7.35 Surface cleaning

7.35.1 Coverage

This chapter covers stack and fugitive VOC emissions from cleaning processes using solvents carried out in industry. The metalworking industries are the major users of solvent cleaning, i. e. automotive, electronic, plumbing, aircraft, refrigeration and business machine industries. Solvent cleaning is also used in activities such as printing, chemical industry, plastic processing, rubber processing, textile processing, mirror manufacturing, paper industry and electric power and solvents are used for paint. Most repair stations for road vehicles and electronic tools use solvent cleaning at least part of the time.

7.35.2 Emission sources

Surface cleaning with solvent (often named solvent degreasing) is the process of using organic solvents to remove water-insoluble residues such as grease, fats, oils, waxes, carbon deposits, fluxes and tars from metal, plastic, fibreglass, printed circuit boards and other surfaces.

Several types of degreasing agents for surface cleaning are used:

- Organic solvents, halogenated or not halogenated,
- Aqueous solutions with use of alkalis, acids, silicates, phosphates and complexing and wetting agents [1],
- Supercritical CO_2,
- Biological agents,
- Ultrasonic degreasing.

Organic solvents used in degreasing applications, are:

- Chlorinated solvents. They are not flammable (no flashpoint) but many of them are classified R40 (perclorethylene and methanedichloride) or R45 (trichlorethylene),
- Hydrocarbon solvents or A3 class solvents (flash point larger than 55°C meaning these solvents are not flammable under current uses but can become flammable during non controlled uses (flammable solvents have a flash point < 55° C)),
- Alcohols and ketones which are flammable,
- HFC hydrofluorocarbons, HFE hydrofluoroethers, PFC perfluorocarbons used in special cleaning applications such as electronic whose main concern is their potential impact on stratospheric ozone even if their ODP (ozone depletion potential) is low but also climate change (PFC and HFC are green house gases regulated under the Kyoto Protocol). HFE are included in the fourth assessment report of IPCC (AR4) [5].

Solvent cleaning is most often used when the metallic part has to be dried after degreasing.

The following parameters have a great influence on the choice of the surface cleaning process:

- The medium to be cleaned,
- The type of impurity to be removed,
- The manufacturing process,
- The requirements induced by subsequent process steps.

The degreasing methodologies can be summarized as follows:

Process	Type of machine	Cleaning product used
Cold cleaning	Manual (with a chiffon as example)	Alcohols Chlorinated solvents
	Open machines	
	Closed machines	
Hot cleaning	Open top machines	Chlorinated solvents
	Covered open top machines	
	Closed machines	
	Closed sealed machines	
	Open top machines	Hydrocarbons
	Covered open top machines	
	Closed machines	
	Closed sealed machines	
Aqueous cleaning	Mono tank machine,	Alkalis, acids, silicates, phosphates, complexing and wetting agents
	Multi tank machines	
	Tunnel machines	

With organic solvents, two types of process exist [1], [2]:

- cold cleaning : cold cleaners are mainly applied in maintenance and manufacturing. They are batch loaded, non-boiling solvent degreasers. Cold cleaner operations include spraying, brushing, flushing, and immersion. In a typical maintenance cleaner, dirty parts are cleaned manually by spraying and then soaking in the tank. After cleaning, the parts are either suspended over the tank to drain or are placed on an external rack that routes the drained solvent back into the cleaner. The cover is intended to be closed whenever parts are not being handled in the cleaner. Typical manufacturing cold cleaners vary widely in design, but there are two basic tank designs: the simple spray sink and the dip tank. Of these, the dip tank provides more thorough cleaning through immersion, and often is made to improve cleaning efficiency by agitation.
- vapour cleaning: vapour degreasers are batch loaded boiling degreasers that clean with condensation of hot solvent vapour on colder metal parts. Vapour degreasing uses halogenated solvents (usually perchloroethylene, trichloroethylene), because they are not flammable and their vapours are heavier than air. A typical vapour degreaser is a sump containing a heater that boils the solvent to generate vapours. Parts to be cleaned are immersed in the vapour zone, and condensation continues until they are heated to the vapour temperature. Residual liquid solvent on the parts rapidly evaporates as they are slowly removed from the vapour zone. Cleaning action is often increased by spraying the parts with solvent below the vapour level or by immersing them in the liquid solvent bath. Nearly all vapour degreasers are equipped with a water separator which allows the solvent to flow back into the degreaser.

For cold cleaners, bath evaporation can be controlled by covering the bath regularly, by using an adequate freeboard height, and by avoiding excessive drafts in the workshop.

For open-top vapour systems, most emissions are due to diffusion and convection, which can be reduced by covering the bath automatically or manually, by spraying below the vapour level, by optimising work loads, or by using a refrigerated freeboard chillers (which may be replaced, on larger units, by a carbon adsorption device).

Vapour cleaning can be carried out in closed sealed machines.

Hermetically sealed machines

These types of machines prevent direct exposure between the solvent and the atmosphere by a series of interlocks, and by the use of a vapour extraction and/or refrigeration system which recycles the vapour back into the solvent sump. This provides an extremely high degree of solvent containment and reduces fugitive emissions. These machines can work either with chlorinated solvents or with other solvents like A3 class hydrocarbons, HFC or HFE. As an option, the complete cleaning device can be operated under a vacuum. This enables distillation at lower temperatures and allows a permanent control of the vapour emissions [3].

Aqueous based cleaning systems

This technique consists of water, detergent and a small amount of solvents, and has been shown to provide a reasonable cleaning efficiency for certain applications. Besides acid cleaning baths, strong till weak alkaline and neutral products are used for industrial cleaning of hard surfaces. Neutral cleaners are predominantly applied for intermediate and final surface cleaning, whereas strong alkaline products aim at obtaining highly cleaned surfaces before surface ennoblement, phosphatation or coating processes. Acid products are found in special applications. Water-based cleaning agents can be used for the cleaning of metals such as steel, aluminium, magnesium, copper, etc., but also for plastics, coated surfaces, glass and electronic parts. In large parts of industrial surface cleaning, water-based systems have been established, leading partly to even better cleaning results as former solvent-based systems. This effect is especially related to further processing of the substrate, such as coating. The two main techniques used in aqueous systems are immersion (small tanks to multi-tanks system) and aspersion (small machines interoperations with complete tunnels).

Biological cleaning process

This technology is based on a water-based cleaning agent combined with an integrated microbiology for the degradation of oils and grease. The water-based cleaning solution is light alkaline to allow the degreasing of a wide range of metals (e. g. copper, iron, aluminium, zinc).The used micro organisms are natural, their living conditions are optimised and continuously controlled via a computer system in order to keep the determinant parameters of the milieu optimal. In order not to endanger the micro organisms, the cleaning temperature is kept between 40 and 45 °C (but can go down to 35°C in certain systems) and the pH-value must remain around 9. The cleaning agent is regenerated via automatic dosage. When comparing to conventional degreasing processes, the amount of generated waste water is in this case much smaller. Some substances cause damage to the micro organisms, or worse kill them; among these substances are chlorinated products, whose degradation has not yet been clarified. The main applications encountered are degreasing fountains for maintenance cleaning in the cold cleaning application.

7.35.3 BAT, Associated Emission Levels (AEL)

General emission reduction options in this sector are [1]:

- Minimisation of the amount of grease and oil, selection of oils greases or systems that allow the use of the most environmentally friendly degreasing systems
- Improvement of equipment:
  - cold cleaning : systematic use of covers, reduction of pulverisation pressure,
  - vapour degreasing : systematic use of closed sealed machines for vapour degreasing with chlorinated solvent, hydrocarbons or other solvents such as HFE, HCFC and PFC
  - Higher freeboards for the reduction of organic solvent losses for degreasing baths; refrigerated freeboards for degreasing baths associated with activated carbon adsorption.

- Substitution of solvent based cleaning agents:

  All solvents such as trichloroethylene which are classified as carcinogenic compounds, have to be substituted if not used in safe and hermetically sealed machines.
  - vapour degreasing : use of aqueous based cleaning agent (using also the BAT defined for these processes [1]),
  - cold cleaning : biological agents, use of fatty acids of natural or synthetic esters [3].
- Regeneration of used organic solvents on-site or by an external regenerator;
- Switch to low-temperature plasma processes (still using some organic solvent).

Examples of emission reduction measures and performances in surface cleaning are presented in table 1

Table 1: Emission sources and selected VOC control measures with associated emission levels for surface cleaning [2]

Emission source	Available techniques	Associated emission levels for VOCs
Vapour cleaning using halogenated solvents or hydrocarbons	Water-based degreasing systems	0 g/kg solvent used*
	Hermetically sealed machines	Less than 0.1 % solvent used*

* sum of I1 the quantity of organic solvents or their quantity in preparations purchased which are used as input into the process in the time frame over which the mass balance is being calculated and I2 the quantity of organic solvents or their quantity in preparations recovered and reused as solvent input into the process. (The recycled solvent is counted every time it is used to carry out the activity).

7.35.4 Emerging techniques

Supercritical CO_2

The principle of this technique is that at supercritical conditions (beyond 75 bars and 35°C), intermediary between liquid and gas, CO_2 has solvent properties which have the advantage to be adjustable with the variation of temperature and pressure. This clean solvent is easily recoverable in making it passing again in a gas stage at the end of the cycle. Nevertheless its cleaning power is limited: it works well for non-polar products but is less efficient with polar products. This difficulty can be surmounted by adding few percent of co-solvent or using an ultra-sonic mechanical effect.

Plasma degreasing

This technology is already applied in some specific production sectors and can be applied to a large variety of substrates leading partly to even better cleaning results than former solvent systems. This effect is especially related to further processing of the substrate, such as coating of certain plastics with water-based paints. Thus, a double emission reduction may be achieved in some cases. Within the plasma degreasing process, surface cleaning is carried out at temperatures below 100 °C and a pressure between 0.1 and 2.10^{-3} hPa. The vacuum chamber is filled with process gas, such as noble gases (e. g. argon, helium), fluorine containing gases (e. g. tetrafluoromethane) or oxygen. An electric field conveys energy to the system, resulting in ionised gas particles. Oxygen is mostly used as process gas. Radicals generated via excitation aim at cutting the hydrocarbon chains and oxidise them to form carbon dioxide and water. The cleaning effect of the plasma is based on this chemical reaction. Organic impurities can be removed by this degreasing process, but plasma technique is not adapted to inorganic impurities such as shavings, mineral dust or salts.

7.35.5 Cost data for emission reduction techniques

Costs are defined in the EGTEI synopsis sheet concerning “surface cleaning“ [2].
Costs range from 0.4 to 56 € / kg VOC abated in the smallest installation and from – 0.3 to 2.97 € / kg VOC in the largest one.

7.35.6 References used for chapter 7.35

[1] European commission BREF for the surface treatment of metals and plastics – August 2006

[2] EGTEI synopsis sheet: Surface cleaning – 2005

http://www.citepa.org/forums/egtei/27-Synopsis-sheet-surface%20cleaning-30-09-05.pdf

[3] Biosolvants – Enjeux et opportunités – 27 mai 2008 – ADEME

[4] AEA energy and environment, OKOPOL and BIPRO: Guidance on VOC substitution and reduction for activities covered by the VOC solvent emissions directive – Guidance 4/5 – Surface cleaning – European commission 2008

[5] A compilation of technical information on the new GHG gases and groups included in the Fourth Assessment Report (AR4) of the Intergovernmental Panel on Climate Change http://unfccc.int/national_reports/annex_i_ghg_inventories/items/4624.php