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

SE Directive - Emission limit values (ELVs) (Annex II A – activity No. 14)				
Activity	**Solvent consumption threshold [tonnes/year]**	**ELVs in waste gases [mg C/Nm³]**	**Fugitive emission values [% of solvent input]**	**Total ELVs [g per pair]**
Footwear manufacture	> 5	--	--	25
Special provisions: Total emission limit values are expressed in grams of solvent emitted per pair of complete footwear produced.				

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.

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.

VOC EMISSION REDUCTION CAN BE ACHIEVED BY SUBSTITUTING VOC BASED ADHESIVES BY VOC-FREE PRODUCTS, BY PROCESS IMPROVENTS AND BY APPLYING WASTE GAS CLEANING.

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.

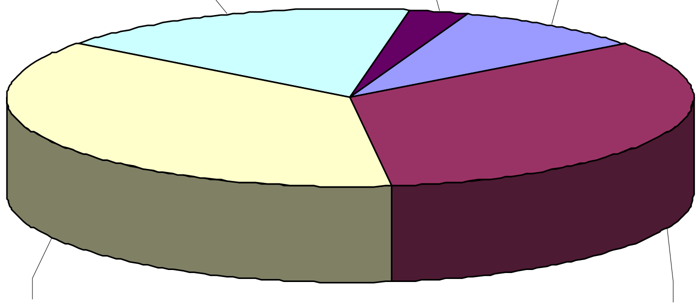
Substitution of solvent-based adhesives is more difficult for the manufacture of heavy duty footwear such as heavy work/safety boots or walking/alpine boots. Installations producing these types of footwear are less likely to be able to meet the SE Directive emission limit values without the use of waste 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]

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.

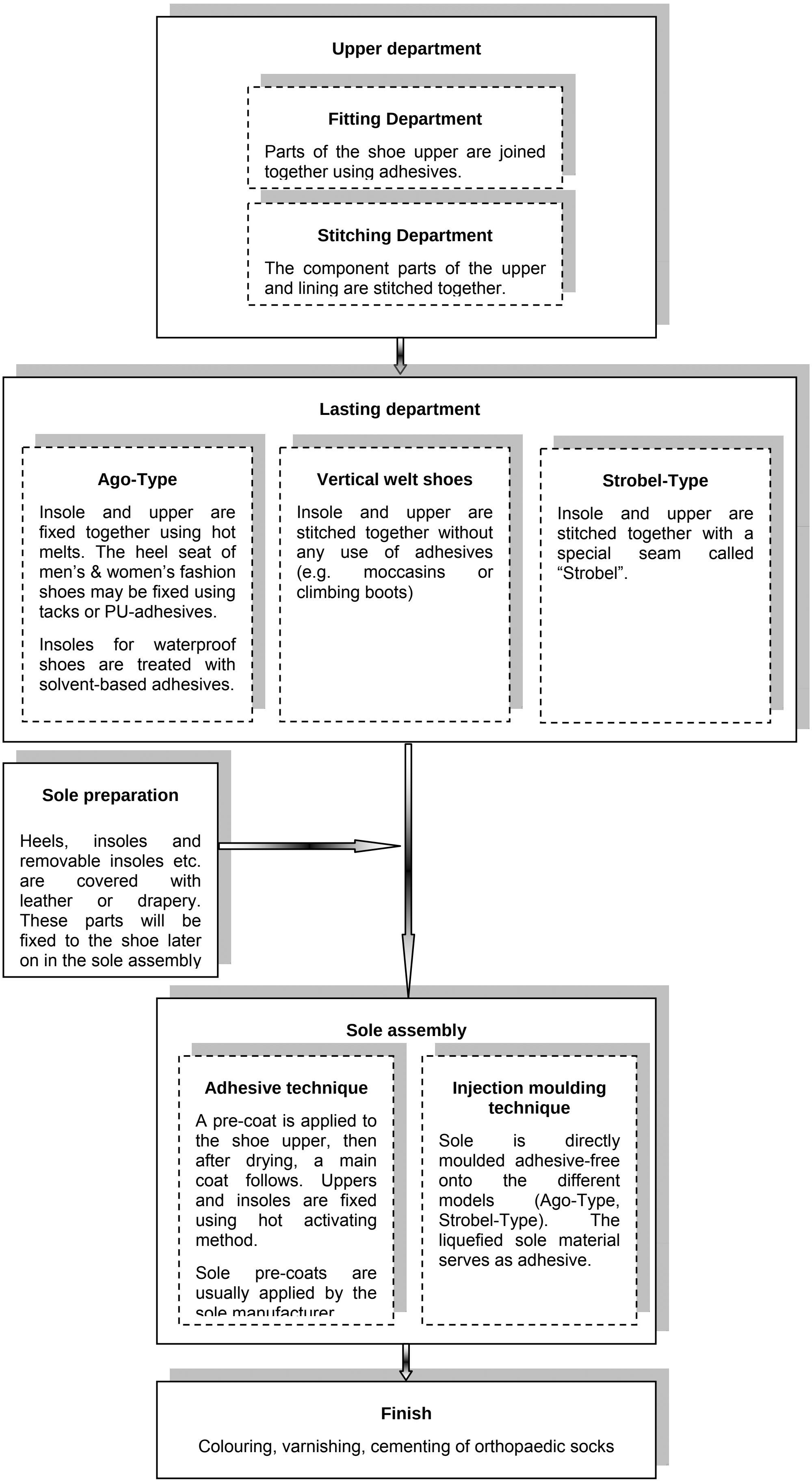


Figure 2: Process steps of footwear production [DFIU 2002]

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 %).

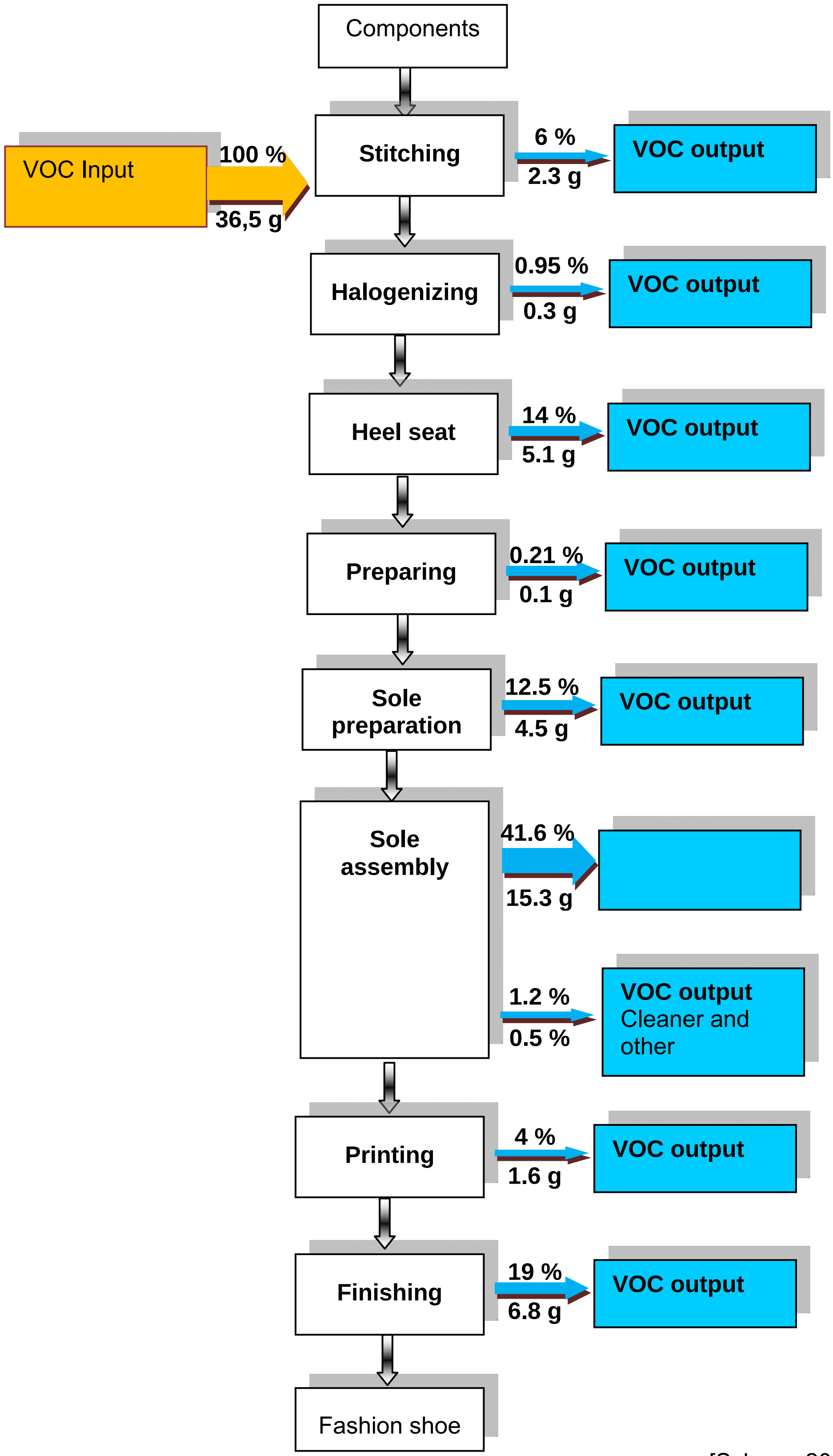
The soles of **children shoes** (figure 5) are injection moulded (see figure 2) and so the emissions are low. There is, nevertheless, a small emission from this process step (0.4 % compared to about 41 % of fashion shoes and 24 % of heavy boots) generated when cleaning the mould.

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)

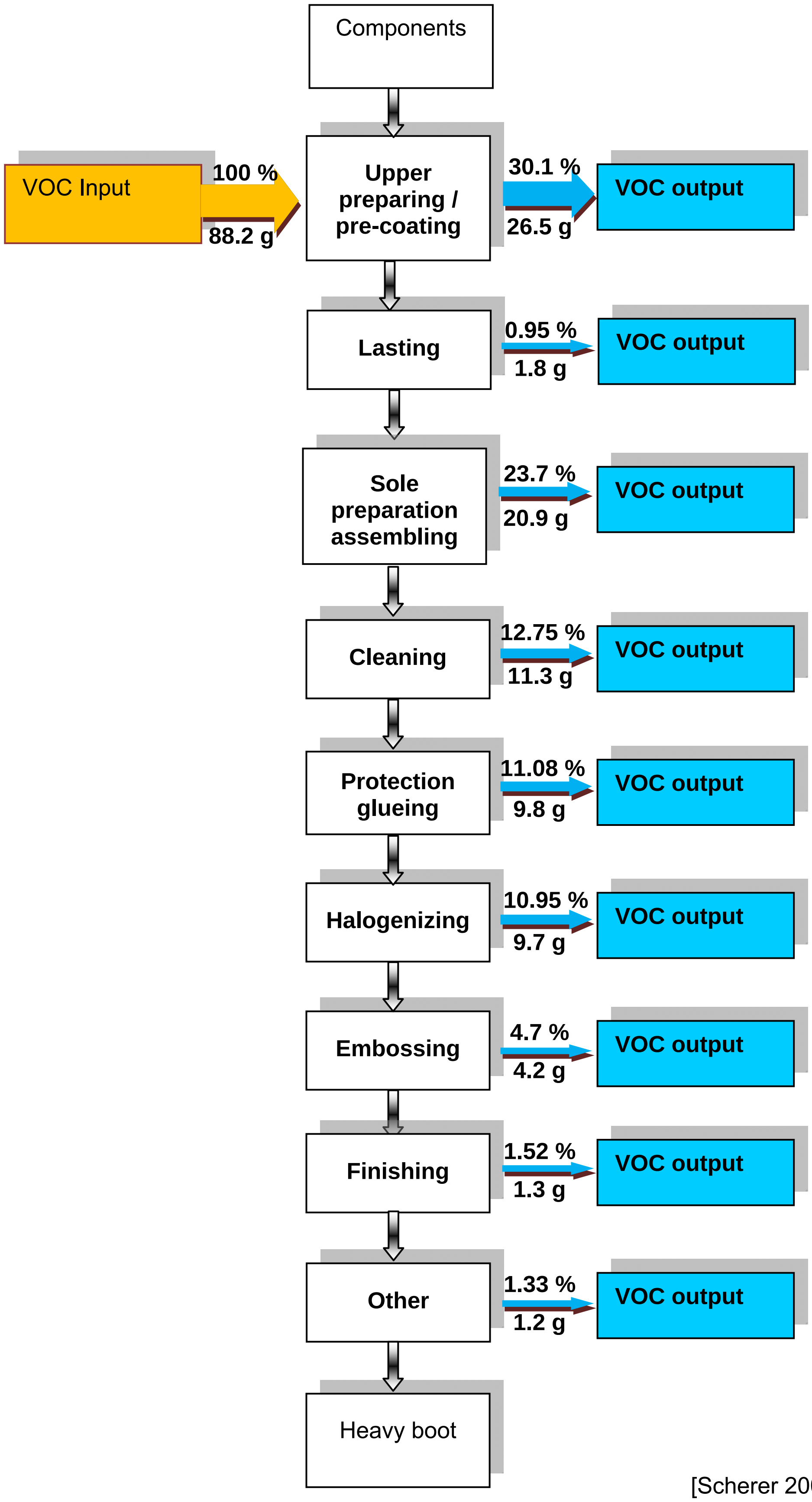


[Scherer 2005]

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)

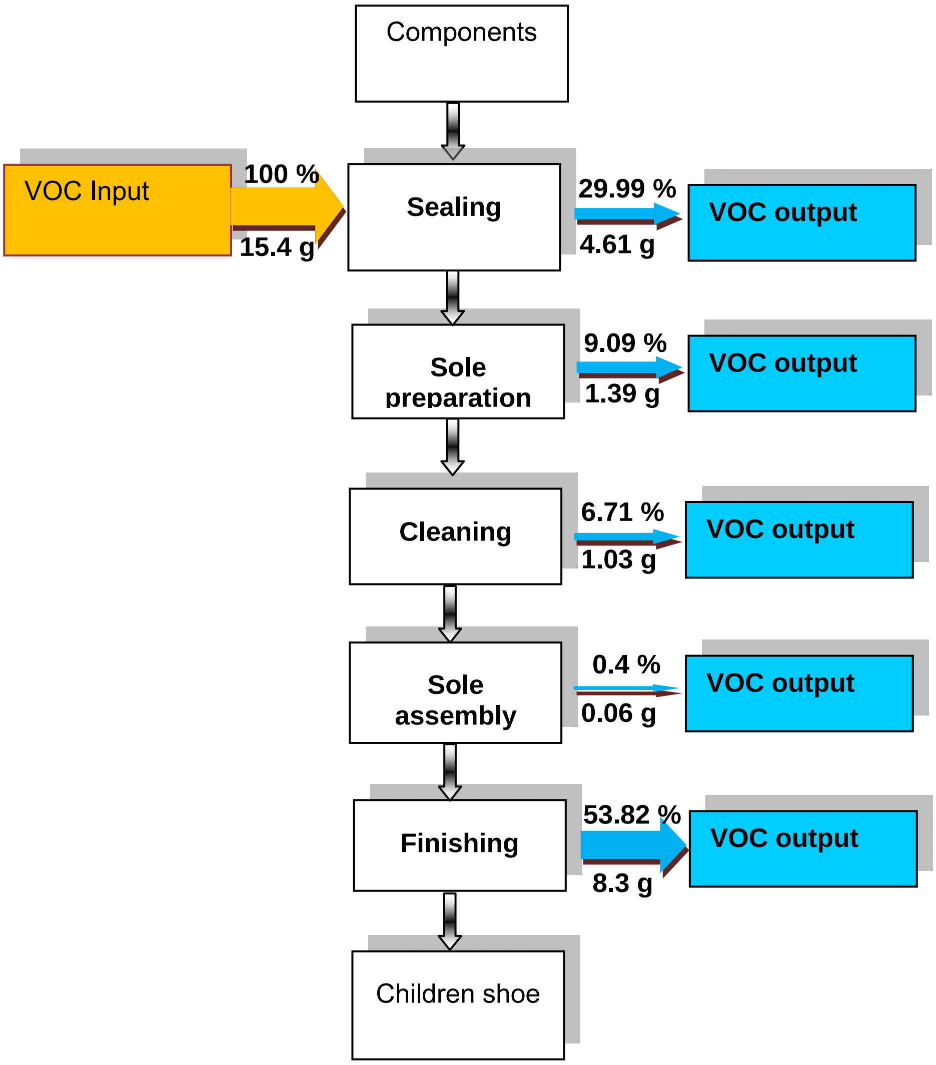


[Scherer 2005]

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.

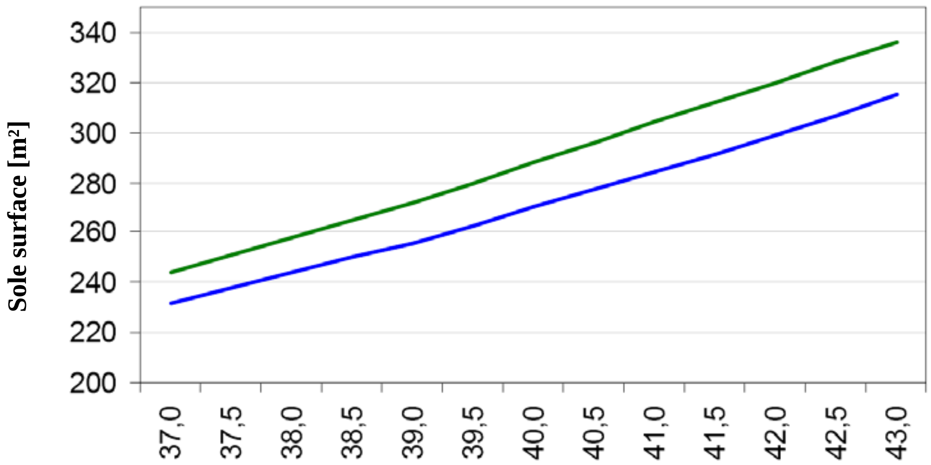
Finishing materials (colouring and varnishing material) may contain solvents.

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]

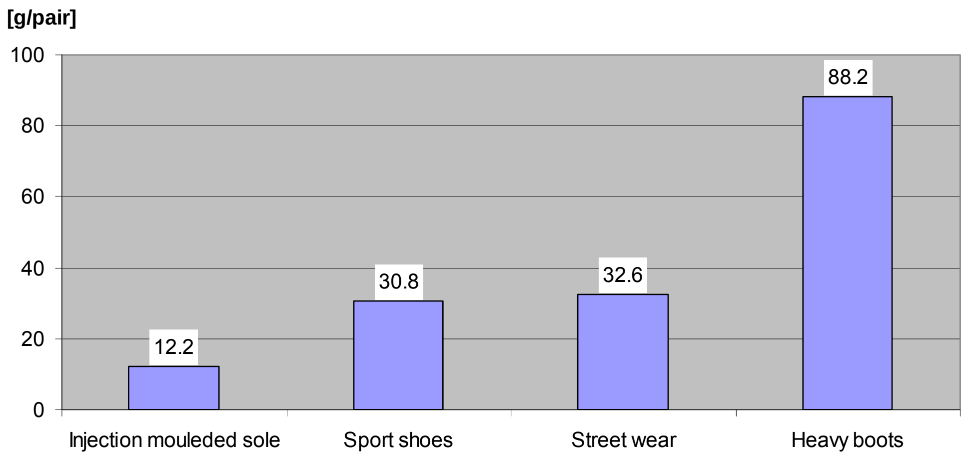
[EWEN 2007]

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]

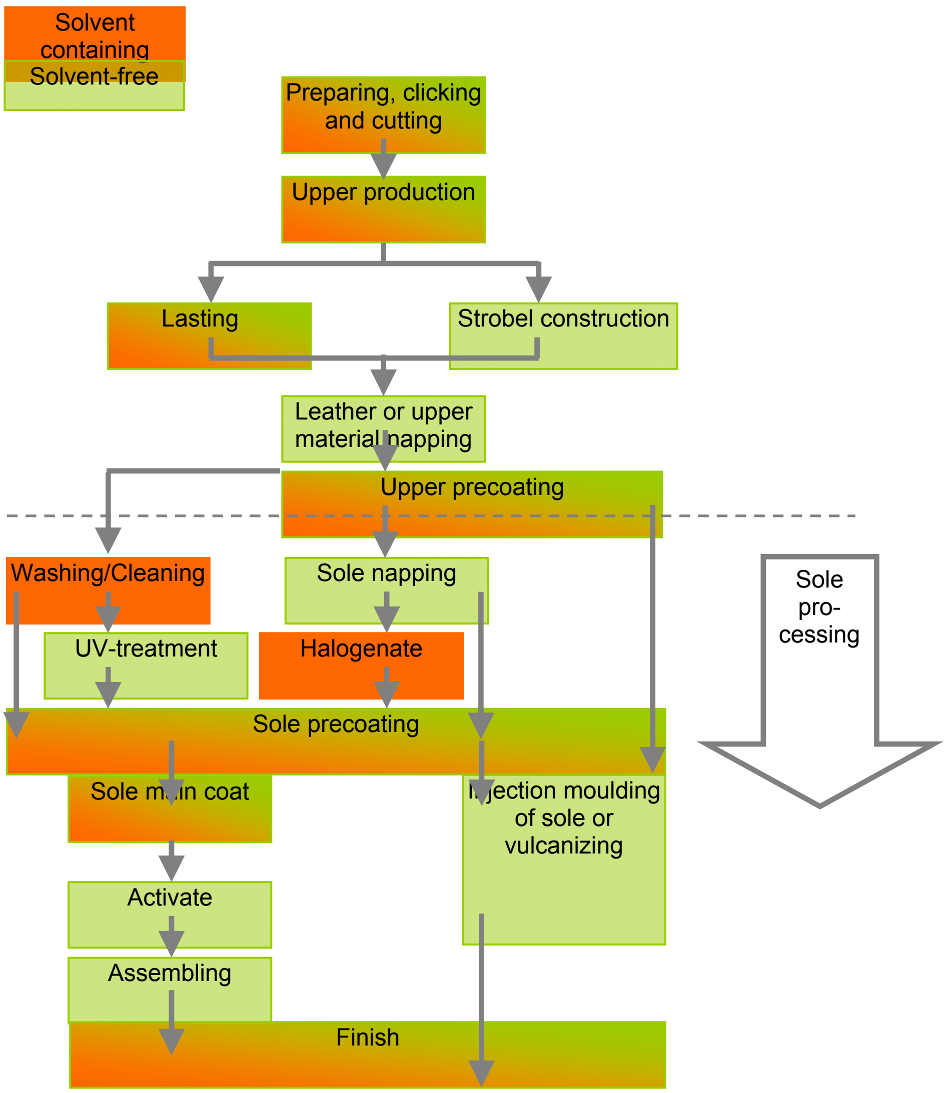
8 Summary of VOC emission reduction measures

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.

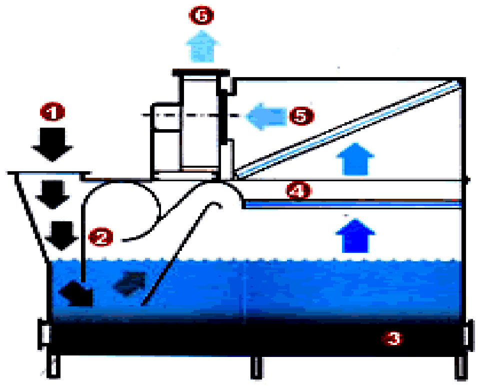


Figure 10: Scheme of the waste gas treatment

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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