond instantly - at present this is only possible with solvent containing adhesives.

6.2.2 Use of products with low VOC content

It is currently not possible to substitute the complete range of solvent-based tapes and labels by hot melt, UV curing or water based product, but continuing technical development is reducing the share of solvent-based product as new products come on line.

These products may still contain up to 20 % organic solvent - to either improve the application or the bonding properties.

In case of primers the solvent content is between 10-15 % and dispersion adhesives may have a residual solvent content of 2-10 %.

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements and abatement techniques can be used to reduce VOC emissions if VOC substitution as described in section 6 is not possible. The following measures are commonly applied for adhesive coating process:

7.1 Abatement technologies / End of pipe measures

Because of the diversity of processes and the different types and amounts of VOC emissions arising, abatement techniques remain important means of reducing VOC emissions from adhesive coating processes. The selection of suitable abatement measures depends more on process parameters, such as flow rate, concentration (and how they vary) than the economic cost of a particular measure and/or approach.

In many cases a combination of different abatement measures - although costly - offers the best solution.

7.1.1 Thermal oxidation (Regenerative /recuperative)

Two types of thermal oxidiser are in common use: regenerative and recuperative oxidisers.

Regenerative oxidation tends to be the more efficient of the two as it uses the recovered energy to pre-heat incoming process air to oxidation temperatures (~ 800 °C). Consequently, its operating costs are significantly lower than for recuperative oxidation systems. Regenerative thermal oxidation systems are particularly effective for process streams with low solvent loading but their operating costs depend highly on the efficiency of the heat exchanger. Regenerative thermal oxidation systems are widely used as they are relatively insensitive to the composition of the solvents in the process air and the concentration.

THERMAL OXIDATION SYSTEMS ARE WIDELY USED TO REDUCE VOC EMISSIONS FROM ADHESIVE COATING

Recuperative systems are useful if the heat of the exhaust gas can be used in different areas of the plant. Steam or thermo-oil is heated via heat exchangers. They are mainly used for small flow rates. At higher rates the systems are not cost effective. They are often used in combination with catalytic oxidation systems.

Thermal oxidation systems are used for inlet concentrations between 1 - 20 g/Nm³. VOC destruction efficiency rates of up to 99.9 % are possible.

The minimum VOC concentration for the oxidation process to be autothermic is 1 - 2 g VOC/Nm³.

6.1.2 Refrigerated condenser

A refrigerated condenser works best with emission streams containing high concentrations of VOC. The air stream is cooled below the dew point of the solvent. Then the solvent condenses and it can be reused. The exhausted air stream leaving the condenser will still contain some solvent. In a closed loop system, the overall solvent emissions are greatly reduced. If the system uses air, care has to be taken, that the solvent concentration in the air is less than 5 % of the lower explosion limit (LEL). While using inert gases (i.e. N_2) concentrations up to 50% LEL can be used, and this option reduces the drying time and the length of the drier. A disadvantage of using inert gases is the required flushing and refilling of the system with inert gas after each equipment down time or outage.

7.2 Process improvements

PROCESS IMPROVEMENTS CAN HELP TO REDUCE VOC EMISSIONS FROM THE APPLICATION PROCESS

Fugitive VOC emissions may arise from solvent storage and handling. The most commonly used measures to reduce them involve process improvements to collect vapours escaping from application systems, drying areas, storage and handling areas etc. in local exhaust ventilation hoods for subsequent treatment or abatement.

A wide range of best practice and process improvements mainly aiming at containing VOC emissions are possible, such as the following (not exhaustive):

- Increased efficiency from optimised application technologies
- Collection of VOCs from different distributed sources using local exhaust ventilation hoods, for subsequent control of point and fugitive emissions
- Back venting to the delivery tanks during bulk storage tank filling
- Improved exhaust air collection systems
- Using closed or covered application systems
- Using closed containers for the transport and intermediate storage of solvents
- Using closed-loop liquid and gas collection equipment for cleaning of reactors and other equipment
- Implementing leak prevention systems

7.3 Organisational measures

The following operational measures are aimed at reducing VOC emissions:

- Optimisation of process parameters
- Effective production and maintenance scheduling
- Reduced quantity of stored solvents

8 Summary of VOC emission reduction measures

The following table summarizes the VOC emission reduction measures discussed in chapters 6 and 7:

Table 5: Measures for VOC substitution and VOC reduction in adhesive coating

Objectives	Description
VOC-free systems	Use of - Water borne adhesives - Hot melt adhesives - UV curing adhesives - VOC free primers
VOC-reduced systems	Reduction of VOC content by using - High solid adhesives - Products with low VOC content
Process Improvements	Good housekeeping Improved collection of exhaust air Proper handling of solvents
Abatement Technologies	Thermal oxidation (regenerative /recuperative) Refrigerated condenser and re-use of solvents

9 Good practice examples

9.1 Example 1: Solvent/water based coating machines

The following information is provided by an equipment manufacturer for solvent or water based coating machines. The example demonstrates the practical possibilities, consequences and differences between solvent and water based adhesive coating machines.

In principle it is possible to convert a machine designed for solvent-based adhesives to use water-based adhesives but it becomes more difficult the older the machine is. In general equipment older than 10 years should not be converted because the control systems are likely to be obsolete

There are two parts of the coating process that differ between water and solvent based coating machines.

One part is the coating system itself. Due to different viscosity requirements, the technical settings will need adjustments. The production costs for the adhesives are about the same.

The more important difference relates to the conversion of the dryer. This is a complex piece of equipment with different sections, fulfilling different tasks and with different settings parameters. Length, temperature and airflow all need to be adjusted when swapping from solvent to water based systems. A dryer for water based adhesive coatings needs about 40% less energy. The reason is the huge amount of air which has to be moved in case of solvent based adhesive to keep the concentration of the solvent at 5 % of LEL.

A typical coating machine costs about 6-8 Million €, with 35-50 % of this cost allocated for the drier.

In general the investment cost for solvent-based adhesive machines are about 20 to 30 % more expensive than comparable machines for water based adhesives (due to the explosion-proof design requirements).

During the production the tape speed of water-based adhesive tapes can be 1,000 m/min whereas solvent based adhesive tapes can only reach 600 m/min maximum.

9.2 Example 2: Abatement technologies

This example describes the situation of a pressure sensitive tape producer (operating in three shifts, 6 days a week). To meet the requirements of the SE directive three different abatement technologies have been implemented:

1) Refrigerated cooling:

The air used to dry the solvent-based adhesive tape is circulated through the system and is condensed at a refrigerated cooler, about 1,100 t per year of solvent is recovered and reused.

The annual maintenance costs are about 10,000 € and the downtime is close to zero. The coating system is an enclosed chamber and emissions from the closed loop are extracted and passed to a recuperative thermal oxidiser.

2) Regenerative thermal oxidation:

The regenerative thermal oxidation system reduces VOC concentrations to 10-18 mg/Nm^3. The capital costs were ~ 400,000 €. The oxidiser has a design throughput of 15,000 Nm^3 per hour. The annual consumption of natural gas is about 200,000 Nm^3. Annual maintenance costs are about 40,000 € with about 200 min downtime during the year.

3) Recuperative thermal oxidation

The plant also operates two recuperative thermal oxidisers. The recovered heat from the combustion is used to produce steam. This equipment is relatively unreliable and has about 400 min of down time each year. About 1,000,000 Nm^3 natural gas is burned each year. The annual maintenance costs are about 50,000 €. Due to the relatively long down time and maintenance costs, the recuperative thermal oxidation is the most inefficient abatement technology. [Lohmann]

9.3 Example 3: Hot melt coating

This example describes the retrofitting of a conventional coating machine used for solvent-based adhesives for the use of hot melt coatings. The drying section is no longer necessary but the following additional equipment has to be provided:

• Drum melter 200 l	~ 35,000 €
• Buffer tank	~ 20,000 €
• Heated tubes	~ 4,000 €
• Slot nozzle	~ 80,000 € (in special cases up to 200,000 €)

In the thermal isolated buffer tank the hot melt which was molten in the drum melter is stored for the further process. From the buffer tank the hot melt is transferred over the heated tubes to the slot nozzles where the coating is applied. The coated area can be 2 meter broad and line speeds up to 1000 m/min are possible. [Glutematic]

10 Emerging techniques and substitutes under development

Currently there are no new techniques or substitutes under development. The on-going research is concentrating on improving existing products, such as UV curing adhesives and hot melts, to make them more competitive with solvent based adhesives.

Ongoing research for water based primers seems promising but the range of application is not known yet.

11 Information sources

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[SE Directive 1999]
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Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Guidance 17:

Manufacturing of coatings, varnishes, inks and adhesives

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses manufacturing of coatings, inks, varnishes and adhesives, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emission Directive (SE Directive)

SE Directive – Scope definition (Annex I)
Manufacturing of coating preparations, varnishes, inks and adhesives is defined by the SE Directive as “the manufacture of the above final products, and of intermediates where carried out at the same site, by mixing of pigments, resins and adhesive materials with organic solvent or other carrier, including dispersion and predispersion activities, viscosity and tint adjustments and operations for filling the final product into its container.”

The SE Directive lays down the following activity specific emission limit values for the manufacturing of coatings, inks, varnishes and adhesives:

Table 2: Emission limit values of the SE Directive

<table>
<tr><th colspan="5">SE Directive - Emission limit values (ELVs)
(Annex II A – activity No. 17)</th></tr>
<tr><th>Activity</th><th>Solvent consumption threshold [tonnes/year]</th><th>ELVs in waste gases [mg C/Nm³]</th><th>Fugitive emission values (% of solvent input)</th><th>Total ELVs (% of solvent input)</th></tr>
<tr><td rowspan="2">Manufacturing of coating preparations, varnishes, inks and adhesives</td><td>≥ 100-1000</td><td>150</td><td>5</td><td>5</td></tr>
<tr><td>> 1000</td><td>150</td><td>3</td><td>3</td></tr>
<tr><td colspan="5">Special provisions:
The fugitive emission value does not include solvent sold as part of a coatings preparation in a sealed container.</td></tr>
</table>

THE SE DIRECTIVE APPLIES TO MANUFACTURING OF COATINGS, INKS, VARHNISHES AND ADHESIVES IF THE SOLVENT CONSUMPTION IS MORE THAN 100 TONNES PER YEAR

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[1] as well as for halogenated VOCs that are assigned the risk phrases R40 or R68[2]. There is a general obligation to replace CMR substances – as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated[3] VOC with R40 the ELVs in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

The main sources of VOC emissions in the manufacturing of paints, varnishes, inks and adhesives are filling of tanks and containers, dissolving, mixing, and blending operations, and product filling/packaging operations as well as the cleaning of equipment and recovery of cleaning solvents.

VOC can be substituted by changing the characteristics of the final product, shifting to water based products, powder products or reactive products. Thus, it may be possible to reduce the annual solvent consumption to less than 100 tonnes.

Emissions can effectively be reduced by keeping vessels closed whenever possible and by using closed systems (e.g. closed mixing and dissolving containers, directly connected with storage tanks via pipes and pumping systems).

VOC reductions can be achieved by appropriate cleaning. Pipes can be emptied using ‘pig systems’.[4] Vessels and valves can be cleaned with enclosed automatic washing systems. Automated washing with VOC cleaners can be combined with VOC recovery by distillation. VOC-free washing systems, using alkaline solutions, have good cleaning properties.

If waste gas abatement is necessary to reduce emissions below the limit values, recovery techniques or thermal and biological treatment can be applied. Further VOC reduction can be realized through technical measures such as effective maintenance and inspection plans, as well as by leak detection and repair programmes. Careful design of storage facilities and work places for mixing and dispersing can enhance VOC reduction by minimising the ambient temperature rise (via underground storages, prevention from exposure to sunlight etc).

[1] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

[2] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: ‘Possible risk of irreversible effects’. The new wording is: ‘Limited evidence of a carcinogenic effect’. In the ‘old’ version mutagenicity (cat 3) was included. This mutagenic effect is now covered separately under R68: ‘Possible risk of irreversible effects’. This new risk phrase does not include carcinogenicity. The ‘new’ version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to this change, a final decision on which version applies can only be given by the European Court

[3] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.

[4] Pig systems clean pipes by moving a small piece of plastic, pushed with compressed air, through the pipe that presses remaining material back into the storage container.

3 Description of the activity and related industry sectors

Paints, inks, varnishes and adhesives are suspensions of finely divided particles in a liquid that when spread over a surface in a layer will form a solid, cohesive, and adherent film.

Products are adapted to coat or glue onto different types of material, e.g. stone, metal, wood, paper, plastic and leather.

The products of the sector can be classified into three different user categories: industry applications (e.g. vehicle coatings, wood coatings, printing inks, tape adhesives), do-it-yourself applications and other professional applications (e.g. decorative paints, vehicle refinishers, protective coatings, flooring adhesives).

In Europe most of the manufacturing of paints, inks, varnishes and adhesives is carried out by small or medium sized, independent, companies. Some installations belong to enterprises with several production sites in one country and a few sites are part of international companies operating throughout Europe or worldwide.

Some 1000 companies are members of CEPE[5] [CEPE 2008] and of these, the ~200 companies that produce inks had estimated sales, in 2002, of about 944,000 tons and a turnover of 3.3 billion Euros [EuPIA 2008].

As an alternative for solvent based paints, varnishes, inks and adhesives, water based products have been developed as well as reactive systems or powder based systems.

[Ökopol 2008]

Figure 1: Dissolvers connected with pipes for direct filling from storage

About 1.4 million tonnes of VOC from conventional systems have been substituted in the past 10 years in Germany by shifting two thirds of the

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[5] European Council of producers and importers of paints, printing inks and artists' colours, Brussels.

production to water based products, high-solids, powder coatings or coatings for electrostatic applications. [VDL 2008]

4 Technical process description

The manufacturing of coating preparations, varnishes, inks and adhesives is a batch process. It is characterised by four major process steps:

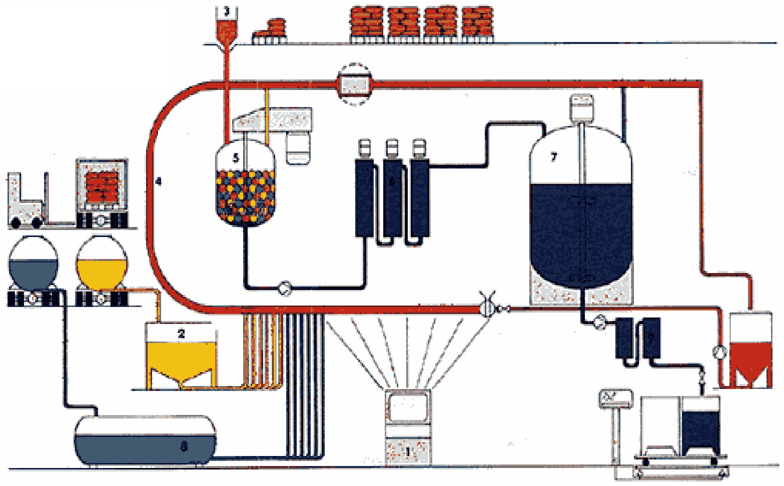
- dosing and pre-mixing;
- milling and dispersing;
- product finishing and blending;
- product filling and packaging.

When calculating VOC emissions from the installation according to the SE Directive, the VOC content sold as part of a coatings preparation in a sealed container does not count as emission. Thus, to reduce VOC emissions without waste gas treatment to < 5 % of the solvent input (respectively < 3%, depending on solvent consumption, see table 2 in section 1), at least 95 % (respectively 97%) of the solvent input has to end up in the product (or may be contained in another controlled output fraction like in waste).

The main sources of VOC emissions in the installation are filling of vessels and containers, leaking and spilling during material transfer, inappropriate handling (open vessels etc.) as well as cleaning of parts and the working environment.

Other process steps with potentially important VOC emissions are storage tank breathing, and emissions from solvents recovery.

VOC emissions reduction depends on the ability to directly pump material into closed containers and on the use of appropriate handling and cleaning. In some cases VOC recovery or an abatement technique are needed to comply with the limit values of the VOC Directive.



[VDL 2002]

Figure 2: Production within a closed system

4.1 Process flow and relevant associated VOC emissions

Figure 3 shows the most important VOC inputs and outputs (arrows indicate the relevance of the VOC amount):

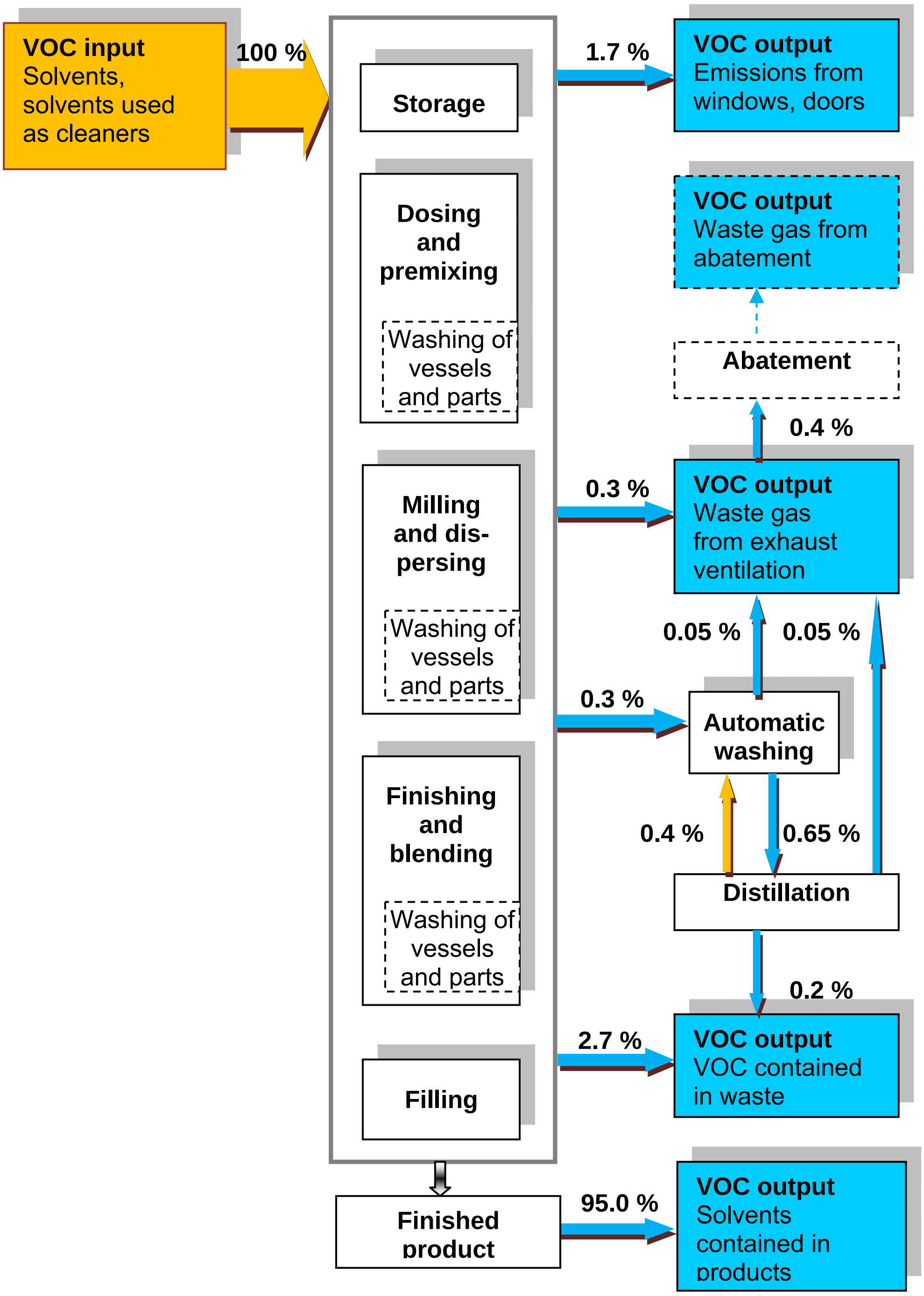


Figure 3: Exemplary VOC emissions from coating manufacturing [Ökopol 2008]

4.2 Process description

Open and semi-open systems are used, particularly in factories regularly producing less than one ton of a specific product. If larger amounts are produced regularly, closed systems tend to be used.

Supply and storage

Liquid commodities are usually supplied in drums or tankers. VOC emissions can occur when solvents are transferred from road tankers to facility storage tanks – which often have a capacity as large as 30 m³ – if no gas displacement device is used.

Emissions from drums can occur if lids or bungs are not properly closed.

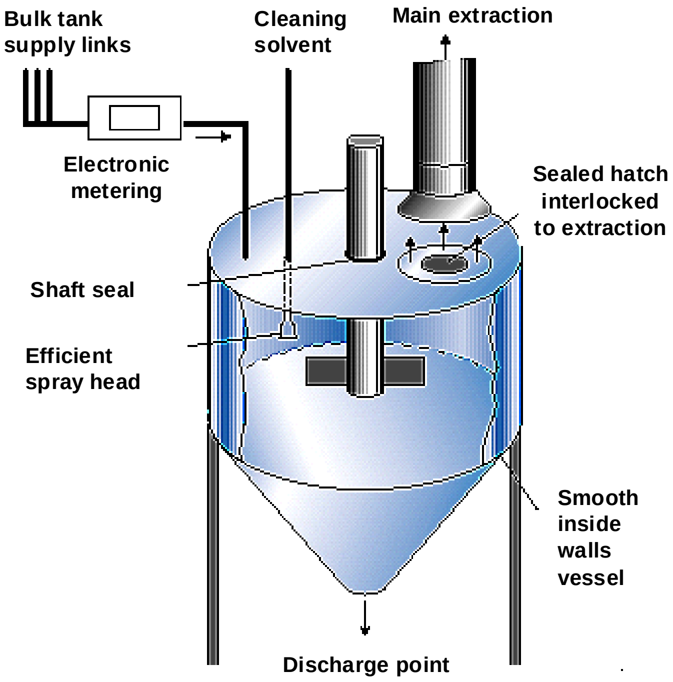
Dosing and pre-mixing

Liquid raw materials are poured into a container and mixed until they form a viscous material, then pigments are added.

Containers with a capacity of one tonne or less are usually portable, so they can be moved to a stationary dissolver. Containers of this size may be open, semi-closed or closed systems. Containers with a capacity of more than one tonne are often closed systems.

In closed systems, components like pigments, resins and solvents are pumped into and out of the container without contact with the ambient air. Often simple wooden or plastic covers are used, providing a cut to pass by the stirring unit. If not properly closed, VOCs are emitted during filling, dosing and mixing.

The mechanical action of mixing large quantities of materials may lead to bulk heating. When resin is added in solid form (instead of fluid) the heating is greater still. The heating may lead to increased VOC emissions unless an enclosed system is used.



[Ökopol 2008]

Figure 4: Closed mixing vessel with extraction, cleaning devices and direct filling

Milling and dispersing

After pre-mixing, the material is milled to obtain fine particle dispersion. For this purpose, the material is filled or pumped into mills, that separate pigment clusters e.g. with small pebbles or balls (‘agitator ball mill’).

Afterwards the material is transferred into a container again and dispersed until it is mingled well and has become a fine dispersion. The disperser may consist of a stirring unit with or without an adapted covering system.

VOC emissions may result from filling, transfer, dispersing and interim storage, if vessels are not properly closed.

Product finishing and blending

To finish the product, materials are added to obtain the coating characteristics, like viscosity, colour and shade. Pigment dispersions, organic solvents and resins are typically added to solvent-based products. Water, preservatives, antifoaming agents, and polyvinyl acetate emulsions are used in water-based coatings.

In closed systems, the adjusting substances are pumped directly into the container. For small production amounts, open or semi-closed systems are often used. Whereas VOC emissions only occur from closed systems when covers are lifted, VOC will be emitted continuously from open and semi-closed systems.

Finally the material is ‘blended’, meaning that mixing and, if necessary, additional milling is carried out to meet product specifications.

VOC emissions may occur during interim storage, if vessels are not properly closed.

Product filling and packaging

The finished product is filled into bins, e.g. containers, drums, pails or cans. The size of the bins and the composition of the product differ according to customer requirements. The filling process varies from manual to fully automatic and from open to completely closed systems. If open systems are used, VOCs are emitted.

Cleaning

At the start of a new batch process, containers and parts generally have to be absolutely clean to prevent residues reducing the quality of the new batch.

Large containers are often cleaned with automatic washing machines. Washing of small containers and parts can also be done in washing machines but manual cleaning predominates. Most cleaning is done with organic solvents; alkaline solutions are rarely applied.

The cleaning frequency depends on volumes produced and on the possibility to combine products that need little or no cleaning (e.g. white colour followed by white colour).

Solvent recovery and abatement

Automatic cleaning systems are often combined with distillation equipment for the recovery of contaminated cleaning agents. These can also be used for the distillation of solvents from returns or from production residues.

If primary measures alone are not sufficient to reduce emissions then systems for recovery or destruction of VOC in waste gases are needed. As solvent recovery is energy intensive and, in most cases, only economical if pure substances (and not mixtures) are recovered, waste gas destruction systems are commonly used. These destruction systems include both thermal and biological methods.

5 Solvent use, emissions and environmental impact

5.1 Solvents used

A great variety of organic solvents are used for paints, inks and varnishes. Table 3 shows the most common solvents in decorative paints.

Table 3: Solvents used for decorative paints and varnishes

Solvent	Boiling point (at 1013 hPa) [°C]	Vapour pressure (at 20°C) [kPa]
Aliphatic hydrocarbons		
n hexane	65-70	20
n heptane	94-99	8.5
Cyclohexane	80.5-81.5	10.4
Methyl cyclohexane	101-103	5.1
White spirits (+ aromatics)	144-165	4.0
1,1,1-trichloroethane	73-75	13.3
Terpenes		
Mineral turpentine	150-180	0.44
Aromatic hydrocarbons		
Toluene	110-111	2.9
Xylene	137-142	0.9
Styrene	145	0.71
Vinyl toluene	164-170	
Ketones		
Acetone	56.2	24.1
Methyl ethyl ketone	79.6	0.1
Methyl isobutyl ketone	114-117	2.15
Methyl n-amyl ketone	147-153	0.5
Cyclohexanone	153-156	0.35

Solvent	Boiling point (at 1013 hPa) [°C]	Vapour pressure (at 20°C) [kPa]
Esters		
Methyl acetate	55-57	22.6
Ethyl acetate	78.3	10.3
Isopropyl acetate	88.4	5.8
Iso butyl acetate	114-118	1.8
Butyl acetate	124-128	1.11
Methoxypropyl acetate	143-150	0.53
Alcohols		
Diacetone alcohol	168	0.1
Methanol	64-65	12.8
Ethanol	78.3	5.9
Propanol	97.2	1.9
Isopropanol	82.4	4.2
Isobutanol	107.7	1.2
Benzyl alcohol	205.2	0.002
n butyl alcohol	116-119	0.67
sec butyl alcohol	99.5	1.6

[Chemiewinkel 2000]

Table 4 lists the solvents, which are most commonly used in the production of inks and varnishes.

Table 4: Most common solvents used in ink and varnish production

Printing technique	Solvents
Publication rotogravure	Toluene
Packaging rotogravure and flexography	Ethanol, isopropanol, n-propanol, toluene, methyl ethyl ketone (MEK)
Offset printing	Mineral oil, natural oil (e.g. soya oil)
Screen printing	Cyclohexanone, di-acetone alcohol, 1-methoxypropylacetate, 2-butoxyethylacetate, 1-methoxy-2-propanol, n-butylacetate

[BREF STS 2007], [LASI 2007], [Ökopol 2008]

Organic solvents used in **adhesives** include aromatic hydrocarbons (toluene, xylene), ketones (acetone), alcohols (methanol, ethanol, isopropanol, glycol, butanol), chlorinated hydrocarbons (dichloromethane), methyl acetate, ethyl acetate and mineral spirits. [AFC/BiPRO/DFIU 2002]

The solvent content of paints, inks and adhesives varies from 0 % to more than 80 % according to the product. [AFC/BiPRO/DFIU 2002], [Chemiewinkel 2000], [German EPA 2003]

5.2 Solvent consumption and emission levels

Solvent consumption at production sites depends on the characteristics of the product range. Manufacturers of interior decorative wall paints, for example, and manufacturers of offset-inks normally use VOC only for cleaning purposes and so do generally not exceed the solvent consumption threshold of 100 tonnes per year. Most producers of solvent based paint, varnish, ink or adhesive systems consume more than 1000 tonnes of solvent per year. [Ökopol 2008]

VOC emissions vary significantly, depending on primary measures (enclosure of systems, cleaning effectiveness, handling) and on the recovery or abatement systems used.

Around 95 % of the VOC input ends up as the VOC content of the final products. VOC output via waste depends on the annual amount of returns and production residues. It also depends on whether internal or external recycling of cleaners is carried out. The amount of VOC in waste (as % of the input) may be around 2 % before recovery and less than 1 % if distillation is carried out on-site. Emissions to air are typically around 1 - 5 % of the solvent input and may require waste gas treatment to be below the emission limits of the SE Directive. [Ökopol 2008]

5.3 Key environmental and health issues

In manufacturing coatings, varnishes, inks and adhesives a broad range of different solvents are used for a wide range of different products.

VOC emissions, together with NOx emissions, are precursors of ground level ozone formation in the presence of sunlight.

Emissions of VOC to air may occur from:

- - the storage of the solvents
- - the process (mixing, dispersing, finishing, filling)
- - cleaning operations (of containers, valves, mixers)

Spills and leaks from storage areas may result in emissions to soil and groundwater.

The process generates waste containing solvents which need to be disposed in a way that emissions to air, soil and groundwater are prevented or limited.

Table 5 shows solvents used in manufacturing of coatings, varnishes, inks and adhesives, which are classified with risk phrases for which specific regulations apply under the SE Directive (see section 1).

Table 5: Exemplary solvents used in manufacturing of coatings, varnishes, inks and adhesives, classified with risk phrases specifically regulated by the SE Directive

Solvents	Risk Phrases
2-methoxy ethanol, CAS 109-86-4	R60, R61
2-methoxyethanol acetate, CAS 110-49-6	R60, R61
2-ethoxy ethanol, CAS 110-80-5	R60, R61
2-ethoxyethanol acetate, CAS 111-15-9	R60, R61
Trichloroethylene, CAS 127-18-4	R45
Dichloromethane (methylene chloride), CAS 75-09-2	R40

[ADEME 2003], [Ökopol 2008]

The risk classification R45 implies that the solvent may cause cancer; the classification with R60 indicates that the solvent may impair fertility, and R61 indicates that the solvent may cause harm to the unborn child. Solvents classified with R40 have a limited evidence of carcinogenic effect.

The SE Directive requires that the abovementioned solvents carrying risk phrases R60, R61 or R45 have to be substituted, if possible, because of their impact on human health. If substitution is not possible, emissions have to be minimized (see section 1).

Existing occupational workplace limits should be taken into consideration.

6 VOC Substitution

In the following chapters potential substitutes for VOC solvents and their associated technologies are presented. This includes application conditions as well as advantages and disadvantages compared to VOC systems.

6.1 Substitution of solvents by shifting to different end products

VOC free water-based systems, reactive systems, and powder-based coatings may be suitable substitutes for solvent-based paints, varnishes, inks and adhesives. They may be used in a wide range of coating, printing and painting products.[6] Possibilities of coating manufacturers to shift to different end products depend on technical innovation, promotion and market acceptance.

Since 2007 the VOC content of decorative paints and vehicle refinishers, has been limited by Directive 2004/42/EC and regulations will become stricter for some decorative paints from 2010. [DECOPAINT Directive 2004]

[6] See for printing guidance documents no. 1, 2 and 3, for the coating of leather guidance document no. 13, and for the coating of vehicles and vehicle refinishing guidance no. 6-Part 1, 6-Part 2 and no. 8.

6.2 Substitution of VOC cleaners

Tenside-based cleaners can substitute for a significant proportion of the solvent-based cleaners used in water based product manufacture.

Alkaline-based cleaners, rather than VOCs, can be used for cleaning process equipment, also when using automatic washing machines. If necessary for more effective cleaning, the cleaning agent can be heated. Figure 5 presents a cleaning result from alkaline automatic washing of a container that was manually cleaned before, showing very good cleaning results even for old multilayer outside contamination, when applied for 30 minutes.

Washing equipment suitable for alkaline cleaners has a similar cost to that of solvent based systems. Dirty cleaning fluid, however, cannot be recovered by distillation - it can be re-used in the system but eventually it will have to be disposed of or treated in a waste water treatment plant.

Before washing **After 10 minutes** **After 30 minutes**

[RENZMANN 2008]

Figure 5: Automatic water based alkaline washing of vessels

Cross-media effects

Alkaline solutions are aggressive to skin and eyes, therefore appropriate material handling and application in closed systems (using fresh-water cleaning in the last stage) are necessary.

7 Other VOC emission prevention measures and abatement techniques

For many cases additional possibilities exist to reduce VOC emission next to substitution of the VOC-solvents. The following measures are commonly applied to reducing VOC emissions from the manufacturing of coatings, inks, varnishes and adhesives.

7.1 Reduction of the solvent content

It is possible to reduce solvent content substantially where alternative products and systems are able to meet customers' requirements. High solid coatings, for example, can reduce the solvent content from a conventional product level of 70-80 % to 30-50 %. If customers are able to shift to water based systems, a reduction to a very low solvent content is possible, for example in flexographic and rotogravure packaging printing (0 – 20 % solvent content). A similar reduction is possible for many decorative paints and primers, etc.

7.2 Process improvements

VOC emissions can be reduced by appropriate materials handling, prevention of leakage from storage and pipes, by application of closed systems, by closed washing systems and by solvent recovery and abatement technology.

Most important measures are those leading to enclosed processes and to reduced emissions from cleaning operations.

Improved handling and process planning

VOC emissions are prevented if workers are trained to keep containers closed whenever possible. Adoption of 'good practice' and daily monitoring can be used to drive continuous improvement. The benefits of good practice can best be gained if appropriate equipment (e.g. size-adapted, lightweight covers) is provided.

Precise batch calculation will avoid VOC emissions related to overproduction, by avoiding the need for extra cleaning and emissions from waste.

Storage and pipes

VOC emission reduction should take into account that some part of the solvent input documented by suppliers may be lost in storage facilities.

VOC emissions arising during transfers from road tankers to storage tanks can be reduced by installing gas displacement devices; these systems use the pressure equalizing line to feed back up to 100 % of the VOC vapour to the tanker. The gas displacement devices can normally be fixed at the overpressure pipe and retrofitting to an existing tank flange connection costs between 5,000 – 6,000 Euros (50 mm pipe, 20 m, stainless steel). [Silbermann 2008]

The following measures can be taken to prevent VOC emissions from tanks and pipes:

- Developing proactive maintenance plans and risk-based inspection plans, such as the risk and reliability based maintenance approach referred to in [BREF Storage 2006]
- Implementing a leak detection and repair programme with a focus on those situations most likely to cause emissions (high volatility liquids, operations employing elevated temperatures) [BREF Monitoring 2003]
- Preventing storage tank and pipe corrosion by the use of suitable construction materials or applying cathodic protection on the inside of tanks. [BREF Storage 2006]
- Ensuring that appropriate gaskets are selected and installed correctly for bolted flange connections, end caps or plugs on open-ended lines (not valves).
- Using automatic devices to avoid overloading storage containers.

Storage containers can be equipped with over/under pressure valves and pressure equalizing lines. This avoids the need to open containers during the extraction of material. It should be ensured that valves close completely. VOC emissions are reduced when holes for venting storage containers are kept as small as possible. [Vineke et al. 2001]

VOC emissions from storage container breathing vents can be avoided if the storage containers are protected from solar radiation i.e. situated in cool, dark, locations; small containers should not be stored outside during warm periods. [ADEME 2003]

Using 'just in time' manufacturing also reduces VOC emissions by minimising the storage times of the bins next to premixing containers. If possible, long transit distances from storage to containers should be avoided. [Vineke et al. 2001]

Processing in closed systems

Direct filling of containers for pre-mixing, dispersing, blending and packaging can reduce VOC emissions. This is achieved by using closed systems with pipes between the storage tanks and mobile or fixed, lidded, containers (see figure 6).

Container lids and covers should fit as closely as possible. If covers are not fixed, they should provide a means of covering the mixer shaft hole.

Depending on the size of containers, retrofitting appropriate covers may be more expensive than investing in new containers (e.g. adapted covers for a medium sized container may cost about 5000 Euros, whereas new containers cost about 3000 - 4000 Euros). [Niemann 2008]

[Ökopol 2008]

Figure 6: Dissolver directly connected with storage tanks

Movable lightweight covers with extraction holes and lids that close properly during interim storage can reduce VOC emissions when mobile containers are moved from one process stage to the next.

Alternatively, antistatic foils, held in place with elastic belts, can be used to cover the containers (see figure 7). [FreiLacke 2008]

[Ökopol 2008]

Figure 7: Interim storage of containers covered with antistatic foil

Optimisation of open systems

If fully closed systems are not available the system should, nevertheless, be kept as closed as possible using temporary coverings with extraction holes. Splashing can be avoided by filling containers using flexible tubes and hoppers. [Vineke et al. 2001]

With regard to extraction of air from mixing vessels, it is possible that too high an extraction rate can result in increased evaporation from the surface of the liquid. Extraction rates should be optimised to minimise losses. In some cases it may only be necessary to operate extraction when the vessel lid is open.

During pre-mixing and dissolving, shearing forces lead to increased temperatures and, potentially, increased VOC emissions. Double-walled containers with water-cooling systems can minimise any warming. Alternatively systems can be applied that cool VOC emissions and return the condensed solvents back into the container (figure 8).

[Niemann 2008]

Figure 8: Dissolver with cooling system for backflow of condensed VOC emissions

Finishing and blending

During finishing and blending, taking samples via small holes without removing the entire covering can prevent VOC emissions. Jet dosing and splashing should be avoided. Flanges are available that enable cleaning from outside the container in order to prevent contamination. [ADEME 2003]

Filling and packaging

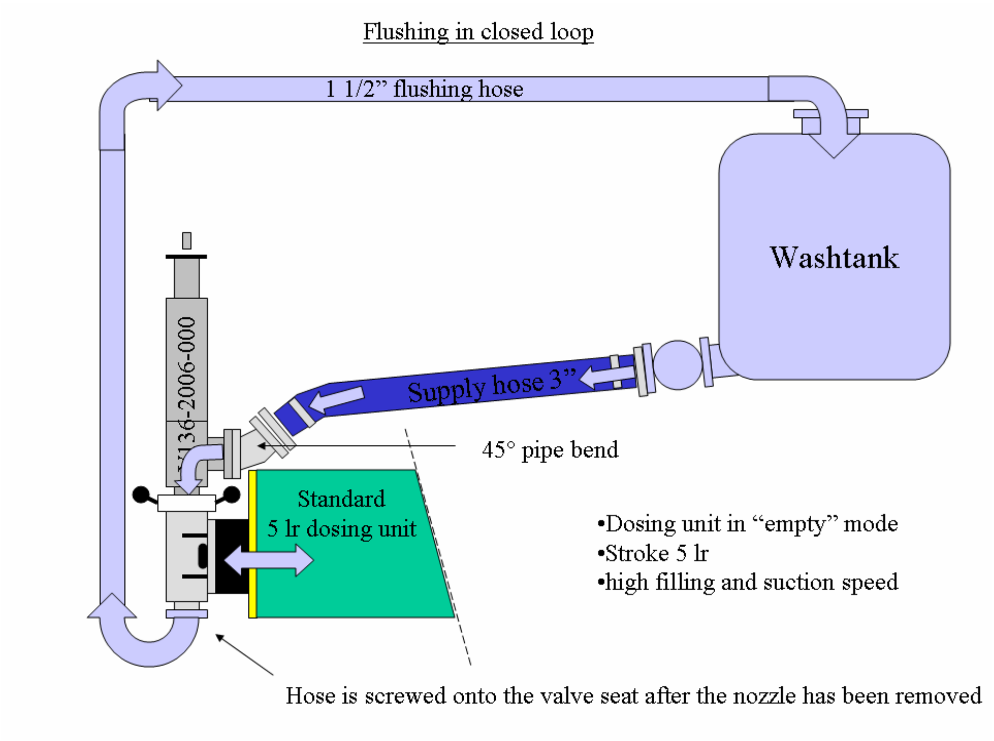
At filling stations, diffuse emissions may be avoided by installing effective extraction hoods and/or by containment [Vineke et al. 2001].

Depending of the kind of bin used (drum, container on pallet, pail or can) it is possible to extract the solvent vapour directly at source, e.g. by bunghole aspiration. [Feige 2008]

Also depending on the kind of bin, VOC emissions can be reduced if the filling device is positioned as low as possible (below-surface or below any open bunghole). [ADEME 2003]

Automatic or semi-automatic filling stations can reduce process time and the time that bins are open awaiting further processing.

Using automatic filling stations that have closed-loop cleaning systems for the filling tubes also reduce emissions; less washing agent is used because residual material can be cleaned up immediately - before it has completely dried. [De Vree 2008]



[DeVree 2008]

Figure 9: Automatic filling system connected with closed loop cleaning system

If filters are used, positioning them directly in the pipe, avoiding open hoppers, can reduce VOC emissions. Filters inside of pipes can be cleaned with blades or with counter flow cleaning. [ADEME 2003]

Cleaning

A high standard of cleanliness is required to maintain product quality, reduce product contamination, and prevent wastage. Manual cleaning of parts and equipment uses large amounts of solvents (e.g. 4 l ethanol for a 500 l drum) [ÖKOPOL 2008]. Fugitive emissions are difficult to avoid during manual cleaning and drying of the parts.

The use of automatic washing machines (for mixing vessels as well as for parts) reduces VOC emissions of cleaning solvents and guarantees a high cleaning quality. VOC emissions can be extracted from the cleaning chamber before doors are opened. Automatic washing not only reduces emissions, but also leads to economic benefits as one person can operate a washing machine whereas manual cleaning of large containers may require two.

Dirty cleaning agents can be re-distilled in directly connected integrated systems. Distillation equipment is available in a range of different sizes and can also be used for recovery of solvents from rejects and remains.

In some cases distillation of used cleaning solvent may not be necessary, for example where a lightly contaminated solvent cleaning residue can be stored separately and directly reused in a subsequent batch of paint without impacting on the quality of the finished product, thus reducing potential emissions from the distillation process, and reducing energy costs.

As mentioned above, under 'substitution', organic cleaning solvents may be replaced by an alkaline solution. It should be noted, however, that these are not suitable for cleaning aluminium and zinc (galvanised) equipment. Containers with electropolished surfaces are the most easily (and efficiently) cleaned. [ÖKOPOL 2008]

If - for small part cleaning - bins have to be used where cleaner surface is long time exposed to ambient air without covering, then the solvent surface may be covered with small, floating, elements. These should have a flatted upside to prevent from rolling and bringing solvents to the upside [ÖKOPOL 2008].

Reduction of VOC emission from parts cleaning may also be achieved by changing the order of product manufacture (e.g. from lighter to darker shades), to reduce the cleaning effort needed. [ÖKOPOL 2008]

Exhaust extraction systems and waste gas treatment

Movable extraction hoods can be used to extract VOC emissions from open systems. Hoods should be available near all potential emission sources i.e. mixing, dispersing, blending, filling or cleaning.

Hoods connected to extraction systems that link to waste gas treatment plant should be designed to allow for proper closing when not in use. This prevents the dilution of waste gases with fresh air.

If waste gas VOC concentrations exceed emission limit values, waste gas treatment systems are needed. Recovery of solvents by condensation or on activated carbon is energy intensive and will only be economic if the recovered solvents are of high quality and value (e.g. toluene recovery). If waste gases contain a mixture of VOCs, then thermal or biological treatment for the destruction of VOC is more cost effective.

8 Summary of VOC emission reduction measures

The following table summarizes the VOC emission reduction measures discussed in chapters 6 and 7:

Table 6: Measures for VOC substitution and VOC reduction in manufacturing of coatings, inks, varnishes and adhesives

Objectives	**Description**	
Substitution/ Solvent free processes	Shift to VOC-free products	Development and manufacturing of solvent free products such as powder coating or 100% water borne systems
	VOC-free cleaners	Use of alkaline solutions or tenside based cleaners
Reduction of the solvent content	Shift to products with low VOC content	Reducing solvent content (water based systems or high solid systems)
Process Improvements	Improved handling and process planning	Train and monitor workers to keep containers closed whenever possible. Avoid overproduction by precise batch calculation.
	Prevent storage emissions	Use of gas displacement devices. Installation of over/under pressure valves. Ensuring venting holes are small and closed whenever possible. Use of overload detection systems. Shielding from solar radiation.
	Prevent storage and pipe leakage	Prevent tanks and pipes from corrosion by use of appropriate materials and cathodic protection. Apply maintenance and inspection plans, and leak and repair programmes. Use end caps or plugs on open-ended lines (not valves). Keep valves fully closed.
	Processing in closed systems	Direct filling of containers from storage tanks.
	Covering of containers	Use movable lightweight covers that close properly or cover containers with antistatic foils and elastic belts.
	Prevent emissions from heating	Reduction of temperature by the use of cooled containers or use of backflow cooling

Objectives	**Description**	
		systems.
	Prevent emissions from interim storage	Avoid long transport distances; avoid temporary storage of containers (just-in-time production)
	Prevent emissions from filling	Use of closed filling systems. Avoid jet dosing and splashing. Keep filling distance as low as possible. Use filling tubes while keeping the covering closed as far as possible during filling. Use below-surface or below bunghole filling if possible.
	Prevent emissions during sample taking	Use small sized holes for sample taking; leave covers open as little time as possible.
	Effective cleaning	Use of enclosed automatic washing systems for containers and parts. Use of closed cleaning systems e.g. for automatic filling devices.
	Prevent emissions from cleaning	Avoid unnecessary cleaning of the working environment like floors, walls or exterior of machines; protect the working environment, e.g. with plastic foil.
	Reduce solvent consumption	Distillation and reuse of solvents from cleaning and rejects. Avoid overproduction to reduce cleaning effort.
	Prevent fugitive emissions	Use flexible or stationary extraction hoods whenever emissions may occur, e.g. during premixing, dispersing, blending, filling and cleaning.
Abatement Technologies	Recovery or destruction of captured VOC emissions	Use recovery systems (by condensation or adsorption on activated carbon). Use thermal oxidation or biofilters.

9 Good practice examples

The following table gives an overview of the emissions achieved at manufacturing sites that have made high efforts to reduce emissions by enclosing the production and – in some cases – by destroying VOC in waste gases from the process and cleaning operations with oxidation.

By these measures total emissions below 3 % of the solvent input are generally achieved, and levels below 1 % when using oxidisation. [Ökopol 2008]

Table 7: Total emission values achieved by different manufacturers

Manufacturing	**VOC abatement**	**Solvent input**	**Total emission**
Manufacturer A Coating preparations and varnishes	**Thermal combustion**	**4000 t/a + recovery (distillation)**	**0.25 %** (and less, as exact input is not known due to distillation)
Manufacturer B Inks (Jan-Jun)	**None**	**569 t/a** **(no distillation)**	**2.8 %**
Inks (Jan-Dec)	**None**	**1092 t/a** **(no distillation)**	**2.3 %**
Manufacturer C Coating preparations and varnishes	**Catalytic combustion**	**3416 t/a**	**0.69 %**
Manufacturer D Inks	**Thermal combustion**	**4500 t/a**	**< 1 %**
Manufacturer E Coating preparations and varnishes	**Thermal combustion**	**10000 t/a**	**~1.8 %**

9.1 Ink manufacturer (solvent and water based products)

Manufacturer B (Benelux), producing flexography and gravure printing inks, made an initial solvent management plan (solvent input/output balance) on the first half of the year and calculated total emissions to be 2.8 % of the solvent input before additional measure were taken.

As one source of fugitive emissions, the opening of containers was detected. When taking solvents out of containers via faucet, the resulting low pressure has to be adjusted. For this purpose a holes of 10 cm in diameter were opened. After July, these holes were replaced by very small and sealable drilled holes. Additionally, the containers next to the milling system were provided with dense closing covering.

As another measure to prevent fugitive emissions cleaning quality requirements were checked. When preparing equipment for the next batch, parts have to be cleaned carefully for not to contaminate the following batch. Manufacturer B introduced, whenever possible, new practice to use the same drums, containers and parts for the same colour or products to reduce demand of absolute cleanness and therefore to reduce the cleaning effort.

At the end of the year, a follow up solvent management plan showed total VOC emissions during the entire balance year of 2.3 % of the solvent input. Reductions were obtained by the above mentioned measures.

9.2 Coating and varnish manufacturer

Manufacturer C (Austria) produces 16,000 t/y of paints, varnishes and stains for wood coating with 10,000 different recipes. 60 % of the total production consists of water-based products.

A manual water-based high pressure cleaning (140 bar) is used for the cleaning of containers and vessels from the production of water-based coatings. Polyethylene drums are automatically cleaned with a brush cleaning system. Dirty water is recycled and clean water is only used for final rinsing, thereby achieving a water recycling rate of 75 %.

For cleaning of containers from the production of solvent-based coatings 6 automatic cleaning devices are used. Only rinsing is done with clean solvents while for the main cleaning the dirty solvents from rinsing are used. All solvents from cleaning are distilled and used for rinsing again. By this concept, only 7 tonnes of new cleaning solvents are needed per year for the production of 5770 tonnes of solvent-based coating.

The company attributes its low total emission value (0.69% of total solvent input) to its very effective extraction system from processes and automatic cleaning. The extraction system is connected with a catalytic combustion system.

Furthermore, the company takes various measures of improved and conscious material handling. Pipes are equipped with a pig-cleaning-system, e.g. all pipes connecting the 30 storage tanks with the production. By this measure cleaning effort for pipes is reduced. At the same time pipes will stay in good condition and VOC emitting leakages are more unlikely.

10 Emerging techniques and substitutes under development

No emerging techniques have been reported.

11 Information sources

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Guidance 18:

Rubber conversion

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses rubber conversion and the related cleaning of equipment, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emission Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
The activity 'rubber conversion' is defined as 'any activity of mixing, milling, blending, calendering, extrusion and vulcanisation of natural or synthetic rubber and any ancillary operations for converting natural or synthetic rubber into a finished product'. The SE Directive covers installations in which this activity is taking place with an annual organic solvent consumption greater than 15 tonnes.

This guidance document does not cover the manufacture of paints or adhesives with rubber.

The SE Directive lays down the following activity specific emission limit values for rubber conversion:

THE SE DIRECTIVE APPLIES TO RUBBER CONVERSION ACTIVITIES IF A SOLVENT CONSUMPTION OF 15 TONNES PER YEAR IS EXCEEDED

Table 2: Emission limit values of the SE Directive

SE Directive - Emission limit values (ELVs) (Annex II A – activity No. 18)				
Activity	**Solvent consumption threshold [tonnes/year]**	**ELVs in waste gases [mg C/Nm³]**	**Fugitive emission values [% of solvent input]**	**Total ELVs [% of solvent input]**
Rubber conversion	>15	20*	25**	25
Special provisions * If techniques are used which allow reuse of recovered solvent, the emission limit value in waste gases shall be 150. **The fugitive emission value does not include solvent sold as part of products or preparations in a sealed container.				

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[1] as well as for halogenated VOCs which are assigned the risk phrases R40 or R68[2]. There is a general obligation to replace CMR substances– as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated[3] VOC with R40/R68 the ELVs in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

PROCESS IMPROVEMENTS ARE MAJOR VOC-REDUCING MEASURES IN THE RUBBER INDUSTRY

In the rubber conversion industry solvents are mainly used as tackifying agents to stick together different types of layers of rubber or rubber coated components and as mould release agents. The substitution or reduction of the solvents as tackifiers is often associated with changes in the production process and compound formulation.

In the tyre industry the use of high tackiness rubber or thin layers of high tackiness rubber bands instead of solvent-based tackifiers during the assembly is a very effective substitution. The combination of production steps (e.g. co-extrusion) is also an effective measure to avoid additional tackifying agents. For the pre-vulcanisation treatment water-based mould release agents are available as VOC substitutes.

The combination of production steps (e.g. co-extrusion), production line re-design to speed-up the process avoiding loss of compound tackiness or other production process improvements are also very effective measures to reduce the usage of tackifying VOC based solutions.

In the general rubber good industry water-based mould release agents are commonly used as solvent-free alternatives. Changes in the production process (e.g. co-extrusion) are also effective measures to reduce VOC emissions.

In case no VOC-free or VOC-reduced products or systems are available abatement technologies like adsorption by activated carbon or the use of regenerative thermal oxidation are effective VOC emission reduction measures.

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[1] CMR substances-carcingenic (R45,R49), mutagenic (R46), or toxic to reproduction (R60,R61)

[2] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: ‘Possible risk of irreversible effects’. The new wording is: ‘Limited evidence of a carcinogenic effect’. In the ‘old’ version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: ‘Possible risk of irreversible effects’. This new risk phrase does not include carcinogenicity. The ‘new’ version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to this change, a final decision on which version applies can only be given by the European Court

[3] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.

3 Description of the activity and related industry sectors

In Europe (EU 27), approximately 4200 companies produce rubber products. The total amount of transformed rubber in 2007 was 4 million tons (35% natural rubber, 65% synthetic rubber). [ETRMA 2008]

The rubber industry can be divided into two main groups of activities: tyre production and general rubber goods industry.

THE TYRE INDUSTRY IS THE MOST IMPORTANT USER OF RUBBER

Worldwide, around 70% of the natural rubber production is supplied to the tyre industry. In 2007, 88 tyre producing plants were operated in Europe. The annual tyre production in Europe[4] was 240 million units in 2006 (228 million units passenger car tyres and light vehicle tyres, 12 million medium & heavy commercial vehicle tyres) which is around 22 % of the worldwide tyre production.

The general rubber goods industry consists of more than 4100 companies, the majority being SMEs. It covers a wide range of products like medical, baby care, construction and automotive rubber goods. The automotive sector, with parts and components such as windscreen wipers, engine mountings, window seals, fan belts, etc., is the biggest consumer of rubber goods with 75% of the EU production [ETRMA 2008].

[4] EU27+ Turkey

4 Technical process description

4.1 Process flow and relevant associated VOC emissions

General rubber goods production

The flow chart in Figure 1 gives an overview of the main process steps of the general rubber goods production applying solvent-based products and provides an overview of possible VOC emissions during the production process:

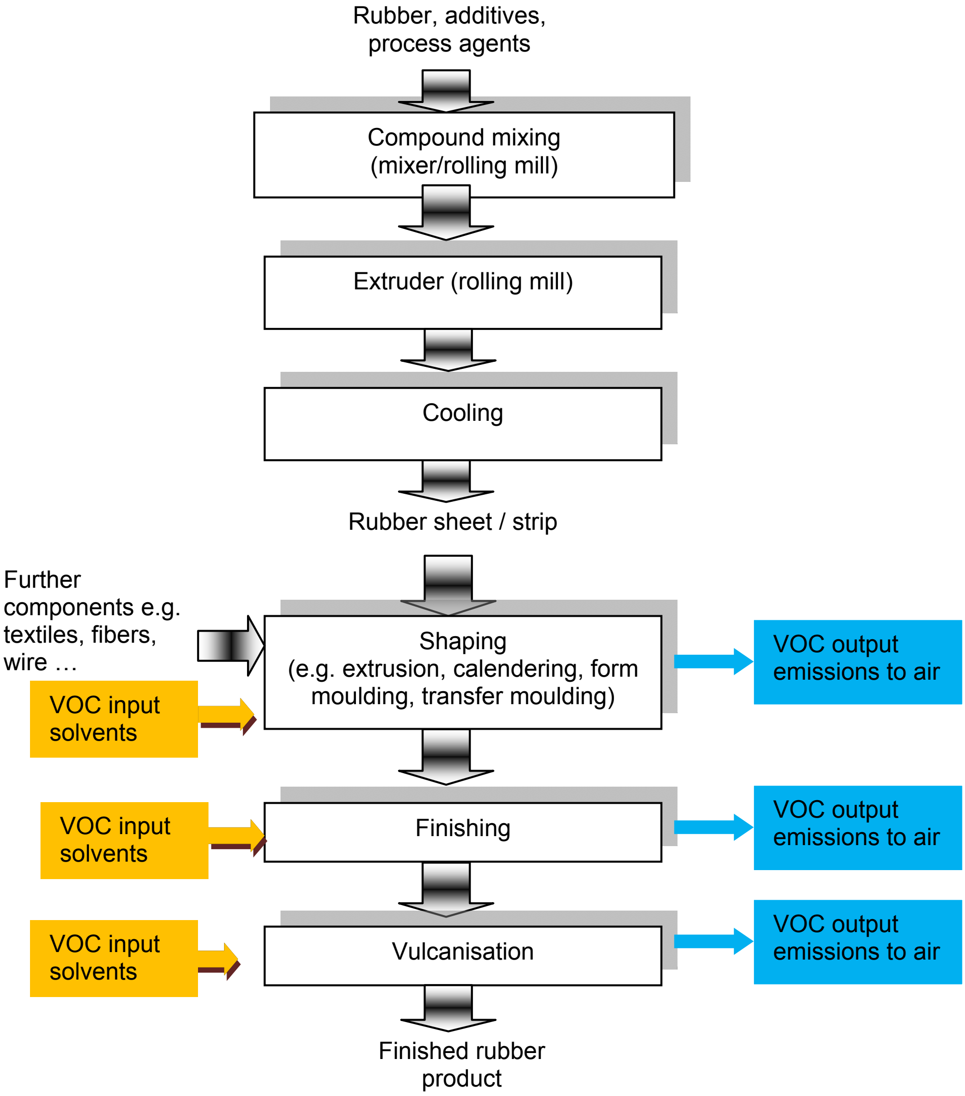

Figure 1: Possible VOC emission sources in general rubber goods production processes using solvent-based products

Tyre production

Figure 2 gives an overview of tyre production using solvent-based products and provides a summary of possible VOC emissions during the production process:

The compounding and mixing of the rubber sheet is analogous to the process described for the general rubber goods sector. In subsequent process steps like preparation of tyre components, assembly, finishing and before the vulcanisation process solvents are used.

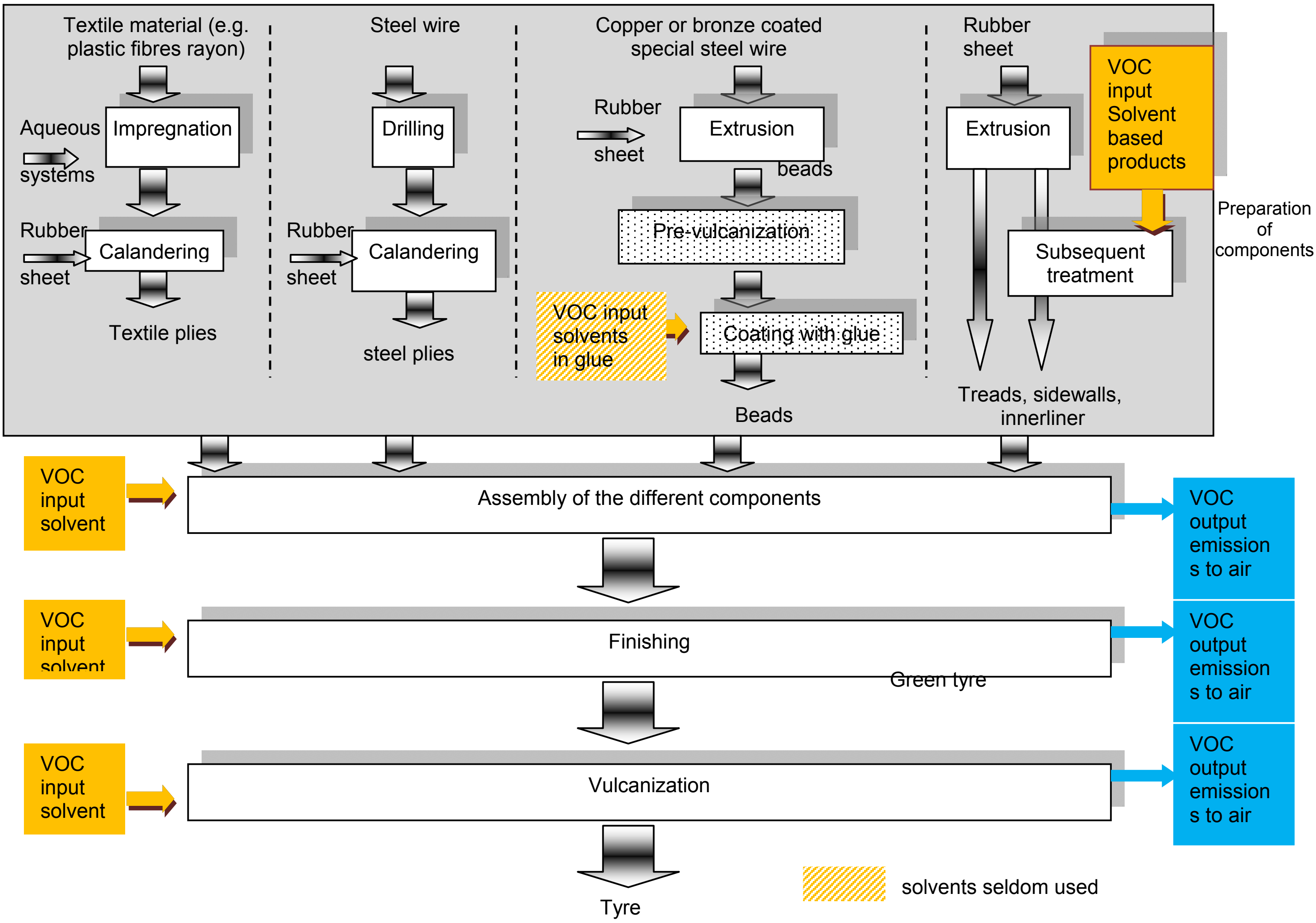

Figure 2: Possible VOC emission sources in tyre production processes using solvent-based products

The main function of the solvents in tyre production is the preparation of the uncured rubber surface before each production step. This is necessary to increase the adhesion by solvent to ensure different layers of compound are sticking together as needed (so called “refreshing” of rubber surfaces). Cleaning of compounds and of machinery in contact with rubber is also carried out using solvents, but is a less significant source of emissions, generally between 3 and 10% of solvent consumption.

The following table shows a typical breakdown of solvent emissions by process stage. This example is for a plant annually producing 46.500 tonnes of agricultural tyres with an input of 252.4 tonnes of solvents [SNCP 2002].

Table 3: Sources of VOC emission during the manufacture of agricultural tyres [SNCP 2002]

Process step	**Annual VOC emissions [t]**	**VOC emissions* [%]**
Preparation of beads	38.6	15
Preparation of treads (2 coatings)	68.4	27
Assembly of the tyre	41.5	17
Coating of the green tyre before vulcanisation	80.5	32
Reparation of tyres**	15	6
Cleaning activities	8.4	3
Total	**252.4**	**100**

* without any abatement technologies
**this production step is relevant after the vulcanisation process for tyres with minor defects

Car and truck and bus tyres production may have slightly different figures in terms of % of allocation of solvents in the production process (in general the tread preparation and extrusion may constitute the dominant factor). The total amount of VOC emissions depends on the dimension of the factory. A typical car tyre factory in the year 2000 was emitting from 400 to 800 tons of solvents per year.

4.2 Process description

General rubber good production

The general rubber goods sector covers a broad range of products with varying shapes, sizes and rubber-composition. As a consequence, different production steps may be necessary for different products. However, the following major process steps are essential for all rubber conversion processes:

- Compounding of rubber mixture
- Shaping
- Finishing

- Vulcanisation

For the compounding and mixing of rubber mixtures no solvents are used.

Preparation of components

Some products require the preparation of components e.g. fibres in the case of tubes or other re-enforced components. The preparation stage may involve the use of solvents.

For many products, a combination of rubber with metal (or another material such as a textile) is used. The metal typically has the function of stabilising or re-enforcing the product.

Shaping

Various techniques are used to shape the rubber mixture including extrusion, calendering, form moulding or transfer moulding.

Extrusion machines are typically used to form rubber into bars, tubes, profiles, or sheets or to encase cables and wires. Where extrusion is the only production process, the shaped rubber products subsequently pass directly to a drying oven for curing. Within the shaping process solvents are partly used.

Calenders are used to form thin sheets of rubber coated materials (e.g. fibres). For this type of production no organic solvents are in use.

Formed articles are produced by processes like pressing, transfer moulding and injection-moulding. These processes typically combine shaping and vulcanisation in one step. Solvents are used as mould release agents (see below vulcanisation).

Finishing

During this production step, the final product is built up from layers of extruded, calendered or re-enforcing materials (e.g. wire, aramid fibres, etc.).

Solvent based adhesives (“cement”) are used to stick together the different layers.

Vulcanisation / Curing

Vulcanisation changes the properties of the rubber from thermoplastic to elastic by cross-linking macromolecules of the rubber at elevated temperatures. No solvents are used for the vulcanisation process itself. But to increase the flow of the rubber mixture into the mould and to avoid sticking of the vulcanised product to the mould, solvent based mould release agents are often applied as pre-treatment before the vulcanisation.

Cleaning of equipment

Organic solvents are partly used for cleaning of equipment.

Tyre production

Tyre production consists of numerous process steps starting with the compounding of the rubber mixture, then the production of the component parts of the green tyre (e.g. textile cord, beads, treads), and finally the assembly and the vulcanisation of the green tyre. The different productions steps are illustrated in section 4.1.

Basically, a tyre consists of the following components:

- Inner rubber liner
- Belt of several layers of steel cord
- Two rings of steel bead wire coated in rubber
- Rubber side walls
- Various plies of re-enforcing fibres sandwiched in rubber
- A thick rubber tread

TYRES ARE BUILT UP BY SEVERAL DIFFERENT LAYERS OF RUBBER AND RUBBER COATED COMPONENTS

The manufacture of certain components of the tyre e.g. impregnated textile cord can take place either in the tyre production plant or at the plant where the textile is produced.

The main production steps are the following:

Mixing/Compounding

The compounding and preparation of the rubber mixture takes place in special mixers ("Banbury mixers"). After extrusion or calendering the final rubber compounds are ready for further application. This production step does not involve the use of solvents.

Preparation

This covers a number of different processes involving the preparation of the different components of the tyre like textile plies, steel belt, beads and treads. Extrusion of treads and other components in these steps are the processes mainly involved in the use of organic solvents in order to tackify the rubber.

Assembly

The individual components of the tyre are assembled during this phase and thus the tyre is built up layer by layer. Solvent-based products are used as “cement” (solvent with a small percentage of compound dissolved in) to adhere the different layers together. The main function of the cement is to prepare or to “refresh” the surface of the different layers, enhancing the tackiness of the different surfaces.

Finishing

After assembly of the components, forming/shaping of the tyre takes place during the finishing phase. During this production step solvents may be used as lubricants, for certain types of tyres. It does not represent a significant contribution to the total solvent consumption of the process.

Vulcanisation

During the vulcanisation process the rubber changes its properties from thermoplastic to elastic. In some cases the “green” tyre is treated with solvent-based mould release agents before the vulcanisation process. These enhance the flow properties of the green tyre into the mould.

Cleaning of equipment

Organic solvents are partly used for cleaning of equipment in contact with rubber.

5 Solvent use, emissions and environmental impact

5.1 Solvents used

General Rubber goods

In the general rubber goods industry the following solvents are commonly used as tackifiers and for cleaning activities.

Table 4: solvents used in the general rubber good manufacture [SNCP 2002]

solvent	**Function**
toluene	Adhesive
ethanol	Cleaning
trichloroethylene	Cleaning
Methyl ethyl ketone (Butanone)	Pre-treatment of components

Tyre industry

In the tyre industry, only heptane or light naphtha fractions are used as solvents in various process steps during manufacture. Heptane is the main component (90%) of the “cement” which is used for tackifying activities in the various assembly stages.

5.2 Solvent consumption and emission levels

The annual solvent consumption by the rubber industry is ~ 4% of total European solvent consumption [ESIG].

THE VOC EMISSION FACTOR IN THE RUBBER INDUSTRY HAS DECREASED SIGNIFICANTLY IN THE LAST 10 YEARS

In the case of tyre manufacture the average emission factor has changed in the last 10 years from 7.1 kg/t of tyre to about or even less than 3 kg/t of tyre for certain types of tyres [SNCP 2002], [Bridgestone 2008A], [Michelin 2007], [Pirelli 2007]. In 2000, VOC emissions from tyre production were estimated to be 22 kt representing 0.21% of the total NMVOC emission in the EU 25 [EGTEI]. In general rubber goods manufacturing the average solvent emissions was reduced from 13.8 kg/t of product (1990) to 8 kg/t of product in 1999 [SNCP 2002]. At present average VOC emissions are below 5 kg/t of product.

5.3 Key environmental and health issues

VOC emissions, together with NO_x emissions, are precursors of ground level ozone formation in the presence of sunlight. Existing occupational workplace limits should be taken into consideration.

Emissions of VOC to air may occur from:

- the storage of the solvents
- the preparation of components

- the assembly of components
- finishing
- vulcanisation
- cleaning operations.

Spills and leaks from storage areas may result in emissions to soil and groundwater.

The process generates waste containing solvents which need to be disposed in a way that emissions to air, soil and groundwater are prevented or limited.

In the general rubber good production the halogenated solvent trichloroethylene (R45, R68; R67; R36/38; R52/53) is of special concern.

6 VOC Substitution

The following sections describe potential substitutes for VOC (using VOC-free and VOC-reduced systems). There are also descriptions of the application technologies or special conditions needed and the advantages and disadvantages compared to systems that use solvents with a high VOC content.

6.1 VOC-free systems

This section describes the ways that VOC-free products or systems can be used to replace the organic solvents currently used.

6.1.1 Water-based systems

General: cleaning

Solvent based cleaning activities can be substituted in most cases by VOC-free products like water-based cleaners with the same cleaning properties.

Tyre production

Water-based systems are available and in use for the pre-vulcanisation treatment, which in conventional systems is a major source of VOC emission.

WATER-BASED MOULD RELEASE AGENTS ARE REDUCE THE USE OF SOLVENTS SIGNIFICANTLY

The use of these water-based mould release agents results in higher energy costs for the drying process. In addition the drying time is prolonged.

General rubber goods production

Water-based alternatives are available for injection, compression or transfer moulds [Henkel 2008].

6.1.2 Switch to VOC-free technology

Tyre production: Use of high tackiness rubber

The assembly of tyre components uses solvent based products as tackifying agents, but the same effect can be achieved using an adhesive rubber strip containing tackifying resins in the formulation and thus solvent based cements are not necessary later in the assembly process.

THE USE OF AN ADHESIVE RUBBER BAND IN THE TYRE ASSEMBLY IS AN EFFECTIVE MEASURE TO REDUCE VOC EMISSIONS

The use of high tackiness rubber or thin layers of high tackiness rubber bands might require both some modifications of the assembly process and high investment costs. In addition the adoption of the tackifying resins and the technical realisation of the reformulated rubber is very time and cost intensive.

Generally the improvement of tackiness performance of compounds is an effective measure to reduce VOC emissions for all extruded compounds.

Tyre-Production: Co-extrusion

Co-extrusion means that different layers or components which are foreseen to be stuck together during the assembling of the tyre are extruded in one production step. With this technology the use of tackifying agents - which are necessary to adhere the layers - can be avoided.

This technology requires high investment costs because the extrusion machines have to be adjusted – in the best case - or replaced by new ones.

For new lines of passenger tyres this technology is state of the art. In some cases solvent application might be still necessary but only to a very limited extent compared to conventional installations.

General rubber goods: Solvent free production of printing blankets

NEW TECHNOLOGY ALLOWS 100% VOC-FREE PRODUCTION OF PRINTING BLANKETS

Printing blankets typically consist of three different rubber layers. The production of printing blankets is conventionally carried out by solvent-intensive painting technology.

Since a few years a new production process is available. The roller-head-installation combined with a three-roll calender allows a 100% free production of printing blankets.

This new technology requires high investment costs.

[Contitech 2008], [KGK 2004]

6.2 VOC-reduced systems

If the complete substitution of organic solvents is impractical then changing to systems with a reduced VOC content, such as those described in this section, can decrease emissions.

Tackifying agents with reduced VOC-content or less volatile components are available, but the applicability of these products needs to be tested for each process. In the tyre industry cements are available with different solid content (e.g. 5, 8, 10, 15 or 20%).

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements and abatement techniques can be used to reduce VOC emissions if VOC substitution as described in section 6 is not possible.

In the rubber industry process improvements play a very important role to reduce VOC emissions and the following measures are commonly applied.

7.1 Process improvements

7.1.1 Tyre production

a) Installation of new extrusion technology (see co-extrusion under section 6.1.2)

With the installation of new extrusion technologies the number of production process using VOC relevant rubber solutions can be reduced (e.g. the different production steps for components can be reduced by combining them in one step)

PROCESS IMPROVEMENTS OFTEN REQUIRE HIGH INVESTMENT COSTS

b) Installation of an assembly machine associated with the extruder

Directly after the extrusion process the rubber surface typically is warm and thus stickier. This tackiness steadily decreases over the course of time. When the extrusion process is associated directly with the assembly this process-related tackiness can be utilised to stick layers together. The use of tackifying agents can be significantly reduced.

c) Installation of a new system replacing the extrusion/coating of textile plies and other plies: this implies the full redesign of the process and therefore can only be applied to completely new installations and only for certain tyre types (passenger tyres)

d) Use of auto-spray systems for the spraying of the solvent-rubber solution (cement) on the extruded components instead of manual wiping of components

e) Installation of peristaltic pumps: accurate deposition of solvent-rubber solution over the extruder to minimize excess usage of solvents instead of hand brushing or dip tanks which often can lead to excessive application of solvent: the dissolution is applied drop by drop on treads

f) Use of closed tank systems like solvent boxes with plunger can instead of open boxes

The measures mentioned under points d) – f) are aiming to optimize the application of solvent/rubber solutions. Apart from the investment costs, these measures may also cause increased maintenance costs (e.g. blockage of the holes from which the rubber solution is applied on components, due to the rubber solids accumulation with time).

7.1.2 General rubber goods production

a) Installation of new extrusion technology (see section 6.1.2) co-extrusion)

b) Use of auto-spray systems instead of manual wiping of components

c) Use of closed solvent tank systems

7.2 Abatement technologies / End of pipe measures

Exhaust gases can be treated to reduce VOC emissions using either carbon filters to adsorb and then reuse VOCs or by thermal oxidation.

7.2.1 Activated carbon adsorption

Activated carbon is suitable for both halogenated and non-halogenated solvents. The recovery of the solvents can either take place on-site or externally. On-site recovery is of limited benefit to small companies as the carbon regeneration equipment is costly and experience is needed to use it properly. This is especially true for the systems for halogenated solvents.

Activated carbon adsorption is applicable for flow rates between 100 and 100,000 m³/h, with solvent concentrations of up to 50 g/m³. The recovery rate depends on, among other things, the type of activated carbon used and the operating conditions. Fresh activated carbon costs about 1 - 1.50 €/kg, while the cost for external recovery of the solvents is about 0.60 €/kg. [Donau Carbon 2008]

Compared with the investment costs for thermal oxidisers (about 150,000 €), those for activated carbon filters are significantly lower (20,000-30,000 €) but the operational costs (replacement of the activated carbon) are higher. [CTP 2008]

In the tyre manufacturing industry activated carbon is only used to a minor extent due to the high flow rates and high VOC concentrations typically occurring in this industry.

7.2.2 Thermal oxidation of solvent emissions

Thermal oxidation is only recommended for non-chlorinated solvents unless high temperature (> 1,100 °C) is used. Otherwise, there is a risk of generating chlorinated pollutants (e.g. dioxins).

Two types of thermal oxidiser are in use in the rubber industry, regenerative and recuperative. Both destroy VOCs by incineration (oxidation), but the systems differ in how waste heat is recovered.

Regenerative thermal oxidation has at least two heat exchangers, consisting of beds filled with material that will allow air to pass while serving as a mass to absorb and store heat. While one bed is heated by the exhaust gas from the burner another bed gives off its stored heat to the VOC laden incoming gas. In recuperative thermal oxidation the heat is transferred directly - via a heat exchanger - from the outgoing air stream to the incoming air stream.

Regenerative oxidation tends to be more efficient than recuperative thermal oxidation as it uses the recovered energy more efficiently to pre-heat incoming process air to oxidation temperatures (~ 800 °C), consequently its operating costs are significantly lower than for recuperative oxidation systems. Regenerative thermal oxidation systems are particularly effective for process streams with relatively low solvent loadings but their operating costs are highly dependent on the efficiency of the heat exchanger.

Regenerative thermal oxidation systems are widely used because they are relatively insensitive to the composition of the solvents in the process air and the concentration.

Recuperative systems are mainly used for small flow rates - at higher rates the systems are not cost effective. They are often used in combination with catalytic oxidation systems. Catalytic systems operate at much lower temperatures (350 – 500 °C) therefore the emission of NO_x is significant lower. Dust and catalyst poisons (e.g. sulphur-compounds) must be avoided.

THE AUTO-THERMIC POINT OF REGENERATIVE THERMAL OXIDATION IS ABOVE 2-3 G VOC/NM³

Natural gas is needed to heat up thermal oxidisers to an operating temperature of 800 °C (or 350-500 °C for catalytic systems) and the process is only autothermic when the VOC concentration of the waste gas is above 2-3 g VOC/Nm³ (for regenerative thermal oxidation). The resulting heat of the burning process, however, can be recovered and can be used for different purposes e.g. steam production.

7.3 Organisational measures

Significant reductions in VOC emissions may be achieved by organisational measures, such as avoidance of interim steps or long waiting times between production steps. Long waiting times between the different production steps require a refreshing of the surfaces as the stickiness of the rubber surface decreases after the production process by and by.

8 Summary of VOC emission reduction measures

Table 5 summarizes the various approaches to substitute or reduce VOC emissions as described in sections 6 and 7:

Table 5: Measures for VOC substitution and VOC reduction for rubber conversion

Objectives	**Description**	
	General rubber goods industry	**Tyre industry**
VOC-free Systems	- Use of water-based mould release agents - Use of water-based cleaning agents - New production technologies (e.g. for printing blankets)	- Use of water-based mould release agents - Use of water-based cleaning agents - Co-extrusion of components - Use of high tackiness rubber
VOC-reduced Systems	- Use of VOC reduced tackifying agents	- Use of VOC reduced tackifying agents
Process Improvements	- use of auto-spray systems instead of hand wiping of components - use of closed tank systems	- installation of an assembly machine associated with the extruder - installation of a new assembly system which replaces the extrusion/coating of the textile plies - use of auto-spray systems instead of hand wiping of components - installation of a dip tank on the extruder instead of hand brushing treads with solutions - use of closed tank systems
Abatement Technologies	- Use of activated carbon adsorption - Use of regenerative or recuperative thermal oxidation	- Use of activated carbon adsorption (only for small production units) - Use of regenerative or recuperative thermal oxidation

9 Good practice examples

9.1 Example 1: Tyre production

At a tyre production plant the major part of solvent input (95%) is in cement (tackifying agent) and the remaining 5% is used for cleaning or mold releasing.

Before making any changes, the average VOC emission was 10-11 kg/t of tyres. The following measures have since been introduced to reduce the VOC consumption and thus the emissions:

- Application of solvent-reduced or solvent-free tackifying agents
- Application of water-based mould release agents
- Installation of an improved extrusion method
- Reformulation of the products
- Installation of peristaltic pumps on the extruder instead of hand brushing or dip tanks
- Redesign of the process (avoidance of interim steps, speeding-up the production process to avoid refreshing of the rubber before next production step.
- Reallocation of process steps to minimize waiting time
- Use of closed tank systems

Major VOC emission reductions could be achieved by a reformulation of compounds, redesign of the process and a reallocation of the process steps. In addition, with these organisational measures the speed of the production line could be increased significantly.

After the implementation of all these measures, VOC emissions have been reduced up to 3 kg/t of tyres. No abatement technologies have been necessary to achieve these reductions.

9.2 Example 2: Tyre production

The company involved produces tyres for the agricultural sector (46,500 tonnes/year). The production steps comprise the mixing of rubber compounds, preparation of components, assembly/finishing and vulcanisation.

The company identified the activities shown in Table as VOC emission relevant:

Table 6: Overview of possible reduction measures and corresponding VOC emission reductions and costs

Description of the technology	**Annual reduction of solvent consumption**	**Costs (constant production) [€]**
Reduction of the solvent use during the extrusion of the beads	-7.92%	0
Elimination of the first coating step for the treads	-13.55%	-15,000
Installation of new equipment for the assembly	-7.92%	5,000,000
Substitution of solvent based solution for the repair of agricultural tyres by water-based products	-5.94%	2,000
Installation of equipment for the production of contact rubber for the treads on the extrusion line	-6.73%	300,000
Elimination of solvent based cleaning agents	-1.35%	-1,500
Replacement of solvent based products for the treatment of the tyres before vulcanisation by water-based systems	-2.18%	2,500
Replacement of the solvent based products used during the assembly of the tyres following process modifications	-15.85%	43,000
Total	**-61.45 %**	**5,326,000**

Apart from the significant VOC reduction also the productivity of the plant will increase with the implementation of the above described measures and new technologies. But the return of investment will be several years due to the high initial investment costs of certain measures.

10 Emerging techniques and substitutes under development

No emerging techniques have been reported.

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Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Guidance 19:

Vegetable oil and animal fat extraction and vegetable oil refining activities

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses vegetable oil and animal fat extraction and vegetable oil refining, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emission Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
The activity "vegetable oil and animal fat extraction and vegetable oil refining activities" is defined as 'any activity to extract vegetable oil from seeds and other vegetable matter, the processing of dry residues to produce animal feed, the purification of fats and vegetable oils derived from seeds, vegetable matter and/or animal matter. The SE Directive covers installations in which this activity is taking place with an annual organic solvent consumption greater than 10 tonnes.

The SE Directive lays down the following activity specific emission limit values for vegetable oil and animal fat extraction and vegetable oil refining activities:

THE SE DIRECTIVE APPLIES TO OIL & FAT EXTRACTION OR REFINING IF A SOLVENT CONSUMPTION OF 10 TONNES PER YEAR IS EXCEEDED

Table 2: Emission limit values of the SE Directive

<table>
<tr><th colspan="5">SE Directive - Emission limit values (ELVs)
(Annex II A – activity No. 19)</th></tr>
<tr><th>Activity</th><th>Solvent consumption threshold [tonnes/year]</th><th>ELVs in waste gases [mg C/Nm^3]</th><th>Fugitive emission values [% of solvent input}</th><th>Total ELVs [kg/tonne]</th></tr>
<tr><td>Vegetable oil and animal fat extraction and vegetable oil refining activities</td><td>> 10</td><td></td><td></td><td>Animal fat: 1.5
Castor: 3
Rape seed: 1
Soya beans (normal crush): 0.8
Soya beans (white flakes): 1.2
Other seeds and other vegetable matter: 3 (1)
1.5 (2)
4 (3)</td></tr>
<tr><td colspan="5">Special provisions:
(1) Total emission values for installations processing individual batches of seeds and other vegetable matter should be set by the competent authority on a case-by-case basis, applying the best available techniques.
(2) Applies to all fractionation processes excluding de-gumming (the removing of gums from the oil)
(3) Applies to de-gumming</td></tr>
</table>

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[1] as well as for halogenated VOCs which are assigned the risk phrases R40 or R68[2]. There is a general obligation to replace CMR substances – as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated[3] VOC with R40/R68 the ELVs in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

NEARLY ALL THE VOC EMISSIONS IN THIS INDUSTRY SECTOR ARISE FROM THE VEGETABLE OIL EXTRACTION

Animal fat extraction is typically carried out by using solvent-free processes like expeller, pusher or a basket centrifuge. Animal fat extraction using solvents is almost phased out in Europe.

In case of vegetable oil solvent based extraction is widely applied since none of the substituting technologies is currently competitive (see section 10). Therefore the application of effective emission prevention and reduction measures (like mineral oil scrubber, condenser, separator and re-boiler) is of great importance for the vegetable oil extraction industry. It is state of the art that the solvent used is in a closed loop process and 99.9 % of the input is reused.

With regard to refining, solvents are only used if a fractionation process is included. This is can lead to additional VOC emissions from refining, which are not related to the extraction process.

3 Description of the activity and related industry sectors

Animal fat extraction

Animal fat extraction (using hexane) is very effective as only 2-8 % of fat remain in the raw material. Other processes using expeller, pusher or a basket centrifuge leave higher percentages (10 to 17 %) of fat behind. As a result of stricter environmental regulations the solvent-based method has, however, largely been ceased in Europe over the past 20 years, with the exception of two companies. [Baert 2008]. The products from the process

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[1] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

[2] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: ‘Possible risk of irreversible effects’. The new wording is: ‘Limited evidence of a carcinogenic effect’. In the ‘old’ version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: ‘Possible risk of irreversible effects’. This new risk phrase does not include carcinogenicity. The ‘new’ version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to this change, a final decision on which version applies can only be given by the European Court

[3] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.

are meal and fat. As long as the price of meal and fat are similar, there is no benefit in extracting higher levels of fat from the raw material and therefore solvent extraction is not advantageous. Because the prices have been similar for many years nearly every company switched voluntarily away from hexane extraction to less efficient melting processes to obtain fat.

In the following this guidance document only deals with the extraction or fractionation of vegetable oil as the share of solvents which is used in animal fat is negligible compared to the use for vegetable oil.

Vegetable oil extraction

Worldwide approximately 22 different vegetable oils are produced on a commercial scale. Since the fruits from tropical plants (e.g. coconut, palm, palm kernel) perish rapidly, they are directly processed into oils in the countries of origin. Most large scale vegetable oil extractions from the three main oilseeds (soybean, rapeseed and sunflower seed) are performed globally by solvent extraction. In Europe (EU 27) the following annual quantities of seeds are processed: soybeans (~13.7 MnT/year), rapeseed (~14.9 MnT/year) and sunflower seeds (~5.2 MnT /year). [FEDIOL 2006]

The structure of the industry has changed significantly in the European Union over the past ten years. Many independent companies have disappeared and large multinational groups have formed. The crushing industry is now rather stable with respect to applied technology, size of operations and seeds. About 75 % of the European capacity now belongs to four major international groups. [FEDIOL 2008]

Across Europe there are about 150 production units employing about 20.000 people. Some concentrate on one type of seed while others process several kinds of seeds, of which some are imported (mainly soybeans, sunflower) and some are produced locally (mainly rapeseed and sunflower seed). [FEDIOL 2008]

Table 33 lists the production of crude vegetable oils and fats from each of the EU-27 (except Luxembourg) in 2006.

Table 3: Production of crude vegetable oils and fats in the EU-27 [weight %]

AT	**1,1%**	**UK**	**6,8%**
DE	**28,5%**	**CY**	**0,0%**
BE	**4,6%**	**CZ**	**3,0%**
DK	**2,1%**	**EE**	**0,2%**
ES	**7,3%**	**HU**	**2,8%**
FI	**0,8%**	**LV**	**0,2%**
FR	**12,6%**	**LT**	**0,1%**
EL	**1,0%**	**MT**	**0,0%**
IE	**0,0%**	**PL**	**4,9%**
IT	**4,7%**	**SI**	**0,0%**
NL	**7,4%**	**SK**	**1,1%**
PT	**4,5%**	**BG**	**1,7%**
SE	**0,8%**	**RO**	**3,6%**

Solvent fractionation

During the fractionation the starting material (oil) is separated into a low melting fraction (olein) and a high melting fraction (stearin). Fractionation with solvents delivers high separation efficiencies and high stearin yield and is therefore chosen if high stearin yields are required or stearin oil ratios need to be adjusted.

4 Technical process description

4.1 Process flow and relevant associated VOC emissions

In the solvent extraction process VOC emissions occur during cooling, storage and transportation of meal and crude oil. The flow chart in Figure 1 does not describe the oil refining process in detail but concentrates on the extraction process, since the amount of residual solvent in the crude oil is much lower than in the extraction step:

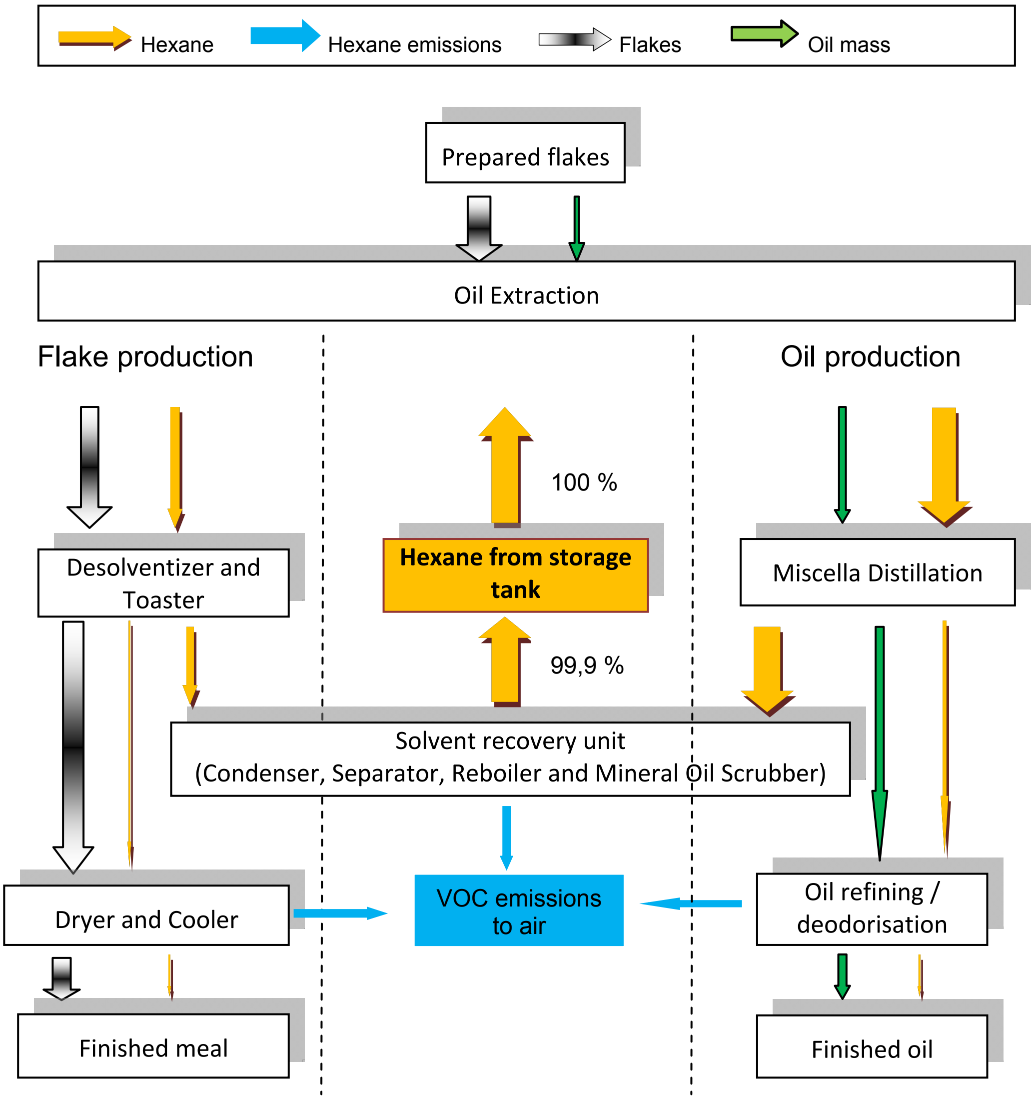

Figure 1: Flow diagram from vegetable oil extraction process [EPA 1995] [NPI 1999]. [VDI 2000]

There are no legal requirements for the amount of residual hexane in meal or oil but general provision are set in Council Directive 88/344/EEC of 13 June 1988 on the approximation of the laws of the Member States on extraction solvents used in the production of foodstuffs and food ingredients[4] and levels generally need to be kept as low as technically possible.

Fugitive emissions can occur during the storage of the meal or the deodorisation of the crude oil. On average, about half of the hexane which is contained in the finished meal is usually emitted during the storage period.

During the process the system is kept under slight vacuum to prevent hexane escaping from process equipment. These vent gases are passed through the condenser and the mineral oil absorption system.

In addition to the hexane used as a solvent in oilseed extraction, solvents can be used in the fractionation process during oil refining.

The hexane emissions from the deodorisation process in the refining process are not treated due to their low concentration and small amount.

Typical process values for hexane based extraction of vegetable oil are summarized in Table 4.

Table 4: Typical hexane value ranges [TC 2008], [VDI 2000] [IU 2008]

Component	**Value**
Oil content in prepared flakes	6 – 11%
Miscella	10 – 30 % oil, 70 - 90 % hexane
Hexane in crude oil	~ 0.02 -0.05 kg per tonne used seed
Finished oil	~ 1 ppm
Mineral oil scrubber hexane emissions	0.05 – 0.15 kg per tonne used seed
Hexane concentration in exhaust air after mineral oil system	10 – 25 g/m³
Hexane emission into exhaust air from Meal dryer/cooler	0.01 – 0.05 kg per tonne used seed
Hexane in finished meal	300 – 500 ppm
Hexane emission during storage of meal	~ 200 ppm
Tank breathing and fugitive emission	~0.01 kg per tonne used seed
Hexane in waste water	< 0.0001 kg per tonne used seed
Total hexane emissions	0.5 – 1.2 kg per tonne used seed*

* for more details see Table 5.

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[4] OJ L 157, 24.6.1988, p. 28

4.2 Process description

Preparation

Oilseeds are prepared for oil extraction by cleaning, dehulling, flaking, conditioning and in many cases pressing.

Extraction

The oil from the rough ground raw materials (oil seeds with a low oil content or expeller pulp produced by previous cold or hot pressing) is extracted using a solvent, such as hexane. The residues, then known as extraction meal, have a residual oil content of only 0.5 – 1.5 % solvent.
Hexane based solvent extraction can be used alone or together with an oil expeller/press. With the expeller 70 to 75 % of the oil can be extracted - depending on the seed. The pulp is then mixed with hexane to extract up to 95 % of the total oil content. The oil dissolved in hexane is then separated by distillation.

Desolventizer & Toaster

The hexane must be removed from the flakes after the solvent extraction. Two removal technologies are established, the `conventional desolventizing' for animal feed and the `flash' desolventizing for human feed. Flakes that enter the desolventizer contain about 35 to 40 % of solvent.

Conventional desolventizing for animal feed

Hexane can be stripped from the flakes using either contact (“toasting”) or non-contact processes. After heat-assisted drying the flakes are cooled with ambient air. The defatted and grounded meal can be used for animal feed.

Flash desolventizing for human food products

In the flash desolventizing process the solvent is removed from the flakes, under vacuum, using non-contact steam or superheated hexane. After the desolventizer a steam stripper step is applied, the gases of the desolventizer and the stripper are collected and passed to the solvent recovery system.

Less than 5 % of the produced flakes are used for human food (white flakes). They are produced separately and are not combined with flakes for animal feed.

FLASH DESOLVENTIZING IS USED FOR THE PRODUCTION OF WHITE FLAKES FOR HUMAN DIET; CONVENTIONAL DESOLVENTIZING IS USED FOR THE PRODUCTION OF MEAL FOR ANIMAL FEED.

Dryer and Cooler

After the desolventizer the meal is dried and cooled before storage. The removed hexane is reused with little fugitive emissions (10-50 g per tonne used seed) to air.

Miscella Distillation

The solvent-oil mixture (Miscella) containing approximately 10 to 30 % oil is undergoing a multi-stage distillation process for solvent recovery. The desolventising of the oil is done by exposing the miscella to steam (contact and non-contact).

Oil refining (deodorisation)

Oil refining is done to prepare the oil for shipment. Unwanted substances as phosphatides, color-producing substances, residual soap or substances with an undesirable smell are removed. During deodorisation volatile compounds are removed by steam injection under a high vacuum.

Solvent recovery system

The solvent recovery system consists of condenser, separator, reboiler and mineral oil scrubber.

Hexane contaminations are either in water or air. The majority of the hexane in the water is removed with a separator. With a reboiler the amount of hexane in the water is further decreased. The majority of the hexane in the air is removed with a condenser, which liquefies the hexane. The final hexane removal from the air is done by a mineral oil scrubber (see also section chapter 7)

5 Solvent use, emissions and environmental impact

5.1 Solvents used

For decades only hexane has been used for solvent-based vegetable oil (and animal fat) extraction in Europe.

5.2 Solvent consumption and emission levels

The overall non methane VOC emissions from vegetable oil extraction were approximately 50 kt in the EU 25 in the year 2000. [Synopsis 2005].

Solvent vegetable oil extraction

Typical hexane emissions from the solvent extraction process are given in Table 5:

Table 5: Typical hexane emissions from the solvent extraction process [VDI 2000] [IU 2008]

Hexane emissions kg hexane per tonne seed	
Soybeans	0.5 – 0.8
Rapeseed	0.5 – 1.0
Sunflower seed	0.5 – 1.0
Linseed	approx. 2
Castor beans	< 3

Solvent fractionation

In case of solvent fractionation emissions only sum up to approximately 3 kg per tonne produced oil due to the use of emission prevention and abatement techniques [Cryo-condensation, membrane systems, good housekeeping, leak detection and repair programme (LDAR-programme)]. Emission might also occur from the vent system, rectification (water removal) or emit as fugitive emissions. [FEDIOL Q 2008]

5.3 Key environmental and health issues

In vegetable oil & animal fat extraction and vegetable oil refining mainly hexane is used for different types of processes e.g. extracting and fractionating.

VOC emissions together with NO_x emissions are precursors of ground level ozone formation in the presence of sunlight. Occupational workplace limits should also be taken into consideration.

Emissions of VOC to air may occur from both the process and the product storage.

Hexane poses a particular health hazard as it may cause peripheral nerve damage following chronic (long- term) exposure [ESIG 2003]. Hexane is flammable, harmful, dangerous to the environment and toxic to reproduction (category 3). As a consequence of its potential environmental and health impact hexane is classified as R48/20 substance with some ‘danger of serious damage to health by prolonged exposure’.

Acetone is extremely flammable as liquid or vapour. It causes skin and eye irritation and is harmful if swallowed. Vapour may cause flash fire and is harmful if inhaled. High vapour concentrations may cause dizziness.

Meal which has been in contact with hexane is only used for animal feeding; meal for human food is completely solvent free.

6 VOC Substitution

Various solvent free extraction processes have been tested for vegetable oil extraction (see section 10) but at the moment none of these technologies is considered economically and/or technically feasible in Europe (see section 10 on emerging techniques).

THERE IS NO VOC FREE COMPETITIVE SUBSTITUTION FOR SOLVENT BASED VEGETABLE OIL EXTRACTION YET

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements and abatement techniques can be used to prevent and reduce VOC emissions, where VOC substitution is not possible. The following measures are commonly applied for vegetable oil solvent extraction:

7.1 Abatement technologies / End of pipe measures

Condenser, hexane/water separator and reboiler

The collected hexane-laden air from the plant is passed through a water shell-tube condenser. The treated air includes the vented air from the surrounding needed to maintain a small vacuum in the process equipment. This small vacuum prevents fugitive emissions from the equipment. Due to the low boiling point of hexane (69°C) a water shell-tube condenser – with low energy consumption and costs - is sufficient to recover most of the solvent. In a separator, the hexane/water mixture is separated into hexane which is reused, and water, which is further treated in the reboiler. The reboiler heats the water to at least 85°C to evaporate remaining solvent [FEDIOL 2007]. The vapour from the reboiler is directed to the condenser and the waste water containing less than 3 mg/l hexane is fed to the waste water system. The air from the condenser still contains small amounts of hexane and is directed to the mineral oil scrubber.

Mineral oil scrubber

Non condensable components and hexane are removed from the air coming from the condenser in a mineral oil scrubber consisting of an absorption column with cold, food grade mineral oil. The hexane-laden mineral oil is then passed through a steam stripping column to recover the hexane for reuse. After cooling the mineral oil is reused in the mineral oil scrubber.

Cryo-condensation

In comparison to the conventional condensation which often uses water as cooling agents in case of cryogenic condensation coolants like nitrogen are used to achieve very low temperatures (e.g. in case of nitrogen -120 °C).

Cryogenic condensation efficiency typically exceeds 99% and so it offers a very high degree of VOC emission reduction. It is also a very versatile process. Since the condensation process is influenced by the vapour pressure of the compound to be separated, adapting the condenser operating conditions allows handling the wide range of concentrations and compounds present in the pharmaceutical industry.

For cryogenic condensation the flow rate can vary between 10 up to 3000 m³/h. The minimum loading should be above 20 g VOC/Nm³ and the pressure between 20 mbar and 6 bar [BREF LVOC, PanGas, Glatt]. Cryogenic condensation is therefore appropriate for low flows and high concentrations. By varying the cooling temperature different types of solvents can be recovered.

CRYOGENIC CONDENSATION IS PARTICULARLY USED FOR CHLORINATED OR OTHER VALUABLE SOLVENTS

Operational costs depend on the cooling gas used; the cost of liquid nitrogen is around 30-50 €cent/l.

This technology is used for the solvent fractionation.

7.2 Process improvements

Diffuse emissions occur during storage, transport and processing of meal containing some residual hexane. In addition, fugitive emission may occur through flanges, valves and pumps, but are largely prevented by the vacuum conditions of the system.

Fugitive VOC emissions may also arise from solvent storage, handling and leaks. The most commonly used measures to reduce these emissions involve process improvements to collect escaping vapours from process systems, storage tanks, and handling areas etc. in local exhaust ventilation hoods for subsequent treatment or abatement. The fugitive emissions in this industry are less than 0.1%

FUGITIVE EMISSIONS CAN BE REDUCED BY GOOD HOUSEKEEPING, LEAKAGE CONTROL AND THROUGHPUT MEASUREMENT INSTALLATIONS

A wide range of best practice and process improvements are possible which aim at containing VOC emissions. The following list is not exhaustive:

- Leakage monitoring
- Process parameter optimisation
- Throughput measurement installations
- Increased efficiency from optimised process technologies
- Back venting to the solvent delivery tanks during bulk storage tank filling
- Improved exhaust air collection systems
- Implementing leak prevention systems

8 Summary of VOC emission reduction measures

The following table summarizes the VOC emission reduction measures discussed in chapters 6 and 7:

Table 6: Measures for VOC substitution and reduction in vegetable oil extraction

Objectives	**Description**	**Applicability**
VOC-free systems	Test phase	
VOC-reduced systems	Test phase	
Process improvements	Collecting of exhaust air Proper handling of solvents Solvent recovery/recycling Good housekeeping	Applicable in all cases and state of the art
Abatement technologies	Condenser, water separator, re-boiler Mineral oil scrubber Counter current de-solventizer and toaster	Applicable in all cases and state of the art

9 Good practice examples

All European companies extracting vegetable oil use the same process and therefore solvent reduction resulted so far mainly from company specific improved process parameters.

Best case examples would include company specific know-how and this might lead to competitiveness issues.

10 Emerging techniques and substitutes under development

MANY SUBSTITUTIONS FOR THE USE OF SOLVENT FOR VEGETABLE OIL PRODUCTION HAVE BEEN TESTED, BUT ONLY WITH MINOR SUCCESS YET.

Different technologies have been developed to obtain vegetable oil. These include enzymatic, supercritical CO_2, osmotic shock and ultrasonic extraction. None of these emerging techniques are realised on an industrial scale. The main unsolved problems are of economic and/or technically nature. These technologies mostly require significantly more energy than the conventional hexane-based extraction.

Supercritical Fluid extraction

Nearly 100% of the seed oils can be extracted with supercritical fluids, such as CO_2. This method, however, needs special equipment for containment and pressure. In this extraction process CO_2 is liquefied under pressure and then heated to the point that the CO_2 has properties of both a liquid and a gas. This occurs at approximately 80°C and 700 bar. Yields with supercritical fluid extraction are typically much higher than those of extractions performed by traditional techniques. [JACOS 2006] This process is 100 % solvent-free but very energy intensive mainly due to the high pressure which has to be reached. [TC 2008].

Enzymatic extraction

Enzymes are used to degrade the cell walls with water acting as the solvent, which makes fractionation of the oil much easier. Although this process would result in process improvements it is not implemented due to the high operational costs [OILGAE] [TC 2008]

Novo Nordisk calculated a pilot plant for enzymatic oil extraction. Table 7 and Table 8 show a comparison between this plant and an existing solvent extraction plant. Both plants were dimensioned for processing 100,000 tonnes of rapeseed per year.

Table 7: Comparison of output form an enzyme process and conventional process processing 100,000 t/y of rapeseed

Product	Enzyme process production t/y	Conventional process production t/y
Oil	35,000	38,000
Protein meal	32,400	---
Fibres	16,302	---
Syrup	28,303	---
Rape meal	---	62,000

Table 8: Comparison costs (mio €/y) for an enzyme process and conventional process processing 100,000 t/y of rapeseed.

	Cost unit	**Enzyme Process [mio €/y]**	**Conventional Process [mio €/y]**
Investment costs	Process equipment	3.25	6.07
	Drying equipment	3.59	
	Utilities	1.51	
	Engineering and installations	1.41	1.49
	Buildings (silos....)	3.28	3.17
	Unexpected costs	1.69	3.03
	Total	**14.73**	**13.76**
Operational and maintenance costs	Manpower	0.62	0.75
	Energy	1.95	0.66
	Subsidiary material enzyme	4.94	0.00
	Subsidiary material chemicals	0.65	0.13
	Production costs per year	**8.16**	**1.55**

The enzyme process provides oil and protein of a higher quality and additional products are manufactured. The enzymatic process is nevertheless uneconomical due to the operational and maintenance costs which are about 5.3 times higher than for a comparable solvent extraction plant. [Novo Nordisk 1998]

Ultrasonic-assisted extraction

Ultrasonic extraction can accelerate the extraction process. The ultrasonic waves are used to create cavitation bubbles. When these bubbles collapse near the cell walls shock waves and liquid jets are created that cause the cell walls to break and release their content into the solvent.

The practical implementation of this technology is very costly and thus it is not yet realised. [OILGAE] [TC 2008]

Osmotic shock

This is a sudden reaction at osmotic pressure which causes cells in a solution to rupture. A realisation of this technology failed so far due to economic reasons. [OILGAE] [TC 2008]

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Guidance on VOC Substitution and Reduction for Activities Covered by the VOC Solvents Emissions Directive (Directive 1999/13/EC)

Guidance 20:

Manufacturing of pharmaceutical products

European Commission - DG Environment

Contract ENV/C.4/FRA/2007/001

Content

1 Introduction

This guidance addresses the manufacturing of pharmaceutical products, presenting options to substitute or reduce the use of VOC and its resulting emissions.

Table 1: Scope definition of the VOC Solvent Emissions Directive (SE Directive)

SE Directive – Scope definitions (Annex I)
The activity 'manufacturing of pharmaceutical products' is defined as synthesis, fermentation, extraction, formulation and finishing of pharmaceutical products and where carried out at the same site, the manufacture of intermediate products. The SE Directive covers installations in which this activity is taking place with an annual organic solvent consumption greater than 50 t.

This activity covers primary pharmaceutical production and activities related to the formulation and finishing of pharmaceutical products (secondary pharmaceutical production). Primary pharmaceutical production includes production of bulk pharmaceuticals, drug intermediates and active pharmaceutical ingredients (API) by means of synthesis, fermentation and extraction. Examples of activities related to formulation and finishing include physical formulation, tablet coating and filling.

The SE Directive lays down the following activity specific emission limit values for manufacture of pharmaceuticals:

Table 2: Emission limit values of the SE Directive

SE Directive - Emission limit values (ELVs) (Annex II A – activity No. 20)				
Activity	**Solvent consumption threshold [tonnes/year]**	**ELVs in waste gases [mg C/Nm³]**	**Fugitive emission values [% of solvent input]**	**Total ELVs [% of solvent input]**
manufacturing of pharmaceutical products	> 50	20*	New installations: 5%** Existing installations: 15%**	New installations: 5% Existing installations: 15%
Special provisions: * If techniques are used which allow reuse of recovered solvent, the emission limit value in waste gases shall be 150 mg C/Nm³. ** The fugitive emission value does not include solvent sold as a part of products or preparations in a sealed container.				

THE SE DIRECTIVE APPLIES TO THE PRODUCTION OF PHARMACEUTICALS IF A SOLVENT CONSUMPTION OF 50 TONNES PER YEAR IS EXCEEDED

Instead of complying with the above ELVs, operators may choose to use a reduction scheme, following the specifications of Annex II (B) of the SE Directive.

Specific requirements apply for VOCs classified as CMR substances[1]as well as for halogenated VOCs that are assigned the risk phrases R40 or R68[2]. There is a general obligation to replace CMR substances– as far as possible – by less harmful substances or preparations within the shortest possible time. In the case of a mass flow ≥10 g/h for VOC classified as CMR substances or ≥100 g/h for halogenated[3] VOC with R40 the ELVs in waste gases are 2 and 20 mg/Nm³ respectively, and these also apply when a reduction scheme is being used.

National legislation may define lower thresholds for solvent consumption, stricter ELVs or additional requirements.

2 Summary of VOC substitution/reduction

VOCs are emitted by many of the diverse processes, such as syntheses, fermentation and extraction, used in primary pharmaceutical production. In secondary pharmaceutical production VOC emissions arise from mixing or granulation processes, tablet coating and filling of liquid preparations.

ABATEMENT TECHNOLOGIES ARE THE MOST IMPORTANT VOC REDUCING MEASURES IN THE PHARMACEUTICAL INDUSTRY

Abatement technologies are the most cost effective means of reducing VOC emissions from existing pharmaceutical manufacturing. Solvent recovery by condensation, absorption and adsorption can be used for waste streams with high VOC loads or valuable solvents. Thermal oxidation (regenerative, recuperative or catalytic) is needed when a broad range of different solvents is present and/or there is a low to medium load of solvent in the waste gas stream. Biological scrubbers are most effective for high volume waste gas emissions with a low VOC load.

Solvent free or reduced solvent production processes should be considered for processes that are still at the development stage - when process modification is possible. The assessment of new compounds should include a review of alternative solvents for processes as standard.

Aqueous products are available that are suitable for the equipment cleaning systems used in a broad range of applications.

Improved equipment, air extraction, and end-of-pipe abatement technology can be used to reduce the fugitive VOC emissions that result from the handling, storage and mixing of solvents.

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[1] CMR substances – carcinogenic (R45, R49), mutagenic (R46), or toxic to reproduction (R60, R61)

[2] After the implementation of the SE Directive a revision of the R-phrase R40 took place. The original wording of R40 was: 'Possible risk of irreversible effects'. The new wording is: 'Limited evidence of a carcinogenic effect'. In the 'old' version mutagenity (cat 3) was included. This mutagenic effect is now covered separately under R68: 'Possible risk of irreversible effects'. This new risk phrase does not include carcinogenicity. The 'new' version of R40 is obviously less restrictive than the old version. Until the SE Directive is adapted to this change, a final decision on which version applies can only be given by the European Court

[3] Halogenated organic solvents are hydrocarbons with one or more of the following halogens: fluorine, chlorine (e.g. trichloroethylene), bromine (e.g. n-propyl bromide) or iodine.

3 Description of the activity and related industry sectors

The European pharmaceutical sector comprises more than 2,200 companies (separate legal entities) [EFPIA 2008] whose activities range from R&D to manufacturing and marketing. The industry structure varies from country to country, reflecting differing medical traditions, intellectual property protection standards and industrial policies. In 2006, the pharmaceutical production was worth an estimated € 190 billion[4] [EFPIA 2008].

Approximately 730 installations were registered and authorised under the SE Directive in the period from 1999 – 2003 as manufacturing pharmaceutical products in EU 15 [Implementation 2006].

The pharmaceuticals sector is composed, predominantly, of very big companies with various production sites and a large number of different products. Nevertheless there are also numerous small and medium sized companies that specialise in the production of specific products.

A very large number of different pharmaceutical products are made using a wide range of different production processes. Although the principle of these processes (e.g. chemical synthesis) may be more or less the same, each pharmaceutical product has its own production parameters, conditions, catalyst requirements, temperature, pressure, solvents, etc.

4 Technical process description

4.1 Process flow and relevant associated VOC emissions

VOC emissions occur during different processes and stages of the manufacture of pharmaceuticals. During primary manufacturing, emissions may arise from extraction, chemical synthesis, and fermentation processes. Fugitive emissions can arise as a result of leakage from reactors, storage vessels, dryers and distillation units as well as from valves, tanks, pumps, and other related equipment (e.g. centrifuges) of the production process. Cleaning of reactors and associated equipment with solvents can also lead to VOC releases.

THE PRIMARY PHARMACEUTICAL MANUFACTURING INCLUDES THE PRODUCTION OF THE ACTIVE PHARMACEUTICAL INGREDIENTS **(API)**

Sources of VOC in the secondary pharmaceutical manufacturing stage may include: storage of ingredients, mixing and blending, compounding, granulation, formulation, drying, tablet manufacture (pressing and coating), production of liquid and aerosol preparations. As with primary production, point and diffuse sources of emission have to be taken into consideration.

The following flow charts illustrate, in a simplified way, production processes and corresponding VOC emission sources for the following processes in the pharmaceutical industry: extraction of the active pharmaceutical ingredient, fermentation process, synthesis process and compounding and formulation:

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[4] EU 27, Norway and Switzerland

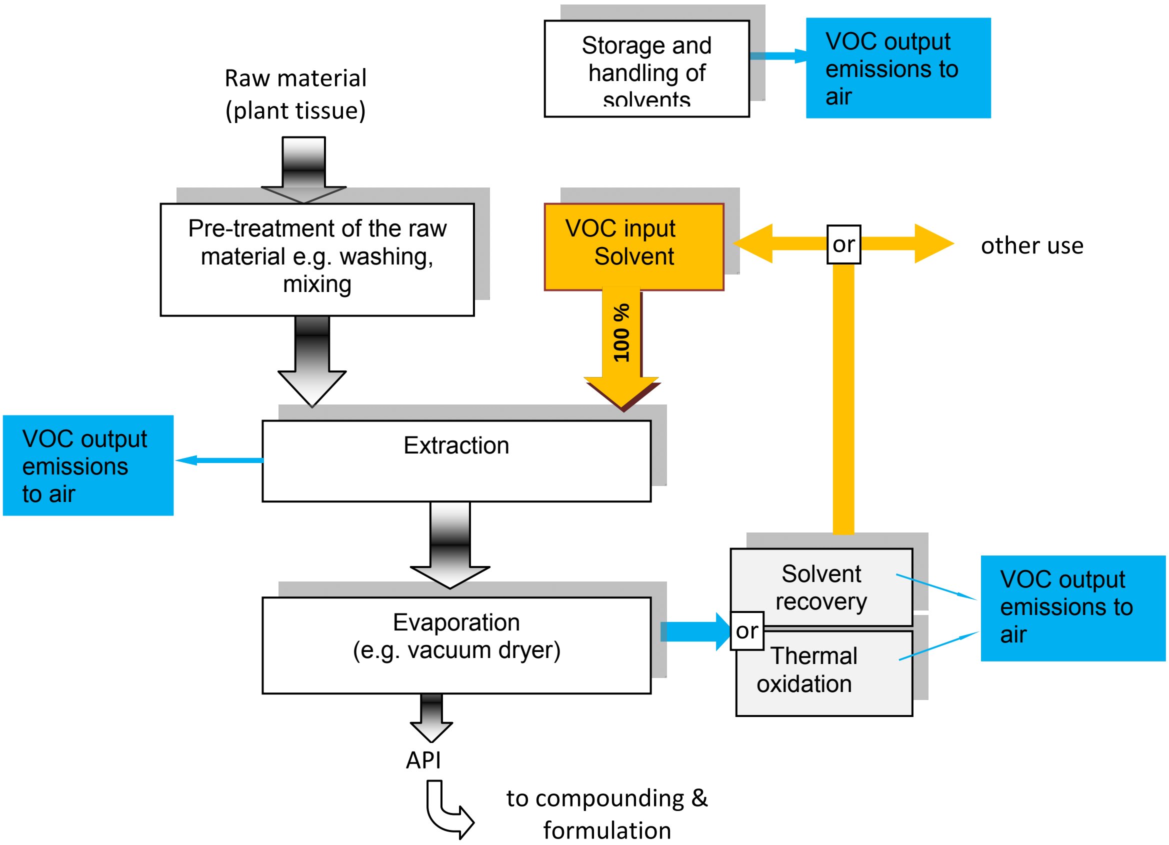

Figure 1: Possible VOC emission sources from **extraction processes** in the pharmaceutical industry (simplified process flow diagram)

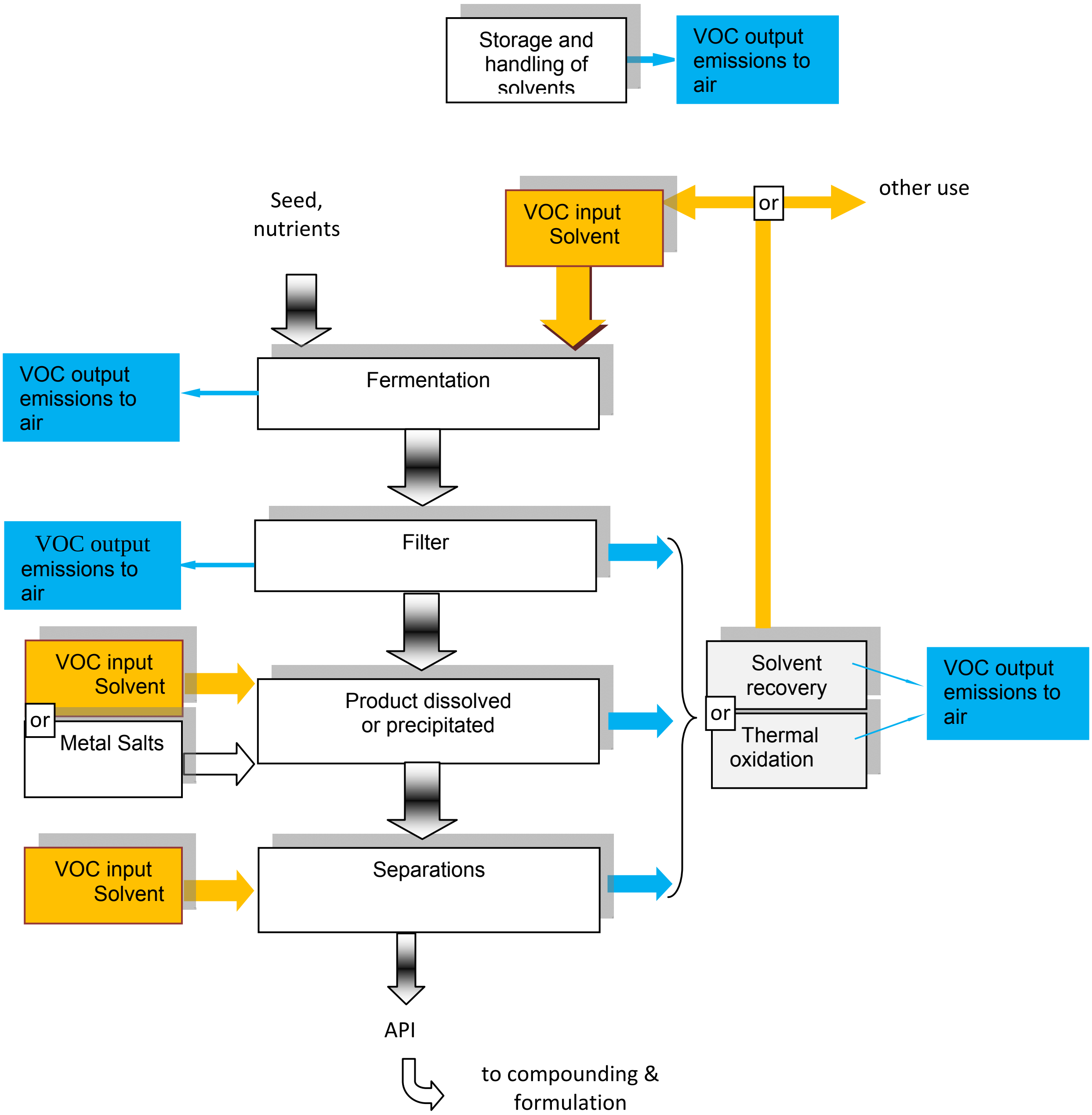

Figure 2: Possible VOC emission sources from **fermentation processes** in the pharmaceutical industry (simplified process flow diagram)

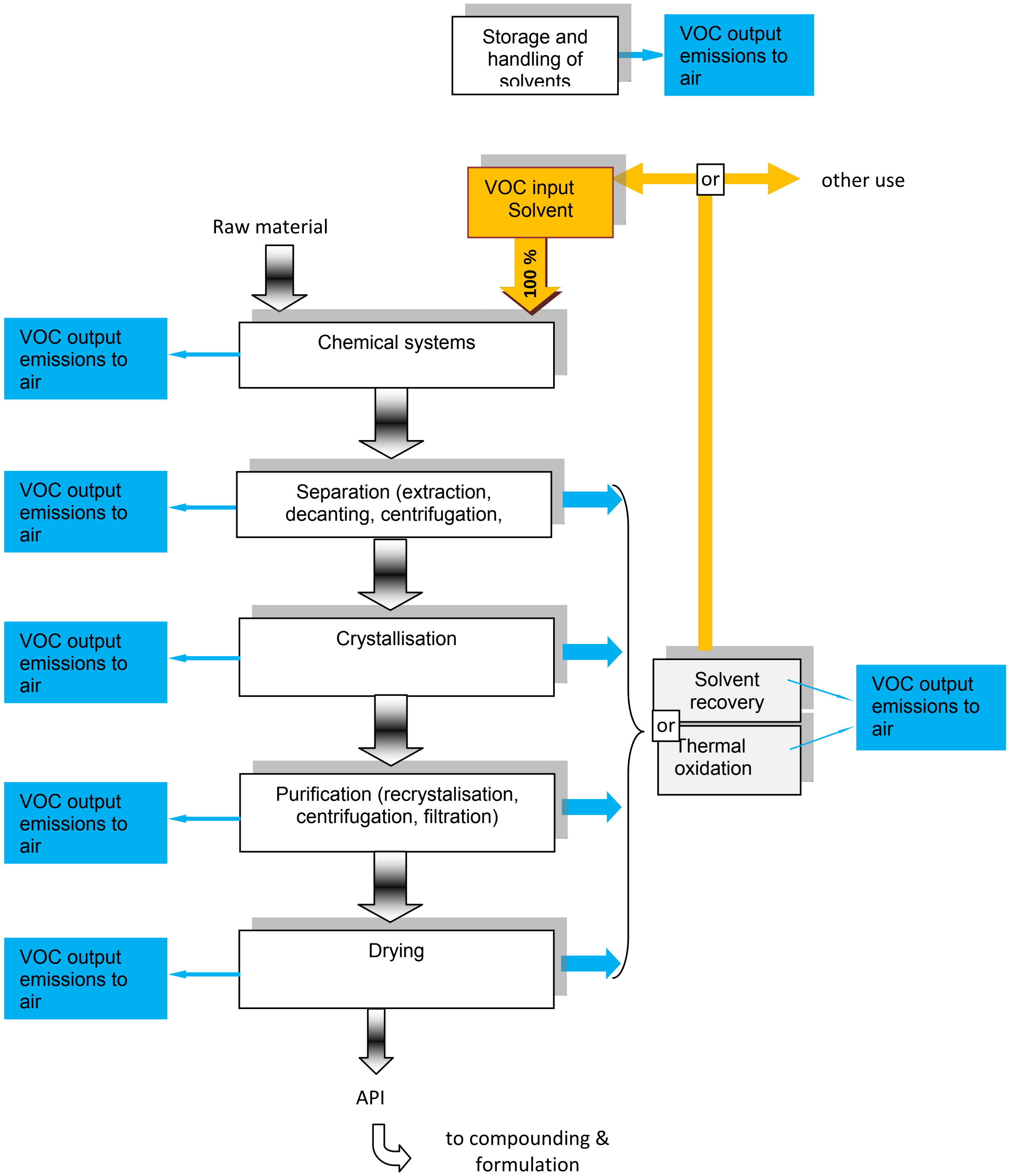

Figure 3: Possible VOC emission sources from **chemical synthesis processes** in the pharmaceutical industry (simplified process flow diagram)

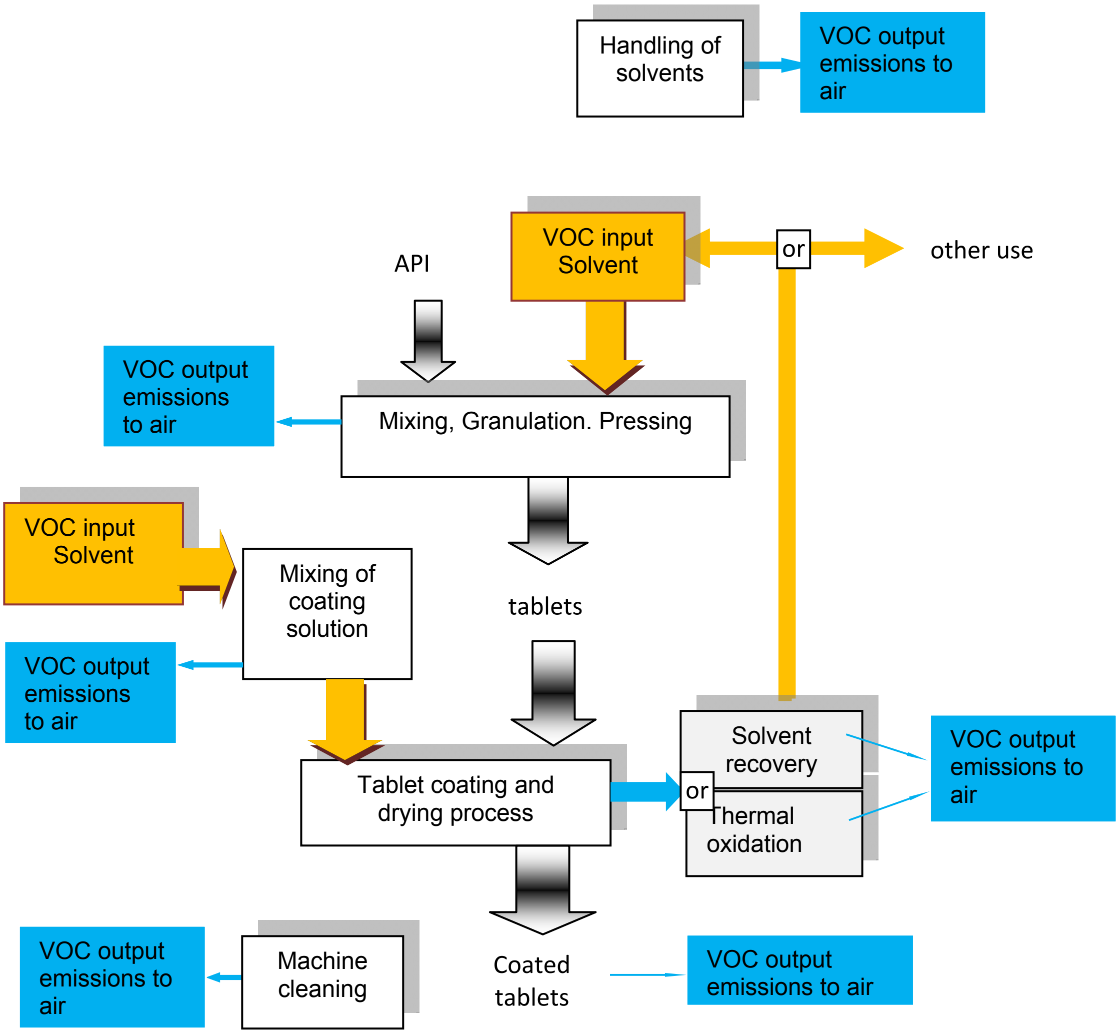

Figure 4: Possible VOC emission sources from **tablet formulation and coating** (simplified process flow diagram)

The average VOC emission from primary manufacturing processes is between 1 and 5% of the organic solvent used. VOC emissions arising from secondary manufacturing processes are between 4-10% of the amount of solvent used [company information]. There are legal restrictions on the residual organic solvent content[5] in finished products (European Pharmacopoeia[6]).

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4.2 Process description

The pharmaceutical industry uses VOCs as solvents in a wide range of processes. The following paragraphs provide a general overview of processes, covered by the SE Directive, where solvents are used for the production of pharmaceutical products. These are:

[5] organic volatile impurities (OVI's)

[6] http://www.edqm.eu/

Synthesis

FOR THE CHEMICAL SYNTHESIS PROCESSES A WIDE RANGE OF DIFFERENT ORGANIC SOLVENTS ARE IN USE

Most active pharmaceutical ingredients (APIs) are created by chemical synthesis and organic solvents are often used to dissolve the components or to act as the reaction medium.

The various types of apparatus and equipment used for synthesis include reactors, condensers, crystallizers, centrifuges and distillation columns. The great variety of chemical synthesis processes requires a wide range of different solvents like acetone, ethanol, toluene, isopropanol, methylene chloride.

Fermentation

The pharmaceutical fermentation process includes the production and separation of medical chemicals such as antibiotics and vitamins from microorganisms. Organic solvents are used for the extraction of the API (e.g. penicillin). The fermentation process takes place in fermentation vessels that are often specifically designed for the process.

Industrial fermentation processes can be divided into two main types - batch fermentation and continuous fermentation - with various combinations and modifications.

Extraction

Extraction is used to separate organic chemicals from vegetative materials or animal tissue in order to manufacture botanical and biological products.

SOLVENTS USED FOR EXTRACTION PROCESSES ARE OFTEN RECOVERED AND REUSED

Extraction can take a variety of forms and, for a particular active ingredient, the type and quantity of organic solvent used is prescribed in specific pharmaceutical manuals or guidebooks (e.g. GMP[7] or cGMP[8]). After several purification steps the extracted component may be dried e.g. in a vacuum dryer to remove the solvent.

Typical solvents used are ethanol, methanol, toluene or heptane and the process takes place in a distillation unit. Since, in many cases, single solvent systems are used, it is often possible to recover and re-use the solvent. The efficiency of the recovery step depends on the solvent and its volatility.

Drying

Drying is an important process, in the production and finishing of pharmaceutical products, whereby solvent content is reduced to a defined maximum residual level. Drying techniques typically used are: tumble, vacuum or freeze-drying, spray drying, fluidized bed dryers, and microwave or infrared heating.

[7] Good manufacturing practice (GMP). To ensure that medicinal products are consistently produced and controlled against the quality standards appropriate to their intended use, the European Union has set quality standards known as Good Manufacturing Practice (COMMISSION DIRECTIVE 2003/94/EC laying down the principles and guidelines of good manufacturing practice in respect of medicinal products for human use and investigational medicinal products for human use) (http://ec.europa.eu/enterprise/pharmaceuticals/eudralex/vol4_en.htm. .

[8] Current good manufacturing practice, The U.S. pharmaceutical product regulations are called "current" Good Manufacturing regulations or "cGMP".

Mixing

Organic solvents are used both as active ingredients in the final product (e.g. liquid preparations) and as auxiliary compounds in the mixing process. If used as an auxiliary compound the solvents have to be removed by drying. Solvents with the function of an active ingredient are not covered by the SE Directive but possible emissions occurring during the mixing.

Granulation

Granulation is the process of producing particles (grains) of the desired size, concentration, and physical properties for compression. Different technologies – batch and continuous systems – are used; fluid bed systems are often used for spray granulation and agglomeration processes; vertical granulators might be used for wet granulation.

Organic solvents are occasionally used as moistening agents as part of the process.

Tablet coating

TABLET COATING IS A PROCESS OF THE SECONDARY PHARMACEUTICAL PRODUCTION WHERE SOLVENTS ARE STILL REQUIRED FOR SPECIFIC APPLICATIONS

Tablet coating, either as a batch or a continuous process, takes place at the end of the manufacturing process. While the majority of tablets are coated for cosmetic reasons or for brand identification they also have specialised functions - such as enteric coating, moisture protective coating, coating for controlled release, flavour coating, taste mask coating, etc. Modern tablet film coaters, typically, are closed rotating drums in which the tablets are suspended in a hot-air fluidized bed. The hot air dries the atomised coating as it is sprayed onto the tablet. Fluidized bed coaters can also be used for continuous tablet coating.

Examples of organic solvents used are isopropanol (2-propanol), dichloromethane (DCM, methylene chloride), acetone, and ethanol. Besides organic solvents, aqueous systems and hydro-alcoholic solvents (e.g. water/ethanol) are also used.

Besides film coatings also sugar coatings are used as protective and/or cosmetic layer for tablets. Sugar coatings are water soluble and contain no solvents. Compared to film coating, sugar coating is more time consuming and the weight of the tablets increases significantly (up to 50%).

Production of liquid preparations

The active ingredients of liquid preparations are firstly dissolved then adjusted to the required concentration for subsequent filling. During the preparation and filling of liquids some evaporation of organic solvents that are part of the product may occur.

Cleaning of equipment

Residue-free surfaces are very important in the production of pharmaceuticals and any cleaning agents used must be capable of ensuring that legally prescribed minimum residue levels are achieved.

Pharmaceutical companies undertake the following cleaning activities:

- Manual cleaning with or without mechanical assistance
- Semi-automatic cleaning processes
- Automatic processes in washers

Fully automated cleaning processes with integrated CIP (Cleaning in place) systems may be used.

Organic solvents are often used to remove organic chemical residues from production equipment.

5 Solvent use, emissions and environmental impact

5.1 Solvents used

In a typical pharmaceutical/fine (non-polymer) batch chemical operation, organic solvent use consistently accounts for 80-90% of mass utilisation [Constable 2007]. They are used to provide the medium in which the reaction takes place, to separate the desired chemical products from unwanted ones and to maximize the purity of the drug. [ESIG]

Overall more than 40 different solvents are in use in pharmaceutical production:

- Alcohols (ethanol, methanol, isopropanol, isobutanol)
- Ketones (acetone, methyl isobutyl ketone (MIBK, 4-methyl-2-pentanone), methyl ethyl ketone (MEK, 2-butanone))
- Alkanes (hexane, heptane, cyclohexane, 2,2,4-trimethylpentane (isooctan))
- Aromatics (toluene, xylene)
- Polar aprotics (N,N-dimethylacetamide (DMA), acetonitrile, N,N-dimethylformamide (DMF), dimethylsulfoxide, 1,4-dioxan, N-methylpyrrolidon, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether)
- Esters (butyl acetate, ethyl acetate, isopropyl acetate)
- Ethers (tetrahydrofuran (THF), methyl-tert-butylether (MTBE))
- Chlorinated hydrocarbons (chloromethane, dichloromethane, trichloromethane (chloroform), 1,2-dichloroethane)

FOR THE PERFORMANCE OF THE DIFFERENT PROCESSES IN THE PHARMACEUTICAL PRODUCTION NUMEROUS DIFFERENT SOLVENTS ARE APPLIED

Which solvents are used depends on the production process parameters to be met. For most processes the type and quantity of solvent are defined in pharmaceutical manuals (e.g. GMP) in order to achieve an end product of a required quality (e.g. in the case of an extraction, a change of solvent might result in different extraction products.)

Methanol is the most widely used cleaning solvent but others that are commonly used include acetone, dimethyl formamide, and ethyl acetate. In many synthesis processes, to avoid contamination, the solvent that is used for the production is also used for the cleaning of the equipment.

5.2 Solvent consumption and emission levels

THE TOTAL SOLVENT CONSUMPTION OF THE PHARMACEUTICAL INDUSTRY INCREASED OVER THE LAST YEARS

The total consumption of solvents by the pharmaceutical sector is growing: the European market shows a steady increase in demand year after year. [ESIG] The current demand for solvent in the pharmaceutical industry is about 9 % (~ 400 kt) of the total solvent consumption in Europe [ESIG]. For 2000, the NMVOC[9] emissions were estimated to be 54.2 kt representing ~ 0.5% of the total NMVOC emission at an EU 25 level. [EGTEI 2005b].

5.3 Key environmental and health issues

In the production of pharmaceuticals a broad range of different solvents are used for a range of processes e.g. synthesis, extraction, tablet coating.

Process emissions of solvents, together with NOx emissions, are precursors of ground level ozone formation in the presence of sunlight. Existing occupational workplace limits should be taken into consideration.

Emissions of VOC to air may occur from:

- the storage of the solvents
- the primary pharmaceutical production (e.g. extraction, syntheses, fermentation)
- the secondary pharmaceutical production (granulation, drying, tablet-coating)
- cleaning operations in the primary and secondary pharmaceutical production

Spills and leaks from storage areas may result in emissions to soil and groundwater.

In the primary pharmaceutical production (mainly for the synthesis process) the halogenated solvents 1,2-dichloroethane, chloromethane, dichloromethane and trichloromethane are of special concern. The solvent 1,2-dichloroethane is classified as CMR substance category 2 (R45, may cause cancer). There is some limited evidence that chloromethane, dichloromethane and trichloromethane (chloroform) have carcinogenic effects (classification as R40 substances).

In addition chloromethane and trichloromethane might cause serious damage to health by prolonged exposure through inhalation.

[9] Non-methane VOC

6 VOC Substitution

The following sections describe potential substitutes for VOC (using VOC-free and VOC-reduced systems). The sections describe associated application technologies and/or special conditions as well as advantages and disadvantages compared to systems that use solvents with a high VOC content.

The manufacture of pharmaceuticals is a highly controlled process. Process modification after the development and authorisation of a new product are not or only to a very limited extent possible. Therefore it is essential that already during the development phase of new products the possible VOC-free or VOC-reduced alternatives receive the necessary attention.

THE SELECTION OF THE SOLVENTS USED DURING THE MANUFACTURING PROCESS IS DETERMINED BY THE AUTHORIZED PROCESS DESCRIPTIONS

6.1 VOC-free systems

In this section alternatives are described where the currently used VOC products are completely replaced by VOC-free products or systems.

6.1.1 Change of solvents or processes (VOC free processes)

The primary production of pharmaceuticals covers a wide range of different processes, solvents and process conditions.

The manufacturing process parameters and special conditions for a particular active ingredient or product are prescribed in specific pharmaceutical manuals or guidebooks (GMP[10] or within other manuals). The quality and purity of the product will depend on the type and amount of solvent that is used.

Recently, however, there has been increased effort in the development of new or improved extraction and synthesis processes designed to avoid the use of organic solvents. Solvent selection guides are available to assist manufacturers in the selection of VOC free/low solvents or less harmful solvents (see section 4.1.3 of [BREF 2006 OFC]) and in the technical literature there are references to a wide range of alternative processes (e.g. solvent free synthesis[129]).

SUPERCRITICAL CO_2 IS NOT SUITABLE FOR POLAR AND HIGH MOLECULAR SUBSTANCES

Supercritical carbon dioxide is widely used as an alternative to conventional solvents in numerous applications, such as: extraction and purification of specialty chemicals and useful natural products. It is also increasingly being used as a solvent for synthetic processes [Green Chemistry 2008]. The main advantages of supercritical CO_2 are that it is non-toxic, non-flammable, recyclable and cheaper than conventional solvents. Supercritical CO_2 is in particular suitable for the extraction of non-polar substances. Polar substances as well as high molecular substances have bad dissolving properties in CO_2. For these substances the addition of co-solvents (e.g. VOCs) is necessary. [Uhde 2008]

For existing technologies the substitution of organic solvents is limited by technological process requirements, patents and – in particular – authorizations for pharmaceutical products. Therefore substitution possibilities have to be evaluated with care and on a case-by-case basis.

The selection and evaluation of the solvent to be used takes place during the research and development stage of new technologies. Therefore attention should be focused, at that early stage, on the selection of VOC-free or low VOC containing solvents in order to avoid VOC emissions in the future. For example enzymatic syntheses in an aqueous solution might substitute for chemical syntheses using organic solvents.

6.1.2 *Use of aqueous cleaning systems*

Drivers for shifting from solvent based cleaning systems to aqueous cleaning for API manufacturing include: the relatively high cost of solvent, difficulties associated with storage and disposal; increasing regulatory pressure; inefficiency and often ineffectiveness of the solvent-based processes; and overall process economics. [Goliath]

The selection of the most appropriate cleaning process depends on the specific process manufacturing parameters used. In many instances a conversion from solvent-based to aqueous-based cleaning is feasible provided there has been appropriate investment in equipment modifications and attention has been given to the details of cleaning process design and validation. [Goliath], [Borer 2008]

CUSTOMIZED VOC FREE CLEANING SOLUTIONS ARE AVAILABLE FOR MANY PROCESSES IN THE PHARMACEUTICAL INDUSTRY

Aqueous cleaning systems are most effective as CIP (Cleaning-in-place) technology. CIP is a system designed for automatic cleaning without major disassembly and assembly work of the parts which have to be cleaned (e.g. vessels). The cleaning system is already part of the equipment. As many installations are not equipped with these specific cleaning facilities a change from solvent-based systems to water-based systems is often linked with high investment costs. On the other hand the cleaning time of water-based systems is significantly shorter than for solvent-based products. Thus – particularly in case of batch processes – the downtime can be reduced significantly. [Borer 2008]

For the tablet processing and coating process also aqueous-based systems are available. For example in case of a product change, the various stamps of a tablet press have to be cleaned. For this activity specific washing machines exist which carry out the cleaning with water-based products [Borer 2008].

A comprehensive review article, published by [Verghese 2003], describes current cleaning practices and the issues to be considered. It also describes users’ experiences of switching from solvent cleaning to aqueous cleaning for API manufacturing.

6.1.3 *Solvent less film coating of tablets*

The use of solvent-free coating systems for tablet coating is steadily increasing. The selection of the coating system depends on the properties of the tablets that have to be coated. The most common alternatives to solvent-based systems are aqueous systems.

SOLVENT-FREE COATING SYSTEMS ARE WELL ESTABLISHED BUT NOT SUITABLE FOR ALL APPLICATIONS

However, aqueous systems cannot be applied to all tablets due to possible interactions with the tablet ingredients, e.g. heat and water might degrade certain active ingredients. In addition, the coating dispersions must be demonstrated to be capable of controlling microbial growth.

The main advantages of aqueous systems are that they contain no solvents and so no VOC control measures are required. Aqueous systems are generally becoming cheaper than solvent-based systems because the price of solvents is linked to oil prices.

Besides aqueous systems, the following different coating techniques are in use:

- Powder coating
- Hot-melt coating
- Supercritical fluid spray coating (CO_2)

Similarly to the aqueous coating, the suitability of these systems depends on specific requirements on the coating and the tablets.

7 Other VOC emission prevention measures and abatement techniques

Preventive measures, process improvements and abatement techniques can be used to reduce VOC emissions if VOC substitution as described in section 6 is not possible. The following measures are commonly applied for the pharmaceutical sector:

7.1 Abatement

ABATEMENT TECHNOLOGIES ARE THE MOST IMPORTANT VOC REDUCTION MEASURES IN THE PHARMACEUTICAL INDUSTRY

As a result of the diversity of processes and different types and amounts of VOC emissions arising, process improvements and abatement techniques are of major importance in the pharmaceutical industry. The selection of suitable abatement measures depends more on process parameters, such as flow rate, concentration and constancy of the same than the economic cost of a particular measure and/or approach.

In many cases a combination of different abatement measures offers the best solution for a pharmaceutical production site. For VOC capture and recovery of valuable and re-usable solvents, condensation, absorption and adsorption offer the best opportunities whilst oxidation techniques which destroy the VOCs are commonly in use for process with varying solvents, concentrations or waste gas volumes.

7.1.1 Condensation

Condensation is a relatively inexpensive (except for cryogenic condensation with liquid nitrogen) and simple technique that is suited to high inlet concentrations, it enables solvents to be recovered and re-used [BREF LVOC].

Condensation of VOCs from a gas stream can be achieved either by increasing the pressure or, more commonly, reducing the temperature of the gas stream. Depending on the characteristics of the vapour, different types of heat exchangers can be used: refrigerated condensers (see section also below), scraped-surface heat exchangers or condensers in series. In general indirect cooling systems should be preferred to reduce effluent formation.

Cryogenic condensation (low temperature condensation)

In comparison to the conventional condensation which often uses water as cooling agents in case of cryogenic condensation coolants like nitrogen are used to achieve very low temperatures (e.g. in case of nitrogen -120 °C).

Cryogenic condensation efficiency typically exceeds 99% and so it offers a very high degree of VOC emission reduction. It is also a very versatile process. Since the condensation process is influenced by the vapour pressure of the compound to be separated, adapting the condenser operating conditions allows handling the wide range of concentrations and compounds present in the pharmaceutical industry.

For cryogenic condensation the flow rate can vary between 10 up to 3000 m^3/h. The minimum loading should be above 20 g VOC/Nm^3 and the pressure between 20 mbar and 6 bar [BREF LVOC, PanGas, Glatt]. Cryogenic condensation is therefore appropriate for low flows and high concentrations. By varying the cooling temperature different types of solvents can be recovered. In comparison to alternative abatement technologies, cryo-condensation units are compact and they tend to be transportable (skid mounted). The system design minimizes moving parts, reducing maintenance and repair [PRAXAIR]

CRYOGENIC CONDENSATION IS PARTICULARLY USED FOR CHLORINATED OR OTHER VALUABLE SOLVENTS

In the pharmaceutical industry cryogenic condensers often use liquid nitrogen as the coolant (< - 196 °C). Investment costs vary from 300.000 € up to more than 2 million €. The technique is particularly useful for the recovery of chlorinated or other valuable solvents, which are frequently re-used in the same process or other processes.

Operational costs depend on the cooling gas used; the cost of liquid nitrogen is around 30-50 €cent/l. As the nitrogen does not come into contact with waste gas it can be used in other processes within the pharmaceutical production site.

Re-use or recycling of solvents

The opportunity to re-use recovered solvent for the same or another pharmaceutical extraction process depends on the process and the solvent system used. In general it is best to recover and re-use solvents in the same process but this is not always possible and allowed ("virgin solvent" requirements for some processes). For example, ethanol can acquire the odour of the extracted medium and so its reuse is often restricted. In such a case external recycling - after the recovery - is necessary.

Recycling of solvents can take place either in-house or off-site. Installations with higher solvent consumption typically have their own integrated recovery and distillation equipment.

External recycling takes place in specialised companies having their own recycling facilities to collect, clean and distil solvents. Recovered solvent can either be re-used by the company of origin or for other applications. Recycled solvents are often used as cleaning agents. They costs about one third as much as virgin solvent -depending on the quality (e.g. almost no contaminants) and solvent type (e.g. very expensive solvents); recycling companies might even pay for the used solvents. [Remondis 2008]

7.1.2 Adsorption

During adsorption, VOCs are removed from the gas stream and collected on the surface of a solid material. The most common adsorption medium is activated carbon (see below). A periodic regeneration of the adsorbents is necessary to ensure the effective functioning and recovery of the VOCs. Besides activated carbon, silica gel, activated alumina and molecular sieve zeolites may be used. [BREF LVOC].

Activated carbon filters

The VOC-loaded air is passed through a filter containing activated carbon until it becomes saturated and then the activated carbon has to be regenerated by heating (using the desorbed VOC often as a fuel). Installations are typically equipped with two parallel filter systems to avoid downtime while one is being regenerated.

Activated carbon filters are very effective for high flow rates with low to medium concentrations. The gas has to be pre-treated e.g. to preset temperature and humidity, to ensure an efficient operation. The recovery rate of activated carbon filters lies between 95 - 99.99%.

ACTIVATED CARBON IS A COST EFFECTIVE MEASURE FOR SOLVENT RECOVERY

Carbon adsorbers which cannot be regenerated are particularly used for treating odours and intermittent processes where total annual VOC emissions are less than ~ 20 tons.

The following table lists some figures related to the operating conditions of activated carbon filters [BREF LVOC]:

Table 3: Operating conditions of activated carbon filters [BREF LVOC]

	Regenerative adsorption	Non regenerative adsorption
Flow	100 - >100,000 m^3/h	10 - >1000 m^3/h
Load	0.01 – 10 g VOC/m^3,	0.01 - 1.2g VOC/m^3
Pressure	1 – 20 atm	

7.1.3 Absorption

In the case of absorption VOCs are removed from the gas stream, by mass transfer, to a scrubbing liquor (e.g. water, caustic, acid). This method is especially suitable for high VOC concentrations and can achieve removal efficiencies of up to 99%. The resulting mixture (absorbents plus VOCs) can be treated by distillation or degassing to recover the solvents for re-use.

7.2 Thermal oxidation (Regenerative / recuperative)

Two types of thermal oxidiser to destroy VOCs are in common use, regenerative and recuperative. Regenerative oxidation tends to be more efficient than recuperative thermal oxidation as it uses the recovered energy to pre-heat incoming process air to oxidation temperatures (~ 800 °C),. Consequently its operating costs are significantly lower than for recuperative oxidation systems. Regenerative thermal oxidation systems are particularly effective for process streams with low solvent loading but their operating costs depend highly on the efficiency of the heat exchanger.

Recuperative systems are mainly used for small flow rates; at higher rates the systems are not cost effective.

Regenerative thermal oxidation systems are widely used in the pharmaceutical industry because they are relatively insensitive to the composition and the concentration of the solvents in the process air. Thermal oxidation systems are used for VOC concentrations between 1-20 g/Nm³. Thermal oxidation efficiency rates of up to 99.9% are possible.

Thermal oxidation systems use the calorific content of the effluent stream VOCs, therefore after a warm up phase no additional fuel is needed for the oxidation process. The minimum VOC concentration for an autothermic oxidation process is 1-2 g VOC/Nm³.

7.3 Catalytic oxidation (CO)

Catalytic oxidation is also suitable for use in the pharmaceutical industry. The advantage of the catalytic oxidation compared to thermal oxidation is that the oxidation takes place at lower temperatures thus energy consumption is lower. For the use of the catalytic oxidation the following conditions have to be in place:

CATALYTIC OXIDATION IS IN PARTICULAR USED FOR WASTE GAS FLOWS WITH A CONSTANT SOLVENT COMPOSITION

- well-defined solvent content and composition
- low flow rates
- free from catalyst poisons (e.g. heavy metals).

Catalytic oxidation (e.g. using a metal oxide, precious metals) can be initiated at temperatures as low as 280-350 °C.

Catalytic oxidation systems are also available with regenerative or recuperative technology. The regenerative catalytic oxidation has significant economic advantages, especially in cases of low VOC concentration and low flow rates.

7.4 Bio-oxidation

Bio-filtration, bio-scrubbing and bioreactors destroy VOCs by biological oxidation using aerobic micro-organisms supported on a substrate.

Biological treatment is particularly effective when there are high flow rates and a relatively low solvent concentration. In this case the operational costs are significantly lower than those of thermal oxidation.

Bio-oxidation is appropriate for a variety of VOCs (also mixtures) e.g. alcohols, esters, amines, ketones, aliphatic, aromatic and to a certain extent also halogenated hydrocarbons. Another very important advantage of bio-oxidation is that odorous compounds are neutralized.

7.5 Process improvements

Fugitive VOC emissions may arise from all processes steps and process improvements should be made to optimise the collection (via local exhaust ventilation hoods) and subsequent treatment or abatement of vapours escaping from reactors, storage and handling areas.

A wide range of best practices and process improvements are possible which aim at containing VOC emissions. The following list is not exhaustive:

- Use of adequate spraying technology in closed systems for tablet coating [Schlick 2008] [Process Pharma 2006]
- Collection of VOCs from different distributed sources using local exhaust ventilation hoods, for subsequent control of point and fugitive emissions
- Working at greater concentration to reduce the consumption of solvents
- Modification of operating conditions for distillation (e.g. distillation under ordinary pressure instead of vacuum distillation)
- Improved condenser efficiency (e.g. increased exchanger surfaces and refrigerating capacities)
- Using dry-sealed vacuum pumps instead of liquid ring vacuum pumps
- Using closed pressure filters or vacuum filters that are more leak free than open filters
- Using vacuum dryers with enhanced solvent condensation
- Fitting pressure vacuum relief valves to storage tanks
- Back venting to the delivery tanks during bulk storage tank filling
- Improved exhaust air collection systems
- Using closed or covered mixing systems
- Using closed containers for the transport and intermediate storage of solvents
- Using closed-loop liquid and gas collection equipment for cleaning of reactors and other equipment

PROCESS IMPROVEMENT LIKE LOCAL EXHAUST VENTILATION HOODS CONTRIBUTE SIGNIFICANTLY TO THE REDUCTION OF FUGITIVE VOC EMISSIONS

- Implementing leak prevention systems
- Better control of reaction parameters (feed rate, mixing, temperature)
- Optimisation of process parameters

The measures described above not only help to reduce fugitive VOC emissions but effective VOC extraction and control may also reduce emission of odours.

7.6 Organisational measures

The following operational measures are aimed at reducing VOC emissions:

- Effective production and maintenance;
- Reduction of the number of batches and increasing batch capacity;
- Reduced quantity of stored solvents
- Employee training on solvent awareness including on guidance on effective handling and storage
- Thorough solvent auditing (mass balance i.e. examine solvent route).

8 Summary of VOC emission reduction measures

The following table summarizes the VOC emission reduction measures discussed in chapters 6 and 7:

Table 4: Measures for VOC substitution and reduction in the pharmaceutical industry

Objectives	**Description**
VOC-free Systems	Change of solvents or processes to VOC free processes Use of aqueous based cleaning systems Use of solvent less film coating of tablets (e.g. aqueous systems, powder coating, hot melt coating) Assessment and review of possible solvents during the development phase
Process improvements	Re-use or recycling of recovered solvents Installation of exhaust air extraction systems Extraction of solvents from storage and handling areas Good maintenance of the installation
Abatement technologies	Recovery of solvents by - Adsorption - Absorption - Condensation (e.g. cryogenic condensation) Thermal oxidation (regenerative or recuperative) Catalytic oxidation Bio-oxidation

9 Good practice examples

9.1 Example: Use of effective abatement technologies

Many suppliers of abatement technology have adjusted their product range to the requirements of the SE Directive. Regenerative thermal oxidation systems are especially suitable for the pharmaceutical industry (e.g. tablet coating). Typical investment and operational costs are listed below:

Nominal waste gas flow: 20,900 Nm³/h

Possible concentration range: 0-12 g/Nm³

Investment costs: ~ 250,000 €

Power consumption for the oxidation process (gas injection): <180 kW

Nominal power for the fan: 29 kW

The operational costs are highly dependent on energy prices - the fuel gas required and electrical consumption. If the VOC concentration exceeds 1,6 g/Nm³, no additional fuel gas is required to maintain the oxidation process and the remaining operating costs of the installation depend only on the power consumption of the fan (29 kW)

[CTP 2008]

10 Emerging techniques and substitutes under development

New production possibilities using biotechnology offer a broad range of new VOC free processes.

New technologies, like photo curable pharmaceuticals, are under investigation for tablet coating [Bose 2006].

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