# 14

# SOLVENT USE IN VARIOUS INDUSTRIES

Attempts to reduce solvent use in the production of various materials require background information on the current inventory, the reasons for selecting certain solvents, the effect of various solvents on the properties of final products, future trends and the possibilities for solvent replacement.

Information on solvent use investigates these areas. This chapter is possible only because of a thorough evaluation by large groups of scientists and engineers assembled by US Environmental Protection Agency. This has produced Compliance Sector Notebooks which contain invaluable information on solvent use. Full documents can be found on the EPA website at http://es.epa.gov/oeca/sector/index.html. These are useful in the investigation of a particular industry. Similar data from other countries were not available but open literature and patents have been included to help the reader to understand changes occurring in other countries.

## 14.1 ADHESIVES AND SEALANTS

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Adhesives and sealants are manufactured from a variety of polymers. Their selection and their combinations used impact solvent selection. Most solvent systems are designed to optimize the solubility of the primary polymer. Adhesives can be divided into ones which bond by chemical reaction and ones which bond due to physical processes.[1] Chemically reactive adhesives are further divided into three more categories for those that bond through polymerization, polyaddition, or polycondensation. Physically bonding adhesives include pressure sensitive and contact adhesives, melt, or solution adhesives, and plastisols. Polymerization adhesives are composed of cyanoacrylates (no solvents), anaerobic adhesives (do not contain solvents but require primers for plastics and some metals which are solutions of copper naphthenate),[2] UV-curable adhesives (solvent-free compositions of polyurethanes and epoxy), rubber modified adhesives (variety solvents discussed below).

Polyaddition adhesives include epoxy and polyurethane polymers which can either be 100% solids, water-based, reactive or non-reactive hot melts or contain solvents mostly to regulate viscosity. Typical solvents include methyl ethyl ketone, acetone, mineral spirits, toluene, and xylene.[3] Polycondensation adhesives include phenol-formaldehyde resin, polyamides, polyesters, silicones and polyimides. With the exception of polyesters (which require ethanol and N-methylpyrrolidone as solvents) and polyimides (which require methyl amyl ketone, butyl acetate, methyl ethyl ketone, 2-ethoxyhexyl acetate as solvents), these adhesives can be made without solvents.

Pressure sensitive and contact adhesives are made from a variety of polymers including acrylic acid esters, polyisobutylene, polyesters, polychloroprene, polyurethane, silicone, styrene-butadiene copolymer and natural rubber. With the exception of acrylic acid ester adhesives which can be processed as solutions, emulsions, UV curable 100% solids and silicones (which may contain only traces of solvents), all remaining rubbers are primarily formulated with substantial amounts of solvents such as hydrocarbon solvents (mainly heptane, hexane, naphtha), ketones (mainly acetone and methyl ethyl ketone), and aromatic solvents (mainly toluene and xylene).

Melt adhesives and plastisols do not contain solvents. The solution adhesives group includes products made from the following polymer-solvent systems: nitrocellulose (typical solvents include solvent combinations usually of a ketone or an ester, an alcohol and a hydrocarbon selected from isopropanol, 2-butylhexanol, amyl acetate, acetone, methyl ethyl ketone), nitrile rubber (main solvent - methyl ethyl ketone), polychloroprene (which is usually dissolved in a mixture of solvents including a ketone or an ester, an aromatic and aliphatic hydrocarbon selected from naphtha, hexane, acetone, methyl ethyl ketone, benzene, toluene), and polyvinyl acetate (water).

In addition to the solvents used in adhesives, solvents are needed for surface preparation[4] and primers. Their composition may vary and is usually designed for a particular substrate, often using fast evaporating solvents and environmentally unfriendly materials with significant adverse health effects.

Detailed data on the total amount of solvents used by adhesive industry could not be found. The adhesive manufacturing industry continues to grow at a very fast pace. Total adhesive production, according to Frost & Sullivan, was $18.25 billion in 1996 and this is expected to grow to $26.2 billion in 2003.[5] Solvent-based materials in 1995 constituted 13% of total production in North America, 14% in Europe, 15% in Japan, and 25% in the Far East.[6] Many industries which use solvent-based adhesives have moved to South America and Asia where regulations restricting emissions are less severe.[5] The shoe industry is now concentrated in South America. There are many initiatives to decrease solvent emissions. For example, World Bank's assistance program for developing countries focuses on this issue.[5] But in spite of the fact that solvent-based adhesives lost some of their markets (3.3% during the period of 1994-1996),[5] they still hold 14-15% of the European market.[6] It is estimated that the use of solvents contributes 24% of all VOC emissions. According to one source adhesives were responsible for a 6% share in these emissions in 1993.[7] Another source[8] blames adhesives for 7% of total VOC emissions in Germany in 1995.

Sealants are divided into groups according to the generic names of polymer base. The main groups include: polyurethanes, silicones, acrylics, polysulfide and others (PVC, polybutylene, styrene-butadiene-styrene copolymers, polychloroprene, and several others). The amount of solvent used in sealants is controlled by the standards which previously divided sealants into two groups: these below 10% VOC and those above. Recently, a provision was made to include water-based acrylics and the limit of VOC for class A sealants was increased to 20%. Polyurethane sealants and structural adhesives can be made without solvent (the first solvent-free polyurethane sealant was made in 1994).[9] Solvents are added to reduce sealant viscosity and to aid in the manufacture of polymer. Typical solvents used are mineral spirits, toluene, and xylene. A small amount of solvent is emitted from curatives which contain methyl ethyl ketone. Most formulations of silicone sealants do not contain solvents. In some sealants, traces of benzene and toluene can be found.

Acrylic sealants are water-based but they may also contain ethylene and propylene glycols, mineral spirits and mineral oil. There are also solvent-based acrylic sealants which contain substantial amounts of solvents such as mineral spirits, toluene and xylene. Polysulfide sealants usually contain toluene but methyl ethyl ketone is also used. The group of class B sealants contains substantially more solvents (up to 40% by volume) but there are some exceptions. PVC sealants are based on plastisols and they can be made without solvents. Butyl rubber based sealants usually contain hydrocarbons ($C_6$-$C_{12}$). Styrene-butadiene-styrene based sealants usually have a large amount of solvents selected from a group including toluene, heptane, hexane, methyl ethyl ketone, isobutyl isobutyrate, n-amyl acetate, n-amyl ketone. They are usually processed in solvent mixtures. Polychloroprene is usually dissolved in a mixture of solvents including ketones or esters, and aromatic and aliphatic hydrocarbons. The list includes naphtha, hexane, acetone, methyl ethyl ketone, benzene, and toluene.

The world market of sealants was estimated in 1996 at $2 billion and was expected to grow in 2003 to $2.75 billion with an annual growth rate of 4.5% which is slightly lower than that expected for adhesives (5.3%).[5]

The changing trends are clearly visible when developments in technology are studied but many barriers to reductions in solvent use exist such as the high investment required, longer processing time, frequently higher material cost of adhesives, and the psychological barrier of changing established adhesive practices. In many instances, adhesive performance is predicted by its superficial characteristics such as strong smell which might suggests that the material has superior properties, its initial green strength which for many indicates good bonding properties, and high viscosity often related to good processing characteristic.[10] Since the alternative materials may not have much odor, or require of longer time to reach strength and have a low viscosity, users are suspicious that their potential performance may be inferior. The following information reviews some recent findings which may contribute to future changes.

In the shoe industry, a major breakthrough occurred in 1928 when polychloroprene was first introduced.[1,10] The first, simple formulation is still manufactured and is used worldwide because the glue can be easily prepared by simply making a solution of the polymer. This gives a product with good adhesion to various substrates. Many new products are available today as potential replacements. Hot melt adhesives can be used in some applications but they still require solvents for cleaning, degreasing, and swelling. Also, their bond strength is frequently inadequate. Reactive systems are not yet used in the shoe industry but reactive hot melts are finding applications. Their broader use is hampered by their sensitivity to moisture which requires special equipment and special care.[10] Water-based adhesives are the most likely replacement product. They also need special equipment for processing because of the high heat of evaporation of water (although water based adhesives contain 50% polymer compared with 15-20% in solvent based adhesives).[10] Two sport shoe manufacturers, Nike and Reebok, already use this technology.

Traditional polychloroprene adhesives can be modified in several ways to be useful in water-based systems. Figure 14.1.1 shows peel strength of several adhesives. The solvent based adhesive (A) has excellent properties both in terms of green strength and bond strength. A simple emulsion of polychloroprene (B) has relatively good ultimate strength

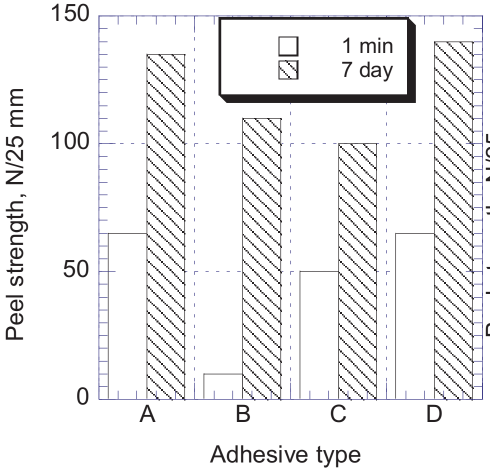

Figure 14.1.1. Green strength and adhesion of several adhesives. Symbols are explained in the text. [Data from B Archer, *International J. Adhesion & Adhesives*, **18**, No.1, 15-8 (1998).]

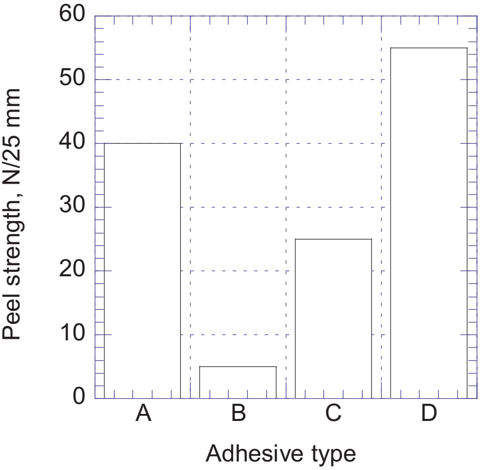

Figure 14.1.2. Contactability of various adhesives. Symbols are explained in the text. [Data from B Archer, *International J. Adhesion & Adhesives*, **18**, No.1, 15-8 (1998).

but lacks green strength and therefore does not meet the performance requirements of shoe manufacturers and other industries.[11] Adhesive (C) is a blend of polychloroprene with polyurethane in a water-based system. This modification gives both green strength and peel strength but Figure 14.1.2 shows that peel strength of a freshly applied adhesive is lower than that of solvent based polychloroprene which may cause problems in holding both adhering surfaces together. The adhesive (D) was developed in an interesting new process which involves the emulsification of a solvent based adhesive obtained from styrene-isoprene-styrene rubber.[11] After emulsification, the solvent is stripped under vacuum to produce a solvent-free adhesive. The reason for emulsification of the complete adhesive as opposed to emulsification of the rubber alone is to produce a homogeneous adhesive system which would otherwise suffer from separation of polymer particles surrounded by a layer of emulsifying agents. Figures 14.1.1 and 14.1.2 show that this system is superior to solvent-based adhesives. Adhesives can be further improved by polymer blending and by adhesive foaming. A foamed adhesive layer requires less material (approximately 4 times less than a conventional adhesive), it requires less drying time (less water and faster evaporation), and provides an improved bond strength. A foamed adhesive has a larger surface area which increases the surface area of contact with the substrate. The compressed rubber foam has a higher tear strength than unfoamed film of the same thickness.[11]

Also, regulations are helping to reduce the solvent content of adhesives.[12,13] The use of chlorinated solvents, frequently used in primers and for cleaning, has been discontinued based on the Montreal Protocol. From June 1998, the production of a pair of shoes in Europe should not involve the use of more than 20 g of solvent. This is only partially successful solution since shoe production is expected to move out of developed countries to less restrictive jurisdictions. Solvent Emission Directive will continue to restrict solvent use in Europe.

Many changes have occurred and more are expected in adhesives based on thermoplastic polyurethanes (TPU).[3,14,15]In the last 30 years, TPU based adhesives were manufactured with solvents for shoes, food packaging, and textile and plastic film lamination. Current technologies use TPU in the form of a hot melt, as a reactive PUR and as a thermoplastic laminating film.[3] Reactive hot-melts were first introduced in the early 1980s and since than have grown very rapidly. After application the adhesive is cured by moisture.[14] These adhesives are already in use by the automotive industry (bonding carpet to door panels, tray assembly, lenses to headlamp housing, and lamination of foam to fabric) and in furniture and building products (moldings, picture frames, decorative foil, edgebanding), in bookbinding, and in the footwear industry. Polyurethane water dispersions are expected to grow 8-10%/year from the current 5,000-6,000 tones/year market in Europe.[14] Applications are similar to those of hot melts.

UV-curable pressure-sensitive adhesives are the most recent application of the advancing radiation curing technology.[16] Low viscosity formulations allow the use of standard application techniques with several advantages such as improved production rate, energy efficiency, improved properties of the final products, and new potential applications for pressure-sensitive additives in thicker films with mechanical performance. It is expected that radiation cured materials will expand at a rate of 10%/year.[17] Adhesives constitute 16% by value and 13% by volume of radiation cured products (two major applications for radiation cured materials are coatings and inks). Henkel introduced a series of water-based laminating adhesives.[18] Hot melt systems, high-solids solvent systems with a 3 times higher solids content, and water based adhesives have been introduced to textile lamination to replace traditional low-solids solvent-based adhesives.[19]

Odor elimination is the additional benefit which has helped to drive the replacement of solvent-based systems.[20] In packaging materials, most odors are related to the solvents used in inks, coatings and adhesives. Also, coalescing solvents from water-based systems caused odors. Elimination of solvent is a priority but solvent replacement may also change the response to the odor because solvents such as toluene and xylene smell like lubricating oils or turpentine whereas isopropanol smells more like a disinfectant. Odors stem not only from solvents but also from products of the thermal and UV degradation of other components and solvents.[20]

In view of the above efforts, it is surprising that the majority of recent patents on adhesives are for solvent-based systems.[21-26] The new inventions include a universal primer,[21] an adhesive composition in which solvents have been selected based on Snyder's polarity (only solvents which belong to group III are useful in adhesive for automotive applications to avoid a deleterious effect on paint),[22] a low VOC adhesive for pipes and fittings,[23] a solvent-containing heat-resistant adhesive based on siloxane polyimide,[24] a water-based polyimide adhesive,[25] and two-component solvent-free polyurethane adhesive system for use in automotive door paneling.[26]

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## 14.2 AEROSPACE

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Figure 14.2.1 shows a schematic diagram of the aerospace manufacturing process.[1] Metal finishing is the process in which most solvents and solvent containing materials are used. The main function of the metal finishing process is corrosion protection which requires proper cleaning, surface preparation, and the selection of suitable coatings.

The functions of coatings used in aircrafts are different from those used in ordinary coating applications therefore an extrapolation of the progress made with solvent replacement in other coating types is not justified. The typical flight conditions of operating altitude (about 10,000 m above the earth), speed (most frequently 900 km/h), temperature (very low in space at about -60°C and substantially higher after landing up to 80°C), humidity (low in space and high at earth level are combined with condensation due to the tempera-

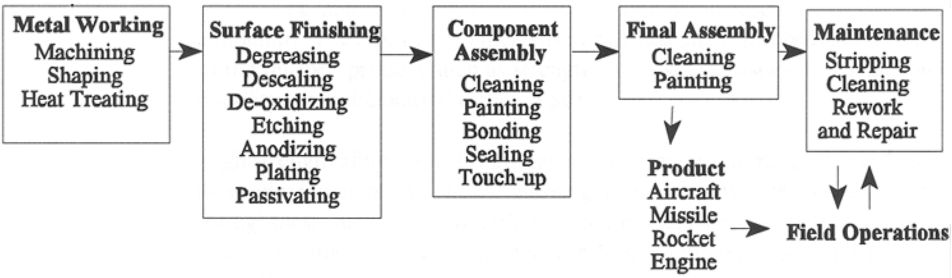

Figure 14.2.1. Schematic diagram of aerospace manufacturing process. [Reproduced from Profile of the Aerospace Industry. EPA Office of Compliance Sector Notebook Project. US Environmental Protection Agency. November 1998.]

**Table 14.2.1. Total releases of solvents by the aerospace industry. [Data from ref. 1]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| benzene | 62,000 | methyl ethyl ketone | 995,000 |
| bromotrifluoromethane | 750 | methyl isobutyl ketone | 47,000 |
| n-butyl alcohol | 7,000 | methyl tetr-butyl ether | 550 |
| sec-butyl alcohol | 10,000 | tetrachloroethylene | 285,000 |
| cyclohexane | 400 | 1,1,1-trichloroethane | 781,000 |
| 1,2-dichlorobenzene | 600 | trichloroethylene | 429,000 |
| 1,1-dichloro-1-fluoroethane | 10,000 | trichlorofluoromethane | 1,800 |
| dichloromethane | 314,000 | toluene | 414,000 |
| isopropyl alcohol | 1,000 | xylene | 103,000 |
| methanol | 21,000 | | |

ture difference), UV radiation (substantially higher during flight), mechanical abrasion due to the high speed of travel, exposure to salt in the atmosphere, exposure to higher level of acids and sulfur dioxide, and exposure to de-icing fluids during winter.[2,3] These unusual conditions should be considered in conjunction with the mechanical movement of the coating caused by rapid changes in temperature and the flexing of aircraft elements because of changes in pressure and severe load variations on wings.[2] In addition, because of their size, aircrafts must often be painted at low temperatures which requires a coating that will cure at these temperatures without leaving entrapped volatiles. These could evaporate in the low pressure conditions at high altitude and cause the formation of voids where corrosion could start. These factors make the design of an effective coating system a severe technological challenge.

Coatings are used by the aerospace industry both for OEM and maintenance purposes. In each case surface cleaning and preparation is required. A paint stripping operation is added to the task in maintenance repainting. Coatings are applied by spraying, brushing, rolling, flow coating, and dipping. Depending on the method of application, the rheological properties of coatings must be adjusted with solvents and, in some cases, with water. An alternative method of viscosity adjustment involves heating the coatings to lower its viscosity by increasing its temperature. This reduces solvent usage. Solvents are also used for equipment cleaning.

In addition to paints, sealants are also used. Sealants are mostly based on polysulfides, containing solvents as discussed in the previous section. Also, non-structural adhesives containing solvents are used as gaskets around windows and for carpeting.

Paint removal is accomplished by either chemical or blast depainting. Dichloromethane is the most common solvent used for this application. Aerospace industry estimates that 15,000 to 30,000 different materials are used for manufacturing some of which are potentially toxic, volatile, flammable, and contain chlorofluorocarbons. Some of these substances may result in air emissions, waste-waters, and solid waste.

**Table 14.2.2. Total transfers of solvents by the aerospace industry. [Data from ref. 1]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| n-butyl alcohol | 2,600 | methyl ethyl ketone | 500,000 |
| cyclohexane | 18,000 | methyl isobutyl ketone | 17,000 |
| 1,2-dichlorobenzene | 4,000 | tetrachloroethylene | 110,000 |
| 1,1-dichloro-1-fluoroethane | 230 | 1,1,1-trichloroethane | 133,000 |
| dichloromethane | 68,000 | trichloroethylene | 98,000 |
| N,N-dimethylformamide | 500 | trichlorofluoromethane | 3,800 |
| ethylene glycol | 14,000 | toluene | 87,000 |
| methanol | 12,000 | xylene | 12,000 |

Air emissions result from sealing, painting, depainting, bonding, as well as from leakage in storage, mixing, drying, and cleaning. The most common solvents involved in coatings are trichloroethylene, 1,1,1-trichloroethane, toluene, xylene, methyl ethyl ketone, and methyl isobutyl ketone. Wastewater is generated through contamination by paints and solvents used for cleaning operations. Solid waste containing solvents comes from paint overspray intercepted by emission control devices, depainting, cleanup, and disposal of unused paint. Solvents used for cleaning are usually a mixture of dimethyl-benzene, acetone, 4-methyl-2-pentanone, butyl ester of acetic acid, naphtha, ethyl benzene, 2-butanone, toluene and 1-butanol. Some solvents used for painting and cleaning are either recycled are burned to recover energy.

In 1996, 199 aerospace facilities (out of 1885 analyzed in the report) released and transferred off-site or discharged to sewers about 12,000 kg of 65 toxic chemicals (solvents in these releases are reported in Table 14.2.1 and transfers in Table 14.2.2).

Methyl ethyl ketone, 1,1,1-trichloroethane, trichloroethylene, and toluene accounted for 66% of all releases. 70% of all transfers was for recycling purposes. The aerospace industry released 10,804 tons of VOC in 1997 which constituted 0.61% of the total releases from 29 industries which were analyzed. Thirteen other industries release more VOC than the aerospace industry.

Recycling and disposal of solvents in the aerospace industry equals the purchase cost of the solvents. Therefore reduction of solvent use is very cost effective. Some chemical stripping operations are now being replaced by cryogenic stripping with liquid nitrogen. Also, supercritical carbon dioxide has been used in Hughes Aircraft Company in some cleaning applications. Solvent emissions can be reduced through control of evaporation (lids, chillers), by dedicating process equipment (reduces cleaning frequency), production scheduling, immediate cleaning of equipment, better operating procedures, reuse of solvent waste, and use of optimized equipment for paint application. There are plans to evaluate powder coatings and water-based paints.[1,2] There are trials to use water as the paint thinner and to lower viscosity of paints by application of resins which have lower viscosity.[2] Work is under the way to replace dichloromethane/phenol stripper with benzyl alcohol.[2] The introduction of an intermediate layer between the primer and the top coat has been proposed.

This will aid the stripping action of the proposed stripping solvent, benzyl alcohol. VOC have already been reduced in several components: bonding primer (from 1030 to 850 g/l), undercoats (from 670 to 350), top coats (from 700-900 to 250-800), clear coats (from 700-800 to 250-520), surface cleaners (from 850 to 250) as well as other materials.[3]

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## 14.3 ASPHALT COMPOUNDING

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Numerous construction products are formulated from asphalt and coal tar for such applications as driveway sealers, cutback asphalts, flashing cements, concrete primers, concrete cold mixes, roof cements, expansion joint fillers, patch liquids, waterproofing liquid-applied membranes, and pipeline coatings. All these products are likely to contain solvents.

The simplest formulations are mixtures of asphalt and (usually) mineral spirits used for sealing , priming, and coating of concrete. These are usually very low performance products which are used in large quantities because of their low price. They release about 40% of their weight to atmosphere during and after application. Since they do not perform well they have to be re-applied at frequent intervals. Driveway sealer is an example of a product which is used every spring, in spite of the fact that, in addition to the pollution it causes, it also produces a gradual degradation and cracking of the driveway. The only solution for elimination of this unnecessary pollution seems to be banning the product by regulation. Some of these products can be replaced by asphalt emulsions which contain water in place of organic solvents.

Several products are used for patching and joint filling purposes. These materials (flashing cement, roof cement, patch liquid, and expansion joint filler) also use solvents to regulate viscosity. The solvents are usually mineral spirits, fuel oil, or polycyclic aromatic hydrocarbons. In addition to the base components, inexpensive fillers such as calcium carbonate or limestone but also still asbestos are added. These products harden on evaporation of the solvent and fill the joints, adhere to surfaces, and provide some waterproofing. These are again, low technology materials, traditionally used because of their very low cost. Most of these products can be replaced by modern sealants which will result in higher initial cost but longer service.

The most technologically advanced products are used for waterproofing and pipeline coatings. These products are also based on dispersion of asphalt in the above mentioned solvents but reinforced with addition of polymer. The addition of polymer modifies the plastic behavior of asphalt and renders it elastomeric. Additional solvents are usually added to improve the solubility of polymeric components. Reactive polyurethanes are the most frequently used modifiers for waterproofing liquid membranes. Toluene and xylene are the most frequently used additional solvents. These materials partially solidify because of evaporation of the solvent. Their elastomeric properties are derived from chain extension and crosslinking reactions which form an internal polymeric network which reinforces asphalt.

There is no data available on the solvent emissions from these materials but their scale of production suggests that their emissions are probably comparable with the entire rubber industry. This is one industry which should be closely monitored not only because of the emission of the above listed solvents but because some of the low grade solvents used contain large quantities of benzene and hexane. It is also cause for concern that asphalt and tar have carcinogenic components.

Recent inventions[1-5] are driven by product improvement needs and environmental aspects of application of these products. Janoski's patent[1] describes a product which is an anhydrous blend of polymer and asphalt and is substantially solvent-free. This technology shows that it is possible for an ingenious designer to produce low viscosity materials without using solvents but by selecting the appropriate type and concentration of bituminous materials, polyurethane components, and plasticizers.

In another invention,[2] a modifier is introduced to increase the adhesion of asphalt/water emulsions to aggregates. Emulsified asphalt is not so deleterious to the environment but its performance suffers from aggregate delamination. In yet another recent invention,[3] terpene solvent, which is a naturally occurring (but never in this high concentration), biodegradable material, was used to replace the mineral spirits, xylene, trichloroethane, toluene, or methyl ethyl ketone normally used in cutback formulations (cutback asphalt is a dispersion of asphalt in a suitable solvent to reduce viscosity and allow for cold application). The two other patents[4,5] discuss inventions leading to an improvement of high and low temperature properties of asphalt with no special impact on reduction of solvents used.

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## 14.4 BIOTECHNOLOGY

### 14.4.1 ORGANIC SOLVENTS IN MICROBIAL PRODUCTION PROCESSES

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### 14.4.1.1 Introduction

Solvents are not dominating compounds in the biosphere of our planet. Under natural conditions, their presence in appreciable amounts is restricted to specific areas. Only a very limited number of solvents is of biological origin and some may reach higher concentrations in nature. The best known example is ethanol. However, also butanol and acetone can be formed readily by microbes and locally high concentrations may occur. In fact, in the beginning of the 20th century, very large production facilities were in operation for the microbial production of butanol and acetone. Furthermore, terpenes are natural solvents that are produced mainly by plants and locally they can reach high concentrations. For instance, limonene is present in tiny droplets in the peel of oranges. All these solvents are toxic to microbial cells. Some others as higher hydrocarbons that are present for instance in olive oil, are not toxic to microbes as will be discussed later.

With the advent of the chemical industry, this picture has changed dramatically. In polluted locations, microorganisms may be confronted with a large number of solvents at high concentrations. With a few exceptions only, it has turned out that microbes can be found that are able to degrade these compounds if their concentration is low. This degradative potential is not unexpected in view of trace amounts that may be present locally in the natural biosphere. But the exposure of cells to unnatural high concentrations of these solvents usually leads to irreversible inactivation and finally to their death.

The chemical industry is largely based on solvent-based processes. But in biotechnological processes, the microbes usually are exploited in a water-based system. This approach is quite understandable in view of the preference of microbes for water and the problems solvents pose to whole cells. Solvents often are used to extract products from the aqueous phase but only after the production process has been completed. At this stage, damage to whole cells is obviously no longer relevant. In both, chemical industry and biotechnology, organic solvents have many advantages over water because of the nature of either product or substrate. Consequently, during the last decades many possibilities have been investigated to use solvents in biocatalytic processes.[1,2] The more simple the biocatalytic system, the less complex it is to use solvents.

Free or immobilized enzymes have been exploited already in a number of systems. Here, biocatalysis may take place in reversed micelles or in an aqueous phase in contact with an organic solvent.[3] In a powdered state some enzymes are able to function in pure organic solvents.[4] Furthermore, modified enzymes such as polymer bound enzymes[5] or surfactant-coated enzymes[6] have been developed so that they can solubilize in organic solvents to overcome diffusion limitation. The advantages of enzymatic reactions using organic solvents can be briefly summarized as follows:[1,3,4]

1) hydrophobic substances can be used;
2) synthetic reactions can take place;
3) substrate or production inhibition can be diminished and
4) bioproducts and biocatalysts can easily be recovered from the systems containing organic solvents.

Although organic solvents have often been used in enzymatic reactions, the application of organic solvents for biotransformation with whole-cell systems is still limited. Cells might be continuously in direct contact with the organic phase in a two-phase water-solvent system during the whole production cycle (Figure 14.4.1.1).[7] Alternatively, cells may remain separated from the bulk organic phase by using membrane bioreactors (Figure14.4.1.2).[8] In these instances, cells encounter phase toxicity[9] or molecular toxicity, respectively.

Because whole bacterial cells are more complex than enzymes, they pose by far greater problems in operating bioproduction processes when organic solvents are present. The most critical problem is the inherent toxicity of solvents to living organisms.[1,2,10,11] As

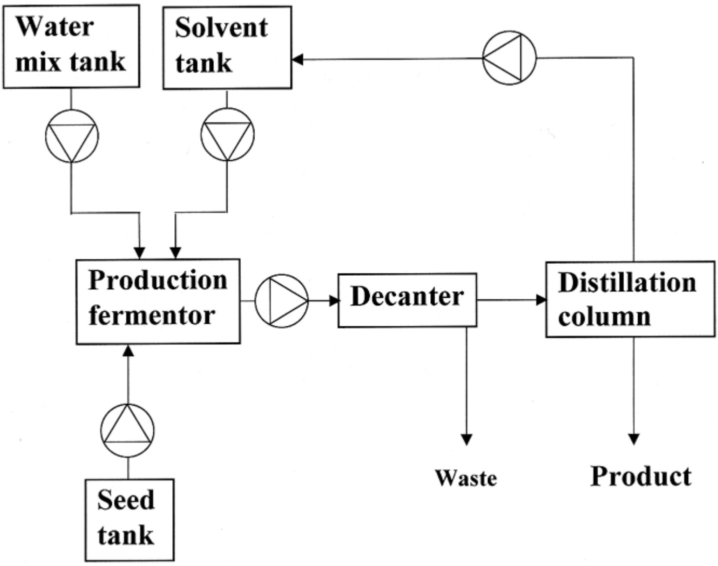

Fig.14.4.1.1. Schematic diagram of a two-phase bioreactor system for continuous 1-octanol production. [After reference 7]. 1-Octanol is produced from n-octane in hexadecene by *Pseudomonas oleovorans* or recombinant strains containing the alkane oxidation genes.

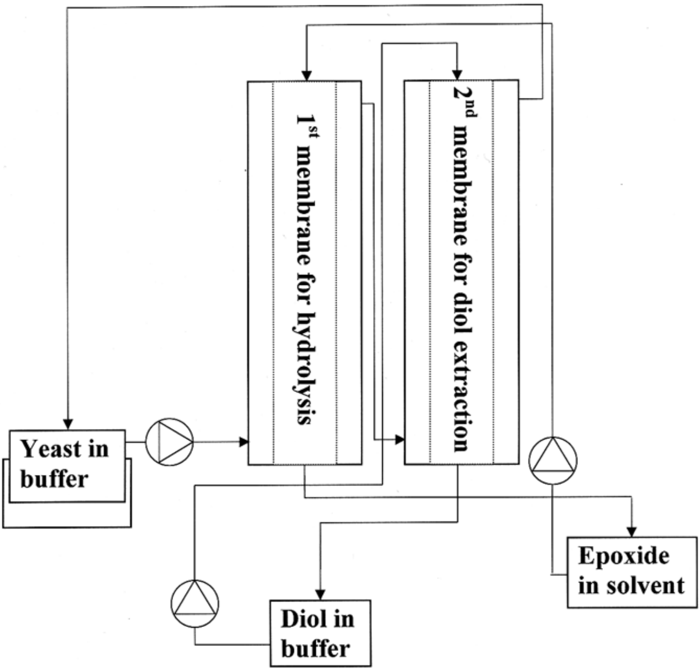

Fig.14.4.1.2. Schematic diagram of a two-phase hollow-fiber membrane bioreactor system for hydrolytic epoxide resolution. [After reference 8]. The yeast cells contain an epoxide hydrolase that enantioselectively hydrolyzes racemic epoxide resulting in enantiopure epoxide that partitions to the organic phase. Diol produced partitions to the water phase.

some solutions have been already found in this area, further progress is expected in the near future. A key problem is the selection of useful solvents in combination with a suitable microbe. Many solvents may be considered with their specific process properties, and many microorganisms may be considered also with their specific advantages or disadvantages. Only on the basis of a detailed understanding of the functioning of a microbial cell in the presence of solvents will it be possible to make a rational selection for a good combination solvent/organism. In the following section we will discuss these key questions. We will also describe recently found solvent-tolerant bacteria and will provide some examples of biotransformation using solvent-tolerant bacteria.

### 14.4.1.2 Toxicity of organic solvents

The toxicity of an organic solvent is closely related to its hydrophobicity, as expressed by the log $P_{O/W}$ values,[12-16] the logarithm of the partition coefficient of the solvent between 1-octanol and water (Table 14.4.1). In general, the Gram-negative bacteria show relatively higher solvent tolerances than the Gram-positive bacteria.[12,14] This may be caused by the difference in the composition of the cell envelope. Solvents with a high log $P_{O/W}$ resulted in the highest activities, but the range of log $P_{O/W}$ tolerated by an organism is dependent on the type of microorganism. In the following section we will describe what happens in the cell in the presence of solvents.

**Table 14.4.1. Relationship between the growth of a cell exposed to an organic solvent and the value of log $P_{O/W}$ of the solvent. [After reference 14]**

| Solvent | log $P_{O/W}$ | *Pseudomonas putida* IH-2000 | *Pseudomonas putida* IFO3738 | *Pseudomonas fluorescens* IFO3507 | *Escherichia coli* IFO3806 | *Achromobacter delicatulus* LAM1433 | *Alcaligenes faecalis* JCM1474 | *Agrobacterium tumefaciens* IFO3058 | *Bacillus subtilis* AHU1219 | *Saccharomyces uvarum* ATCC26602 |
|---|---|---|---|---|---|---|---|---|---|---|
| dodecane | 7.0 | + | + | + | + | + | + | + | + | + |
| decane | 6.0 | + | + | + | + | + | + | + | + | - |
| nonane | 5.5 | + | + | + | + | + | + | + | + | - |
| *n*-hexyl ether | 5.1 | + | + | + | + | + | + | + | + | - |
| octane | 4.9 | + | + | + | + | + | + | + | + | - |
| isooctane | 4.8 | + | + | + | + | + | + | + | - | - |
| cyclooctane | 4.5 | + | + | + | + | + | + | - | - | - |
| diphenyl ether | 4.2 | + | + | + | + | + | - | - | - | - |
| *n*-hexane | 3.9 | + | + | + | + | + | - | - | - | - |
| propylbenzene | 3.7 | + | + | + | + | - | - | - | - | - |
| *o*-dichlorobenzene | 3.5 | + | + | + | - | - | - | - | - | - |
| cyclohexane | 3.4 | + | + | + | - | - | - | - | - | - |
| ethylbenzene | 3.2 | + | + | - | - | - | - | - | - | - |

| Solvent | log $P_{O/W}$ | *Pseudomonas putida* IH-2000 | *Pseudomonas putida* IFO3738 | *Pseudomonas fluorescens* IFO3507 | *Escherichia coli* IFO3806 | *Achromobacter delicatulus* LAM1433 | *Alcaligenes faecalis* JCM1474 | *Agrobacterium tumefaciens* IFO3058 | *Bacillus subtilis* AHU1219 | *Saccharomyces uvarum* ATCC26602 |
|---|---|---|---|---|---|---|---|---|---|---|
| *p*-xylene | 3.1 | + | + | - | - | - | - | - | - | - |
| styrene | 2.9 | + | - | - | - | - | - | - | - | - |
| toluene | 2.6 | + | - | - | - | - | - | - | - | - |
| benzene | 2.1 | - | - | - | - | - | - | - | - | - |

+, growth; -, no growth

Bar[9] suggested that the toxicity in two-phase systems was caused by both the presence of a second phase (phase toxicity) and solvent molecules which dissolved in the aqueous phase (molecular toxicity). Basically, both mechanisms are governed by the same principle in that the solvent accumulates in the microbial membrane. In case of the direct contact between cells and pure solvent, the rate of entry of solvents in a membrane will be very high. If the solvent has to diffuse via the water phase, then the accumulation in membranes will be slower. This latter mechanism on the molecular toxicity has been investigated in more detail.[17] In experiments with liposomes from *E. coli*, and ten representative organic solvents labeled by $^{14}C$ under aqueous-saturating levels, it was observed that the solvents accumulate preferentially in the cell membrane. The partition coefficients (log $P_{M/B}$) of the solvents between the model liposome membrane and buffer correlate with those (log $P_{O/W}$) in a standard 1-octanol-water system:

$$\log P_{M/B} = 0.97 \times \log P_{O/W} - 0.64 \qquad [14.4.1.1]^{17}$$

The accumulation of an organic solvent in the membrane causes changes in the membrane structure. Organic solvents residing in the hydrophobic part of the membrane disturb the interactions between the acyl chains of the phospholipids. This leads to a modification of membrane fluidity which eventually results in the swelling of the bilayer.[10] In addition to this, conformations of the membrane-embedded proteins may be altered.[10] These changes in the integrity of the membrane also affect the membrane function.

The principal functions of the cytoplasmic membrane involve:

1) barrier function,
2) energy transduction and
3) formation of a matrix for proteins.

The disruption of lipid-lipid and lipid-protein interactions by the accumulation of organic solvents has a strong effect on the membrane's function as a selective barrier for ions and hydrophilic molecules. Permeability is of particular importance for protons because the leakage of protons directly affects the primary energy transducing properties of the membrane. The initial rates of proton influx in the absence and presence of different amounts of hydrocarbon were measured.[17] The permeability for protons increases with increasing amounts of hydrocarbon. Hence, leakage of protons occurs in the presence of organic sol-

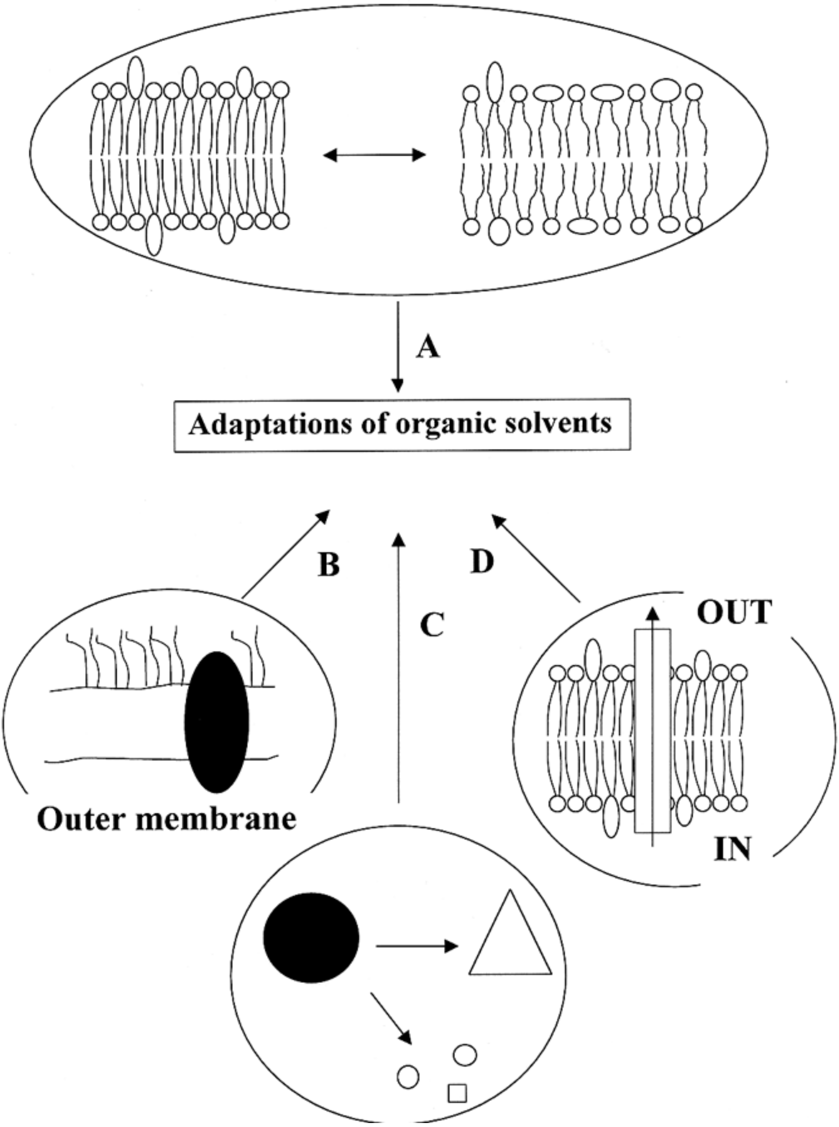

Figure 14.4.1.3 Schematic presentation of possible mechanisms of solvent tolerance. **A** Changes in the structure of cytoplasmic membrane. **B** Changes in the structure of outer membrane. **C** Transformation of the solvent. **D** Active export of the solvents [After reference 32]

vents.[17] Not only the impairment of the barrier function is caused by the alterations that occur in the membrane structure when it interacts with organic solvents. It is well known that the activities of the proteins embedded in the membrane are regulated by the membrane thickness, head group hydration, fluidity and fatty acid composition.[18,19] All these parameters are also known to be affected by the accumulation of organic solvents. The effects of solvents on these parameters were reviewed by Sikkema et al.[10]

### 14.4.1.3 Solvent-tolerant bacteria

As described in the previous section, the organic solvents with $1 < \log P_{O/W} < 4$ are considered to be toxic to microorganisms. In 1989, Inoue and Horikoshi[21] found a toluene-tolerant *Pseudomonas putida* strain that grew in a two-phase toluene-water system ($\log P_{O/W} = 2.5$ for toluene). This finding was surprising and went against the dominant paradigm at that time. Solvent tolerance was confirmed by other strains of *P. putida*[22-26] and by other representatives of the genus *Pseudomonas*.[27-30] Furthermore, solvent tolerance has been found in the strains of Gram-positive bacteria *Bacillus*[31,32] and *Rhodococcus*.[33] The key question now is: How do solvent-tolerant bacteria overcome the toxic effects of organic solvents? Some of the possible mechanisms involved in solvent tolerance according to various researchers are shown in Fig.14.4.1.3.[32]

Current research on changes in the structure of the cytoplasmic membrane shows the involvement of: 1) the composition of the fatty acids of the phospholipids like the *cis/trans* isomerization of unsaturated fatty acids; 2) composition of phospholipid headgroups and 3) rate of turnover of membrane components.

Organic solvents cause a shift in the ratio of saturated to unsaturated fatty acids.[34,35] In a solvent-tolerant strain, an increase in the saturation degree has been observed during adaptation to the presence of toluene. Solvent-tolerant strains also have the ability to synthesize *trans*-unsaturated fatty acids from the *cis*-form in response to the presence of organic solvents.[34,36-38] Increases in the saturation degree and the ratio of *trans*-form change the fluidity of the membrane and the swelling effects caused by solvents are depressed.

Alterations in the headgroups of lipids during the adaptation to solvents have also been observed in some solvent-tolerant strains.[37,39] The changes in the composition of the headgroups cause changes in the affinity of the lipids with the organic solvents and in the stability of membrane due to an alteration of bilayer surface charge density. These changes compensate the effect caused by the solvents. In one strain, the rate of phospholipid synthesis increases after exposure to a solvent.[40] This strain has a repairing system which is faster than the rate of damage caused by the organic solvent.

Unlike Gram-positive bacteria, Gram-negative bacteria such as *Pseudomonas* have an outer membrane. The outer membrane has been shown to play a role in the protection of the cell from solvent toxicity. Ions such as $Mg^{2+}$ or $Ca^{2+}$ stabilize the organization of the outer membrane and contribute to solvent tolerance.[38] Low cell surface hydrophobicity caused by changes in the lipopolysaccharide (LPS) content has been reported to serve as a defensive mechanism.[41,42] It has also been reported that the porins which are embedded in the outer membrane are relevant to solvent tolerance.[37,42-44]

The metabolism of organic solvents in solvent-tolerant strains contributes to solvent tolerance by degradation of the toxic compounds. This contribution, however, is considered to be limited[33,45] because many solvent-tolerant strains show non-specific tolerance against various organic compounds.

Non-specific tolerance to toxic compounds is well known in the field of antibiotic resistance. A wide range of structurally dissimilar antibiotics can be exported out of the cell by multidrug-efflux pumps. Could the export of organic solvents contribute to solvent tolerance?

Isken and de Bont[46] conducted experiments to determine whether the solvent tolerant *Pseudomonas putida* S12 was able to export toluene by monitoring the accumulation of $^{14}C$ labeled toluene in the cells. Toluene-adapted cells were able to export toluene from their

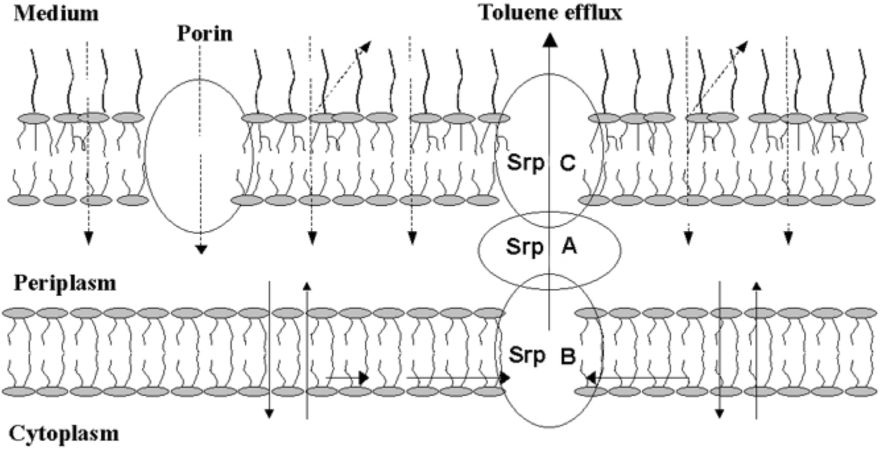

Figure 14.4.1.4. Schematic picture of toluene penetration and efflux in the solvent-tolerant *Pseudomonas putida* S12 [After reference 20].

membranes whereas the non-adapted cells were not. Furthermore, it was observed that in the presence of energy coupling inhibitors, toluene accumulation was the same as in the non-adapted cells. The amount of toluene in the cell was concluded to be kept at a low level by an active efflux system. The presence of a toluene-efflux system is supported by genetic research.[47,48] The pump has a striking resemblance to multidrug-efflux systems. Active efflux pumps for solvents have also been detected in other *Pseudomonas* strains.[25,26,30,37]

It is obvious that solvent tolerance is caused by a combination of the mechanisms described above. Figure 14.4.1.4 shows a schematic picture of toluene penetration and efflux in the solvent tolerant strain *P. putida* S12.[20] Toluene enters the cell through the outer membrane. At present, it is unclear whether toluene passes through porins or through the phospholipid part of the cell. The efflux pump recognizes and interacts with toluene in the cytoplasmic membrane. Toluene is then pumped into the extracellular medium.

### 14.4.1.4 Biotransformation using solvent-tolerant microorganisms

Many important fine chemicals, including catechols, phenols, aldehydes and ketones, low molecular epoxides and diepoxides, medium-chain alcohols, and terpenoids fall within the range of $1 < \log P_{O/W} < 4$. The discovery of solvent-tolerant bacteria leads to the new possibility of biocatalytic reaction systems containing organic solvents. By using solvent-tolerant bacteria, a variety of fine chemicals can be formed in microbial production processes.

The organic solvents used so far in published research had to be very hydrophobic ($\log P_{O/W} > 5$) in order to prevent microbial inactivation.[1] Consequently, many fine chemicals can not beneficially produced in the presence of such solvents because they simply would remain in the water phase and would not partition to the organic phase. The use of solvent-tolerant microorganisms enables the use of less hydrophobic solvents ($2.5 < \log P_{O/W} < 4$) and in such a system, chemicals with a $1 < \log P_{O/W} < 4$ preferentially will go into the organic phase. Up to now, however, only a few applications using solvent-tolerant microorganisms have been reported.

Aono et al.[49] reported the oxidative bioconversion of cholesterol as a model biocatalytic reaction using a solvent-tolerant *Pseudomonas* species. Cholesterol and its products are insoluble in an aqueous solution but dissolve in some organic solvents. The attempt was successful. The conversion of cholesterol was more than 98% and the yield of oxidative products was 80%.

Speelmans et al.[50] reported on the bioconversion of limonene to perillic acid by a solvent-tolerant *Pseudomonas putida*. The microbial toxicity of limonene is known to be very high. It is a major component of citrus essential oil and is a cheap and readily available base material. By using a solvent-tolerant strain perillic acid was obtained at a high concentration. This finding brings commercial production nearer.

The applications of solvent-tolerant strains in microbial production processes are at present limited, but two strategic options are currently available to use such bacteria.[20] Relevant genes can be introduced into solvent-tolerant organisms in order to produce the required product. This approach has been followed successfully by J. Wery in our laboratory who employed an 1-octanol-aqueous system. Methylcatechol was produced from toluene by solvent tolerant *P. putida* S12. Alternatively, the efflux pump can be expressed in a suitable solvent-sensitive host which would then be more tolerant for a particular solvent.

Other benefits may arrive from solvent-resistant bacteria. Ogino et al.[26] isolated *Pseudomonas aeruginosa* LST-03 which can grow in organic solvents with $\log P_{O/W} > 2.4$ and secrets organic solvent-stable lipolytic enzymes. They were able to purify an organic solvent-stable protease which was more stable than the commercially available proteases.[51] Hence, solvent-tolerant strains have become a source for new enzymes.[52]

In the near future, the use of solvent-tolerant strains will make the application of organic solvents in biotransformations by whole cells a more realistic option.

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## 14.4.2 SOLVENT-RESISTANT MICROORGANISMS

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### 14.4.2.1 Introduction

Several main properties of microorganisms in relation to solvents can be considered:

- Toxic or antimicrobial effects of solvents
- Solvent resistance or adaptation of microorganisms
- Metabolic activities of microorganisms

Antimicrobial effects or solvent-resistant microorganisms are the main topic of this section.

### 14.4.2.2 Toxicity of solvents for microorganisms

#### *14.4.2.2.1 Spectrum of microorganisms and solvents*

The growth-inhibiting effects of several solvents on microorganisms are described.[1,2] Organic solvents have toxic effect on microorganisms. Table 14.4.2.1 summarizes the relevant organic solvents and their toxicity concerning selected microorganisms.

**Table 14.4.2.1. Toxicity of organic solvents - examples**

| Solvent | Microorganisms | References |
|---|---|---|
| Toluene, benzene, ethylbenzene, propylbenzene, xylene, hexane, cyclohexane | *Pseudomonas putida* | Isken et al. (1999)[3]<br>Gibson et al. (1970)[4] |
| Terpenes, e.g., alpha-pinene, limonene, β-pinene, terpinolene | *Bacillus sp., Saccharomyces cerevisiae*, isolated mitochondria | Andrews et al. (1980)[5]<br>Uribe et al. (1985)[6] |
| Styrene | soil microorganisms | Hartmans et al. (1990)[7] |
| Cyclohexane | yeast cells, isolated mitochondria | Uribe et al. (1990)[8] |
| Aromatic hydrocarbons | isolated bacterial and liposomal membranes | Sikkema et al. (1992)[9]<br>Sikkema et al. (1994)[1] |
| Ethanol | yeasts | Cartwright et al. (1986)[10]<br>Leao and van Uden (1984)[11] |

### *14.4.2.2.2 Mechanisms of solvent toxicity for microorganisms*

The toxicity of organic solvents or hydrophobic substances for microorganisms depends mainly on their effects on biological membranes[1,9,12-14] - similar to membrane effects of several anesthetics. This concerns especially effects on cytoplasmatic membranes. The following main changes of membrane structures and functions have been observed:

- Accumulation of hydrophobic substances such as organic solvents in cytoplasmatic membranes. This accumulation causes structural and functional changes in the cytoplasmatic membranes and microbial cells.
- Structural changes in cytoplasmatic membranes, e.g., swelling of membrane bilayers, increase of surface and thickness of the membranes, changes in the composition of the membrane (e.g., changes in the fatty acid composition), modification of the microviscosity, damage of membrane structures (see below).
- Loss of membrane integrity, especially disruption of cytoplasmatic membranes, less damage of outer membranes. Because of these damages often complex cellular structures (e.g., vesicula) or cell functions (decrease of respiratory activities of mitochondria) are destroyed or inhibited.
- Interactions of the accumulated lipophilic substances with the cytoplasmatic membranes and especially hydrophobic parts of the cell or cell membranes. Lipid-lipid interactions and interactions between proteins and lipids of the membrane structure (lipid bilayers, membrane-embedded proteins) are discussed.
- Effects on passive and active membrane transport systems, e.g., increase of passive efflux and flux of ions such as protons, cations $Mg^{++}$ and $Ca^{++}$ or small molecules, stimulation of the leakage of protons and potassium, changes in the uptake of compounds (e.g., solvents) and excretion (e.g., metabolic products), inhibition of active transport systems (e.g., ATP depletion).
- Damage of cellular homeostasis and cell physiology, e.g., reduction of transmembrane electrical potentials and proton chemical potentials or proton motive forces as a result of membrane changes (efflux of ions), changes of pH gradients.

- Changes in enzyme activities, e.g., inhibition of oxidases and depletion of ATP. Of special relevance are various interactions with enzymes (proteins) in the membrane, e.g., lipid-protein interactions.
- Loss of particular cellular functions, e.g., respiratory system of mitochondria or active transport systems (see above).
- Loss of complex cell functions, e.g., reduced growth rates and activities of microorganisms.

The extent of solvent toxicity to microorganisms is determined by various factors:

(a) Hydrophobic or lipophilic properties of solvents. The toxicity of solvents to microorganisms can be described by a partition coefficient (log $P_{o/w}$) between organic compounds (solvents) and water which is specific for the applied substance. This partition coefficient is based on a standard octanol-water system model.[1,15,16]

The toxicity and the affinity of solvents to cell structures increase with hydrophobic properties of solvents, e.g., high toxicities with $P_{o/w}$ values of 1-5.[1,14] The partition coefficient correlates with the membrane-buffer partition coefficient between membrane and aqueous system.[1,14,16] They also depend on membrane characteristics.[17,18]

(b) Accumulation, partitioning and concentrations of solvents in cell structures (membranes). Dissolution and partitioning of solvents depend essentially on solvent properties, e.g., polarity (specific partition coefficients), or membrane characteristics (influence on partition coefficients). Both dissolution and partitioning can be influenced by additional factors, e.g., cosolvents. The effects on microorganisms can depend typically on solvent concentrations, e.g., dose response effects.

(c) Biomass, ratio of concentrations of solvents and biomass. Effect of solvents depends on this ratio.

(d) Surrounding conditions, e.g., temperature which influences the proton leakage and microbial activities.[19]

The toxicity of solvents for microorganisms shows positive and negative consequences, e.g.:

- Positive aspects such as antibacterial effects[20] which are found in several products.
- Negative aspects such as reduced stability of biotransformation and bioremediation processes because of the inactivation of microorganisms.

## 14.4.2.3 Adaption of microorganisms to solvents - solvent-resistant microorganisms

### *14.4.2.3.1 Spectrum of solvent-resistant microorganisms*

Different microorganisms are able to adapt and even to grow in the presence of solvents. Some relevant examples are given in Table 14.4.2.2.

**Table 14.4.2.2. Solvent-tolerant microorganisms and their resistance to organic solvents**

| Solvent-tolerant microorganisms | Solvents | References |
|---|---|---|
| bacteria from deep sea (1.168 m, Japan) | benzene, toluene, p-xylene, biphenyl, naphthalene | Abe et al. (1995)[21] |

| **Solvent-tolerant microorganisms** | **Solvents** | **References** |
|---|---|---|
| deep sea isolates,<br>*Flavobacterium* strain DS-711,<br>*Bacillus* strain DS-994 | hydrocarbons | Moriya and Horikoshi (1993)[22] |
| marine yeasts | n-alkanes | Fukamaki et al. (1994)[23] |
| *Pseudomonas putida* | toluene, m-, p-xylene, 1,2,4-trimethylbenzene, 3-ethyltoluene | Inoue and Horikoshi (1989)[24]<br>Cruden et al. (1992)[25] |
| *Pseudomonas sp.* | alpha-pinene | Sikkema et al. (1995)[14] |
| *E. coli* K-12 | p-xylene | Aono et al. (1991)[26] |

The concentration of organic solvents which can be tolerated by the microorganisms varies extensively, e.g., growth of *Pseudomonas putida* in the presence of more than 50 % toluene[27] but tolerance of *E. coli* K-12 in the presence of only up to 10 % p-xylene.[26]

The growth characteristics of different species can differ to a great extent, e.g., no growth, growth with or without metabolizing solvents. Generally higher solvent tolerance of Gram-negative bacteria compared to Gram-positive bacteria is observed.[28] Some solvent-tolerant microorganisms cannot use organic solvents as substrate for growth and need other substrates in complex media.[26,27] Other microorganisms can use organic solvents in minimal media as a source of energy or carbon, e.g., *Pseudomonas putida* in the presence of xylene or toluene.[25]

### 14.4.2.3.2 Adaption mechanisms of microorganisms to solvents

The mechanisms of solvent tolerance are only partly known.[29-31] Relevant microbial adaptation mechanisms are:

- *Changes in the composition of the cytoplasmatic membrane*. The compounds of the membranes such as lipids or proteins can influence the membrane characteristics and, therefore, the adaption to solvents. Mainly phospholipids in the membrane bilayer determine the partitioning of solutes and especially the resistance to solvents[17,18] A reduction of the partition coefficient has been observed when the fatty acid composition was changed.[32] An increase of monounsaturated fatty acids and a decrease of saturated fatty acids correlated with a higher ethanol tolerance of *S. cerevisiae, E. coli,* and *Lactobacillus* strains.[33-35] An increase of unsaturated fatty acids is induced by polar solvents and low temperatures, an increase of saturated fatty acids is connected with more apolar solvents and high temperatures.[36] Even changes in the configuration of fatty acids, which are provoked by solvents, can lead to adaption mechanisms, e.g., *cis-trans* conversions.[29]

- *Changes in the microbial structure*. Various structural changes can cause a reduction of toxic solvent effects, e.g., the increase of membrane fluidity which is connected with an increase of unsaturated fatty acids (see above) and results in a decrease of the membrane permeability.

- *Specific structural characteristics of microorganisms*. Typical structures of microorganisms vary according to the microbial species, e.g., outer membrane characteristics of bacteria. For instance, Gram-negative bacteria such as *Pseudomonas sp.* tolerate higher concentrations of hydrophobic compounds compared to Gram-positive bacteria. The resistance of the outer membrane correlates with the solvent-tolerance.[28]

- *Alterations of the cell envelope structure (cell wall)*. Mechanical alterations and chemical modifications of the cell wall can reduce the microbial resistance to solvents. The most interesting chemical modification concerns hydrophobic or hydrophilic abilities of the cell wall.[37] Decreasing hydrophobicity of the cell wall enhances the adaption of microorganisms to solvents.[38]
- *Suppression of the effects of solvents on membrane stability*.
- *Limitation of solvent diffusion into the cell* (see above).
- *Repairing mechanisms*, e.g. enhanced phospholipid biosynthesis.
- *Transport or export systems*. The excretion of compounds out of the microbial cell and cytoplasmatic membrane is well known but only documented for some substances, e.g., for drugs.[39] Passive and active transport systems are relevant, e.g., ATP driven systems. Export systems for the several solvents must be assumed.
- *Immobilization and mobilization of microorganisms and solvents*. The adsorption of solvents to microorganisms can be reduced if the contact is decreased. For instance, immobilization of microorganisms or solvents minimizes the contact. An immobilization and reduction of toxicity was shown if adsorption materials were added.[40]
- *Surrounding conditions*, e.g., low temperature, which can induce higher solvent resistance of microorganisms (see above).

### 14.4.2.4 Solvents and microorganisms in the environment and industry - examples

Microorganisms are frequently observed in organic-aqueous systems containing solvents are essential in natural and in industrial processes. The occurrence and role of microorganisms and organic compounds in these two-phase organic-aqueous systems are similar to the effects described above (see Section 14.4.2.2). Although toxic effects on microorganisms in these natural and industrial processes are well known, reliable data concerning solvent-resistant microorganisms are not available.

#### *14.4.2.4.1 Examples*

##### 14.4.2.4.1.1 Biofilms, biofouling, biocorrosion

Important examples for organic-aqueous systems are surface-associated biofilms which are a form of existence of microorganisms. Microorganisms, mostly bacteria, are embedded into a glycocalyx matrix of these biofilms.[41,42] This biofilm matrix mediates the adhesion of microorganisms to surfaces, concentrates substances and protects microorganisms from antimicrobial agents.[41,42] Several organic-aqueous systems can be observed, especially surface of surrounding materials (pipes, etc.) in relation to water or ingredients (e.g., oil in pipes) related to water between ingredients and surrounding materials (pipes, etc.).

Some aspects of solvents in these organic-aqueous biofilm systems are studied. Solvents can occur in water systems emitted from surrounding organic materials.[43] It was shown that solvents are important concerning microbial biocorrosion and biofouling processes, e.g., by swelling and hydrolysis of materials.[44]

Despite these well-known aspects, reliable data and studies concerning solvent-resistant microorganisms in biofilm, biofouling, or biocorrossion processes are not shown. Nevertheless similar mechanisms in biofilms must be assumed as described above (see Section 14.4.2.3) because similar conditions occur (organic-aqueous systems).

### 14.4.2.4.1.2 Antimicrobial effects, microbial test systems

The toxic mechanisms of solvents to microorganisms described above (see Section 14.4.2.2) are frequently used in effects of antimicrobial agents.

The damage of microbial biomembranes is fundamentally connected with the antimicrobial effects of several solvents on bacteria.[45]

Biomembranes and other microbial structures can be affected by solvents via similar processes as described. Relevant examples are naked viruses which are generally more resistant to viruzi agents because the envelopes of viruses are damaged by viruzi substances such as some solvents. Another example of solvent-like interactions are effects of antimicrobial agents to capsules of bacterial spores, e.g., Bacillus species.

Bacterial or enzymatic toxicity tests are used to assay the activity of organic compounds including solvents. A survey of environmental bacterial or enzymatic test systems is given by Bitton and Koopman.[46] The principles of these test systems are based on bacterial properties (growth, viability, bioluminescence, etc.) or enzymatic activities and biosynthesis. The toxicity of several solvents were tested in bacterial or enzymatic systems, e.g., pure solvents such as phenol in growth inhibition assays (Aeromonas sp.),[46] solvents in complex compounds such as oil derivates,[46,47] solvents in environmental samples such as sediments or solvents used in the test systems.[46,48,49] The efficiency of several test systems, e.g., Microtox tests or ATP assays, vary, e.g., looking at the effects of solvents.[46]

### 14.4.2.4.1.3 Industrial processes

In industrial processes the main microbial activities connected with solvents are:

- Processes in biotechnology, biotransformation and biocatalysis,[50,51] e.g., production of chemicals from hydrophobic substrates or use of solvents as starting materials for microbiological reactions.
- Bioremediation: degradation of environmental pollutants, e.g., wastewater treatment or bioremediation in biofilm reactors.[52-55]

Various microorganisms and microbial mechanisms are relevant in these industrial processes. Examples are conversion processes of organic substances, e.g., by bacterial oxygenases.[56,57] Normally low-molecular-weight aromatic hydrocarbons including solvents are converted in these biotransformation processes.[58]

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# 14.4.3 CHOICE OF SOLVENT FOR ENZYMATIC REACTION IN ORGANIC SOLVENT

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## 14.4.3.1 Introduction

The ability of enzymes to catalyze useful synthetic biotransformations in organic media is now beyond doubt. There are some advantages in using enzymes in organic media as opposed to aqueous medium, including

1) shifting thermodynamic equilibrium to favor synthesis over hydrolysis,
2) reduction in water-dependent side reaction,
3) immobilization of the enzyme is often unnecessary (even if it is desired, merely physical deposition onto solid surfaces is enough),
4) elimination of microbial contamination,
5) suitable for reaction of substrates insoluble and/or unstable in water, etc.

Here organic media as the reaction system are classified into two categories: substrates dissolved in neat organic solvents and solvent-free liquid substrates. Although the latter seems preferable to the former, if it works, there are a number of cases where the former is the system of choice: for example, when the substrate is solid at the temperature of the reaction, when high concentration of the substrate is inhibitory for the reaction, when the solvent used gives better environment (accelerating effect) for the enzyme, and so forth.

Prior to carrying out an enzymatic reaction in an organic solvent, one faces choice of a suitable solvent in the vast kinds of organic solvents. From active basic researches having been carried out in the past two decades, there has been a remarkable progress in our understanding of properties of enzymes in organic media, and in how organic solvents affect them. Some researchers call the achievement ‘medium engineering’. A comprehensive monograph was published in 1996 reviewing the progress.[1]

In this article organic solvents often used for enzymatic reactions are roughly classified, followed by influence of solvent properties on enzymatic reactions and then properties of the enzymes affected by the nature of the organic solvents are briefly summarized.

## 14.4.3.2 Classification of organic solvents

Among numerous kinds of organic solvents, the ones often used for enzymatic reactions are not so many, and may be classified into three categories (Table 14.4.3.1),[2] in view of the importance of water content of the organic solvent concerned (see Section 14.4.3.3).

1) water-miscible organic solvents

These organic solvents are miscible with water at the temperature of the reaction. Any cosolvent system having 0 - 100% ratio of the solvent/water can be prepared from this kind of solvent. Note that some organic solvents having limited water solubility at ambient temperature, and hence are not regarded as water-miscible, become miscible at elevated temperature.

2) Water-immiscible organic solvents

**Table 14.4.3.1. Classification of solvents commonly used for enzymatic reactions in organic media. [Adapted, by permission, from T. Yamane, Nippon Nogeikagaku Kaishi, 65, 1104(1991)]**

1) Water-miscible organic solvents

Methanol, ethanol, ethylene glycol, glycerol, N,N'-dimethylformamide, dimethylsulfoxide, acetone, formaldehyde, dioxane, etc.

2) Water-immiscible organic solvents (water solubility [g/l] at the temperature indicated)

- alcohols
  (n-, iso-) propyl alcohol, (n-, s-, t-) butyl alcohol, (n-, s-, t-) amyl alcohol, n-octanol, etc.
- esters
  methyl acetate, ethyl acetate (37.8, 40°C), n-butyl acetate, hexyl acetate, etc.
- alkyl halides
  dichloromethane (2, 30°C), chloroform, carbon tetrachloride, trichloroethane (0.4, 40°C), etc.
- ethers
  diethyl ether (12, 20°C), dipropyl ether, diisopropyl ether, dibutyl ether, dipentyl ether, etc.

3) Water-insoluble organic solvents (water solubility [ppm] at the temperature indicated)

- aliphatic hydrocarbons
  n-hexane (320, 40°C), n-heptane (310, 30°C), isooctane (180, 30°C), etc.
- aromatic hydrocarbons
  benzene (1200, 40°C), toluene (880, 30°C), etc.
- allicyclic hydrocarbons
  cyclohexane (160, 30°C), etc.

These organic solvents have noticeable but limited solubility of water, ranging roughly 0.1 - 10 % its solubility. The water solubility is of course increased as the temperature is raised.

3) Water-insoluble organic solvents

These solvents are also water-immiscible and have very low water solubility so that they are regarded as water-insoluble, i.e., water is practically insoluble in the organic solvents. Most aliphatic and aromatic hydrocarbons belong to this category.

In Table 14.4.3.1 organic solvents often used for enzymatic reactions are listed together with their water solubilities (although not for all of them).

### 14.4.3.3 Influence of solvent parameters on nature of enzymatic reactions in organic media

Factors that influence the activity and stability of enzymes in organic media have been mostly elucidated. Several of them are mentioned below.

1) Water activity, $a_w$

Among factors, the amount of water existing in the reaction system is no doubt the most influential. To emphasize the effect of water, the author once proposed to say 'enzymatic reaction in microaqueous organic solvent', instead of merely say 'enzymatic reaction in organic solvent'.[3-5]

Very trace amount of water or nearly anhydrous state renders practically no enzymatic reaction. In this context, it should be reminded that commercially available enzyme preparations, or the enzymes even after lyophilization or other drying procedures, contain some water bound to the enzyme proteins. Whereas, excess water in the reaction system results in hydrolysis of the substrate, which is often unfavorable side reaction, giving rise to lower yield of product. Thus, there exist usually the optimal water content for each enzymatic reaction of concern.

Water molecules in the microaqueous system exist in three different states: 1) water bound to the enzyme protein, 2) water dissolved freely in the solvent (plus dissolved substrate), and 3) water bound to impurities existing in the enzyme preparation or bound to the support materials if immobilized enzyme particles are used. Therefore, the following equation with respect to water holds:

Total water = (Water bound to the enzyme) + (Water dissolved in the solvent) [14.4.3.1]

+ (Water bound to the immobilization support or to impurities of the enzyme preparation)

Water affecting most of the catalytic activity of the enzyme is the one bound to the enzyme protein.[6] From the above equation, it can be well understood that the effect of water varies depending on the amount of enzyme used and/or its purity, kind of solvent, and nature of immobilization support, etc. as far as the total water content is used as the sole variable. Also, it is often asked what is the minimal water content sufficient for enzymatic activity? It should be recognized that a relation between the degree of hydration of the enzyme and its catalytic activity changes continuously. There exist a thermodynamic isotherm-type equilibrium between the protein-bound water and freely dissolved water, and its relationship is quite different between water-miscible and water-insoluble solvents.[4]

A parameter better than the water content, water activity, $a_w$, was proposed to generalize the degree of hydration of a biocatalyst in organic media.[7] $a_w$ is a thermodynamic parameter which determines how much water is bound to the enzyme and in turn decides the catalytic activity to a large extent among different kinds of the organic solvents. $a_w$ is especially useful when water-insoluble organic solvent is used because the precise water content is hard to be measured due to its low solubility. It was shown that profiles between $a_w$ and the reaction rate were similar when the same reaction was carried out in different solvents at varying water contents.[8] In dif-

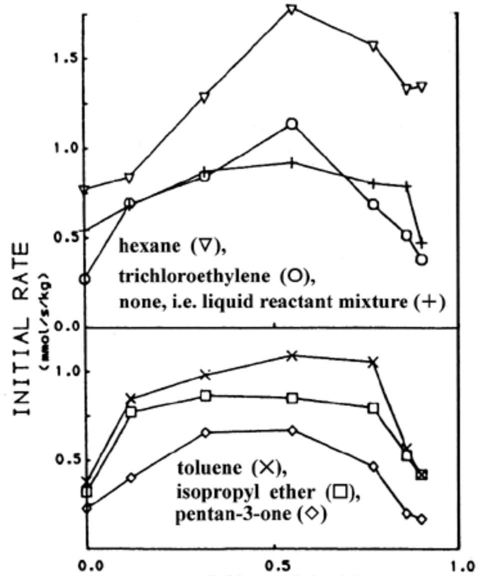

Figure 14.4.3.1 Activity of Lipozyme catalyst as a function of water activity in a range of solvents. [Adapted, by permission, from R.H. Valivety, P.J. Halling and A.R. Macrae, *Biochim. Biophys. Acta*, **1118**, 221 (1992)].

ferent solvents, maximum reaction rate was observed at widely different water content, but if water content was qualified in terms of $a_w$, the optimum was observed at almost the same $a_w$ (Figure 14.4.3.1). However, as seen from Figure 14.4.3.1, the profile does not lay on a single curve, and the absolute optimal reaction rate varies depending on the kind of the solvent, implying that $a_w$ is not almighty.

2) Hydrophobicity (or polarity), logP

A hydrophobicity parameter, logP, was first proposed for microbial epoxidation of propene and 1-butene.[9,10] logP is the logarithm of P, where P is defined as the partition coefficient of a given compound in the standard n-octanol/water two phase:

$$P = \frac{\text{solubility of a given compound in } n-\text{octanol phase}}{\text{solubility of a given compound in water phase}} \qquad [14.4.3.2]$$

Laane et al.[10] concluded as a general rule that biocatalysis in organic solvents is low in polar solvents having a logP < 2, is moderate in solvents having a logP between 2 and 4, and is high in apolar solvents having a logP > 4. They also stated that this correlation between polarity and activity paralleled the ability of organic solvents to distort the essential water layer bound to the enzyme that stabilized the enzyme. Since logP can easily be determined experimentally, or be estimated from hydrophobic fragmental constants, many biotechnologists have tried since then to correlate effects of organic solvents on biocatalysts they studied with logP approach. Their results have been successful, not completely but only partially. A number of exceptions to the ‘logP rule’ have been in fact reported.

3) Dielectric constant (or dipole moment), ε (or D)

Interactions between an enzyme and a solvent in which the enzyme is suspended are mostly non-covalent ones as opposed to interactions in water. These strong non-covalent interactions are essentially of electrostatic origin, and thus according to Coulomb’s law, their strength is imposed dependent on the dielectric constant, ε, (which is higher for water than for almost all organic solvents). It is likely that enzymes are more rigid in anhydrous solvents of low ε than in those of high ε. Thus, ε of a solvent can be used as a criterion of rigidity of the enzyme molecule. For the enzyme to exhibit its activity, it must be dynamically flexible during its whole catalytic action so that its activity in a solvent of lower ε should be less than in a solvent of higher ε. On the other hand, its selectivity or specificity becomes higher when its flexibility decreases so that the selectivity in a solvent of lower ε should be higher than in a solvent of higher ε.

## 14.4.3.4 Properties of enzymes affected by organic solvents

1) Thermal stability (half-life), $t_{1/2}$

Stability of an enzyme in an organic solvent is estimated by its half-life, $t_{1/2}$, when its activity is plotted as a function of incubation time. Although, $t_{1/2}$ during the enzymatic reaction is more informative for practical purposes, $t_{1/2}$ under no substrate is often reported because of its easiness of measurement. Inactivation of an enzyme is caused mostly by change in its native conformation, or irreversible unfolding of its native structure. Water, especially enzyme-bound water makes a major contribution to the protein folding through van der Waals interaction, salt-bridges, hydrogen bonds, hydrophobic interaction, etc. When the enzyme molecule is put into organic solvent, water molecules bound to the enzyme molecule are more or less re-equilibrated, depending on the free water content. Therefore, both the nature of organic solvent and the free water content have profound effects on its stability.

It has been shown that a number of enzymes suspended in anhydrous (dry) organic solvents exhibit thermal stability far superior to that in aqueous solutions (Table 14.4.3.2).[11] This is because most of chemical processes that occur in the thermal inactivation involve water, and therefore do not take place in a water-free environment. Furthermore, increased rigidity in dry organic solvents hinders any unfolding process. The increased thermal stability in the dry organic solvent drops down to the stability in aqueous solution by adding small amount of water as demonstrated by Zaks and Klibanov[12] and others. Thus, thermal stability of the enzyme in organic solvent strongly depends on its free water content.

**Table 14.4.3.2. Stability of enzymes in non-aqueous vs. aqueous media. [Adapted, by permission, from 'Enzymatic Reactions in organic Media', A. M. P. Koskinen and A. M. Klibanov, Blackie Academic & Professional (An Imprint of Chapman & Hall), Glasgow, 1996, p. 84]**

| Enzyme | Conditions | Thermal property | References |
|---|---|---|---|
| PLL | tributyrin<br>aqueous, pH 7.0 | $t_{1/2} < 26$ h<br>$t_{1/2} < 2$ min | Zaks & Klibanov (1984) |
| *Candida* lipase | tributyrin/heptanol<br>aqueous, pH 7.0 | $t_{1/2} = 1.5$ h<br>$t_{1/2} < 2$ min | Zaks & Klibanov (1984) |
| Chymotrypsin | octane, 100°C<br>aqueous, pH 8.0, 55°C | $t_{1/2} = 80$ min<br>$t_{1/2} =15$ min | Zaks & Klibanov (1988)<br>Martinek et al. (1977) |
| Subtilisin | octane, 110°C | $t_{1/2} = 80$ min | Russell & Klibanov (1988) |
| Lysozyme | cyclohexane, 110°C<br>aqueous | $t_{1/2} = 140$ h<br>$t_{1/2} < 10$ min | Ahen & Klibanov (1986) |
| Ribonuclease | nonane, 110°C, 6 h<br>aqueous, pH 8.0, 90°C | 95% activity remains<br>$t_{1/2} < 10$ min | Volkin & Klibanov (1990) |
| $F_1$-ATPase | toluene, 70°C<br>aqueous, 70°C | $t_{1/2} > 24$ h<br>$t_{1/2} < 10$ min | Garza-Ramos et al. (1989) |
| Alcohol dehydrogenase | heptane, 55°C | $t_{1/2} > 50$ days | Kaul &Mattiasson (1993) |
| HindIII | heptane, 55°C, 30 days | no loss of activity | Kaul & Mattiasson (1993) |
| Lipoprotein lipase | toluene, 90°C, 400 h | 40% activity remains | Ottoline et al. (1992) |
| β-Glucosidase | 2-propanol, 50°C, 30 h | 80% activity remains | Tsitsimpikou et al. (1994) |
| Tyrosinase | chloroform, 50°C<br>aqueous solution, 50°C | $t_{1/2} = 90$ min<br>$t_{1/2} = 10$ min | Yang & Robb (1993) |
| Acid phosphatase | hexadecane, 80°C<br>aqueous, 70°C | $t_{1/2} = 8$ min<br>$t_{1/2} = 1$ min | Toscano et al. (1990) |
| Cytochrome oxidase | toluene, 0.3% water<br>toluene, 1.3% water | $t_{1/2} = 4.0$ h<br>$t_{1/2} = 1.7$ min | Ayala et al. (1986) |

For References, refer to Ref. 11.

2) Specificity and selectivity, $k_{cat}/K_m$

It is the most exciting and significant feature that the substrate specificity, enantioselectivity and regioselectivity can be profoundly affected by nature of solvents in which the enzyme molecule exists. This phenomenon has opened an alternative approach for changing specificity and selectivity of an enzyme other than both screening from nature and protein engineering in the field of synthetic organic chemistry. The ability of enzymes to discriminate substrate specificity among different, but structurally similar substrates, enantioselectivity among enantiomers, eantiofaces or identical functional groups linked to a prochiral center, and regioselectivity among identical functional groups on the same molecule, is expressed quantitatively on E value, which is the ratio of the specificity constants, $k_{cat}/K_m$, for the two kinds of substrate (or entiomers), i.e., $(k_{cat}/K_m)_1/(k_{cat}/K_m)_2$. For kinetic resolution of racemic mixture by the enzyme, E is called enantiomeric ratio. The higher E, the higher the enantiomeric excess (i.e., the optical purity), ee, of the product (or remaining substrate). It is said that an E value higher than 100 is preferable for pharmaceutical or biotechnological applications. For overview of this topic, see Refs. 13 and 14.

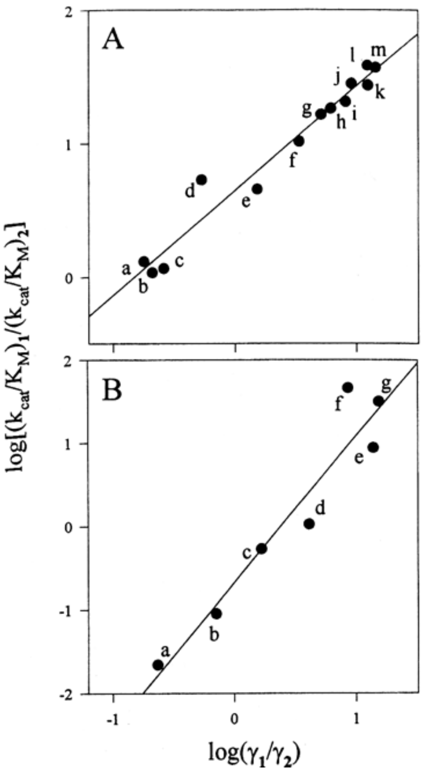

Figure 14.4.3.2. The dependence of (A) subtilisin Carlsberg and (B) a-chymotrypsin substrate specificity for substrates 1 and 2 on the ratio of their Raoult's law activity coefficients. For the structures of the substrates 1 and 2, and the solvents a through m in (A) and a to g in (B), refer to Ref. 16. [Adapted, by permission, from C.R. Wescott and A.M. Klibanov, *Biotechnol. Bioeng.*, **56**, 343(1997)].

(2a) Substrate specificity

Zaks and Klibanov reported that the substrate specificity of α-chymotrypsin, subtilisin, and esterase changed with an organic solvent.[15] The substrate specificity in octane was reversed compared to that in water. A thermodynamical model that predicted the substrate specificity of subtilisin Carlsberg and α-chymotrypsin in organic media on the basis of specificity of the enzyme in water and physicochemical characteristics of the solvents was developed by Wescott and Klibanov.[16] They determined $k_{cat}/K_m$ for the transesterification of N-acetyl-L-phenylalanine and N-acetyl-L-serine with propanol in 20 anhydrous solvents, and correlated the data of $(k_{cat}/K_m)_{Ser}/(k_{cat}/K_m)_{Phe}$, first with the solvent to water partition coefficients for the substrate, $P_{Phe}/P_{Ser}$. Later they examined the selectivity of subtilisin toward two different substrates with the Raoult's law activity coefficients, γ, by the following equation:[15]

$$\log\left[\left(k_{cat}/K_m\right)_1/\left(k_{cat}/K_m\right)_2\right]=\log\left(\gamma_1/\gamma_2\right)+constant \qquad [14.4.3.3]$$

The correlation was unexpectedly high as seen in Figure 14.4.3.2,[15] implying that the change of substrate specificity of enzyme in organic solvent stems to a large extent from the energy of desolvation of the substrate.

(2b) Enantioselectivity

Changes in enantioselectivity in various organic solvents was first discovered by Sakurai et al.[17] Later Fitzpatrick and Klibanov studied enantioselectivity of subtilisin, Carsberg in the transesterification between the sec-phenethyl alcohol (a chiral alcohol) and vinyl butyrate to find that it was greatly affected by the solvent. Only the correlations with ε or with D gave good agreements.[18] The enzyme enantioselectivity was inversed by changing solvents.[19] Nakamura et al. studied lipase (Amano AK from *Pseudomonas sp.*)-catalyzed transesterification of *cis*- and *trans*-methylcycolhexanols with vinyl acetate in various organic solvents, and investigated the effect of solvent on activity and stereoselectivity of the lipase.[20] They correlated their stereoselectivity with good linearity (except for dioxane and dibutyl ether) by the following two-parameter equation (Figure 14.4.3.3):

$$E=a(\varepsilon-1)/(2\varepsilon+1)+bV_m+c \qquad [14.4.3.4]$$

where ε and $V_m$ are dielectric constant and molar volume of the solvent, respectively, and a, b, and c are constants which should be experimentally determined.

Bianchi et al. also reported that for the resolution of antitussive agent, Dropropizine, using both hydrolysis in aqueous buffer and transesterification techniques in various organic solvents, by a lipase (Amano PS from *Pseudomonas cepacia*), E depended very much on organic solvents (Table 14.4.3.3), with the highest E value (589) in n-amyl alcohol and the lowest one (17) in water.[21] In this case, however, there was no correlation between the enantioselectivity and the physico-chemical properties of the solvents such as logP or ε.

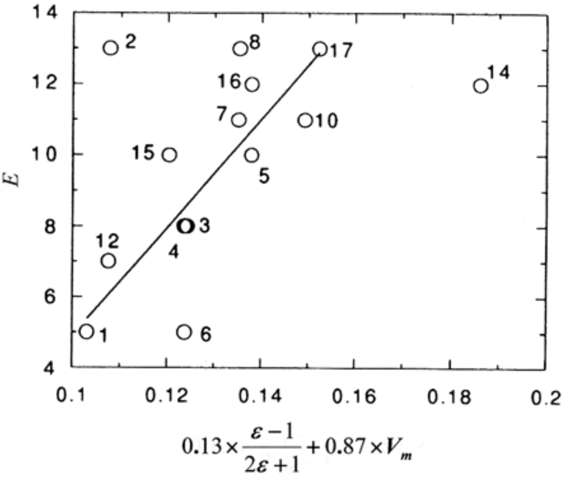

Figure 14.4.3.3. Linear relationship between f(ε, $V_m$) and E for lipase-catalyzed transesterification of *cis*- and *trans*-4-methylcyclohexanols with vinyl acetate in various organic solvents. For the organic solvents 1 through 18, refer to Ref. 20. [Adapted, by permission, from K. Nakamura, M. Kinoshita and A. Ohno, *Tetrahedron*, **50**, 4686(1994)].

**Table 14.4.3.3. Effect of the solvent on enantioselectivity of lipase PS. [Adapted, by permission, from D. Bianchi, A. Bosetti, P. Cesti and P. Golini, Tetrahedron Lett., 33, 3233(1992)].**

| Solvent | logP | ε | Nucleophile | E |
|---|---|---|---|---|
| $H_2O$ | | 78.54 | $H_2O$ | 17 |
| hexane | 3.5 | 1.89 | n-propanol | 146 |
| $CCl_4$ | 3.0 | 2.24 | n-propanol | 502 |
| toluene | 2.5 | 2.37 | n-propanol | 120 |
| iso-propyl ether | 1.9 | 3.88 | n-propanol | 152 |
| 2-methyl-2-butanol | 1.45 | 5.82 | n-propanol | 589 |
| 2-methyl-2-butanol | 1.45 | 5.82 | $H_2O$ | 63 |
| n-propanol | 0.28 | 20.1 | n-propanol | 181 |
| acetonitrile | -0.33 | 36.2 | n-propanol | 82 |
| 1,4-dioxane | -1.1 | 2.2 | n-propanol | 164 |

As mentioned above, no correlation was reported in a large number of articles on the effects of solvents on the enzyme specificity/selectivity, although correlations between the specificity/selectivity and physico-chemical properties of the solvents were successful in some combinations of an enzymatic reaction for a set of solvents. Therefore, attempts to rationalize the phenomena based on either physico-chemical properties of the solvents or on their structure, are at present clearly unsatisfactory from the point of view of predictable value. Further experiments carried out under more strictly defined condition are necessary to reach the quantitative explanation of the whole phenomena.

### 14.4.3.5 Concluding remarks

Activity, stability, and selectivity of an enzyme are affected considerably by nature of organic solvents as well as free water content in the enzyme-catalyzed reaction in the organic solvents. However, rational criteria for the selection of a proper solvent among vast variety of the organic solvents are very limited so far. Researchers are obliged to resort to empirical approach by examining some kinds of solvent for the enzyme-catalyzed reaction concerned at the present state of art.

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## 14.5 COIL COATING

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The coil coating industry is under pressure to eliminate the use of solvents. Polyester coil coatings contain up to 40% of solvents such as glycol esters, aromatic hydrocarbons (e.g., Solvesso 150), alcohols, ketones, and butyl glycol.[1,2] A recent book[1] predicted that the solvent-based technology will not change during the next decade because the industry heavily invested in equipment to deal with solvents. Such changes in technology require long testing before they can be implemented. The coil coating industry normally recovers energy from evaporated solvents either by at-source incineration or by a recycling process which lowers emissions. Because of the large amount of solvents used, the use of PVC and fluorocarbon resins in some formulations, and the use of chromates in pretreatments the pressure remains on the industry to make improvements.[3] The coil coating industry is estimated to be consuming about 50,000 tons of solvents both in Europe and in the USA.[1] About half of these solvents are hydrocarbons.

According to the published studies,[3,4] efforts to change this situation did start in the early 1990s and by mid nineties research data were available to show that the technology can be changed. Two directions will most likely challenge the current technology: radiation curing and powder coating.

Coil coats are thin (about 30 μm wet thickness) but contain a high pigment loading. Consequently, UV curing is less suitable than electron beam curing. The application of this technology requires a change to the polymer system and acrylic oligomers are the most suitable for this application. This system can be processed without solvents. If a reduction of viscosity is required, it can be accomplished by the use of plasticizers (the best candidates are branched phthalates and linear adipates) and/or reactive diluents such as multifunctional monomers. Results[3] show that the UV stability of the system needs to be improved by using a polyester top coat or fluoropolymer. With top coat, material performs very well as learned from laboratory exposures and exposures in industrial environment.[3] At the time of the study (about 6 years ago), process of coating was less efficient than solvent-based system because production speed was about 6 times slower than the highest production rates in the industry (120 m/min). At the same time, it is known[2] that the quality of solvent-based coatings suffers from excessive production rates as well. Radiation curing has a disadvantage because of its high capital investment but it does have an economical advantage because the process is very energy efficient. Previous experiences with radiation curing technology show that the process has been successfully implemented in several industries such as paper, plastic processing, and wood coating where long term economic gains made the changes viable.

Comparison of solvent-based fluoropolymer and fluorocarbon powder coating developed in Japan[4] shows that elimination of solvent is not only good for environment but also improves performance (UV stability especially is improved). The study was carried out with a very well designed testing program to evaluate the weathering performance of the material.

These two technologies show that there is extensive activity to improve coil coatings with simultaneous elimination of solvents. Two recent patents contribute more information on the developments in the coil coating industry.[5,6] One problem in the industry is with the poor adhesion of the coating to steel.[2,3] A primer developed contains dipropylene glycol methyl ether and PM acetate which allows the deposition of relatively thick layers (20-40 μm) without blistering and at suitable rate of processing. However, the primer has a low solids content (30-45%).[5] A new retroreflective coating was also developed[6] which is based on ethyl acrylate-styrene copolymer and contains a mixture of xylene with another aromatic hydrocarbon (Solvesso 150) at relatively low concentration (11-12%).

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## 14.6 COSMETICS AND PERSONAL CARE PRODUCTS

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Several cosmetic products contain solvents. These include nail polish, nail polish remover, fragrances, hair dyes, general cleaners, hair sprays and setting lotions. In most cases, ethanol is the only solvent. Nail polish and nail polish remover contain a large variety of solvents. Several recent patents[3-6] give information on current developmental work in this area.

Nitrocellulose, polyester, acrylic and methacrylic ester copolymer, formaldehyde resin, rosin, cellulose acetate butyrate are the most frequently used polymers in nail polish formulations. Solvents were selected to suit the polymer used. These include acetone, methyl acetate, ethyl acetate, butyl acetate, methyl glycol acetate, methyl ethyl ketone, methyl isobutyl ketone, toluene, xylene, isopropyl alcohol, methyl chloroform, and naphtha. Solvents constitute a substantial fraction of the composition usually around 70%. Reformulation is ongoing to improve the flexibility and durability of the nail polish.[3] Other efforts are directed to improve antifungal properties,[4] to eliminate ketones and formaldehyde resin (ketones because of their toxicity and irritating smell and formaldehyde resins because they contribute to dermatitis),[5] and elimination of yellowing.[6] All efforts are directed towards improvements in drying properties and adhesion to the nails. These properties are partially influenced by solvent selection. The current trend is to greater use of ethyl acetate, butyl acetate, naphtha, and isopropanol which are preferable combinations to the solvents listed above.

Acetone used to be the sole component of many nail polish removers. It is still in use but there is a current effort to eliminate the use of ketones in nail polish removers. The combinations used most frequently are isopropanol/ethyl acetate and ethyl acetate/isopropanol/1,3-butanediol.

General cleaners used in hairdressing salons contain isopropanol and ethanol. Hair spray contains ethanol and propellants which are mixtures of ethane, propane, isobutane, and butane. The reported study[2] of chemical exposure in hairdresser salons found that although there were high concentrations of ethanol the detected levels were still below the NIOSH limit. The concentrations were substantially higher in non-ventilated salons (about 3 times higher) than those measured in well ventilated salons. Small concentrations of toluene were found as well, probably coming from dye components.

Recent patents[7,8] show that solvents may enter cosmetic products from other ingredients, such as components of powders and thickening agents. Some solvents such as dichloromethane and benzene, even though they are present is smaller quantities are reason for concern.

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# 14.7 DRY CLEANING - TREATMENT OF TEXTILES IN SOLVENTS

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Most processes in manufacturing and finishing of textiles are aqueous. In order to prevent water pollution, some years ago developments were made to transform dyeing-, cleaning- and finishing-processes from water to solvents. During 1970-1980 solvent processes for degreasing, milling, dyeing and waterproofing of textiles could get limited economic importance. All these processes were done with tetrachloroethylene (TCE). After getting knowledge about the quality of TCE penetrating solid floors, stone and ground, contaminating groundwater, this technology was stopped.

Today the main importance of solvents in connection with textiles is given to dry cleaning, spotting and some special textile finishing processes.

## 14.7.1 DRY CLEANING

### 14.7.1.1 History of dry cleaning

Development of dry cleaning solvents

The exact date of discovery of dry cleaning is not known. An anecdote tells us that in about 1820 in Paris, a lamp filled with turpentine fell down by accident and wetted a textile. After the turpentine was vaporized, the wetted areas of the textile were clean, because the turpentine dissolved oily and greasy stains from it.

In 1825, Jolly Belin founded the first commercial “dry laundry” in Paris. He soaked textile apparel in a wooden tub filled with turpentine, cleaned them by manual mechanical action, and dried them by evaporating the turpentine in the air.

After getting the know-how to distill benzene from tar of hard coal in 1849, this was used as a solvent for dry cleaning because of its far better cleaning power. But benzene is a strong poison, so it was changed some decades later to petrol, which is explosive. In order to reduce this risk, petrol as dry cleaning solvent was changed to white spirit (USA: Stoddard solvent) with a flash point of 40 - 60°C (100 - 140°F) in 1925.

The flammability of the hydrocarbon solvents in dry cleaning plants was judged to be risky because of fire accidents. After finding the technology for producing inflammable chlorinated hydrocarbons, trichloroethane and tetrachloroethylene (TCE) were introduced in dry cleaning since about 1925. These solvents gave the opportunity for good cleaning results and economic handling. Up to 1980, TCE was the most important solvent for dry cleaning worldwide.

Compared to TCE, fluorinated chlorinated hydrocarbons (CFC) offer benefits to dry cleaning because of their lower boiling points and their more gentle action to dyestuffs and fabrics. So since 1960 these solvents have had some importance in North America, Western Europe, and the Far East. They were banned because of their influence on the ozone layer in the stratosphere by the UNESCO’s Montreal Protocol in 1985.

At the same time, TCE was classified as a contaminant to groundwater and as a dangerous chemical to human health with the possible potential of cancerogenic properties. As a result of this, hydrocarbon solvents on the basis of isoparaffins with a flash point higher than 55°C (130°F) were at first used in Japanese and German dry cleaning operations since 1990.

Also, alternatives to conventional dry cleaning were developed. Wet cleaning was introduced by Kreussler in 1991 (Miele System Kreussler) and textile cleaning in liquid carbon dioxide was exhibited by Global Technologies at the Clean Show Las Vegas in 1997.

Development of dry cleaning machines

In the beginning, dry cleaning was done manually in wooden tubs filled with turpentine or benzene. About 1860, the Frenchman Petitdidier developed a wooden cylindrical cage, which was rotated in a tub filled with solvent. The apparel to be dry cleaned was brought into the cage and moved through the solvent by the rotation of the cylinder. This machine got the name "La Turbulente".

The next step was the addition of a centrifuge to the wooden machine. The dry cleaned apparel was transferred from the machine into the centrifuge and then dried by vaporizing the solvent in the open air.

About 1920, a tumble dryer was used for drying the dry cleaned textiles. Fresh air was heated up, blown through the dryer, where the air was saturated with solvent vapor and then blown out to be exhausted into the environment. The used solvent was cleaned to be recycled by separation of solid matter by centrifugal power with a separator and to be cleaned from dissolved contamination by distilling.

In 1950, dry to dry machines were developed by Wacker in Germany for use with TCE. The principle of working is as follows: The cage, filled with textiles, is rotating in a closed steel cylinder. The dry cleaning solvent is pumped from the storage tank into the cylinder so that the textiles in the cage are swimming in the solvent. After ending the cleaning process, the solvent is pumped back into the storage tank and the cage rotates with high speed (spinning) in order to separate the rest of the solvent from the textile. Then air is circulated through a heat exchanger to be heated up. This hot air is blown into the rotating cage in order to vaporize the remaining solvent from the textiles. The air saturated with solvent vapor is cleaned in a condenser, where the solvent is condensed and separated from the air. The air now goes back into the heat exchanger to be heated up again. This circulation continues until textiles are dry. The separated solvent is collected in a tank to be reused.

In order to reduce solvent losses and solvent emissions, since 1970 charcoal filters have been used in the drying cycle of dry cleaning machines, so that modern dry cleaning systems are separated from the surrounding air.

### 14.7.1.2 Basis of dry cleaning

Dry cleaning means a cleaning process for textiles, which is done in apolar solvents instead of water. If water is used, such cleaning process is called "washing" or "laundering".

Natural textile fibers, such as wool, cotton, silk and linen, swell in water because of their tendency to absorb water molecules in themselves. This causes an increase of their diameter and a change of the surface of yarns and fabrics. The result is shrinkage, felting and creasing.

Apolar solvents, such as hydrocarbons, are not absorbed by natural textile fibers because of the high polarity of the fibers. So there is no swelling, no shrinkage, no felting and no creasing. From the solvent activity, dry cleaning is very gentle to textiles, with the result that the risk of damaging garments is very low.

Because of the apolar character of dry cleaning solvents cleaning activity also deals with apolar contamination. Oils, fats, grease and other similar substances are dissolved in the dry cleaning operation. Polar contamination, such as, salt, sugar, and most nutrition and body excrements are not dissolved.

In the same way that water has no cleaning activity with regard to oils, fat, or grease, in dry cleaning there is no activity with regard to salts, sugar, nutrition and body excrements. And in the same way that water dissolves these polar substances, cleaning of textiles from these contaminants does not pose any problems in a washing process.

To make washing active to clean oils, fat and grease from textiles, soap (detergent) has to be added to water. To make dry cleaning active to clean salts, sugar and the like from textiles, dry cleaning detergent has to be added to the solvent.

In washing, fresh water is used for the process. After being used, the dirty washing liquid is drained off. In dry cleaning the solvent is stored in a tank. To be used for cleaning it is pumped into the dry cleaning machine. After being used, the solvent is pumped back into the storage tank. To keep the solvent clean it is constantly filtered during the cleaning time. In addition to this, a part of the solvent is pumped into a distilling vessel after each batch to be cleaned by distilling.

Dry cleaning solvents are recycled. The solvent consumption in modern machines is in the range of about 1 - 2 % per weight of the dry cleaned textiles.

### 14.7.1.3 Behavior of textiles in solvents and water

Fibers used for manufacturing textiles can be classified into three main groups:

| | |
|---|---|
| • Cellulosic fibers: | cotton, linen, rayon, acetate. |
| • Albumin fibers: | wool, silk, mohair, camelhair, cashmere. |
| • Synthetic fibers: | polyamide, polyester, acrylic. |

Textiles made from cellulosic fibers and synthetics can be washed without problems. Apparel and higher class garments are made from wool and silk. Washing very often bears a high risk. So these kinds of textiles are typically dry cleaned.

Dependent to the relative moisture of the surrounding air fabrics absorb different quantities of water. The higher the polarity of the the fiber, the higher is their moisture content. The higher the swelling (% increase of fiber diameter) under moisture influence, the higher is the tendency of shrinkage in a washing or dry cleaning process.

**Table 14.7.1. Water content (%) in textile fibers dependent on relative humidity**

| Fiber | Relative humidity, % | | | Swelling, % |
|---|---|---|---|---|
| | 70 | 90 | max. | |
| Viscose | 14.1 | 23.5 | 24.8 | 115 |
| Wool | 15.6 | 22.2 | 28.7 | 39 |
| Silk | 11.2 | 16.2 | 17.7 | 31 |
| Cotton | 8.1 | 11.8 | 12.9 | 43 |
| Acetate | 5.4 | 8.5 | 9.3 | 62 |
| Polyamide | 5.1 | 7.5 | 8.5 | 11 |
| Acrylic | 2.1 | 4.0 | 4.8 | 9 |
| Polyester | 0.5 | 0.6 | 0.7 | 0 |

The same absorption of water occurs if textiles are immersed in solvent in a dry cleaning machine. If the relative humidity in the air space of the cylinder of a dry cleaning machine is higher, textiles absorb more water. The water content of textiles in solvent is equal to the water content of textiles in the open air if the relative humidity is the same.

If water additions are given to the dry cleaning solvent in order to intensify the cleaning effect with regard to polar contamination, then the relative humidity in the air space of the cylinder of the dry cleaning machine increases. As a result of this, the water content in the dry cleaned textiles increases, too, so that swelling begins and shrinkage may occur.

Woolen fabrics are particularly sensitive to shrinkage and felting because of the scales on the surface of the wool fiber. Not only in washing, but also in dry cleaning there is a risk of shrinkage on woolen garments. This risk is higher when the dry cleaning process is influenced by water addition. If the relative humidity in the air space of a dry cleaning machine is more than 70%, shrinkage and felting may occur, if the dry cleaning solvent is tetrachloroethylene (TCE). In hydrocarbon solvents wool is safe up to 80% relative humidity, because of the lower density of hydrocarbons compared to TCE, which reduces mechanical action.

### 14.7.1.4 Removal of soiling in dry cleaning

"Soiling" means all the contamination on textiles during their use. This contamination is of very different sources. For cleaning purposes, the easiest way of classification of "soiling" is by solubility of soiling components. The classification can be done by definition of four groups:

| | |
|---|---|
| • Pigments: | Substances are insoluble in water and in solvents. Examples are: dust, particles of stone, metal, rubber; soot, scale of skin. |
| • Water soluble material: | Examples are: salts, sugar, body excrements, sap and juice. |
| • Polymers: | Substances are insoluble in solvents but can be soaked and swell in water. Examples are: starch, albumin and those containing material such as blood, milk, eggs, sauce. |
| • Solvent soluble material: | Examples are: oil, fat, grease, wax, resins. |

**Table 14.7.2 Average soiling of garments (apparel) in Europe**

| Soil type | Proportion, % | Solubility | Components |
|---|---|---|---|
| Pigments | 50 | not | dust, soot, metal oxides, rub-off, pollen, aerosols |
| Water soluble | 30 | water | sugar, salt, drinks, body excretions |
| Polymers | 10 | water | starch, albumin, milk, food |
| Solvent soluble | 10 | solvents | skin grease, resin, wax, oils, fats |

In practice, the situation is not so simple as it seems to appear after this classification. That is because soiling on garments almost always contains a mixture of different substances. For example, a spot of motor oil on a pair of trousers consists of solvent soluble oil, but also pigments of soot, metal oxides and other particles. The oil works as an adhesive for the pigments, binding them to fabric. In order to remove this spot, first the oil has to be dissolved then pigments can be removed.

The removal of solvent soluble "soiling" in dry cleaning is very simple. It will be just dissolved by physical action. Polymers can be removed by the combined activity of detergents, water and mechanical action. The efficiency of this process depends on the quality and concentration of detergent, the amount of water added into the system, and the operating time. Higher water additions and longer operating time increase the risk of shrinkage and felting of the textiles.

Water soluble "soiling" can be removed by water, emulsified in the solvent. The efficiency here depends on the emulsifying character of the detergent and the amount of water addition. The more water is emulsified in the solvent, the higher is the efficiency of the process and the higher is the risk of shrinkage and felting of the textiles.

Pigments can be removed by mechanical action and by dispersing activity of detergents. The higher the intensity of mechanical action, influenced by cage diameter, rotation, gravity of the solvent and operating time and the better the dispersing activity of the detergent, the better is the removal of pigments. The same parameters influence the care of the textiles. The better the cleaning efficiency, the higher the risk for textile damage.

### 14.7.1.5 Activity of detergents in dry cleaning

The main component of detergents is surfactant. The eldest known surfactant is soap. Chemically soap is an alkaline salt of fatty acid. Characteristic of soap (and surfactant) is the molecular structure consisting of apolar - hydrophobic - part (fatty acid) and a polar - hydrophilic - part (-COONa), causing surface activity in aqueous solution.

Surface activity has its function in the insolubility of the hydrophobic part of molecule in water and the hydrophilic part of molecule influences water solubility. This gives a tension within soap molecules in water forming layers on every available surface and forming micelles if there is a surplus of soap molecules compared to the available surface. This soap behavior stands as an example of mechanism of action of surfactants in general.

Micelles of surfactants in water are formed by molecular aggregates of surfactants oriented in such a way that the hydrophobic parts are directed internally, so that the hydrophilic parts are directed outwards. In this way the aggregates form spheres, cylinders, or laminar layers, dependent on its concentration.

Because of this behavior, it is possible to remove oil, fat or grease from substrates in aqueous solutions, if surfactants are present. The surfactants act to disperse the oil into small particles and build up micelles around these particles, so that oil, fat or grease incorporated inside the micelle (Figure 14.7.1). If aggregates are small, the solution is clear. If aggregates are larger, the solution (emulsion - type oil in water) becomes milky.

In the same way, but in the opposite direction, surfactants form micelles in solvents (Figure 14.7.2). In this case, not the hydrophobic, but the hydrophilic part is directed internally and the hydrophobic outwards. Emulsions in this case are not formed by oil in water, but by water in oil (solvent).

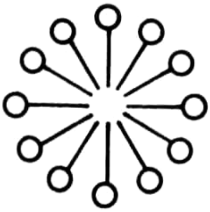

Figure 14.7.1. Schematic diagram of surfactants aggregated in micelle in aqueous solution.

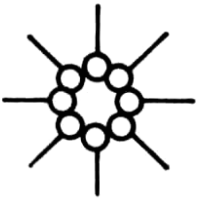

Figure 14.7.2. Schematic diagram of surfactants aggregated in micelle in solvent solution.

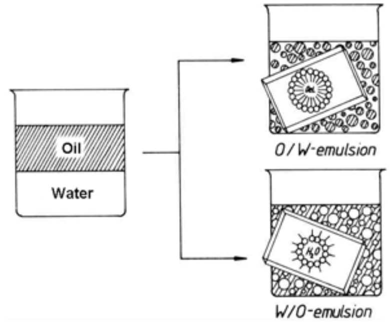

Figure 14.7.3. Aggregation of surfactants in emulsions of type oil in water (O/W) and water in oil (W/O).

Because of this behavior, it is possible to remove water soluble (polar) material from substrates in solvents, if surfactants are at present. The surfactants disperse the polar material into very small particles and build up micelles around the particles, so that the polar material is totally incorporated inside micelle. If the aggregates are small, the solution is clear. If they are large, the solution (emulsion - type water in oil) becomes milky.

Drycleaning detergents consist of surfactants, cosolvents, lubricants, antistatic compounds and water. They are used in order to increase the cleaning efficiency, to improve the handle of dry cleaned textiles, and to prevent electrostatic charge on textiles. They are formulated as liquids in order to be easily added to the solvent by automatic dosing equipment. In dry cleaning the drycleaning detergents play the same role as soap or laundry detergents in textile washing.

### 14.7.1.6 Dry cleaning processes

Process technology in dry cleaning has the target to clean garments as good as possible without damaging them, at lowest possible costs and with highest possible safety. Because of the environmental risks dependent on the use of TCE or hydrocarbon solvents, safe operation is the most important. Modern dry cleaning machines are hermetically enclosed, preventing infiltration of surrounding air, operating with electronic sensor systems, and they are computer controlled. The main part is the cylinder with the cleaning cage, the solvent storage tanks, the solvent recovering system, the solvent filter system and the distillation equipment (Figure 4.9.4).

Cylinder/cage:

A cage capacity is 20 liters per kg load capacity of the machine (about 3 gal per lb). That means, an average sized dry cleaning machine with load capacity of 25 kg (50 lbs) has a cage capacity of 500 liters (130 gal). This size is necessary because the same cage is used for cleaning and drying.

During the cleaning cycle, 3 - 5 liters of solvent per kg load (0.5 - 0.8 gal/lb) are pumped into the cylinder. In a 25 kg machine, it is 80 - 125 liters (25-40 gal). This solvent is filtered during the cleaning time.

Solvent storage tanks:

A dry cleaning machine has 2 - 3 solvent storage tanks. The biggest - the working tank - has a capacity in liters ten times the load capacity in kg. The clean solvent tank and optional retex tank have half the capacity. All the tanks are connected to each other with an overflow pipe.

The working tank with its inlet and outlet is connected to the cylinder of the machine. The inlet of the clean tank is connected to the distilling equipment, the outlet to the cylinder.

Filter system:

The filter is fed with solvent from the cylinder by pump pressure. The filtered solvent goes back into the cylinder. The filter has a further connection to the distilling equipment used as drain for the residue.

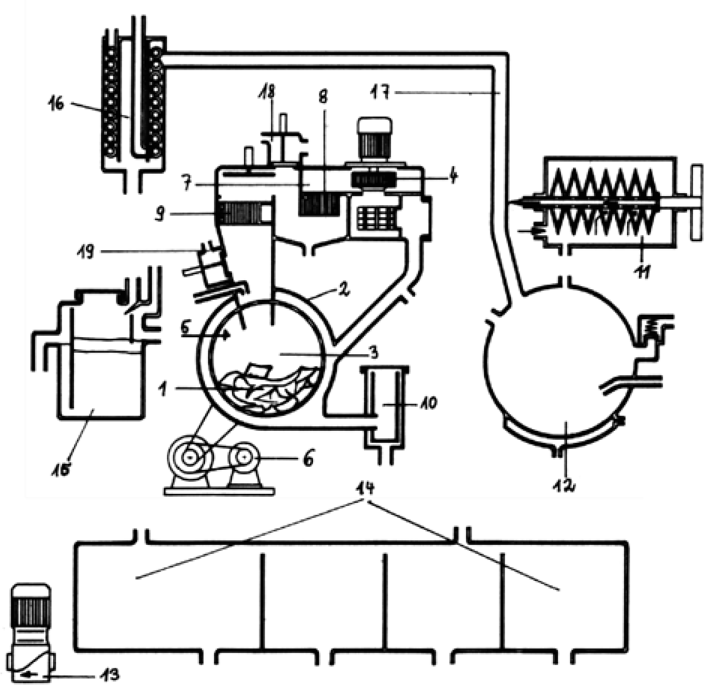

Figure 14.7.4. Scheme of a dry cleaning machine. 1 textiles to be cleaned, 2 cylinder, 3 cage, 4 fan, 5 heater, 6 drive for cage, 7 air canal, 8 cooler, 9 lint filter, 10 button trap, 11 filter, 12 distilling vessel, 13 pump, 14 solvent storage tanks, 15 water separator, 16 condenser, 17 steam pipe, 18 outlet to charcoal filter, 19 dosing unit.

Distilling equipment:

The distilling vessel has the same capacity as the biggest storage tank. Solvent to be distilled is pumped into the vessel from the cylinder or from the filter. The vessel is steam or electrical heated. The solvent vapor is directed into a condenser (water cooling) and then to a water separator, from where it flows into the clean solvent tank. The residue after distillation remains in the vessel and is pumped into special residue drums.

Recovering system:

In order to dry the dry cleaned garments from the solvent residue which remains after spinning, a fan extracts air out of the cylinder into a condenser, where solvent vapor is condensed out of the air. From there the air is blown into a heater and directed by fan back into the cylinder. In this way the solvent is vaporized away from the garment and after condensing, reused for cleaning.

Dosing equipment:

In order to get the right additions of dry cleaning detergent into the solvent, a dry cleaning machine has dosing equipment working on the basis of a piston pump, which doses the right amount of detergent at the right time into the system.

Computer control:

All the processes are computer controlled. Drying/Recovering, Distilling/Filtration operate according to fixed programs; the cleaning cycle can be varied with regard to the requirements of the garment. The most common program works as follows:

Loading the machine, closing the door, starting computer control:

1 min pumping solvent from working tank into cylinder up to low dip level (3 l/kg);
3 min pre-cleaning by rotating the cage in the cylinder;
1 min pumping the solvent from the cylinder into the distillation vessel;
1 min spinning;
2 min pumping solvent from working tank into cylinder up to high dip level (5 l/kg); addition of detergent (2-5 ml/l of solvent);
8 min cleaning by rotating the cage in the cylinder together with filter action;
1 min pumping the solvent from the cylinder back to the working tank (the solvent in working tank is filled by overflow from clean tank);
3 min spinning
8 min drying /recovering solvent with recovery system
5 min drying/recovering solvent with charcoal filter.

After the sensor has indicated that the load is free of solvent residue, opening the door and unloading the machine. After the cleaning process, the garment is controlled for cleaning quality and can be finished or if necessary, it undergoes spotting/recleaning before finishing.

### 14.7.1.7 Recycling of solvents in dry cleaning

The recycling of solvents in dry cleaning is very important, because solvents are too expensive for single use. Three different systems are used for the cleaning of the solvent in order for it to be recycled:

- Filtration
- Adsorption
- Distillation

Filtration is a simple physical process, separating insoluble parts from the solvent. It is done during the cleaning cycle.

Adsorption is mainly used together with hydrocarbon solvents, because their high boiling temperature is insufficient to separate lower boiling contaminants from the solvent. Adsorption systems use charcoal or bentonites. The solvent is pumped to filters where contaminants with higher polarity than solvent are adsorbed by the adsorbing material. The adsorbing material can adsorb contaminants in a quantity of about 20% of its own weight. After being saturated, the adsorbing material must be replaced and changed to fresh material. The charged adsorbing material is disposed according to regulations, which is cost intensive.

Distillation is the best cleaning method if the boiling point of solvent is significantly lower than the boiling point of possible contaminants. With dry cleaning machines using TCE, distilling is the normal recycling method. The boiling point of TCE is 122°C, which makes steam heating possible, so that the process can be done safely and cost effectively. The distillation residue consists of removed soil and detergents. Its quantity is much lower than in the adsorption systems, because there is no waste from adsorbing material. Disposal costs are much lower than with adsorption.

## 14.7.2 SPOTTING

### 14.7.2.1 Spotting in dry cleaning

Spotting is the removal of stains from textiles during professional textile cleaning. Correct cleaning, good lighting conditions, appropriate equipment, effective spotting agents, and expert knowledge are indispensable.

Lighting conditions

Lighting of the spotting table with composite artificial light consisting of a bluish and a yellowish fluorescent tube attached above the table approx. 80 cm from the standing point is better suited than daylight. This ensures high-contrast, shadow-free lighting of the work surface and allows for working without fatigue.

Equipment

Basic equipment should comprise a spotting table with vacuum facility, sleeve board, steam and compressed air guns, and a spray gun for water. Spotting brushes should have soft bristles for gentle treatment of textiles. Use brushes with bright bristles for bright textiles and brushes with dark bristles for dark textiles. Use spatulas with rounded edges for removing substantial staining.

### 14.7.2.2 Spotting agents

In dry cleaning, normally three groups of spotting agents are used:

Brushing agents

Brushing agents containing surfactants and glycol ethers dissolved in low viscosity mineral oil and water. Brushing agents are used for pre-spotting to remove large stains from textiles. They are applied undiluted with a soft brush or sprayed onto the heavily stained areas before dry cleaning.

Special spotting agents

Special spotting agents are used for removing particular stains from textiles. The range consists of three different products in order to cover a wide range of different stains. The products are applied as drops directly from special spotting bottles onto the stain and are allowed to react. The three products are:

- Acidic solution of citric acid, glycerol surfactants, alcohol and water for removing stains originating from tannin, tanning agent, and fruit dye.
- Basic solution of ammonia, enzymes, surfactants, glycol ethers and water for removing stains originating from blood, albumin, starch, and pigments.
- Neutral solution of esters, glycol ethers, hydrocarbon solvents and surfactants for removing stains originating from paint, lacquer, resin, and adhesives.

Post-spotting agents

Stains that could not be removed during basic cleaning must be treated with post-spotting agents. Most common is a range of six products, which are used in the same way, as the special spotting agents:

- Alkaline spotting agent for stains originating from starch, albumin, blood, pigments
- Neutral spotting agent for stains originating from paint, lacquer, grease, and make-up.
- Acidic spotting agent for stains originating from tannin, fruits, beverages, and rust.
- Acidic rust remover without hydrofluoric acid.

- Solvent combination for removing oily and greasy stains from textiles.
- Bleaching percarbonate as color and ink remover.

### 14.7.2.3 Spotting procedure

Correct procedure for spotting

It is recommended to integrate the three stages of spotting

- Brushing
- Special spotting
- Post-spotting

into the process of textile cleaning. Perform brushing and special spotting when examining and sorting the textiles to be cleaned.

Brushing

Examine textiles for excessive dirt, particularly at collars, pockets, sleeves, and trouser legs. If textiles are to be dry cleaned check them particularly for stains originating from food or body secretions.

If the textiles are to be wet-cleaned check them particularly for greasy stains. Apply a small quantity of brushing agent onto the stained areas and allow to react for 10-20 minutes before loading the cleaning equipment.

Special spotting

Intensive staining found during the examination of the textiles can be treated with special spotting agents. The stain substance must be identified and related to one of the following categories:

- coffee, tea, fruit, red wine, grass, urine
- blood, food, pigments, sweat
- wax, paint, lacquer, make-up, pen ink, adhesives

Depending on the category of the stain substance, apply the special product with the dripping spouts in the work bottle onto the stain and tamp it gently with a soft spotting brush. Allow to react for 10-20 minutes before loading the cleaning equipment.

Post-spotting

Stains that could not be removed during dry-cleaning or wet cleaning with machines are subject to post-spotting. Proceed as follows:

- Place the garment with the stain area onto the perforated vacuum surface of the spotting table.
- Identify stain, drip appropriate product undiluted onto the stain and tamp it gently with the brush.
- For stubborn stains, allow product to react for up to 3 minutes.
- Use vacuum to remove product and rinse spotted area with steam gun.
- Dry with compressed air, moving the air gun from the edges to the center of the spotted area.

Hidden spot test

If it is suspected that a stain cannot be removed safely due to the textile material, the compatibility of the spotting agent should be checked by applying a small quantity of the agent at a hidden part of the garment. If the garment passes the test, the spotting agent is expected to be successful without damaging the garment.

## 14.7.3 TEXTILE FINISHING

The use of solvents for textile finishing has only some importance for the treatment of fully fashioned articles. The processes are done in industrial dry cleaning machines. The advantages are the same as in dry cleaning compared to washing: lower risk against shrinkage and damage of sensitive garments.

### 14.7.3.1 Waterproofing

In Northern Europe, North America and Japan, some kinds of sportsware need to be waterproofed. The treatment is done in dry cleaning machines with a load capacity larger than 30 kg ( > 60 lbs). The machines need to be equipped with a special spraying unit, which allows one to spray a solution of waterproofing agent into the cage of the machine.

The waterproofing agents consists of fluorocarbon resins dissolved in a mixture of glycol ethers, hydrocarbon solvents and TCE. This solution is sprayed onto the garments, which are brought into the cage of the machine. The spraying process needs about 5 - 10 min. After spraying, the solvent is vaporized in the same way as drying in dry cleaning, so that the fluorocarbon resin will stay on the fibers of the garments. In order to get good results and the highest possible permanence of water resistance, the resin needs to be thermally fixed. In order to meet these requirements, a drying temperature of > 80°C (= 175°F) is necessary.

### 14.7.3.2 Milling

Solvent milling has some importance for the treatment of fully fashioned woolen knitwear. The process is very similar to normal dry cleaning. The specific difference is the addition of water together with the detergent, in order to force an exact degree of shrinkage and/or felting.

Milling agents are similar to dry cleaning detergent. They have specific emulsifying behavior, but no cleaning efficiency. The process runs like this: textiles are loaded into the machine, then solvent (TCE) is filled in before the milling agent diluted with water is added. After this addition, the cage rotates for 10 - 20 min. The higher the water addition, the higher the shrinkage; the longer the process time, the higher the felting. After this treatment, the solvent is distilled and textile load is dried. High drying temperature causes a rather stiff handle, low drying temperatures give more elastic handle.

### 14.7.3.3 Antistatic finishing

Antistatic finishing is used for fully fashioned knitwear - pullovers made from wool or mixtures of wool and acrylic. The process is equal to dry cleaning. Instead of dry cleaning detergent, the antistatic agent is added.

Antistatic agents for the treatment of wool consist of cationic surfactants such as dialkyl-dimethylammonium chloride, imidazolidione or etherquats. Antistatic agents for the treatment of acrylic fibers are based on phosphoric acid esters.

# 14.8 ELECTRONIC INDUSTRY - CFC-FREE ALTERNATIVES FOR CLEANING IN ELECTRONIC INDUSTRY

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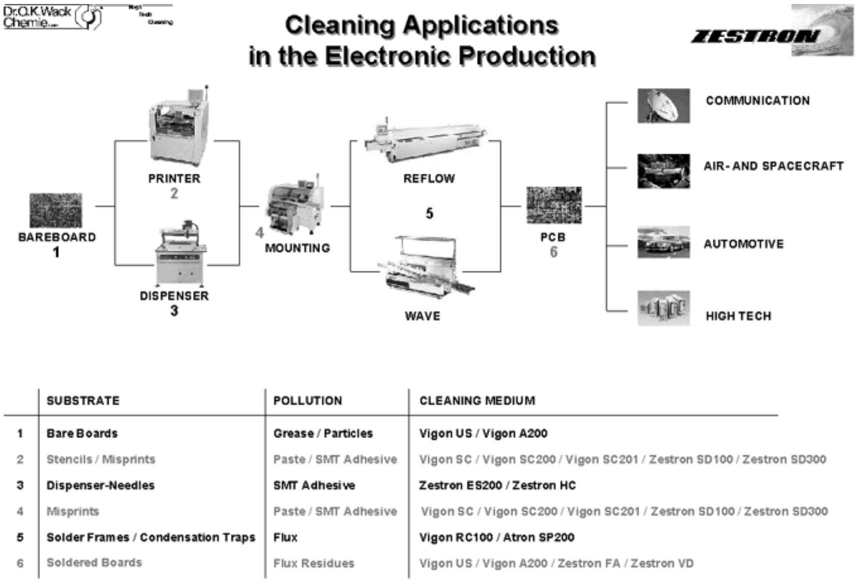
## 14.8.1 CLEANING REQUIREMENTS IN THE ELECTRONIC INDUSTRY

The global ban of the CFCs has fundamentally changed cleaning in the electronic industry. Manufacturing processes were developed with the goal of avoiding cleaning. However, this objective has only be partially realized.

Furthermore, there are still a lot of different areas in the electronic industry where cleaning of assemblies is highly recommended and necessary. Examples of such applications can be found in the aviation and space industries and in addition in the rapidly growing telecommunication industry. When investigating the production process of printed circuit assemblies, there are several important cleaning applications that have varying degrees of impact on the quality of the manufactured assemblies (see Figure 14.8.1).



| | SUBSTRATE | POLLUTION | CLEANING MEDIUM |
|---|---|---|---|
| 1 | Bare Boards | Grease / Particles | Vigon US / Vigon A200 |
| 2 | Stencils / Misprints | Paste / SMT Adhesive | Vigon SC / Vigon SC200 / Vigon SC201 / Zestron SD100 / Zestron SD300 |
| 3 | Dispenser-Needles | SMT Adhesive | Zestron ES200 / Zestron HC |
| 4 | Misprints | Paste / SMT Adhesive | Vigon SC / Vigon SC200 / Vigon SC201 / Zestron SD100 / Zestron SD300 |
| 5 | Solder Frames / Condensation Traps | Flux | Vigon RC100 / Atron SP200 |
| 6 | Soldered Boards | Flux Residues | Vigon US / Vigon A200 / Zestron FA / Zestron VD |

Figure 14.8.1. Cleaning applications in the electronic production.

Cleaning applications in the SMT assembly line typically start with the cleaning of the bare boards (1). The preliminary substrates have to be cleaned in order to remove a variety of residues (particles, chemicals used in the manufacturing process of the bare boards). These residues may have a negative impact on the subsequent production steps. A detailed analysis[1] of different kinds of contamination which might occur on the bare boards revealed that these residues might cause failures in production steps far beyond the initial printing process. Therefore it is important to assure clean surfaces in each production step.

The cleaning applications (2-4) outlined in the SMT process line, shown in Figure 14.8.1, refer to the soldering process. Within this production step the components are placed on the bare board using solder paste that is printed on the solder pads through a stencil. The stencil can be cleaned continuously during the printing process by using a stencil printer underside wiping system. However, it has definitely to be cleaned after removing the stencil from the printer. The solder paste is removed from the apertures of the stencils in order to assure an accurate printing image (3).[2,3] If the assemblies are to be mounted on both sides, the components are placed on one side by using an epoxy adhesive (SMT adhesive), in order to prevent them from being accidentally removed during the reflow process (3).[3] The soldering process is carried out in a specially designed reflow oven. The cooling coils which contain condensed flux residue of such reflow ovens also have to be cleaned (5). In the case of wave soldering processes, the flux contaminated solder frames in addition must be cleaned.

The contamination that must be removed after the soldering process is predominantly from flux residues. The removal of flux residues from the soldered assemblies (6) is generally the most critical application. Thus it is the important that the assemblies are cleaned. A subsequent coating process demands a very clean and residue-free surface to assure long term stability of the coating against environmental stresses such as humidity.[1]

Asked for the reasons for cleaning most of the process engineers give the following answers:

1) Stencils and other tools, such as squeegees, are cleaned in order to assure a reproductive and qualitative satisfying printing process.[2]
2) Contaminations from printed circuit assemblies are removed to achieve long-term reliability.
3) Cleaning is an important manufacturing step within the SMT process line if subsequent processes such as coating and bonding are required.

In recent times an additional process step, which cleaning definitely is, was regarded to be time and cost inexpedient. Therefore a lot off optimization techniques have been applied to the SMT production process to try to avoid cleaning. However, considering new technologies in the electronic industry like fine pitch, flip chip and micro-BGA applications, the above statement is no longer true. The question if the removal of flux residues from printed circuit boards is necessary can only be answered by carrying out a detailed process analysis including the costs for cleaning and the increased reliability of the products. A large number of global players in the electronic industry prefer the advantages of better field reliability of their products. This aspect is even more important taking into consideration the outstanding competition in these industries.

Whether a product has to be cleaned, and, especially, when cleaning is necessary in the SMT production depends on the following factors.

- Process costs: cleaning is an additional process step that demands additional investment and resources. However, failures and downtime in other process steps can be diminished.
- Process reliability: due to a larger process window, the manufacturing process as a whole is more stable.
- Product reliability: the functionality and long term reliability of the products has to be assured.

After the decision has been made in order to choose the most suitable cleaning process, the following two questions have to be answered in advance:

- Which contamination has to be removed?
- What are the requirements regarding cleanliness of the surface, especially taking the subsequent process steps into account.

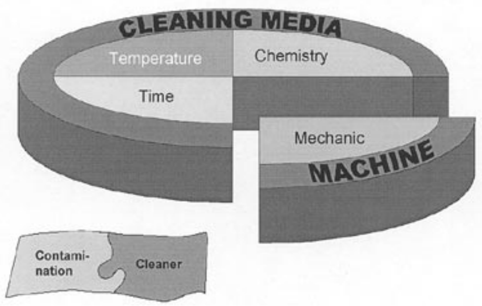


Figure 14.8.2. Factors influencing the cleaning process.

The most important consideration in achieving an optimal cleaning result, is the interaction between the chemistry of the cleaning agent and the type of contamination. This is explicitly shown in the below presented lock and key principle.

However, the cleaning result is not only depended on the nature of the chemistry used for cleaning. Other important factors in the cleaning process are the type of cleaning equipment used and the applied process parameters such as temperature, time and method of application of the cleaning agent (see Figure 14.8.2).

In order to optimize a cleaning process for the specific requirements, detailed information on the nature and composition of the kind of contamination that has to be removed is necessary. This tailoring of the chemistry is achieved by carrying out time consuming screenings matching typical contamination with suitable solvents.

Another very important aspect is the material compatibility of the cleaning agent and the substrates that need to be cleaned. The cleaning chemistry should not attack the different materials of the components in any manner. Consequently, a number of long-term compatibility tests have to be carried out to assure this very important process requirement.

Also, more environmental and worker safety issues are ever increasing when evaluating a new cleaning process. Cleaning processes approved by the industry have to pass even higher standards than are demanded from the government. They have to show, under the worst case scenario, a large process window and a large process margin of safety with respect to personal and environmental exposure.

If all of the above mentioned process requirements such as

- excellent cleaning result,
- long-term functional reliability of the substrates after cleaning,
- material compatibility between cleaning chemistry and the substrates, and
- no drawbacks due to environmental and safety issues

should be fulfilled, a lot of time and know-how has to be invested.

## 14.8.2 AVAILABLE ALTERNATIVES

Due to the global ban of the CFCs, a large number of different cleaning processes[4] have been developed. Each of them has advantages and disadvantages regarding the above mentioned process requirements. The available cleaning processes can be divided into the following main groups:

1) aqueous processes,
2) semi-aqueous processes,
3) water-free processes based on solvents, and

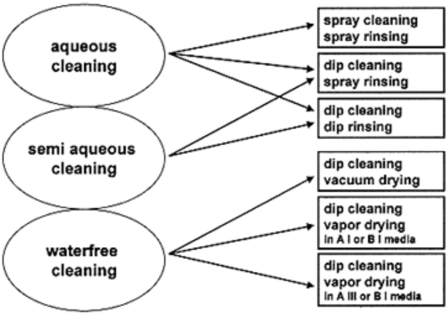


Figure 14.8.3. PCB cleaning.

4) special cleaning processes.

In an aqueous cleaning process,[5] cleaning is achieved by using water or a water-based cleaning agent. In order to avoid drying spots, rinsing is carried out with deionized water. By soldering with water-soluble solder pastes only hot water is necessary for cleaning. However, the use of an alkaline water-based cleaning agent is effective to remove more critical flux residues with low or high pressure spray in cleaning equipment.

In semi-aqueous processes,[4] cleaning is carried out using a high boiling mixture of organic solvents. Rinsing is achieved by using deionized water. The organic solvents used for these cleaners are predominantly based on alkoxypropanols, terpenes, high-boiling alcohols, or mixtures of different chemistries.

In applications based on solvents such as isopropanol or alkoxypropanols[6] a rinse with deionized water is not imperative, since these chemistries do not leave any residues if used for rinsing. Especially when using an uniformly boiling solvent-based cleaning agent, vapor rinsing with solvent vapor is possible. All there mentioned cleaning process will be discussed more detailed in the following sections.

Less widespread applications in the electronic industry include:

- Cleaning using supercritical carbon dioxide (SCF).[7]
- Cleaning using plasma.[7]

SCF cleaning alternative is especially useful for extremely sensitive and complex assemblies. At temperatures above 31°C and pressures above 73 bar, carbon dioxide transforms into a supercritical phase. Supercritical carbon dioxide reveals an extremely low surface tension. Consequently, the wetting of small gaps and complex assembly architectures can be achieved. However, the contamination that should be removed has to be nonpolar, and the compounds should be resistant to high pressures. Due to these basic limitations and the high costs of this cleaning process, this process does not play an important part in the electronic industry.

The advantage of plasma cleaning is in almost waste-free removal of contaminations. The contaminations are transformed into carbon dioxide and water. However, this cleaning process is only suitable for removal of the small amounts of residue from the substrate surface. Combinations with aqueous cleaning processes are feasible and common in the field.

### 14.8.2.1 Water based systems; advantages and disadvantages

#### *14.8.2.1.1 Cleaning with DI - water*

Cleaning without using any kind of cleaning agent in the electronic assembly process is possible when water-based fluxes are used for the soldering process. Since these aqueous fluxes are highly activated, aggressive residues occur after the soldering process. These residues have to be removed immediately to avoid severe corrosion of solder joints. The use of water-based fluxes is very common in the US electronic market due to the main advantage of a large soldering process window for soldering. DI-water is used for this purpose since it is able to solubilize the polar residues. However, physical energy, such as high-spray-pressure, is in most cases necessary to assure complete and residue-free removal of the contamination. However, since pure deionized water reveals a relatively high surface tension, the wetting ability is extremely low.[8] Consequently, being confronted with the situation of constant increase of the packaging densities on PCBs, flux residues especially, between or under components, are very difficult to be removed.[8] As a result this presently predominant cleaning process will be in decline in the future.

#### *14.8.2.1.2 Cleaning with alkaline water-based media*

The principle of this kind of cleaning process is based on the presence of saponifiers in the cleaning fluid. These saponifiers are able to react with the non-soluble organic acids, that are the main ingredients of the flux residues. In other words, the non-soluble flux residues are transformed into water-soluble soaps due to a chemical reaction between the saponifier and the flux. This reaction is called saponification. For such a cleaning process an effective rinse with deionized water is imperative to minimize the level of ionic contamination.[1,5]

However, the presence of alkaline components in the aqueous cleaning fluid may cause the phenomenon of corrosion on different metals (Al, Cu, Sn) resulting in the visible dulling or discoloration of solder joints and pads.[9,10]

The chemical nature of the saponifiers is either organic or inorganic. Organic saponifiers are for example monoethanolamine or morpholine.[5] These soft bases transform the insoluble organic carboxylic acids to soluble soaps acting, in addition, as a kind of buffer to stabilize the pH of the cleaning solution. However, the above mentioned organic amines have an associated odor, and more important, are classified as volatile organic compounds (VOCs). Inorganic saponifiers based on the system sodium carbonate/sodium hydrogen carbonate are also very attractive alternatives exhibiting sufficient cleaning ability at pH-values below 11. By using these chemistries the VOC and odor issue can be avoided.[5]

Besides organic or inorganic saponifiers a large scale of different anionic, cationic or nonionic surfactants are present in water-based alkaline cleaning solutions. The main reason for adding surfactants is the requirement for lower surface tension in order to increase the wetting of the substrates. However, using surfactants in cleaning median in high-pressure spray in air cleaning applications, the issue of foaming has to be taken into consideration.

#### *14.8.2.1.3 Aqueous-based cleaning agents containing water soluble organic components*

There is a large number of products on the market that are mixtures of water and water-soluble organic solvents. These media are recommended for the removal of solder paste, SMT adhesives and flux residues from stencils, misprints and populated reflowed PCBs.[11]

The water-soluble organic solvents are predominantly natural long chain alcohols, glycol ether derivatives or furfuryl alcohol. The basic principle of the cleaning process using such fluids is based on the removal of lipophilic contamination such as oil, grease, flux or adhesive through the organic components of the mixtures. After the removal from the surface of the substrates, the lipophilic contamination precipitates out of the water-based cleaning agent and can be removed by using a filtration devices. In order to guarantee a sufficient cleaning performance, these mixtures contain organic components up to 50%. Consequently, these formulations tend to be classified as cleaning agents with high content of volatile organic compounds (VOCs).

### *14.8.2.1.4 Water-based cleaning agents based on MPC® Technology (MPC = Micro Phase Cleaning)*

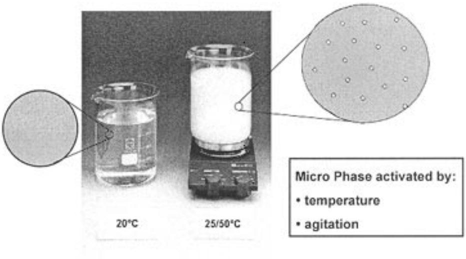


Figure 14.8.4. MPC® cleaning technology.

Cleaning agents based on MPC Technology can be formulated either neutral or alkaline. The media combine the advantages of solvent and aqueous-based formulations revealing an extremely large process window.[2,3] The principle of MPC systems is shown in Figure 14.8.4.

The MPC media are based on formulations consisting of alkoxypropanols and water. Their phase behavior is dependent on the temperature, agitation, and the dragged in contamination. The microphase, which is generated through temperature or media agitation, is responsible for the removal of the lipophilic components of the contamination. The ionics are removed by the aqueous phase.[12] Since the ability to keep the organic contamination in the microphase is limited through the degree of loading, the lipophilic substances are expedited into the aqueous phase. Due to their lipophilic character, they precipitate out of the fluid and can be removed by a simple filtration device. As a result the loading of the cleaning fluid with contamination is minimal thereby minimizing the amount of organic components that finally pollute the subsequent rinsing stages.[3]

Alkaline pH, that is essential for the saponification process, can be realized through biochemical buffer systems, predominately aminoalkanoles.

Due to the described cleaning principle, extremely long bath life times can be guaranteed with excellent cleaning results.[2,3,12] The MPC® media are tailor made for all kinds of different cleaning equipments such as high and low pressure spray systems, spray under immersion, and ultrasonic applications.[3] These cleaning agents based on MPC® Technology also contain low quantities of volatile organic compounds. However, due to this state of the art technology the percentage of VOCs are reduced to a minimal level.

### *14.8.2.1.5 Advantages and disadvantages of aqueous cleaning media*

Prior to the implementation of a cleaning process in a production line, the following criteria need to be taken into consideration:

1) Cleaning performance

The substrates that have to be cleaned should be free of all kinds of residues that might have some negative influence on the functionality of the substrates. The contamination consist predominantly of flux residues, solder paste or SMT adhesive. Another important aspect with respect to the cleaning result is the compatibility between substrates and the cleaning chemistry. It is painless to remove the contamination while destroying the substrates.

2) Process reliability and process costs

Every engineer tries to implement a process with a wide process window, and minimizing potential problems during production. While evaluating a cleaning process, the process parameters should be stable over a long period of time. As a result the equipment down time can be minimized, due to maintenance thereby optimizing the overall process cost.

3) Environmental aspects

A cleaning agent should not only be considered based on its content of volatile organic compounds. A medium that does not contain any VOCs may on the one hand have no influence on air pollution. However, on the other hand, soil and water may be influenced. A VOC containing cleaning fluid has an inherently longer bath life. Consequently, the overall environmental calculation for some VOC containing cleaning fluid are better than by using VOC-free media.

4) Personal safety

Another very important aspect for the evaluation of a new cleaning process is the issue on personal safety. The following topics have to be taken into consideration:

- No risks during handling of the cleaning agent, especially regarding toxicity and flash point.
- Low odor of the cleaning fluid.

If the evaluated cleaning agent fulfils these important requirements, the chemistry will be accepted by the operator.

Taking the discussed issues (1-4) into account, the advantages (+) and disadvantages (-) for the different aqueous cleaning fluids are as follows:

a) Aqueous fluids using amines for saponification:
  + excellent removal of flux residues and unsoldered solder paste
  + predominantly VOC-free formulations
  - low solid flux residues are difficult to remove
  - limited removal of adhesives due to curing of the adhesive
  - short bath life times resulting in high costs for media disposal

b) Aqueous fluids using inorganic saponifiers and buffer systems:
  + satisfying cleaning results on flux residues and solder paste
  + VOC-free formulations
  + longer bath life due to constant pH level caused by the buffering systems
  - low solid flux residues and SMT adhesives are difficult to remove

c) Mixtures of organic solvents and water:
  - small process window regarding flux residues and SMT adhesives
  - VOC containing mixtures
  - short bath life

d) pH neutral and alkaline fluids based on MPC® Technology:
  + extremely large process window regarding flux residues, solder paste and adhesive removal
  + extremely long bath life-times due to previous described cleaning principle
  + economical cleaning process
  - small amounts of VOCs.

### 14.8.2.2 Semi-aqueous cleaners based on halogen-free solvents, advantages and disadvantages

A semi-aqueous cleaning process consists of a wash cycle using a mixture of different organic solvents followed by a rinse with deionized water. Organic contaminations, predominantly rosin flux residues, are removed through the lipophilic solvents, whereas the ionics are minimized by the polar rinse media. The different kinds of solvent formulations that are available on the market reveal an extremely wide process window. Almost all different fluxes that occur in the electronic assembly process can be removed efficiently.

In principle, the media that can be used for semi-aqueous cleaning processes can be classified into two main groups:[4]

- solvent-based mixtures that are not soluble in water, and
- water-soluble cleaning fluids.

The water solubility of the solvent-based cleaning agent is very important for the treatment of the subsequent water rinse.

#### *14.8.2.2.1 Water insoluble cleaning fluids*

The first media designed for this application were predominantly based on terpenes[13] and different mixtures of hydrocarbons and esters. In order to increase the rinse ability of the solvent-based mixtures with deionized water, different surfactants were added.[14] The principle of using a water insoluble cleaning fluid was based on the idea to avoid contaminating the rinse sections through the cleaning fluid. The lipophilic contamination should be kept in the organic cleaning media that can be easily separated from the rinse water by a skimming device. However, experience in the field revealed that this kind of media have some critical drawbacks.

Since the surface tension of the organic cleaning formulations are lower than the surface tension of deionized water (approx. 72 mN/m), the cleaning fluid stays on the surface and will not rinse off. Consequently, the cleaning result is not acceptable with regard to ionic contamination and surface resistivities.[1] Acceptable cleaning results can only be realized through complicated multi-stage rinse processes. Another important disadvantage is the potential risk of re-contamination of the substrate when lifting the substrate out of the rinse section, since the top layer of the rinse section consists of polluted cleaning media. Consequently, effective agitation and skimming of the rinse water is imperative to avoid this phenomenon.[4]

#### *14.8.2.2.2 Water-soluble, water-based cleaning agents*

The solvents used for this application are based on water soluble alcohols, alkoxypropanols and aminoalcohols.[4,6] The chemical structure of these compounds combines a hydrophobic and hydrophilic groups. Due to this ambivalent structure it is possible to optimize the water solubility and lipophilic character for an optimal cleaning performance. Consequently, cleaning fluids based on this principle reveal the largest process window. All different kinds of flux residues, especially low rosin fluxes, are easily rinseable with water resulting in an residue-free cleaning process. The quality and long-term stability of these processes are proven through many applications in the field.[8,15,16] Applications and processes will be discussed more detailed later on.

#### *14.8.2.2.3 Comparison of the advantages (+) and disadvantages (-) of semi-aqueous cleaning fluids*

In order to quantify the effectiveness of the two main groups of solvent based cleaning agents that can be used for semi-aqueous processes, the following key aspects has to be taken into consideration:

- cleaning performance,
- process reliability,
- environmental aspects, and

- personal safety.

a) Non water soluble cleaning agents:

\+ wide process window regarding fluxes, solder pastes and adhesives

\- low rosin flux residues are critical to remove

\- possibility of re-contamination of the substrate in the rinsing stage

\- cleaning fluids contain volatile organic compounds.

b) Water soluble solvent based cleaning agents:

\+ extremely wide process window regarding all kinds of fluxes, solder pastes and adhesives

\+ residue-free removal of the cleaning fluid due to excellent rinse ability

\- VOC containing formulations

### 14.8.2.3 Other solvent based cleaning systems

Besides the already mentioned solvent based cleaners, there are some special solvents on the market. However, due to their physical and toxicological character, most of them are used for special applications. The advantages and disadvantages of the different products are summarized below.

14.8.2.3.1 Isopropanol

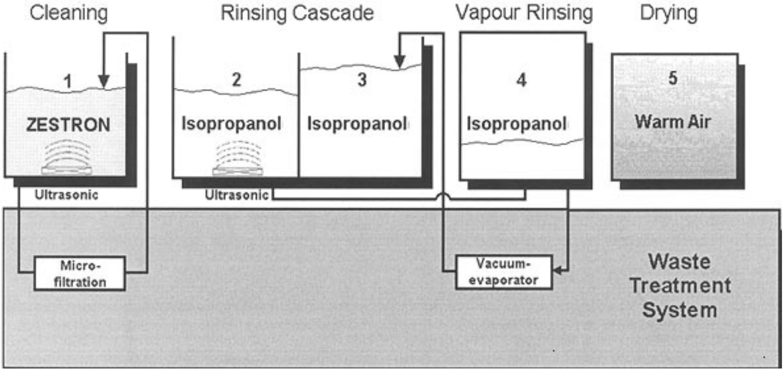


Figure. 14.8.5. Zestron FA/IPA.

Isopropanol is sometimes used for the cleaning of assemblies. More common, however, is the use of this solvent in stencil cleaning applications. Isopropanol is often also used as a rinsing media when cleaning with a solvent for hybrid or ceramic applications prior to bonding (see Figure 14.8.5). However, when using isopropanol for any kind of cleaning application there are some essential disadvantages that have to be taken into consideration:

- Flammability due to low flash point,
- Requires explosion-proof cleaning equipment,
- Small process window with respect to the ability to flux residues,
- Limited removal of adhesives due to curing of the adhesives, and
- White residues formation with some flux residues.

14.8.2.3.2 Volatile siloxanes

Due to their extremely low surface tensions combined with excellent wetting character, siloxanes were recommended for electronic cleaning applications. While siloxanes can be used for the removal of non-polar contaminations, ionic contaminations cannot be readily removed. Consequently, for an effective cleaning process, formulations containing siloxanes and alkoxypropanols are needed. However, the use of siloxanes containing cleaning fluids does not play an important role in electronic assembly cleaning applications with respect to the above mentioned disadvantages.

### 14.8.2.3.3 Chlorinated solvents

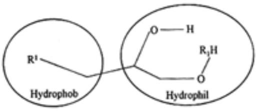
Chlorinated solvents such as trichloroethylene or 1.1.1-trichloroethane are nonflammable and excellent cleaning results can be achieved on especially non-polar residues. However, ionic contamination cannot be removed sufficiently.

There are predominant environmental issues, in particular, their ozone depletion potential, which makes their use in electronic cleaning applications obsolete.

### 14.8.2.3.4 n-Propylbromide (nPB)

Cleaning fluids based on formulations using n-propylbromide (nPB) have to be regarded very critically. Since these products also contain halogens, they cannot be considered to be real alternatives for chlorinated or fluorinated hydrocarbon mixtures. Due to these open environmental questions, cleaning applications using n-propylbromide formulations are still not very common, especially in Europe.

### 14.8.2.3.5 Alkoxypropanols



Cleaning agents based on alkoxypropanols show extremely satisfying cleaning results due to their chemical structure. The lipophilic part of the molecule is capable of removing organic soils such as greases or oils from the substrate surface, whereas the hydrophilic part is able to remove the ionic contaminations.

Furthermore, products based on this kind of chemistry show a large process window on all different types of flux residues. Different applications and processes will be discussed in detail in the following sections.

### 14.8.2.3.6 Hydrofluorinated ethers

Hydroflourinated ethers are a new generation of cleaning fluids revealing no ozone depletion potential. Since they have no flash point there is no need to use explosion-proof cleaning equipment, thereby the cost of cleaning equipment is dramatically reduced. In addition, with their extremely low surface tension and viscosity, they are able to penetrate the tightest spaces of assemblies with high packing densities. Physical properties and different applications and processes will be discussed in more detail below.

### 14.8.2.3.7 Advantages and disadvantages of solvent-based cleaning agents

*Advantages*:

- Solvents exhibit a large process window on all different kinds of fluxes, adhesives and solder pastes
- Most solvents can be regenerated through distillation,
- There is no need of extensive treatment systems for the rinse water,

*Disadvantages*:

- Higher proven costs due to investment in explosion-proof cleaning equipment,
- VOC containing solvents,

*Process*:

- Handling risks for the operator due to flammability, toxicity and odor, and

- Good material compatibility with respect to materials commonly found on assemblies.

## 14.8.3 CLEANING OF TOOLS AND AUXILIARIES

The prohibition of CFCs in 1993 in Europe found the electronic industry scrambling to undertake appropriate actions. Various alternative technologies have asserted themselves during the conversion to environmentally friendly processes. Basically, two courses have evolved as alternative to the use of CFCs for changing applications:

- New soldering techniques that avoid cleaning as a process have been developed and introduced in the electronic industry.
- New environmentally friendly cleaning processes have been introduced.

A large number of European companies decided in favor of no-clean processes, in spite of the associated disadvantages. In the USA cleaning has not be abandoned; it is still an important step in the SMT production line. However, with the increase of packing density and increased quality demands, more and more European companies are now returning to cleaning processes. In general, the purpose of changing is for the removal of contamination which might otherwise harm the operation of the electronic circuit assembly.

Ensuring high reliability for a circuit assembly by effective cleaning is extremely important in such domains as the military, aviation, telecommunications, and in the automotive industry. The need for change to high reliability can be expected to grow appreciably because of different factors. These factors range from more complicated assemblies with higher density to the greatly accelerating use of conformal coatings in the automotive, niche computer, consumer electronics, and telecommunications markets. Dramatic growth is expected to occur in the USA, Europe and Asia. The applications where cleaning is necessary can be divided into three main applications:

- the removal of flux residues from printed circuit assemblies (PCBs) after reflow or wave soldering;
- the removal of solder paste and/or SMT-adhesive from stencils screens or misprints, and
- the tool cleaning (dispensing nozzles, solder frames, cooling coils from reflow or wave soldering ovens, and squeegees).

### 14.8.3.1 Cleaning substrates and contamination

In recent years stencil and misprint cleaning has become a significant issue for many users. Normally, in a typical PCB assembly line, the solder paste is printed through screens or stencils. As an alternative to glue dispensing, specially formulated SMT adhesives can now be printed through a stencil. Consequently, the stencils must be cleaned periodically to maintain the quality and yield of the process. However, the removal of SMT adhesive gives rise to completely new demands on the cleaning process and the condition of the stencils. The following specifies the points that must be observed in connection with stencil cleaning. Great importance has therefore been given to comparison of different cleaning chemistries, cleaning equipment, and comparison of manual and automated cleaning.

Ever-increasing component density and the result expected from the printed image give rise to stringent requirements regarding stencil cleanliness. A flawless printed image is very important because misprinted boards can no longer be used without cleaning. This can be very expensive, particularly if components have already been mounted onto one side of a board. As a consequence, stencil printing for the application of solder paste on SMT boards has become a standard. Stainless steel stencils with apertures that are either etched or cut with a laser are used for this purpose. They can also be used for fine-pitch apertures. Studies have revealed that more than 60% of the defects arising in the SMT process are caused by inadequate paste printing. This, in return, can be traced to insufficient cleaning that is often done manually. Consequently, a well working stencil cleaning process is an imperative.

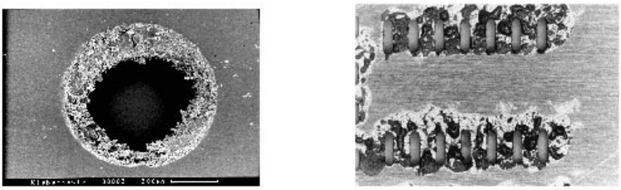


Figure 14.8.6. Left: Residues of SMT adhesive cured in the aperture of a stainless steel stencil. Right: Stainless steel stencil encrusted with solder paste.

With regard to the cleaning process it is very important that no paste or cleaner residues remain in a stencil aperture, as this will inevitably cause misprints (see Figure 14.8.6, right). The printing of adhesives, on the other hand, requires some points to be taken into consideration since this method has to produce different dot heights. The ratio between the stencil thickness and a hole opening is the decisive factor with this technology. Stencils for adhesive application are made of either stainless steel or plastic and are usually thicker than those used for paste printing. Cleaning is complicated by the thickness of the stencils (often exceeding 1 mm). Consequently, small holes require a cleaner with intense dissolving properties to ensure that the adhesives are completely removed (see Figure 14.8.6, left).

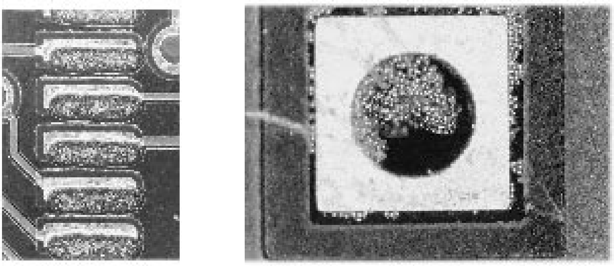


Figure 14.8.7. Left: Misprinted PCB, Right: Via filled with solder paste.

Although cleaning of stencils improves the printing results drastically, the production of misprints during the printing process cannot be avoided completely. However, the cleaning of misprinted assemblies is an application that is still frequently ignored. This involves the removal of misprinted or smeared solder paste or SMT adhesive. The removal of solder paste as the most widespread application gives rise to the following demands:

- No solder paste must remain on the surface, or the vias (see Figure 14.8.7).
- The surface must be perfectly clean and dry to ensure immaculate renewed printing.
- The solder flux on double-sided PCBs must also be removed from the side where soldering has been finished.

### 14.8.3.2 Compatibility of stencil and cleaning agent

In some cases, repeated washing can damage stencils cleaned in automated washing stations. This damage usually occurs through degradation of the frame-to-screen glue. This degradation occurs at the junction of the stencil and the mesh and also at the junction of the mesh and the frame. The causes for this degradation lay in two factors. First, the high temperatures that are needed to clean stencils with aqueous cleaners cause thermal stresses along the glue boundaries. Secondly, the glue itself, which in most cases is a cured epoxy material, may dissolve in the cleaning medium. The combination of these two factors can lead to severe stencil defects. A protective coating can be applied to the glue in cases where it is known that the glue is not stable towards the cleaning medium. Advanced cleaning agent manufacturers work closely with stencil manufacturers to avoid this problem. However, testing in advance of installed cleaning operation ensures that no unexpected stencil defects will affect the production process.

### 14.8.3.3 Different cleaning media

When selecting a cleaning process, the chemistry should be selected first, because the cleaning chemistry has to be adopted to the chemical ingredients of the contamination. Only after the evaluation of the proper chemistry, can the method of applying the cleaning agent be evaluated.

Solvent-based cleaning agents such as hydrocarbons, alcohols, terpenes, and esters offer properties that make them effective cleaning agents for the electronics industry. Low surface tension, high solubility, and ease of drying allow organic solvents to clean effectively where water-based cleaning agents are less effective. These benefits are very similar to the physical properties of the chlorofluorocarbons (CFC) that were once in widespread use in electronics manufacturing operations. Solvents, however, have several significant drawbacks that have limited their use including:

- Flame and explosion hazards,
- Higher equipment costs, due to required explosion protection,
- Personal exposure concerns,
- Material costs, and
- Disposal of used solvents.

And while water-based cleaning agents have been much improved in recent times, their performance does not always match that of their solvent forerunners. In fact, an ideal water-based cleaning agent would combine the physical properties of solvent-based cleaning agents with the safety and convenience of water-based materials.

Solvent-based cleaning agents

Cleaning with solvents such as isopropanol or acetone still remains the most widely applied method because any type of solder paste or SMT adhesive can be removed from the stencils by specially formulated mixtures. Consequently, the cleaning process window for such modern solvents is sufficiently wide to ensure the required results when changing over to another paste or adhesive. Normally, such cleaning processes are performed in machines designed specifically for solvent cleaning. The use of cleaners with flash points in excess of 104ºF (40°C) means that the machines can be set up without having to maintain an explosion protected area. Moreover installation in a special room may be necessary. However, the handling requirements of highly flammable cleaners, for such as isopropanol (IPA, flash point of 54ºF, 12°C), are far more critical, and cleaning is not so effective, particularly with fine-pitch stencils and SMT adhesives. Besides, modern solvent cleaners have been formulated in such a manner that health hazards are minimized - provided, they are properly used.

Water-based cleaning agents

The benefits of cleaning with water-based agents are straightforward. They include:

- Ease of use,
- Absence of fire or explosive hazards,
- Simple disposal,

- Environmental and personal safety rules.

In some cases even pure water can be used as the cleaning medium (presupposing that the contaminants are fully water-soluble). In most cases, however, water requires the addition of chemical or mechanical energy to obtain good cleaning performance. This can come in the form of:

- A cosolvent,
- A chemical activator,
- Elevated temperature,
- Mechanical action, or
- High-pressure spray or ultrasonics.

Contaminants such as oils, greases and SMT adhesives that feature high organic matter content are not readily soluble in water. Adding chemical activators such as saponifiers to the formulation can increase their solubility. Unfortunately, saponifiers require in most cases elevated temperatures (38-60°C) in order to react with the contamination. However, temperatures in this range will most likely damage the stencil. Saponifiers improve cleaning by reducing the surface tension of the cleaning solution, permitting the agent to penetrate void spaces and stand-off gaps that pure water cannot reach. The saponifiers in water-based cleaning agents are either organic or inorganic. Organic saponifiers are, in most cases, fully miscible with water and can easily be rinsed from the stencil. Any residues remaining after rinsing evaporate during drying. Inorganic saponifiers are usually water-soluble materials applied as a solution in water. They are nonvolatile, and residues remaining after rinsing might leave contamination on the substrate. The alkaline saponifier is consumed during the cleaning process and requires constant replenishment. In addition, the high pH value and the elevated application temperatures can also cause an oxidative attack of the aluminum frame of the stencil.

Elevated temperatures are also commonly used to increase cleaning performance. An increase in temperature will lead to a corresponding increase in the solubilizing properties of the cleaning medium. There is of course a point at which the thermal stress induced by high temperature cleaning can damage the stencil adhesion.

Lastly, high pressures or ultrasonics are used as a way to remove contaminants by transferring mechanical energy to particulate contamination. Pressure helps to force the cleaning agent into void spaces and stand-off gaps. Pressure can only marginally improve cleaning performance when the contaminant is not in particulate form or when solubility is the limiting factor.

Water-based cleaners based on MPC® technology

Satisfactory results in stencil cleaning with aqueous systems can only be achieved for the removal of solder paste. Most aqueous systems used to remove adhesives failed in the past because the water caused the adhesives to set.

Micro Phase Cleaning (MPC)[2,3,12] refers to the use of a cleaning agent formulated to undergo a phase change at elevated temperature. When heated above a threshold temperature (typically 100-120ºF, 40-50°C) a microphase cleaner changes from a clear colorless solution to a turbid milky mixture.

The phase transition produces a cleaning mixture that exhibits the properties of both solvent-based and water-based cleaners. “Water-like” properties allow the cleaning agent to effectively dissolve ionic contaminants and remove them from the substrate’s surface.

Non-polar and organic residues are removed by contact with the hydrophobic or "solvent-like" phase.[12]

No specialized equipment is needed to handle microphase cleaning agents. In most cases a microphase cleaning agent can be used as a drop-in replacement in existing equipment. Microphase cleaners are effective in all types of cleaning equipment capable of applying the cleaning agent in a liquid form. This includes spray and ultrasonic equipment.

**Table 14.8.1. Comparison of different cleaner types**

| Cleaning Agent | Pros | Cons |
|---|---|---|
| Modern solvents | Removal of adhesives and solder paste<br>Wide process window<br>Cleaning at room temperature<br>Do not oxidize/corrode stencil | Flammable<br>Emits solvent vapors into work area<br>Slow drying<br>VOC (volatile organic compound)<br>Ozone depletion potential<br>Require explosion proof equipment |
| Aqueous alkaline cleaner | Cheap<br>Non-flammable<br>Non ozone depleting<br>No VOCs<br>Mild odor | Do not remove adhesives<br>Short bath life times<br>Narrow process window<br>Water rinse necessary |
| Aqueous based cleaners of MPC Technology | Removal of adhesives and solder paste<br>Wide process window<br>Non-flammable<br>Rapid drying<br>Residue-free drying<br>Long bath life | Agitation of the cleaner (spray, ultrasonic, spray under immersion, overflow) necessary |

Table 14.8.2 presents the typical technical characteristics of different cleaning agents developed by Dr. O.K. Wack Chemie for stencil and misprint cleaning applications.

#### 14.8.3.4 Comparison of manual cleaning vs. automated cleaning

Printing screens are often cleaned manually (Figure 14.8.8) as users still shy away from the purchase of a cleaning machine because of the associated investment costs ($6,500 to $60,000). However, a more accurate assessment must take the following points into account:

**Table 14.8.2. Technical data of typical cleaning agents (water-based and solvent)**

| Cleaning Agent | Vigon® SC200 | Zestron® SD300 |
|---|---|---|
| Chemistry | water based | solvent based |
| Flash point | none | 106°F |
| Appl. Temp. | 77°F | 77°F |
| Process | spray in air ultrasonic manual | spray in air (ex proofed) manual |

(1) The mechanical rubbing action of the repeated manual cleaning impairs the stencil surface. This is particularly apparent with plastic stencils. These changes to the stencil surface can result in misprints and shorten the service life of the stencil, making it very difficult to track the source of the problem.

(2) Precise repeatability of the cleaning results is not guaranteed with manual

cleaning because manual applications are not based on precisely defined cleaning processes. This can also result in fluctuations of the printing result.

(3) Manual cleaning must be completed with the utmost care. Such care costs time and money, thus making it very expensive. The investments for a cleaning machine can be recovered within a very short period, independent of the number of substrates that are to be cleaned.

Example: A worker requires 1 hour per day for stencil cleaning. On the basis of $40.00/h and 220 workdays, a small machine ($8,700) can be a worthwhile investment within a year.

Some users clean misprinted assemblies manually. This can prove to be very labor and cost intensive when larger quantities are involved. The cleaning results and their reproducibility will be rather inconsistent. Manual cleaning of PCBs with vias and blind holes with a brush or cloth can mean that solder beads are actually rubbed into the holes. Such holes can only be satisfactorily freed by ultrasonic or other mechanical means. It is imperative that the via are free of solder particles, otherwise the consequential damage can be very expensive.

### 14.8.3.5 Cleaning equipment for stencil cleaning applications

As previously mentioned, it may well prove to be an economical proposition to invest in a specially designed cleaning machine if this can be justified by the number of substrates that have to be cleaned. In general, PCB assemblers use the following different types of cleaning equipment for stencil and misprint cleaning:

- Spray in air,
- Spray under immersion, and
- Ultrasonic.

Spray in air cleaning equipment

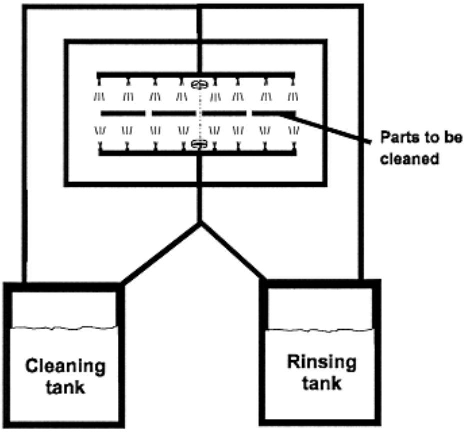


Figure 14.8.8. Scheme of typical spray in air type of cleaning equipment.

Spray in-air machines consist of either a single or multiple reservoirs containing wash and rinse fluids (detergents, solvents, saponifiers, water, etc.). The stencils are placed in a separate chamber, and the wash/rinse fluids are then pumped from the reservoirs into the stencil chamber, and delivered onto the stencil via low pressure (<70 psi) spray wands. These arms may be either co- or counter-rotating. When designed for using a solvent as a wash medium, these machines must be designed to be explosion protected (intrinsically safe electronics, pneumatic or TEFC pumps, sealed conduits, etc.). These machines may also be outfitted to use an inert atmosphere, such as nitrogen, in the stencil chamber.

When used with aqueous-based media, they may often be equipped with a wash and or rinse tank heater. Advantages of this type of machine are:

- Relatively inexpensive (although explosion protecting oftentimes significantly increases the cost of the machine),
- Easy to use,
- A large number of options (add-ons) available (in-line filtration, closed loop water recirculation, programming options, etc.),
- Do not require as much media as other types of stencil cleaners, because they do not require total immersion of the stencil,
- The stencil is also washed, rinsed, and dried in the same chamber, thus eliminating the need to move the stencil around manually.

Disadvantages include the sometimes large footprint that results from having to provide up to three separate chambers (wash, rinse, and stencil), and the sometimes inadequate agitation (spray pressure) generated by the machine. This can make it difficult to clean fine-pitch apertures.

Spray under immersion cleaning equipment

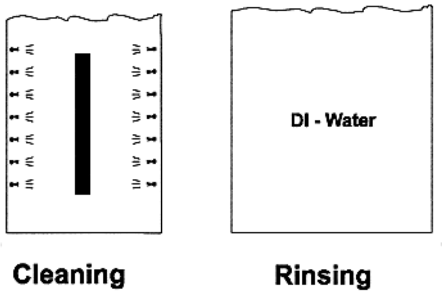


Figure 14.8.9. Scheme of typical spray under immersion batch cleaner.

In spray under immersion equipment, the stencil is placed into a bath (immersed) containing the cleaning medium. The medium is then recirculated using submerged spargers to provide agitation to the stencil surface. A separate chamber is then used for rinsing and drying. Advantages of this type of machine are that it is:

- Most gentle on the stencil, and
- The capital expense is relatively low.

However, because of the low pressure, cleaning cycles may require longer cleaning times. Also, the size of the machine and the quantity of cleaner required are dictated by the size of the stencil to be cleaned.

Ultrasonic cleaning equipment

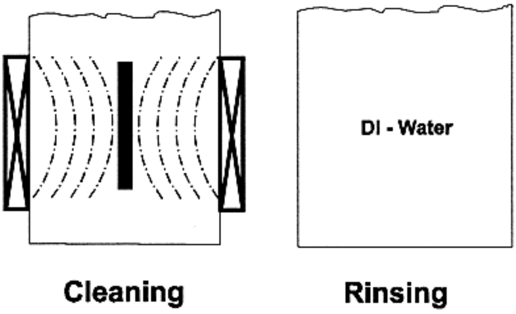


Figure 14.8.10. Scheme of typical ultrasonic batch cleaning equipment.

Ultrasonic machines, as the name implies, use ultrasonic “vibratory” energy to clean stencils. The stencil is immersed in a bath containing the cleaning medium, and exposed to ultrasonic energy. The ultrasonic frequency varies, but is typically between 40 and 100 kHz. Options for the ultrasonic cleaning machine include overflow recirculation of the medium, as well as spray under immersion jets to aid cleaning and bath agitation. The equipment also varies greatly in size (from tabletop models to large footprint models that include rinsing baths, air dryers, and robot arms). Advantages of this unit are that:

- The ultrasonic energy is much better suited to cleaning fine pitch openings, and

- External heaters often may not be needed when using aqueous medium, because of the bath heating that the ultrasonic energy accomplishes.

However, because of this heating, these units are not recommended for use with solvent cleaners. Also, precise control of the ultrasonic energy is required to prevent possible damage to the stencil and apertures. Comparatively, also, ultrasonic machines are more expensive than either type of spray equipment. The size, and thus the cost, is directly proportional to the size of the stencil to be cleaned.

### 14.8.3.6 Stencil cleaning in screen printing machines

Today, many screen printers incorporate an automatic cleaning system for the undersides of stencils. During the process a wiper is moistened with a cleaner that wipes the stencil. On high-end printers this unit is programmable to permit subsequent dry wiping and vacuum drying. Cleaning the underside of stencils may not replace machine stencil cleaning, but it does extend the time, in some cases significantly, until machine cleaning becomes necessary.

A disadvantage of these automatic-cleaning units is the fact that only solder paste removal is possible. The main problem associated with cleaning the stencil underside of adhesive stencils is that it does not remove the adhesive from the stencil holes. This means that only the surface is cleaned, while the holes are untouched. Cleaning agents suitable for this application already exist.

### 14.8.3.7 Summary

The cleaning process, which a user finally selects, depends to a major extent on the operating conditions. Each process has its own specific advantages and disadvantages, so users are supported by advice and testing. These can be accomplished under tightly simulated process conditions by a technical center.

## 14.8.4 CLEANING AGENTS AND PROCESS TECHNOLOGY AVAILABLE FOR CLEANING PCBs

### 14.8.4.1 Flux remove and aqueous process

With the banning of CFCs - enforced in Germany since January 1993 - users have been confronted with the problem of ensuring cost effective elimination of ozone depleting chemicals from the production process while having to satisfy constantly rising quality requirements. In the electronic industry it is customary to set certain quality standards in the manufacturing process of electronic assemblies. Nevertheless, it is often not enough to check the quality of a part immediately after it has been manufactured as long-term quality must also be taken into account. However, technically proficient and efficient processes are available that can exclude long-term risks and even reduce overall costs.

A large number of companies have decided in favor of no-clean processes. Though, with the expansion of packing density and increased quality demands, more and more companies are now returning to cleaning processes.

#### *14.8.4.1.1 The limits of a no-clean process*

The no-clean concept (i.e., no cleaning after soldering) proceeds from the following assumptions:

(1) The used soldering fluxes have a low solid content of approx. 2 to 3% and contain strong activators. These activators, however, are critical as they can easily form highly conductive electrolytes under humid climatic conditions.

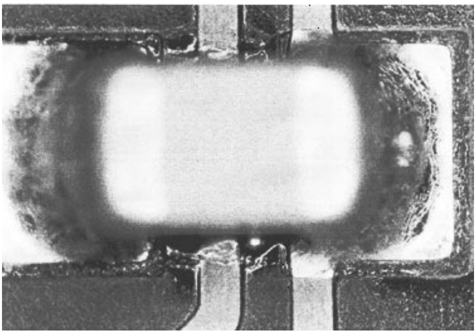


Figure 14.8.11. Soldering flux residues on a component.

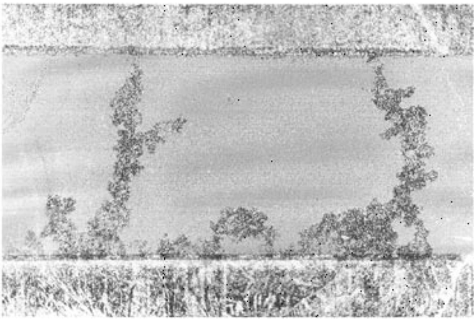


Figure 14.8.12. Dentride growth between connecting contacts.

(2) Reduction of the resin content and quantity of activators simultaneously diminishes the risk of leakage current, electro-migration and corrosion.

After soldering, cleaning removes all residues from the pc-boards, whereas the no-clean soldering process leaves residues on the pc-boards surface, thereby exposing them to the influence of humidity. Consequently, the presence of soldering flux residues on assemblies (Figure 14.8.11) can cause significant functional disruptions. To guarantee quality assurance with no-clean fluxes, the standard tests previously employed in the days of CFC cleaning where transferred accordingly to no-clean pc-boards, including:

- Testing for impurity,
- Testing for surface resistance (SIR test),
- Testing for electro-migration,
- Testing for bondability, and
- Testing under climatic stresses.

Testing for ionic contamination and establishing the surface resistance usually produces good results with pc-boards soldered in a no-clean process. Nevertheless, the values are still significantly poorer than with cleaned assemblies. The migration and precipitation of metal ions can cause the dangerous growth of dendrites (Figure 14.8.12). These metal dendrites are outstanding electric conductors that diminish the surface resistance and, in the long-term, result in short-circuits. Coating can significantly reduce the risk of electro-migration. However, this demands a clean surface, otherwise homogeneous adhesion of the coating is not assured.

### *14.8.4.1.2 Different cleaning media and cleaning processes*

When selecting a cleaning process, the cleaning chemistry is the most sensitive parameter, because the cleaning agent has to be adapted to the chemical ingredients of the contamination. Only after determining the most suitable chemistry, should the method of application be evaluated. In principle cleaning processes can be split into three separate categories:

(1) Semi-aqueous cleaning,
(2) Aqueous cleaning, and
(3) Solvent cleaning.

### 14.8.4.1.3 Semi-aqueous cleaning

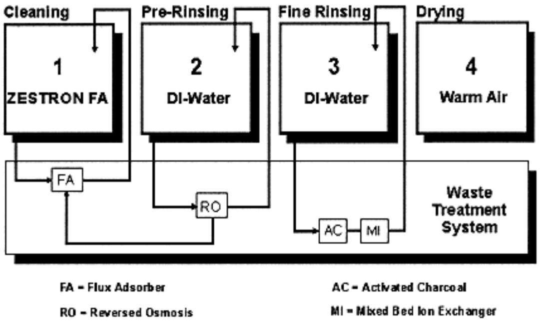


Figure 14.8.13. Diagram of a semi-aqueous cleaning process with ZESTRON® FA.

A process that has found widespread use in practice is semi-aqueous cleaning with ZESTRON® FA. This cleaner was especially developed for removal of no-clean soldering fluxes in ultrasonic batch or spray under immersion cleaning systems. It is used in the cleaning bath, rinsed with demineralized water, and then dried with hot air (see scheme in Figure 14.8.13.).

The carried-in flux constituents can be removed by a flux absorber system to ensure the cleaning medium maintains a constant quality. Cartridge filters also remove precipitated flux residues and particles. Two cascaded rinsing units - a pre-rinse and a fine rinse - follow the wash stage. The rinsing water contaminated with carried-over cleaning medium is passed through different sized particle filters, mixed-bed ion exchangers, and activated carbon filters. The quality of the rinsing water can be continuously monitored by conductivity measurement to establish its residual ion content. The conductivity value should be below 1 μS/cm.

The complete process in based on a closed-loop principle. Consequently, the cleaning process merely liberates those substances that are to be removed from the pc-boards (i.e., soldering flux residues). Closed-loop operation is not only advisable for ecological reasons, but is also a very sound economic proposition as it significantly minimizes process costs.

### 14.8.4.1.4 Aqueous cleaning in spray in air cleaning equipment

Low pressure spray in air batch cleaning systems (see Figure 14.8.14) can be attractive propositions for users who only have a low volume of pc-boards to clean and are required to furnish proof of a specified cleaning process to their customers. The water-based mildly alkaline cleaning agent VIGON® A200 was specifically developed for this application.

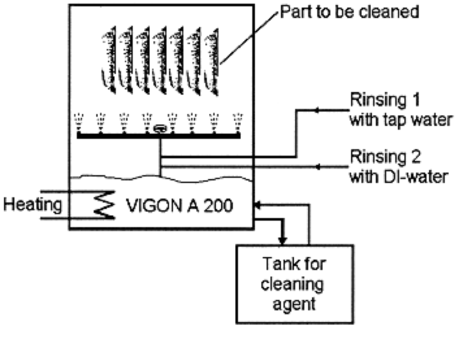


Figure 14.8.14. Diagram of an aqueous in-line cleaning process with VIGON® A200.

High-pressure spray in air in-line cleaning processes that remove flux residues from PCBs, are often employed by manufactures to clean large quantities of boards. This still represents the most economical way to clean large quantities of PCBs. Especially for contract manufactures that are required to clean different types of PCBs, often with several different flux residues.

The parts to be cleaned are fed, one after the other, into a continuous spray cleaner where they pass through the different process stages indicated in Figure 14.8.15. The

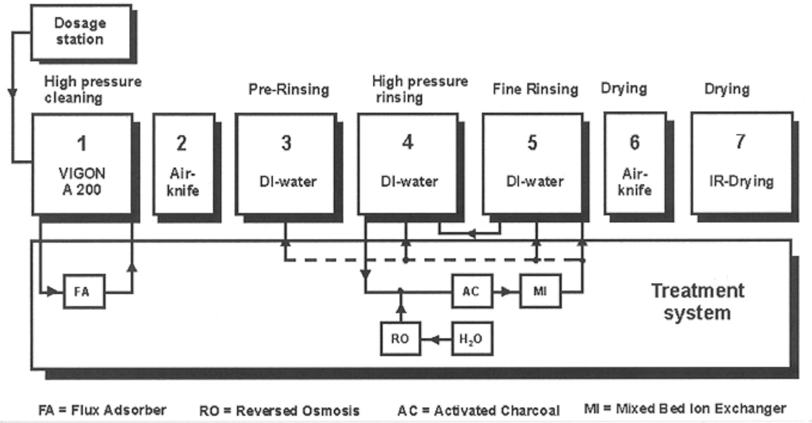


Figure 14.8.15. Scheme of a low-pressure batch cleaning system.

high-pressure cleaning unit is supplied with VIGON® A200 by a chemical dosing station. Cleaning medium quality can be maintained by installing a flux absorber system. The cleaned parts are blown-out with an air knife to minimize carry-over losses from the high-pressure cleaning section. Pre-rinsing the parts with deionized water follows the cleaning section. A fine rinse unit ensures minimum ionic contamination on the PCBs. Finally, the cleaned parts are then blown off with hot air. Complete drying, particularly of parts that retain a great deal of liquid, can be performed with an infrared dryer.[20,21]

### 14.8.4.2 Flux removal from printed circuit boards - water-free cleaning processes

In the European Community, the production and sales of chlorinated fluorocarbons (CFCs) have been banned since 1995. Due to their ozone depletion potential (ODP) hydrochlorinated fluorocarbons (HCFCs) are also subject to be phased-out. The revision of EC Direction 3094/95 proposed in Article 5 the ban of HCFCs as solvents for parts cleaning. HCFCs are not allowed in open solvent applications and their use in contained cleaning systems, such as industrial equipment with ultrasonic agitation, will be banned by January 1, 2002. However, the aerospace and aeronautic industries are allowed to use HCFC until January 1, 2002. Furthermore, in some countries, including Germany and Switzerland, national ordinances have prohibited the use of HCFCs to replace CFC solvents for several years. Consequently, the search for alternative solutions to avoid cleaning (no clean technology) or to use environmentally acceptable solvents leads to new cleaning processes including new cleaning agents and new cleaning equipment.

- Novec™ hydrofluoroether (HFE) in combination with a cosolvent, and
- High boiling cleaning agents that can be recycled continuously by vacuum distillation.

These two new processes can permanently replace both 1,1,1-trichlorochlorethane and CFC-113, as well as, chlorinated solvents such as dichloromethane, trichloroethylene (TCE) , perchloroethylene and HCFC-141b.

#### *14.8.4.2.1 Water-free cleaning processes using HFE (hydrofluoroethers) in combination with a cosolvent*

The cleaning process:

A cosolvent cleaning process is one, in which the cleaning and rinsing solvents are of significantly different composition. For example, in semi-aqueous systems (see Cleaning Technologies on the PCB Assembly Shop Floor (Part II) in EPP Europe, October 1999) cleaning is done with organic solvents and water is used for rinsing. In the cosolvent cleaning process, cleaning is accomplished primarily by the organic cosolvent, and rinsing is effected by a fluorochemical. Typically, in cosolvent systems, the boil (wash) sump contains a mixture of cosolvent and fluorochemical rinsing agent. The rinse sump normally contains essentially 100% fluorochemical rinsing agent.

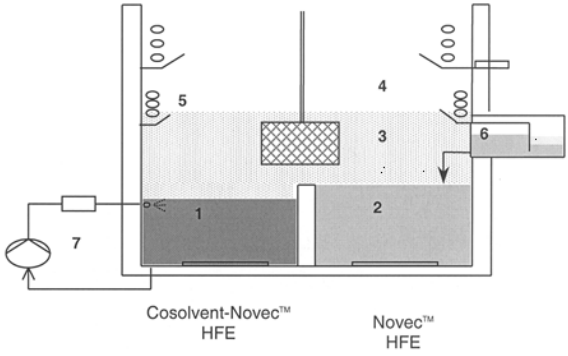


Figure 14.8.16. Typical vapor degreasing equipment.

Referring to Figure 14.8.16, a cosolvent process operation can be summarized as follows. Printed circuit boards containing flux residues are immersed into the boil sump, which contains a mixture of cosolvent and fluorochemical rinsing agent, typically about equal volumes of each. After being cleaned in the boil sump, the substitutes are immersed in the rinse sump, which contains nearly 100% fluorochemical.

The primary function of the rinse sump is to remove the fluorochemical/cosolvent mixture and the soil dissolved in it. Following immersion in the rinse liquid, the parts are moved into the vapor phase for a final rinse with pure fluorochemical vapor. Finally, the parts are lifted into the freeboard zone, where any remaining fluorochemical rinsing agent evaporates from the parts and returns to the sump by condensation from cooling coils. At this point, the cleaning cycle is complete and the parts are clean and dry.

Furthermore, pure Novec$^{\text{TM}}$ HFEs can be used for the removal of light soils, halogenated compounds like fluorinated greases or oils, and other particles.

The increasing popularity of the cosolvent process is mainly due to its flexibility in allowing independent selection of both the solvating and rinsing agents that best meet the needs of a particular cleaning application. The fluorochemical cosolvent process is even capable of defluxing components with very complex geometry due to the advanced physical properties of the cosolvent.

The cleaning chemistry:

Novec$^{\text{TM}}$ hydrofluoroethers (Novec$^{\text{TM}}$ HFEs) are rapidly becoming recognized as the solvents of choice for superior cleaning in the electronics and precision engineering industries. The combined properties of these new materials have proven to be very effective alternatives to ozone depleting substances (ODSs) like the previously mentioned CFCs and HCFCs. The new developed chemical compounds methoxyfluorobuthylether (HFE 7100) and ethoxyfluorobuthylether (HFE 7200). HFE rinsing agents can be used in combination with respective cosolvents. The most effective cosolvents for defluxing applications in the market are based on alcoxypropanols which are specially designed for applications in combination with HFEs.

Since the boiling points of these two HFEs lie at the upper range covered by the traditional ODSs such as HCFC-141b, CFC-113 and 1,1,1-trichloroethane, a better cleaning efficiency is provided due to the increase in solubility of most soils with temperature.

Like ODS solvents, the HFEs are non-flammable, which leads to very simple and thus inexpensive equipment designs.

The low surface tension of HFEs helps these fluids to easily penetrate tight spaces, especially between and under components of populated printed circuit boards. In addition, this is supported by the low viscosity of the HFEs that also allow it to quickly drain from the parts that have been cleaned.

One useful parameter for assessing the potential performance of a cleaning agent is the wetting index, which is defined as the ratio of the solvent's density to its viscosity and surface tension. The wetting index indicates how well a solvent will wet a surface and penetrate into tight spaces of complex cleaning substrates. The higher the index, the better the surface penetration.

**Table 14.8.3. Properties of HFEs compared to common CFCs and HCFCs**

| Property | HFE-7100 | HFE-7200 | HCFC-141b | CFC-113 |
|---|---|---|---|---|
| Boiling point, °C | 60 | 73 | 32 | 48 |
| Flash point, °C | none | none | none | none |
| Surface tension at 25°C | 13.6 | 13.6 | 19.3 | 17.3 |
| Viscosity, Pa s | 0.61 | 0.61 | 0.43 | 0.7 |
| Wetting index | 181 | 172 | 149 | 133 |

Since HFEs contain no chlorine nor bromine, they do not have an ozone depletion potential. In addition, their atmospheric lifetime is short compared to CFCs. Furthermore, the Global Warming Potential of HFE fluids is significantly lower than other proposed fluorinated solvent replacements. Practical studies as well as laboratory tests have found that HFE solvent emissions are 5-10 times lower than the emissions of CFCs or HCFCs. Although, HFEs are volatile organic compounds (VOC), they are not controlled by related US directive regulations. Finally, toxicological tests have shown, that these products have extremely low toxicity which allows for higher worker exposure guidelines, unlike many of the chlorinated and brominated solvents offered as ODS alternatives.

### *14.8.4.2.2 Water-free cleaning processes in closed, one-chamber vapor defluxing systems*

Liquid vapor degreasing using solvents has been an accepted method of precision cleaning for over 50 years. This cleaning process incorporates washing, rinsing, drying and solvent reclamation in a compact, cost-effective unit. Consequently, this makes it a very attractive process for many production cleaning applications. Environmental concerns raised in the last decade have changed both the chemistry and equipment technology for degreasing. Solvents have been modified or replaced to eliminate ozone depletion potential and other haz-

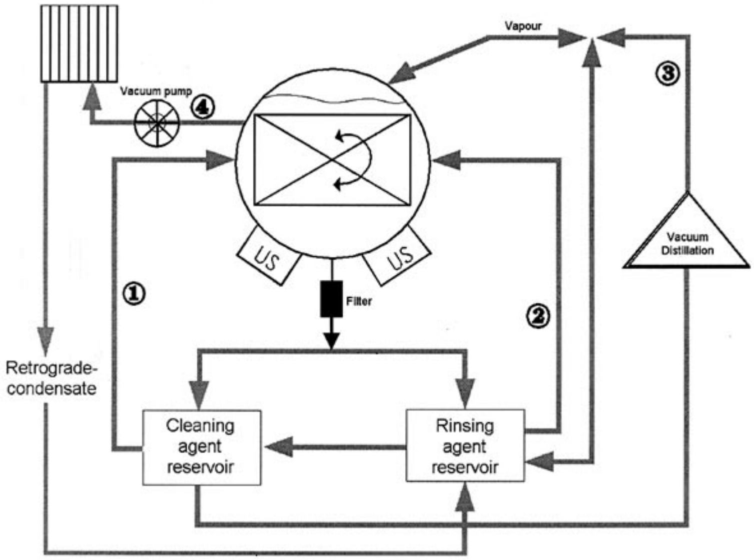


Figure 14.8.17. Closed-loop batch vapor degreasing process.

ards. Equipment designs and operating processes have been totally re-engineered to reduce solvent losses to near zero.

Referring to Figure 14.8.17, a modern vapor defluxing process can be described as follows. The cleaning equipment contains a cylindrical process chamber within which the complete cleaning, rinsing and drying process takes place. The process chamber may include spray manifolds and/or ultrasonic transducers (frequency of 40kHz) to provide the mechanical energy necessary for advanced precision cleaning. Following the final vapor rinse, remaining vapors are passed through a heat exchanger to condense the vapors to liquid, which is returned to the solvent recovering device. The vacuum then extracts any remaining solvent molecules, which are either exhausted from the machines directly or passed through carbon absorption system in order to limit solvent emissions to extremely low levels. The use of vacuum distillation for solvent recovery and vacuum drying assures minimal solvent consumption. Distillable solvents with a flash point above 55°C like Zestron® VD by Dr.O.K. Wack Chemie are suitable for such a process.

Many benefits provided by solvent cleaning are evident. Among these are:

- no process chemistry to mix or maintain,
- solvent is reclaimed automatically in the cleaning equipment,
- only few process variables to be managed,
- very easy and cost-effective to operate, and
- typically small footprint of the cleaning equipment.

## 14.8.5 CRITERIA FOR ASSESSMENT AND EVALUATION OF CLEANING RESULTS

There are a number of different processes that can be customized to monitor the cleaning process and cleaning results. Depending upon the existing requirements, simple “qualitative tests” can be applied to produce a “Good” or “Poor” rating, or more elaborate quantitative tests may be required to furnish a more in-depth statement of regarding the condition of the cleaning bath.

Refractive index:

An optical method by which a change of the refractive index of liquids, depending upon the content of liquid or solid contaminants, is used to measure the level of bath contamination.

Solid residue from evaporation:

This method establishes the non-volatile residues in cleaning and rinsing baths. This produces a very accurate statement of the bath contamination level.

Electrochemical potential:

The electrochemical potential is determined by the pH value, which furnishes an indirect statement of the level of contamination.

Conductivity measurement:

This is used to check the quality of the rinsing bath in assembly cleaning processes. The conductivity measurement indicates the amount of process-related ionic, and therefore conductive, contaminants carried over into the rinse medium.

Ionic contamination measurement:

Ionic contamination-expressed in sodium chloride equivalents is primarily used to assess the climatic resistance of electronic assemblies. Ionic measurement is suitable for statistical process control, but it does not furnish an absolute statement concerning the climatic resistance of an assembly.

Ink test:

Most organic residues on assemblies are not detected by ionic contamination meters. However, such residues do change the surface tension of assemblies, thereby influencing the adhesion of subsequent coatings. This method determines the surface tension by iterative use of corresponding testing inks.

Furthermore, the remaining protective ability of organic solder (OSP-coatings) on copper can be estimated. This test also provides an indication of the adhesion of lacquers and conformal coatings to the assembly.

Water-immersion test:

This economical test exposes the climatically unstable points of electronic components. Due to the nature of the test, the entire board is evaluated. This test accelerates the mechanisms of electrochemical migration. Consequently, faults that previously would appear after months or even years can be detected during the development process. To identify potential weak points, the assembly is operated in standby mode and immersed in deionized water. Testing while the assembly is in full operation is even more effective. The sensitivity of the circuit to moisture exposure is assessed on the basis of the recorded test current, combined with a subsequent examination of the assembly. Through weak point analysis, a Yes/No decision can be determined concerning the expected service life, of the assembly.

The growing diversity of cleaning media, cleaning equipment, and cleaning processes, together with more stringent legal requirements and quality expectations, are making it increasingly difficult for companies to develop their own cost-effective and result-optimized cleaning processes. Consequently, a lot of well known manufacturing companies opted for turnkey solutions for the entire development and installation of complete cleaning processes.

## 14.8.6 COST COMPARISON OF DIFFERENT CLEANING PROCESSES

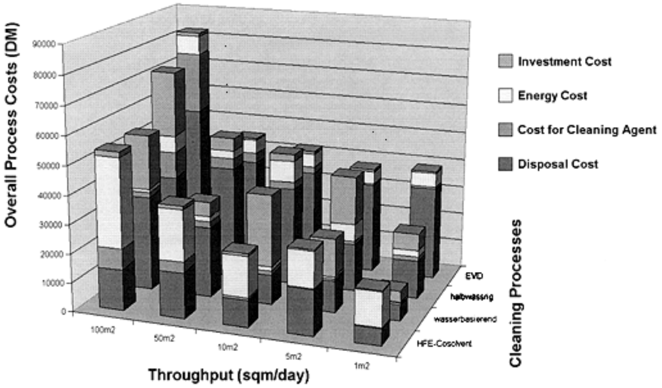


Figure 14.8.18. Comparison of overall process costs between different cleaning processes.

Long-term cost analysis experience on different cleaning processes have been summarized in Figure 14.8.18 which describes the overall process costs of the different cleaning applications discussed. Whereby the overall process costs are divided into four main sections:

- Investment costs,
- Costs for the cleaning agent,
- Costs for the disposal of used media/ recycling cost, and
- Energy costs.

By analyzing the numbers, the following key conclusions on the different cleaning processes are substantial:

- The total annual process costs are always connected with the throughput, but not necessarily in a linear function.
- The lowest investment costs can be achieved by using an aqueous-based or Novec$^{TM}$ HFE-cosolvent cleaning process.
- Closed vapor degreasing and Novec$^{TM}$ HFE-cosolvent processes are more competitive regarding waste disposal.
- A water-based cleaning process is the most competitive regarding media costs.

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## 14.9 FABRICATED METAL PRODUCTS

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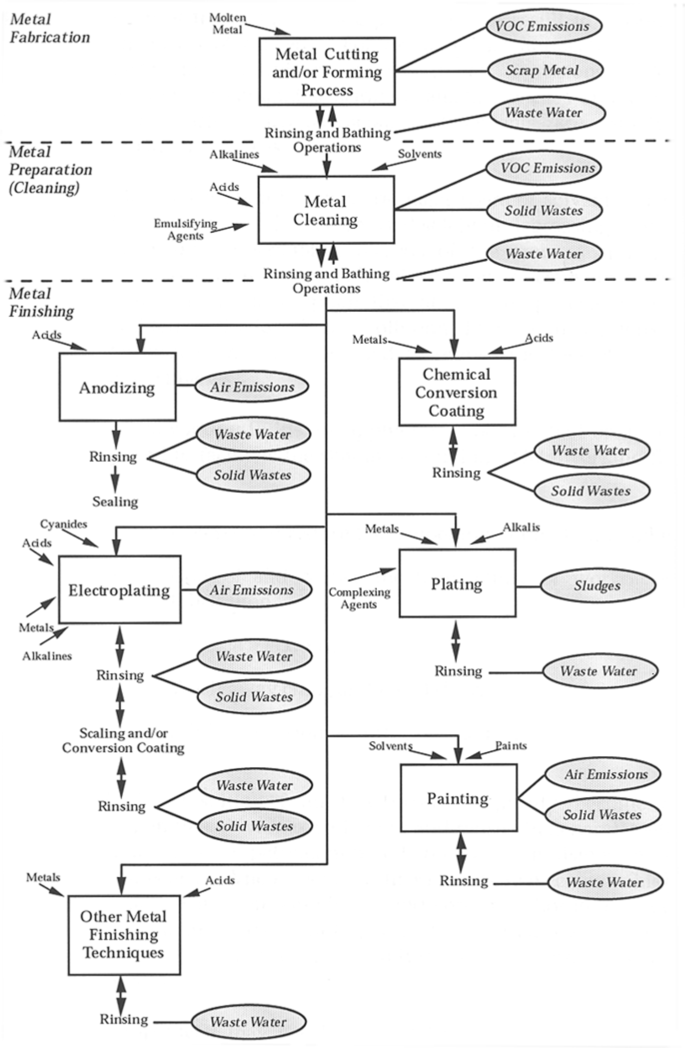

Figure 14.9.1. Schematic diagram of operations in fabricated metal products manufacturing process. [Reproduced from EPA Office of Compliance Sector Notebook Project. Profile of the Fabricated Metal Products Industry. US Environmental Protection Agency, 1995.]

**Table 14.9.1. Reported solvent releases from the metal fabricating and finishing facilities in 1993 [Data from Ref. 1]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| acetone | 870,400 | 2-methoxyethanol | 22,800 |
| benzene | 1,800 | methyl ethyl ketone | 4,540,000 |
| n-butyl alcohol | 495,000 | methyl isobutyl ketone | 934,000 |
| sec-butyl alcohol | 13,600 | tetrachloroethylene | 844,000 |
| cyclohexanone | 303,000 | toluene | 3,015,000 |
| 1,2-dichlorobenzene | 10,900 | 1,1,1-trichloroethane | 2,889,000 |
| dichlorofluoromethane | 10,800 | trichloroethylene | 3,187,000 |
| dichloromethane | 1,350,000 | trichlorofluoromethane | 82,000 |
| ethylbenzene | 299,000 | 1,2,4-trimethylbenzene | 262,000 |
| ethylene glycol | 99,000 | xylene (mixture) | 4,814,000 |
| 2-ethoxy ethanol | 18,600 | m-xylene | 8,800 |
| isopropyl alcohol | 23,400 | o-xylene | 17,000 |
| methanol | 199,000 | p-xylene | 10 |

Figure 14.9.1 shows a schematic diagram of the operations in a fabricated metal products manufacturing process.[1] The diagram shows that solvent emissions, waste waters, and solid wastes are produced from three operations: the metal cutting and forming process, metal cleaning, and painting. In metal cutting and forming the major solvents used are 1,1,1-trichloethane, acetone, toluene, and xylene. In surface cleaning, the straight solvents are used for cleaning or some solvents such as kerosene or glycols are emulsified in water and the emulsion is used for cleaning. When emulsions are used the amount of solvent is decreased. Solvents are released due to evaporation, volatilization during storage, and direct ventilation of fumes. Waste waters are generated from rinse waters. These waste waters are typically cleaned on-site by conventional hydroxide precipitation. Solid wastes are generated from waste water cleaning sludge, still bottoms, cleaning tank residues, and machining fluid residues. In painting, two methods are used: spray painting and electrodeposition. Painting operations release benzene, methyl ethyl ketone, methyl isobutyl ketone, toluene, and xylene. Paint cleanup operations also contribute to emissions and waste generation. The predominant solvents used for equipment cleaning are tetrachloride, dichloromethane, 1,1,1-trichloroethane, and perchloroethylene. Sources of solid and liquid waste include components of emission controlling devices (e.g., paint booth collection system and ventilation filters), equipment washing, paint disposal, overspray, and excess paint discarded after expiration of paint's shelf-life.

Table 14.9.1 shows reported solvent releases from metal fabricating and finishing facilities and Table 14.9.2 shows reported solvent transfers from the same industry.

Xylene, methyl ethyl ketone, trichloroethylene, 1,1,1-trichloroethane, and dichloromethane are released in the largest quantities. Methyl ethyl ketone, xylene, toluene,

**Table 14.9.2. Reported solvent transfers from the metal fabricating and finishing facilities in 1993 [Data from Ref. 1]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| acetone | 767,000 | methyl ethyl ketone | 5,130,000 |
| n-butyl alcohol | 282,000 | methyl isobutyl ketone | 846,000 |
| sec-butyl alcohol | 495 | tetrachloroethylene | 415,000 |
| cyclohexanone | 1,025 | toluene | 1,935,000 |
| dichloromethane | 237,000 | 1,1,1-trichloroethane | 920,000 |
| ethylbenzene | 263,000 | trichloroethylene | 707,000 |
| ethylene glycol | 68,000 | 1,2,4-trimethylbenzene | 42,000 |
| 2-ethoxy ethanol | 1,800 | xylene (mixture) | 2,335,000 |
| isopropyl alcohol | 41,000 | m-xylene | 27,000 |
| methanol | 138,000 | o-xylene | 37 |
| 2-methoxyethanol | 7,800 | p-xylene | 23 |

trichloroethylene, and methyl isobutyl ketone are transferred in largest quantities outside industry for treatment and disposal. The metal fabrication and finishing industry's contribution to reported releases and transfers in 1995 was 9.3% of the total for 21 analyzed industries. This industry is the fourth largest contributor to total reported releases and transfers.

Among the potential actions to reduce pollution, these are the most effective: recycling of solvents, employing better waste control techniques, and substituting raw materials. For solvent cleaning, several techniques are suggested. Employees should be required to obtain solvent from their supervisor. It is estimated that this will reduce waste by 49%. Pre-cleaning (wipe, blow part with air, etc.) should be adopted or the parts should be first washed with used solvent. Equipment for vapor degreasing should be modified by increasing its head space, covering degreasing units, installing refrigerator coils, rotating parts before removing, installing thermostatic controls, and adding filters. Trichloroethylene and other halogenated solvents should be replaced with liquid aqueous alkali cleaning compounds.

Other waste reduction can be realized by the better production scheduling, use of dry filters in the spray booth, prevention of leakage from the spray gun, separation of wastes, and recycling of solvents by distillation.

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# 14.10 FOOD INDUSTRY - SOLVENTS FOR EXTRACTING VEGETABLE OILS

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## 14.10.1 INTRODUCTION

Many materials including oils, fats, and proteins, for both food and nonfood use, are recovered from diverse biological sources by solvent extraction.[1,2] These materials include animal tissues (e.g., beef, chicken, pork and fish); crops specifically produced for oil or protein (e.g., soy, sunflower, safflower, rape/canola, palm, and olive); by-products of crops grown for fiber (e.g., cottonseed and flax); food (e.g., corn germ, wheat germ, rice bran, and coconut); confections (e.g., peanuts, sesame, walnuts, and almonds); nonedible oils and fats (castor, tung, jojoba); and other oil sources (oils and fats from microbial products, algae, and seaweed). There are many physical and chemical differences between these diverse biological materials. However, the similarities are that oils (edible and industrial) and other useful materials (e.g., vitamins, nutriceuticals, fatty acids, phytosterols, etc.) can be extracted from these materials by mechanical pressing, solvent extracting, or a combination of pressing and solvent extraction. The preparation of the various materials to be extracted varies. Some need extensive cleaning, drying, fiber removal (cottonseed), dehulling, flaking, extruding, etc., all of which affect the solvent-substrate interaction and, therefore, the yield, composition, and quality of the oils and other materials obtained.

Historically, the advancement of processing technology for recovering oils and other useful materials has been primarily driven by economics. For thousands of years stone mills, and for several centuries simple hydraulic or lever presses were used as batch systems. The continuous mechanical presses only became reality during the early 1900s. It was not until the 1930s, that extraction solvents were used more widely, which greatly enhanced the recovery of oil from oilseeds or other oil bearing materials.

In solvent extraction crude vegetable oil and other useful materials are dissolved in a solvent to separate them from the insoluble meal. Many solvents have been evaluated for commercial extraction. Commercial hexane has been the main solvent for the oilseed processing industry since the 1940s[1,2] because of its availability at reasonable cost and its suitable functional characteristics for oil extraction. However, the interest in alternative solvents to hexane has continued and is motivated by one of a combination of factors: desire for a nonflammable solvent, more efficient solvent, more energy efficient solvent, less hazardous and environmentally friendly solvent, solvent with improved product quality, and solvents for niche/specialty markets. Today commercial isohexane (hexane isomers) is replacing commercial hexane in a few oilseed extraction operations and other solvents (e.g., isopropanol, ethanol, acetone, etc.) are also being used for various extraction processes or have been evaluated for use as extracting solvents.[3-6]

With greater flexibility of operating hardware and availability of various solvents with tailored composition, the oilseed industry does have expanded options to choose the unique composition of solvents to obtain the desired final products. While the availability, cost, ease-of-use (i.e., no specialty processing hardware required and with low retrofitting costs), and acceptable product quality continue to be the principle factors used to choose a solvent for oil extraction, in recent years environmental concerns and health risk have become increasingly important criteria to be considered in selecting an oil extraction solvent.

This chapter presents information on solvents for extracting oilseeds and other biological materials for oils, fats, and other materials.

## 14.10.2 REGULATORY CONCERNS

Many workplace, environmental, food safety, and other regulations (see Tables 14.10.1 and 14.10.2 for summary information on U.S. laws and regulations) apply to the use of solvents for the extraction of oilseeds and other diverse biological materials. Some solvent may have fewer workplace and environmental regulatory requirements; offer benefits, such as an improved product quality and energy efficiency;[7] as well as other advantages, such as the ability to remove undesirable (e.g., gossypol from cottonseed) and desirable (e.g., vitamin E, tocopherols, lecithins, phytosterols, and long chain polyunsaturated fatty acids) constituents of oilseeds and other biological materials more selectively. Some of the regulations required in the United States are discussed. Many other countries have similar requirements, but if they do not, it would be prudent to consider meeting these regulations in solvent extraction and to have environmental, health and safety, and quality management programs.[19,44]

**Table 14.10.1. U.S. Worker health and safety laws and regulations**

**Laws**:

Occupational Safety and Health Act of 1970 (OSHA) (PL 91-596 as amended by PL 101 552; 29 U.S. Code 651 et. seq.)

**OSHA Health Standards**:

Air Contaminants Rule, 29 CFR 1910.1000
Hazard Communication Standard, 29 CFR 1910.1200

**OSHA Safety Standards**:

Process Safety Management, 29 CFR 1910.119
Emergency Action Plan, 29 CFR 1910.38(a)(1)
Fire Prevention Plan, 29 CFR 1910.38(b)(1)
Fire Brigades, 29 CFR 1910.156
Personal Protection Equipment (General Requirements 29 CFR 1910.132; eye and face protection, .133; respiratory protection, .134)

**Table 14.10.2. U.S. Environmental laws and regulations**

| Law or Regulation | Purpose |
|---|---|
| Environmental Protection Agency (EPA) (established 1970) | To protect human health and welfare and the environment |
| Clean Air Act (CAA) (42 U.S. Code 7401 et seq.) | To protect the public health and welfare. Provides EPA with the authority to set NAAQS, to control emissions from new stationary sources, and to control HAP. |
| Federal Water Pollution Control Act (known as the Clean Water Act) (CWA) (33 U.S. Code 1251 et seq.) | The major law protecting the "chemical, physical and biological integrity of the nation's waters." Allows the EPA to establish federal Limits on the amounts of specific Pollutants that can be released by municipal and industrial facilities. |

| | |
|---|---|
| Toxic Substances Control Act (TSCA) (15 U.S. Code 2601 et seq.) | Provides a system for identifying and evaluating the environmental and health effects of new chemicals and chemicals already in commerce. |
| Resource Conservation and Recovery Act (RCRA) (42 U.S. Code 6901 et seq.) | A system for handling and disposal of non-hazardous and hazardous waste. |
| Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) (42 U.S. Code 9601 et seq.) | Known as "Superfund", gives the EPA power to recover costs for containment, other response actions, and cleanup of hazardous waste disposal sites and other hazardous substance releases. |
| Emergency Planning and Community Right-to-Know Act (EPCRA; also "SARA 313")<br>(42 U.S. Code 1101 et seq.) | (Part of Superfund) Provides authority for communities to devise plans for preventing and responding to chemical spills and release into the environment; requires public notification of the types of hazardous substances handled or release by facilities; requires state and local emergency plans. |

### 14.10.2.1 Workplace regulations

Workplace regulations (see Table 14.10.1) are promulgated and enforced in the U.S. by the Occupational Safety and Health Administration (OSHA), which is in the Department of Labor. The purpose of OSHA is to ensure that the employers maintain a safe and healthful workplace. Several workplace standards that affect extraction solvents are discussed.

#### *14.10.2.1.1 Air Contaminants Standard (29 CFR 1910.1000)*

The purpose of the air contaminants standards are to reduce risk of occupational illness for workers by reducing permissible exposure limits (PEL) for chemicals. Table 14.10.3 lists the PELs [8-hr time-weighted average (TWA) exposure] for the solvents discussed. To achieve compliance with the PEL, administrative or engineering controls must first be determined and implemented, whenever feasible. When such controls are not feasible to achieve full compliance, personal protective equipment, work practices, or any other protective measures are to be used to keep employee exposure below the PEL.

**Table 14.10.3. U.S. Workplace regulations,[a] air contaminants**

| Chemical Name (CAS No.) | Permissible Exposure Limit (PEL) [Health Risk: Basis for the PEL] |
|---|---|
| n-Hexane (110-54-3) | 500 ppm/1800 mg/m$^3$; new PEL was 50 ppm/180 mg/m$^3$ same as ACGIH (TLV); [neuropathy] |
| Commercial hexane[b] (none) | (Same as n-hexane) |
| n-Heptane (142-82-5) | 500 ppm/200 mg/m$^3$; new PEL was 400 ppm/1640 mg/m$^3$, (500 ppm STEL) same as ACGIH (TLV); [narcosis] |
| Cyclohexane (110-82-7) | 300 ppm/1050 mg/m$^3$; ACGIH (TLV) 300 ppm/1030 mg/m$^3$; [sensory irritation] |
| Cyclopentane (287-92-3) | None; new PEL was 600 ppm, same as ACGIH (TLV); [narcosis] |
| Hexane isomers | None; new PEL was 500 ppm/1760 mg/m$^3$ (1000 ppm STEL) same as ACGIH (TLV); [narosis] |
| Commercial isohexane[c] (none) | (Same as hexane isomer) |

| Chemical Name (CAS No.) | Permissible Exposure Limit (PEL) [Health Risk: Basis for the PEL] |
|---|---|
| 2-Methyl pentane (isohexane) (2-MP) (107-83-5) | (Same as hexane isomer) |
| 3-Methyl pentane (3-MP) (96-14-0) | (Same as hexane isomer) |
| Methyl cyclopentane (MCP) (96-37-7) | (Same as hexane isomer) |
| 2,2 Dimethyl butane (neohexane) (2,2-DMB) (75-83-2) | (Same as hexane isomer) |
| 2,3 Dimethyl butane (2,3-DMB) (79-29-8) | (Same as hexane isomer) |
| Methyl cyclohexane (108-87-2) | 500 ppm; new PEL was 400 ppm/1610 mg/m$^3$, same as ACGIH (TLV); [narcosis] |
| Isopropyl alcohol (2-propanol) (IPA) (67-17-5) | 400 ppm/980 mg/m$^3$; ACGIH (TLV) same plus 500 ppm/1230 mg/m$^3$ STEL; [sensory irritation] |
| Ethyl alcohol (ethanol) (64-17-5) | 1000 ppm/1880 mg/m$^3$; ACGIH (TLV) same; [narcosis, irritation] |
| Acetone (67-64-1) | 1000 ppm/2400 mg/m$^3$; ACGIH (TLV) 750 ppm (1000 ppm STEL); [sensory irritation] |

[a] CAS No. is the Chemical Abstracts Service Registry Number; PEL is from 29 CFR 1910.1000, Table Z-1; American Conference on Governmental Industrial Hygienists (ACGIH), threshold limit value (TLV); under the HCS, a MSDS is required for all of the compounds (physical and/or chemical hazard); all of the solvents are flammable liquids or gasses, under the OSHA definition, and are regulated under the PSM Standard.

[b] Commercial hexane as used in the U.S. is usually about 65% n-hexane, and the rest is hexane isomers (e.g., methyl cyclopentane (MCP), 2-methyl pentane (2-MP), and 3-methyl pentane (3-MP)), and it contains less than 10 ppm benzene.

[c] Mixture of 2-MP (45-50%), 3-MP, 2,2-DMB, and 2,3-DMB. (ref 7)

In the case of a mixture of contaminants, an employer has to compute the equivalent exposure when the components in the mixture pose a synergistic threat (toxic effect on the same target organ) to worker health.[8,9]

### *14.10.2.1.2 Hazard Communication Standard (HCS) (29 CFR 1910.1200)*

The HCS requires information on hazardous chemicals to be transmitted to employees through labels, material safety data sheets (MSDS), and training programs. A written hazard communications program and record keeping are also required.

A substance is a “hazardous chemical” if it is a “physical hazard” or a “health hazard”. A flammable or explosive liquid is a “physical hazard”. A flammable liquid means “any liquid having a flash point below 110ºF (37.8ºC), except any mixture having components with flash points of 100ºF (37.8ºC) or higher, the total of which make up 99% or more of the total volume of the mixture”. “Health hazard” means “a chemical for which there is statistically significant evidence based on at least one valid study that acute or chronic health effects may occur in exposed employees”. Hexane and all the solvents listed in Table 14.10.3 would require a MSDS, since all are flammable liquids (physical hazards) as defined by OSHA and/or possible health hazards because all, except hexane isomers, have an U.S. OSHA PEL. However, hexane isomers have an American Conference of Industrial Hygienist (ACGIH) threshold limit value (TLV),[10] which many states and countries enforce as a mandatory standard.

Chemical manufacturers and importers are required to review the available scientific evidence concerning the hazards of chemicals they produce or import, and to report the information to manufacturing employers who use their products. If a chemical mixture has not been tested as a whole to determine whether the mixture is a hazardous chemical, the mixture is assumed to present the same hazards as do the components that comprise 1% or greater of the mixture or a carcinogenic hazard if it contains a component in concentration of 0.1% or greater that is a carcinogen. Commercial hexane containing 52% n-hexane has been tested and found not to be neurotoxic unlike pure n-hexane.[11-13] So mixtures with less than 52% n-hexane should not be considered to be a neurotoxin, although n-hexane would have to be listed on the MSDS, if in greater quantity than 1% of the mixture.

#### *14.10.2.1.3 Process Safety Management (PSM) Standard (29 CFR 1910.119)*

PSM is for the prevention or minimization of the consequences of catastrophic releases of toxic, reactive, flammable, or explosive chemicals. This regulation applies to all processes that involve one or more of 137 listed chemicals (29 CFR 1910.119, Appendix A) above their threshold quantities or have 10,000 lbs. or more of a flammable liquid or gas, as defined by the U.S. OSHA HCS [29 CFR 1910.1200(c)]. This includes n-hexane, hexane isomers, and all solvents listed in Table 14.10.3.

In addition to the PSM standard, U.S. OSHA has been enforcing two other regulations for operations/processes with flammable liquids. First, under Personal Protective Equipment - General Requirements (29 CFR 1910.132), OSHA has cited or obtained voluntary agreement from organizations relative to flame-resistant (FR) clothing. Operators and other employees working in the area of a flammable process are being required to wear flame-resistant work clothing. For facilities that use hexane and other flammable solvents, it would be prudent to require FR clothing for all personnel working in areas where there is an exposure to a flammable liquid. Second, OSHA has cited organizations for failure to meet related safety regulations under Fire Brigades (29 CFR 1910.156), specifically for standards such as: training, both initial and annual refresher training; protective equipment availability and testing; and fitness for duty including periodic physicals. If an on-site fire brigade is part of the site's Emergency Response Plan (29 CFR 1910.38), then these requirements must also be met. In addition, the requirement of the PSM standard for an Emergency Response Plan triggers the requirements of Emergency Action Plan [29 CFR 1910.38(a)].

### 14.10.2.2 Environmental regulations

The role of the U.S. Environmental Protection Agency (EPA) is to protect human health and welfare and the environment. The U.S. EPA administers all regulations affecting the environment and chemicals in commerce. The individual states and state environmental regulatory control boards implement and enforce most of the regulations. The legislation that serves as the basis for the regulations can be divided into: statutes that are media-specific [Clean Air Act (CAA) and Clean Water Act (CWA)]; statutes that manage solid and hazardous waste [Resources Conservation and Recovery Act (RCRA) and Comprehensive Environmental Response, Compensation and Liability Act (CERCLA; "Superfund")]; and, statutes that directly limit the production rather than the release of chemical substance [Toxic Substances Control Act (TSCA) and Federal Insecticide, Fungicide and Rodenicide Act (FIFRA)]. See Table 14.10.2 for a summary of the information on environmental laws and regulations, and Tables 14.10.4 and 14.10.5 for an overview of environmental requirements that apply to each solvent.

### Table 14.10.4. U.S. Environmental regulations, air and water

| Chemical Name (CAS No.) | VOC | HAP | CWA[a] | Sol. in $H_2O$ |
|---|---|---|---|---|
| n-Hexane (110-54-3) | Yes | Yes | Yes | I |
| Commercial hexane(none) | Yes | | | |
| n-Heptane (148-82-5) | Yes | No | Yes | I |
| Cyclohexane (110-82-7) | Yes | No | Yes | 0.01 |
| Cyclopentane (287-92-3) | Yes | No | Yes | I |
| Hexane isomers (none) | Yes | No | Yes | |
| Commercial isohexane (none) | (same as hexane isomers) | No | Yes | |
| 2-Methyl pentane (isohexane) (107-83-5) | (a hexane isomer) Yes | No | Yes | 0.0014 |
| 3-Methyl pentane (96-14-0) | (a hexane isomer) Yes | No | Yes | 0.0013 |
| Methyl cyclopentane (96-37-7) | (a hexane isomer) Yes | No | Yes | 0.0013 |
| 2,2 dimethyl butane (neohexane) (75-83-2) | (a hexane isomer) Yes | No | Yes | 0.0018 |
| 2,3 dimethyl butane (79-29-8) | (a hexane isomer) Yes | No | Yes | 0.0011 |
| Methyl cyclohexane(108-87-2) | Yes | No | Yes | 0.0014 |
| Isopropyl alcohol (2-propanol) (67-17-5) | Yes | No | Yes | Misc. |
| Ethyl alcohol (ethanol) (64-17-5) | Yes | No | Yes | Misc. |
| Acetone (67-64-1) | No[b] | No | Yes | Misc. |

[a] Under the Clean Water Act there could be stormwater and NPDES permit requirements; none of the solvents are listed as priority toxic pollutants in 40 CFR 401.15.

[b] Acetone is considered by the U.S. EPA not be a VOC (60 FR 31643; June 16, 1995)

Abbreviations: CAS No., Chemical Abstracts Service Registry number; VOC, volatile organic chemical; HAP, hazardous air pollutant; CWA, Clean Water Act; I, insoluble in $H_2O$; MISC., miscible in $H_2O$; and 0.01, 0.01 parts soluble in 100 parts $H_2O$. Source for water solubility: Ref 47.

### Table 14.10.5 U.S. Environmental regulations, waste

| Chemical Name (CAS No.) | (RCRA) | | (EPCRA/SARA Title III)[a] | |
|---|---|---|---|---|
| | RCRA Code[b] | Sec. 304 CERCLA RQ | Sec.311/312 | Sec.313 (TRI) |
| n-hexane (110-54-3) | | 5000[c] | Yes | Yes |
| Commercial hexane (none) | | | | Yes[d] |
| n-heptane (142-82-5) | | | Yes | No |

| Chemical Name (CAS No.) | (RCRA) | | (EPCRA/SARA Title III)[a] | |
|---|---|---|---|---|
| | RCRA Code[b] | Sec. 304 CERCLA RQ | Sec.311/312 | Sec.313 (TRI) |
| Cyclohexane (110-87-7) | U056 | 1000 | Yes | Yes |
| Cyclopentane (287-92-3) | | | Yes | No |
| Hexane isomers (none) | | | Yes | No[e] |
| Commercial isohexane (none) | | | | No[e] |
| 2-Methyl pentane (also called isohexane) (107-83-5) | | | Yes | No[e] |
| 3-Methyl pentane (96-14-0) | | | Yes | No[e] |
| Methyl cyclopentane (96-37-7) | | | Yes | No[e] |
| 2,2 Dimethyl butane (neohexane) (75-83-2) | | | Yes | No[e] |
| 2,3 Dimethyl butane (79-29-8) | | | Yes | No[e] |
| Methyl cyclohexane (108-87-2) | | | Yes | No |
| Isopropyl alcohol (2-propanol) (67-63-0) | | | Yes | No[f] |
| Ethyl alcohol (64-17-5) | | | Yes | No |
| Acetone (67-64-1) | U002 | 5000 | Yes | No |

[a] From Title III Lists of Lists, U.S. EPA, EPA 740-R-95-001 (April 1995); 40 CFR 52-99; (59 FR 4478; January 31, 1994) hexane added to TRI list; (60 FR 31633; June 16, 1995) acetone removed from TRI list.

[b] 40 CFR 261.33, listed hazardous waste - EPA RCRA Hazardous Waste Number. All the solvents that are on the RCRA list are listed because of Section 3001 of RCRA (part for identification and listing of hazardous waste) except hexane which is on because of CAA Section 112 (HAP).

[c] RQ for hexane finalized June 12, 1995 (60 FR 30939).

[d] Only the amount of commercial hexane that is n-hexane has to be reported (e.g., if the commercial hexane is 62% n-hexane, only 62% of the emissions have to be reported for TRI).

[e] The EPA clarrified that the listing for hexane was only for n-hexane, other isomers of hexane are not included. (59 FR 61457; Nov. 30, 1994).

[f] The EPA has indicated (62 FR 22318, April 25, 1997) that IPA itself does not meet the criteria for listing on the TRI list. The EPA will remove IPA from the TRI list. Abbreviations: RQ, reportable quantity in pounds/24 h.

#### *14.10.2.2.1 Clean Air Act (CAA; 42 U.S. Code 7401 et seq.)*

To satisfy the CAA requirements, states and state air control boards are required to implement regulations and develop state implementation plans (SIP).[14,15] Criteria pollutants (e.g., ozone, oxides of nitrogen, carbon monoxide) are regulated with National Ambient Air Quality Standards (NAAQS) and hazardous air pollutants (HAP), such as hexane, with National Emissions Standards for Hazardous Air Pollutants (NESHAP).

The NAAQS are set at levels sufficient to protect public health (primary air quality standards) and welfare (secondary air quality standards; “welfare effects” include wildlife, visibility, climate, damage to and deterioration of property and effects on economic value and on personal comfort and well being) from any known or anticipated adverse effect of the pollutant with an adequate (appropriate) margin of safety. The 1990 CAA expanded the list of HAP to 188, including hexane, and more strictly regulates nonattainment areas for criteria pollutants such as ozone, particulate matter, carbon monoxide and oxides of nitrogen.

*NAAQS*: Volatile organic compounds (VOC) are essentially considered the same as the criteria pollutant ozone.[16,17] VOCs are very broadly defined by the U.S. EPA (40 CFR 51.100): any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, that participates in atmospheric photochemical reactions. This includes any organic compound other than those specifically listed as having been determined to have negligible photochemical reactivity. Reactive VOCs are essentially all those judged to be clearly more reactive than ethane - the most reactive member of the “negligibly reactive” class. $C_4$ - $C_6$ paraffins are of relatively low kinetic reactivity but produce $NO_2$, and potentially ozone.[18] Hexane and all of the solvents discussed, except acetone, would be considered VOCs (see Table 14.10.4) that can undergo photochemical oxidation in the atmosphere to form ozone. In the U.S., acetone was added to the list of compounds excluded from the definition of VOCs in 1995, because it was determined to have negligible photochemical reactivity.[19]

Most U.S. vegetable-oil extracting facilities would be major sources of VOCs and would be covered by the requirements for ozone emissions and attainment, unless they used a solvent that was not classified as a VOC. (The definition of “major source” changes as the severity of the ozone nonattainment area increases. Plants in marginal and moderate areas are major if they emit 100 tons VOC/yr; in serious areas, 50 tons/yr; in severe areas, 25 tons/yr; and in extreme areas 10 tons/yr). All facilities in ozone non-attainment areas could be required to reduce emissions through implementing Reasonable Available Control Measures (RACM) standards or Best Available Control Measures (BACM). Any new or significantly modified facility would have to comply with the new source review (NSR) requirements and prevention of significant deterioration (PSD) requirements.

*Hazardous air pollutants (HAP) or air toxics*: If a facility is a major emitter of any of the chemicals on the CAA list of HAPs, EPA requires sources to meet emissions standards.[14,16,17] n-Hexane is on the HAP list but isohexane, acetone and other solvents listed in Table 14.10.4 are not.

The air toxic requirements of the CAA for establishing control measures for source categories are technology-based emission standards (not health based) established for major sources (10 tons/yr of one HAP or 25 tons/yr of total HAP) that require the maximum degree of reduction emissions, taking costs, other health and environmental impacts, and energy requirements into account. Standards are set based on known or anticipated effects of pollutants on the public health and the environment, the quantity emitted, and the location of emissions. Compliance involves the installation of Maximum Achievable Control Technology (MACT) - MACT essentially is maximum achievable emission reduction. For new sources, MACT standards must be no less stringent than the emission control achieved in practice by the best controlled similar source. The MACT standards for vegetable oil processing using n-hexane are expected to be issued in 2001. Once a standard has been promulgated for a source category, a source will have three years after the due date to comply. The requirements cover normal operations and startup, shutdown, and malfunction (SSM). The allowable emissions for solvent extraction for vegetable oil production in the U.S., as a 12-month rolling average based on a 64% n-hexane content, will vary from 0.2 gal/ton to greater than 0.7 gal/ton depending on the oilseed (65FR34252; May 26, 2000) (see Table

12.14.6). There are also variable emission requirements depending on the oilseed for allowable emissions for solvent extraction for vegetable oil production in Europe.

**Table 14.10.6. Oilseed solvent loss factors for allowable HAP loss (12-mo. rolling ave.)**

| **Type of Oilseed Process** | **A source that...** | **Oilseed Solvent Loss Factor (gal/ton)** | |
|---|---|---|---|
| | | Existing Sources | New Sources |
| Corn Germ, Wet Milling | processes corn germ that has been separated from other corn components using a wet process of centrifuging a slurry steeped in a dilute sulfurous acid solution | 0.4 | 0.3 |
| Corn Germ, Dry Milling | processes corn germ that has been separated from the other corn components using a dry process of mechanical chafing and air sifting | 0.7 | 0.7 |
| Cottonseed, Large | processes 120,000 tons or more of a combination of cottonseed and other listed oilseeds during all normal operating periods in a 12 operating month period | 0.5 | 0.4 |
| Cottonseed, Small | processes less than 120,000 tons of a combination of cottonseed and other listed oilseeds during all normal operating periods in a 12 operating month period | 0.7 | 0.4 |
| Flax | processes flax | 0.6 | 0.6 |
| Peanuts | processes peanuts | 1.2 | 0.7 |
| Rapeseed | processes rapeseed | 0.7 | 0.3 |
| Safflower | processes safflower | 0.7 | 0.7 |
| Soybean, Conventional | uses a conventional style desolventizer to produce crude soybean oil products and soybean animal feed products | 0.2 | 0.2 |
| Soybean, Specialty | uses a special style desolventizer to produce soybean meal products for human and animal consumption | 1.7 | 1.5 |
| Soybean, Small Combination Plant | processes soybeans in both specialty and conventional desolventizers and the quantity of soybeans processed in specialty desolventizers during normal operating periods is less than 3.3 percent of total soybeans processed during all normal operating periods in a 12 operating month period. The corresponding solvent loss factor is an overall value and applies to the total quantity of soybeans processed | 0.25 | 0.25 |
| Sunflower | processes sunflower | 0.4 | 0.3 |

A health-based standard would be for a boundary line level of a solvent (e.g., n-hexane) based on the inhalation reference concentration (RfC).[20] The current RfC for n-hexane is 200μg/m$^3$. Recent research suggests that the RfC for hexane should be at least 10 times higher (> 2000 μg/m$^3$).

*Federal permits*: All major sources of regulated solvents are required to have federally enforceable operating permits (FOP)[14,15] (also referred to as Title V permits).

*State permits:* Most states require state permits for facilities that emit listed air pollutants.[14,15] In some states federal permits and state permits are combined, while in other states facilities are required to have both a state or county (air district) permit and a federal permit. As part of annual emission inventory reporting requirements, many states already require reporting of HAP and VOC because of their state implementation plan (SIP).

### *14.10.2.2.2 Clean Water Act (CWA; 33 U.S. Code 1251 et seq.)*

The CWA is the major law protecting the "chemical, physical and biological integrity of the nation's waters." Under it, the U.S. EPA establishes water-quality criteria used to develop water quality standards, technology-based effluent limitation guidelines, and pretreatment standards and has established a national permit program [National Pollution Discharge Elimination System (NPDES) permits; 40 CFR 122] to regulate the discharge of pollutants. The states have responsibility to develop water-quality management programs.

For extraction solvents vegetable oil extracting facilities are covered by basic discharge effluent limitations [direct discharges to receiving waters or indirect discharges to publicly owned treatment works (POTW)], and stormwater regulations.[15] The amount of solvent in effluent discharges and in stormwater (for those covered) needs to be determined and possibly monitored as part of an NPDES permit and as part of the visual examination or testing of stormwater quality.

### *14.10.2.2.3 Resource Conservation and Recovery Act (RCRA; 42 U.S.Code 6901 et seq.)*

RCRA subtitle C (40 CFR 261) is a federal "cradle-to-grave" system to manage hazardous waste (including provisions for cleaning up releases and setting statutory and regulatory requirements). Subtitle D covers nonhazardous wastes. Materials or items are hazardous wastes if and when they are discarded or intended to be discarded. The act requires generators, transporters, and disposers to maintain written records of waste transfers, and requires the U.S. EPA to establish standards, procedures, and permit requirements for disposal. The act also requires states to have solid waste management plans, prohibits open dumping, and requires the EPA to establish criteria for sanitary landfills. EPA under RCRA also regulates underground storage tanks that store or have stored petroleum or hazardous substances.

Hazardous wastes are either listed wastes (40 CFR 261.30-.33) or characteristic wastes (40 CFR 261.21-.24). The U.S. EPA defines four characteristics for hazardous waste: ignitability (40 CFR 260.21); corrosivity (40 CFR 260.22); reactivity (40 CFR 260.23); and toxicity (40 CFR 260.24). Any waste that exhibits one or more of these characteristics is classified as hazardous under RCRA. The ignitability definition includes a liquid that has a flash point less than 60°C (140°F); the EPA included ignitability to identify wastes that could cause fires during transport, storage, or disposal (e.g., used solvents). All of the solvents in Table 14.10.5 have flash points less than 60°C, so all could be a RCRA ignitability waste.

#### *14.10.2.2.4 Emergency Planning and Community Right-to-Know Act (EPCRA; 42 U.S. Code 11001 et seq.)*

Enacted as Title III of the 1986 Superfund Amendments and Reauthorization Act ("SARA"), the Act mandates the EPA to monitor and protect communities regarding releases of chemicals into the environment. It requires states to establish emergency planning districts with local committees to devise plans for preventing and responding to chemical spills and releases. ["Superfund" is the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) of 1980 that gives the U.S. EPA authority to force those responsible for hazardous waste sites or other releases of hazardous substances, pollutants, and contaminants to conduct cleanup or other effective response actions.]

*Section 304 (40 CFR 355.40)*: Facilities are subject to state and local reporting for accidental releases, in quantities equal to or greater than their reportable quantities (RQ), of extremely hazardous substances (EHS) or CERCLA hazardous substances (40 CFR 302, Table 302.4) under Section 304. n-Hexane, cyclohexane, acetone, and some of the other solvents discussed are CERCLA hazardous substances and have CERCLA RQ for spills (Table 14.10.5).

*Section 311, 312 (40 CFR 370.20-.21)*: Business must make MSDSs, for chemicals that are required to have an MSDS, available to state and local officials. Since all of the solvents discussed require MSDSs under the OSHA HCS, all are covered by these requirements.

*Section 313 (40 CFR 372), Toxic Release Inventory (TRI)*: Businesses are required to file annual reports with federal and state authorities of releases to air, water, and land above a certain threshold for chemicals on the TRI/Section 313 list (40 CFR 372.65) by July 1 each year for the previous year's releases.[21] TRI requirements are triggered if a facility is involved in manufacturing with 10 or more full-time employees, manufactures, processes, or otherwise uses with one or more listed substance(s) in a quantity above the statutory reporting threshold of 25,000 lbs./yr (manufactured or processed) or 10,000 lbs./yr (otherwise used). Beginning with the 1991 reporting year, such facilities also must report pollution prevention and recycling data for such chemicals pursuant to Section 6607 of the Pollution Prevention Act (42 U.S. Code 13106).

n-Hexane was added to the TRI list in 1994 with reporting for 1995 emissions.[19] The other solvents discussed are not on the TRI list. The EPA can add new chemicals to or delete chemicals from the TRI list as it deemed necessary and any person may petition the EPA to add chemicals or delete chemicals from the list.

#### *14.10.2.2.5 Toxic Substances Control Act (TSCA; 15 U.S. Code 2601 et seq.)*

If a chemical's manufacture, processing, distribution, use, or disposal would create unreasonable risks, the U.S. EPA, under the TSCA, can regulate it, ban it, or require additional testing. TSCA mandates the U.S. EPA to monitor and control the use of toxic substances by requiring the Agency to review the health and environmental effects of new chemicals [referred to as "Premanufacturing Notice" or "PMN"; Section 5(a)(1) of TSCA] and chemicals already in commerce. The U.S. EPA also has Significant New Use Rules (SNUR) under Section 5(a)(2) of TSCA which provides a way for the U.S. EPA to restrict uses of a chemical substance already in commerce that are proposed for new uses. All of the solvents discussed are already commercially available, so a PMN would not apply; some could be subjected to SNUR (40 CFR 721, subpart A), since some are not presently being used as extraction solvents in large quantities.

Under Section 4(a) of TSCA, the U.S. EPA can require testing of a chemical substance or mixture to develop data relevant for assessing the risks to health and the environment. Section 8(d) of TSCA requires that lists of health and safety studies conducted or initiated with respect to a substance or mixture be submitted to the U.S. EPA. All new toxicological data of the effects of a chemical not previously mentioned must be reported immediately if the data reasonably supports the conclusion that such substance or mixture presents a substantial risk of injury to health or the environment [Section 8(e) of TSCA]. Testing (Section 4 test rule) was required for several of the solvents earlier (e.g., commercial hexane for which new toxicological information was reported to the U.S. EPA since 1992),[22] and any new toxicological information will have to be reported to the U.S. EPA under Section 8(e) and 8(d).

### 14.10.2.3 Food safety

In the U.S. the use of a solvent to extract oil, that is a human food product or used in a food product, from oilseeds and biological materials falls under the rules and regulatory jurisdiction of the U.S. Food and Drug Administration (FDA), which regulates all aspects of food, including food ingredients and labeling in the U.S. In order to be legally used as an oilseed extraction solvent in the U.S., a substance must have been subject to an approval by the U.S. FDA or the U.S. Department of Agriculture (USDA) during 1938-1958 for this use ("prior sanction"); be generally recognized as safe (GRAS) for this use; or be used in accordance with food additive regulations promulgated by the U.S. FDA.

Many prior sanctions and GRAS determinations are not codified in the U.S. FDA regulations. However, extracting solvents used in food manufacturing, such as n-hexane, have been labeled as a food additive, solvent, defoaming agent, component of a secondary food and color additives, minor constituent, or incidental additives (i.e., "additives that are present in a food at significant levels and do not have any technical or functional effect in that food") depending on the application. Incidental additives can be "processing aids," (i.e., "substances that are added to a food during processing but removed from the food before it is packaged"). Most food-processing substances, including solvents, can be regarded as "incidental additives" and thus are exempt from label declaration in the finished food product. Even if exempt from label declaration, all extraction solvents must be used in accordance with the U.S. FDA good manufacturing practices (GMP; 21 CFR 100).

In the U.S., the Flavor and Extract Manufacturers' Association (FEMA) has conducted a program since 1958 using a panel of expert pharmacologists and toxicologists to determine substances that are GRAS. This panel uses all available data, including experience based on common uses in food. This safety assessment program ("FEMA GRAS") is widely accepted and considered an industry/government partnership with the U.S. FDA.[23] A number of papers published in Food Technology since 1961[24,25] list the substances that the panel has determined to be GRAS and the average maximum levels in parts per million (ppm) at which each has been reported to be GRAS for different categories of food. The U.S. FDA has not incorporated these substances in their regulations but does recognize the findings of the Expert Panel of FEMA as GRAS substances.

Since vegetable oil and other human food grade oils undergo deodorization (steam distillation) and other purification processes (i.e., refining and bleaching) as part of the manufacturing process prior to being used as a food product, they should not contain any of

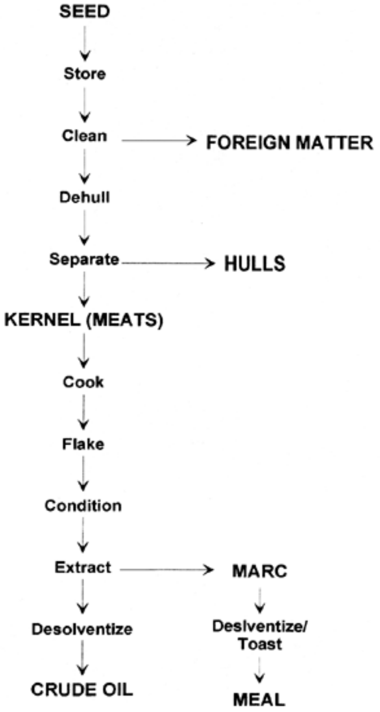

Figure 14.10.1a. Flow diagram of oilseed extraction process from seed to crude oil and meal.

the extraction solvent, if proper manufacturing practices are followed. (see Section 14.10.3.3 Processing crude oil, for more details.) Refining removes free fatty acids and other non-oil compounds (e.g., phospholipids, color, and trace metals); bleaching with acid-activated bleaching earth or clay (e.g., bentonite), removes color-producing substances and residual soaps; and deodorization, the last major processing step in edible oils refining removes volatile compounds (undesirable ingredients occurring in natural oils and those that may be imparted by prior unit processes or even storage, many of which are associated with undesirable flavors and odors).[26,27] Most commercial deodorizers operate at a temperature of 245-275°C (475-525°F) under a negative pressure of 2-10 mm Hg.[26,27] It has been reported that no hexane residue remains in the finished oil after processing due to its high volatility.[28] In addition, animal-feeding studies with expeller and solvent-extracted meals have not indicated any adverse health affects related to the extraction solvent.[29]

Hexane has been used since the 1940's as an oilseed-extraction solvent on the determination that it is GRAS and it may also be subject to a prior sanction. However, like many other food-processing substances, there is no U.S. FDA regulation specifically listing hexane as GRAS or prior sanctioned.

GRAS status may be determined by a company ("GRAS self-determination"), an industry, an independent professional scientific organization (e.g., FEMA GRAS), or the U.S. FDA. The Federal Food, Drug and Cosmetic Act (FFDCA; 21 U.S. Code 321 et seq.) does not provide for the U.S. FDA to approve all ingredients used in food, and the U.S. FDA explicitly recognizes that its published GRAS list is not meant to be a complete listing of all substances that are in fact GRAS food substances. Although there is no requirement to inform the U.S. FDA of a GRAS self-determination or to request FDA review or approval on the matter, the U.S. FDA has established a voluntary GRAS affirmation program under which such advice will be provided by the agency. Solvents that do not have prior sanction, a GRAS determination, or a tolerance set, probably should be evaluated for compliance under food safety requirements, if a facility is considering changing its extracting solvent or using a solvent for the extraction of the various biological materials for specialty markets.

## 14.10.3 THE SOLVENT EXTRACTION PROCESS

Three types of processing systems are used to extract oil from oil-bearing materials: expeller pressing, prepress solvent extraction, and direct solvent extraction. Only prepress solvent extraction and direct solvent extraction, which remove the oil from the conditioned, prepared seed with an organic solvent, will be discussed here[1,27] (see Figure 14.10.1). Oil-bearing materials have to be prepared for extraction to separate the crude oil from the

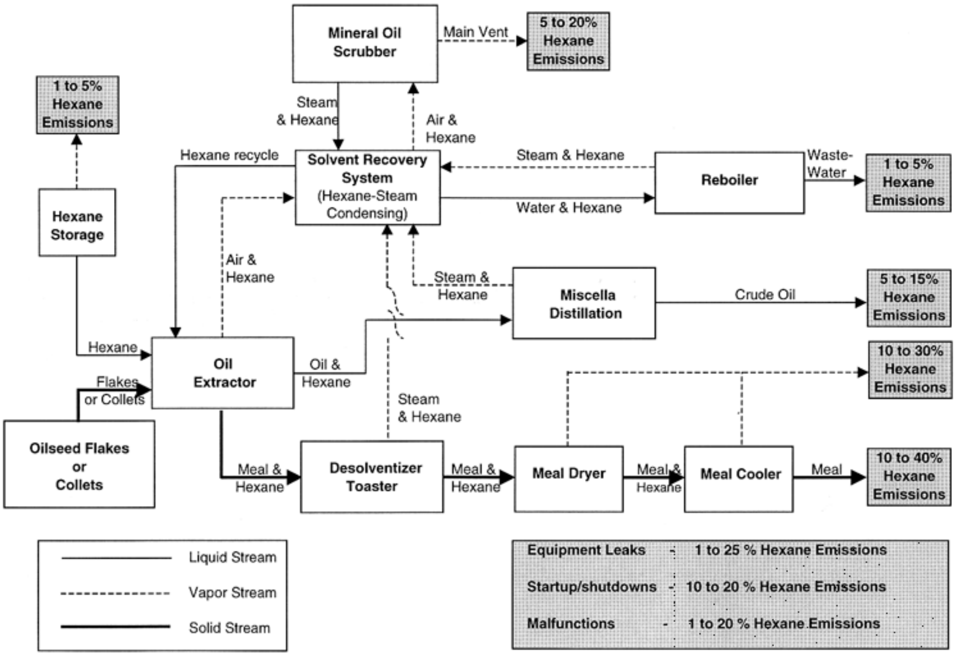

Figure 14.10.1b. Flow diagram of oilseed extraction process. Overview of extraction operation and identification of emission sources.

meal. Careful control of moisture and temperature during processing must be exercised to maintain the quality of the protein in the meal and to minimize the damage to the oil. Crude oils are refined by conditioning with phosphoric acid and treating with sodium hydroxide (alkali-refining) (see Figure 14.10.2). Refined oil is bleached with activated clay to remove color pigments. Bleached oils are then deodorized by steam distillation. The refined, bleached, and deodorized oil (RBD oil) is used to produce finished products, e.g., salad and cooking oils, shortening and margarine. Some of the finished products also require the oil to be hydrogenated, which changes the consistency of the oil, and increases stability to oxidation, which extends the shelf life of the finished products. Also some of the oils are winterized to remove the higher melting constituents, which can be used in confectionary products; the winterized oil is less likely to become cloudy in refrigerated storage.

### 14.10.3.1 Preparation for extraction

*Storage*: For optimum extraction and quality of oil, the oil-bearing material should be stored so that it remains dry and at relatively low temperature. If it is wet, it should be processed as soon as possible after harvest. Oils in the presence of water can deteriorate rapidly, forming free fatty acids and causing greater refining loss.

*Seed cleaning*: The first step in the commercial processing of oilseeds is “cleaning”, to remove foreign materials, such as sticks, stems, leaves, other seeds, sand, and dirt using dry screeners and a combination of screens and aspiration. Permanent electromagnets are also used for the removal of trash iron objects. Final cleaning of the seed usually is done at the extraction plant just prior to processing.

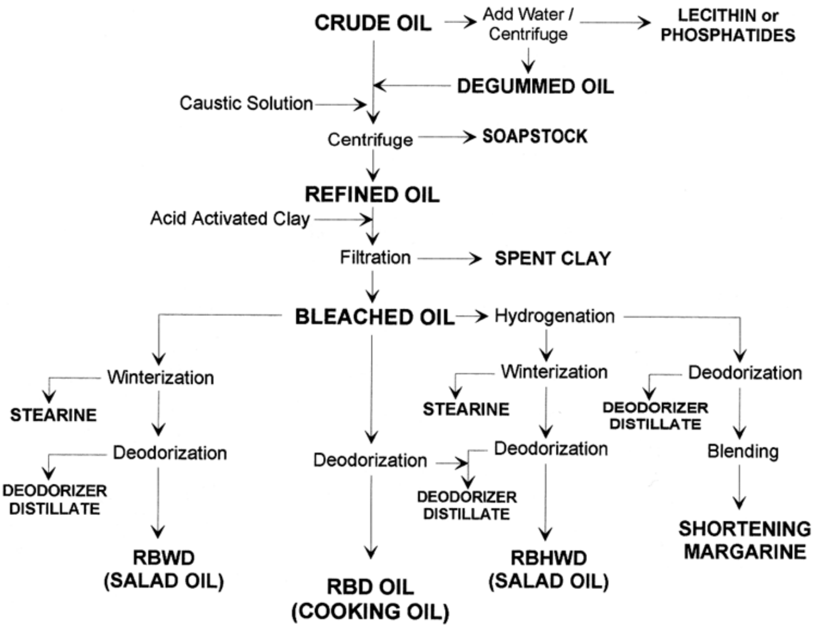

Figure 14.10.2. Flow diagram of edible oil processing.

*Dehulling*: After cleaning, it may be necessary to remove the seed's outer seed- coat (hull). The seedcoat contains little or no oil, so its inclusion makes the extraction less efficient. Also, the next processing step is grinding to reduce particle size, and any tough seedcoats would interfere with this process. If the hulls are not removed prior to extraction, they will reduce the total yield of oil by absorbing and retaining oil in the press cake. An acceptable level of hull removal must be determined, depending on the desired protein level of the final meal. Hulls are removed by aspirator and undehulled seeds are removed from the kernels by screening and returned to the huller. Some meats still adhere to the hulls, which are beaten, then screened again to obtain the meat.

*Grinding, rolling, or flaking*: After dehulling, the meats are reduced in size, or "flaked," to facilitate oil removal. Proper moisture content of the seeds is essential for flaking, and if the moisture level is too low, the seeds are "conditioned," with water or steam, to raise the moisture to about 11%. For solvent extraction, flakes are commonly not less than 0.203-0.254 mm (0.008-0.010 inch), which can be solvent extracted efficiently with less than 1% residual oil. Thinner flakes tend to disintegrate during the solvent extraction process and reduce the miscella percolation rate.

*Cooking*: Prior to extraction, the flakes are heated. The purpose of cooking the flakes is: (1) cell walls are broken down, allowing the oil to escape; (2) oil viscosity is reduced; (3) moisture content is controlled; (4) protein is coagulated; (5) enzymes are inactivated and microorganisms are killed; and (6) certain phosphatides are fixed in the cake, which helps to minimize subsequent refining losses. Flakes are cooked in stack cookers to over 87.8°C (190°F) in the upper kettle. Flakes with high phosphatide content may benefit from being cooked at slightly lower temperatures to avoid elevating refining losses. The temperature of the flakes is raised to 110-132.2°C (230-270°F) in the lower kettles. The seeds are cooked for up to 120 min. Overcooking lowers the nutritional quality of the meal and can darken both the oil and meal. Poor-quality seeds with high levels of free fatty acids cannot be cooked for as long a period as high-quality seeds because of darkening. Darker oil requires additional refining to achieve a certain bleach color.

*Expanders*: Sometimes low shear extruders called expanders are used. This equipment has the capability to process both low- and high-oil content materials. The meats are fed into an extruder after dehulling, flaking, and cooking and are heated as they are conveyed by a screw press through the extruder barrel. The meats are under considerable pressure and temperature when they reach the exit of the extruder. The change in pressure as the material leaves the extruder causes it to expand and the oil cells are ruptured, releasing the oil, which is rapidly reabsorbed. The expanded "collets" produced are then cooled and extracted with solvent.

### 14.10.3.2 Oil extraction

*Prepress solvent extraction*: In this process the oil-bearing material are first mildly pressed mechanically by means of a continuous screw press operation to reduce the oil by half to two-thirds of its original level before solvent extraction to remove the remaining oil in the pre-pressed cake. Pressing follow by solvent extraction is more commonly used when high oil content materials (e.g., canola/rapeseed, flaxseed, corn germ) are processed.

*Direct solvent extraction*: This process involves the use of a nonpolar solvent, usually hexane, to dissolve the oil without removing proteins and other non-oil soluble compounds. Solvent extraction yields about 11.5% more oil than does the screw press method, and less oil remains in the meal. The cooked flakes or collets (if expanders are used) are mixed with hexane in a batch or continuous operation. The hexane vapor pressure limits the practical operating temperature of the extraction and its contents to about 50-55ºC. The resulting miscella (oil-solvent mixture) and the marc (solvent laiden collets) are heated to evaporate the solvent, which is collected and reused. The oil is freed from the miscella, by using a series of stills, stripping columns, and associated condensers. The hexane-free oil (i.e., crude oil) is cooled and filtered before leaving the solvent-extraction plant for storage or further treatment. This is the crude oil normally traded in the commodity market. Occasional overheating of the oil-solvent miscella will cause irreversible color changes in the oil.

### 14.10.3.3 Processing crude oil

Most crude edible oils, obtained from oil-bearing materials, consist primarily of triglycerides (triacylglycerols). The triglycerides (approximately 95% of the crude oil) are the constituents recovered for use as neutral oil in the manufacture of finished products. The remaining nontriglyceride portion contains variable amounts of other lipophilic compounds, such as free fatty acids (FFA), nonfatty materials generally classified as "gums," phospholipids (phosphatides), tocopherols, color pigments, trace metals, sterols, meal, oxidized materials, waxes, moisture, and dirt. Most of these minor lipid components are detrimental to finished product color, flavor, and smoking stability, and so must be removed from the neutral oil by a processing/purification process. The object of the processing/purification steps is to remove the objectionable impurities while minimizing possible damage to the neutral oil and tocopherols and loss of oil during such processing.

Lecithin and cephalin are common phosphatides found in edible oils. Soybean, canola/rapeseed, corn, and cottonseed are the major oils that contain significant quantities of phosphatides. Alkaline treatment used for FFA reduction is also capable of removing most of the phosphatides from these crude oils. Tocopherols are important minor constituents of vegetable oils, which are natural antioxidant that retard the development of rancidity.

Refining, bleaching, and deodorization are the steps that are necessary if the oil is to be used in food applications. Oil that has only gone through these three steps is called "RBD" oil. Figure 14.10.2 illustrates the processing pathways.

*Refining*: Refining involves the removal of nonglyceride materials (phospholipids, color, and trace materials) and FFA. The goal is to produce a high-quality refined oil with the highest yield of purified triglycerides. Refining is by far the most important step in processing. An improperly refined oil will present problems in bleaching and deodorization and reduce quality.

Some solvent-extracted crude oils, including soybean or canola/rapeseed, contain approximately 2-3% gums, which are mainly phosphatides and require degumming. The principal phosphatides are lecithin and cephalin. Gums can cause problems through higher then necessary refining losses, or by settling out in storage tanks. The degumming operation exploits the affinity of most phosphatides for water, converting them to hydrated gums that are insoluble in oil and readily separated by centrifugal action. Lecithin can be recovered and concentrated from the gums in a separate solvent extraction process, usually with acetone.

Either water-degummed oil or crude oil can be treated with sodium hydroxide solution to saponify free fatty acids that are subsequently removed as soapstock by a primary refining centrifuge. Conventional alkali refining is by far the most widespread method of edible oil refining. The success of the alkali refining operation is the coordination of five prime factors: (1) use of the proper amount of reagent (sodium hydroxide), (2) proper mixing, (3) proper temperature control, (4) proper residual contact time, and (5) efficient separation.

Oil is alkali-refined by the addition of sodium hydroxide solution at a level sufficient to neutralize the FFA content of the oil. An excess of sodium hydroxide is required to reduce the color of the refined oil and to ensure the completion of the saponification reaction and to remove other trace elements. The amount and strength of the sodium hydroxide solution needed to neutralize the FFA is dependent on the amount of both FFAs and phosphatides present in the crude oil. Water-soluble soaps are formed in the primary reaction between the sodium hydroxide and FFAs. The hydratable phosphatides react with the caustic forming oil-insoluble hydrates. The caustic used in alkali refining is normally diluted to about 8-14% NaOH, although higher concentrations are occasionally used to reduce color. The proper amount of NaOH solution added to the oil will produce an adequately refined oil with the minimum of triglyceride oil loss. The amount of NaOH solution (neutralizing dose plus excess) is determined by experience and adjusted according to laboratory results.

After the NaOH solution is injected, it is mixed for 6-10 minutes to ensure thorough contact. The treated oil is then heated to assist in breaking of the emulsion prior to separation of the soapstock from oil in continuous centrifuges.

Any soap remaining, after the primary soapstock separation, is removed through continuous hot water washings. In this step, water is added at 10-15% at a temperature sufficient to prevent emulsification, generally 82-90.5ºC (180-195ºF). The oil is again separated from the soapy phase in water wash separators and drier prior to bleaching.

*Bleaching*: The oil is further purified by "bleaching", which removes color bodies and trace metals as well as entrained soaps, and products of oxidation that are adsorbed onto the surface of bleaching agents or adsorbents. Types of adsorbents most commonly used include neutral clay, acid activated clay, and activated carbon. The choice of adsorbent will depend on a balance between activity of the adsorbent, oil retention loss, and adsorbent cost.

The process is generally carried out via batch or continuous bleaching. Adsorbent is mixed with the refined oil creating a slurry that is agitated to enhance contact between the oil and the adsorbent. This is generally carried out under a vacuum at 90-95ºC (194-203ºF) for 15-30 minutes. Vacuum bleaching offers the advantages of an oil with improved oxidative and flavor stability. Finally the adsorbent is filtered from the oil using pressure leaf filters precoated with diatomaceous earth. Spent clay is steamed for efficient oil recovery.

*Deodorization*: Deodorization, which removes the volatile compounds along with residual FFA, is a critical step in ensuring the purity of any vegetable oil and improves flavor, odor, color, and oxidative stability. Many of the volatile compounds removed are formed by the auto-oxidation of fat, which produces aldehydes, ketones, alcohols, and hydrocarbons that are associated with undesirable flavors and odors. The process also is effective in removing any remaining pesticide residues or metabolites that may be in the oil.

Deodorization, which can be conducted as a batch operation in smaller plants or as a continuous or semicontinuous process by larger deodorizing facilities, consists of a steam distillation process in which the oil is heated to 230ºC (446ºF) under a vacuum of 2-10 mm Hg. Steam is sparged through the oil to carry away the volatiles and provide agitation. The odor and flavor compounds, which are more volatile than the triglycerides, are preferentially removed. After deodorization and during the cooling stage, 0.005-0.01% citric acid is generally added to chelate trace metals, which can promote oxidation. Deodorized oils preferably are stored in an inert atmosphere of nitrogen to prevent oxidation. Tocopherols and sterols are also partially removed in the deodorization process. Tocopherols can be recovered from the deodorizer distillate in a separate operation.

## 14.10.4 REVIEW OF SOLVENTS STUDIED FOR EXTRACTION EFFICIENCY

Research on solvents for extraction has been carried out for more than 150 years and has intensified since the first patent was issued to Deiss of France in 1855.[1,3,48] In the early effort of selecting an extraction solvent, the availability, operation safety, extraction efficiency, product quality and cost were the major concerns. In recent decades, toxicity, bio-renewability, environmental friendliness have been added to the solvent selection criteria. Among the solvents tested, a majority of the candidate solvents were excluded on the ground of toxicity and safety. Only a handful of solvents are used to any degree. These are acetone, alcohol, hexanes, heptane, and water.[1,4-7,49] Water is used in rendering of fat from animal tissues and fish and in coconut processing,[49] alcohol for spice and flavorants extraction,[5,49] acetone for lecithin separation and purification.[4] For commodity oils derived from vegetable sources, only hydrocarbon solvents have been used since 1930's. Acetone was used by an Italian cottonseed oil mill during the 1970's.[4] Aqueous acetone and acetone-hexane-water azeotrope were studied by the scientists at the Southern Regional Research Center of Agricultural Research Service, USDA during the 1960's and 1970's.[4] The effort was stopped due to the cost of retrofit required, the difficulties in managing the mixture of solvents with the presence of water and product quality concerns - a strong undesirable odor associated with the acetone extracted meals.[4] Ethanol and isopropanol were studied in the 1980's as a potential replacement of hexane for oil extraction. Both were proven technically feasible but economically unacceptable.[5,6] n-Hexane is listed as a HAP under the CAA[14,15] (See Section 14.10.2.2.1 CAA) and there are other regulatory requirements. As a way to meet environmental regulations, a short term option to commercial hexane appears to be hydrocarbons with significantly reduced n-hexane content.

### 14.10.4.1 Hydrocarbon solvents

Extraction of oils has largely relied on mechanical or heat rendering process for centuries.[50] Increased demand of productivity to separate oils from oilseeds has been the principal factor driving the changes of oilseed processing from the ancient hydraulic press to a continuous screw press or expeller in early 1900's.[51,52] This operation still left more than 4-5% residual oil in the pressed cake.[51] More complete recovery of oil can only be effectively accomplished by solvent extraction.[53,54]

Solvent extraction of oils had an early beginning. Deiss in France received a patent to extract fat from bone and wool with carbon bisulfide in 1855.[53] A year later, Deiss received additional patents covering the extraction of oil bearing seeds. Large scale solvent extraction already was established in Europe in 1870.[55] The earliest extractors were unagitated single-unit batch extractors of small capacity and not very efficient.[56,57] These extractors were gradually modified by the addition of agitation. They were organized in a battery of ten batch extractors which can be operated in a countercurrent principle. Extractors of this type operated in European plants during the last three decades of the 19th century.[57]

Further development in solvent extraction technology was relatively slow until early twentieth century. Solvent extraction spread from Europe to various parts of the world including the United States and South America.[57] The first extraction plant in the United States was used to recover grease from garbage, bones, cracklings, and other packing-house wastes and to recover residual oil from castor pomace.[57] Wesson[58] reported his efforts applying solvent extraction to recover cottonseed oil from 1889 till the close of World War I. During the 1930's solvent extraction was introduced in the United States for the recovery of oil from soybeans and the German equipment of the continuous type was used almost exclusively.[57-61] Just prior to World War II the installation of continuous solvent extraction equipment was greatly accelerated and throughout the period of the War new plants were erected in an effort to keep pace with the constantly increasing production of soybeans. All of the later installations have been of American manufacture and in a number of cases of American design.[57-61]

Solvents used in the early effort to extract grease and oils were diverse. Besides carbon bisulfide used by Deiss,[53] chlorinated hydrocarbons, benzene, and alcohols were all being tried. Extracting oil from corn and cottonseed with both aviation gasoline and petroleum distillate was performed in the United States in 1915 and 1917 respectively.[62] The hydrocarbon paraffins became the preferred solvents for oilseed extraction during 1930's through the process of elimination.[63-71] Due to the prominent defects of early solvent extraction: dark crude oil, strong solvent odor in meal and high cost associated with solvent loss, low boiling hydrocarbons such as propane and butane were recommended as oil extraction media.[72] The flammability of hydrocarbons also prompted much research in 1940's using chlorinated hydrocarbons as the extraction solvents[73,75] before its meal was found unsafe as feed.[75-77] For the purpose of improved protein and oil quality[75,78] and of processing safety and biorenewable solvents,[75,79,80] both ethanol and isopropanol were investigated as the oil extracting solvents. While these alcohols offer various advantages in product quality and process safety and are renewable, they are still not economically feasible to replace hydrocarbons as oilseed extraction solvents.[81] Hexane rich solvent became popular for the oilseed industry,[54,57,82,83] because it is the most efficient solvent, extracts minimum non-oil material and is easy to separate from the crude oil and marc.[63] A thorough comparison of various hydrocarbon solvents for cottonseed oil extraction on a lab scale basis was reported by Ayers and Dooley in 1948.[84] A more recent study by Wan et al.[85] used a laboratory scale dynamic percolation extractor which operates at the conditions similar to those applied in the oil mill practice. Plant trials of isohexane and heptane solvents versus hexane in a 300 tons/day cottonseed factory revealed some interesting findings.[7]

### 14.10.4.1.1 Nomenclature, structure, composition and properties of hydrocarbons

Petroleum and natural gas are the most abundant and affordable sources of hydrocarbon. Sometimes naphtha is used to describe the low boiling liquid petroleum and liquid products of natural gas with a boiling range from 15.6ºC (60ºF) to 221ºC (430ºF). This large group of compounds can be structurally classified as aliphatic and aromatic. Aliphatic hydrocarbons include saturated alkanes (paraffins), unsaturated alkenes (olefins) and alkynes (acetylenes), and cycloparaffins (naphthenes). Paraffins can be linear such as n-butane, n-pentane, and n-hexane, and branched such as isobutane, isopentane, isohexane, etc. Example of olefins is ethylene; of cycloparaffins, cyclopentane and cyclohexane; and of an aromatic, benzene.[8,86,87] These compounds are derived from natural gas and petroleum oils which normally contain thousands of hydrocarbons with molecular weight ranging from methane to about 50,000 - 100,000 Daltons. Upon refining, the crude petroleum is divided into hydrocarbon gases (methane, ethane, propane and butane), light distillates (naphthas and refined oils), intermediate distillates (gas oil and absorber oil), heavy distillates (technical oils, paraffin wax and lubricating oils), residues (petroleum grease, residual fuel oil still wax, asphalts and coke), and refinery sludges (acid coke, sulphonic acid, heavy fuel oils and sulfuric acid).[88] Historically, various fractions of petroleum naphthas, pentane and hexane from the light naphthas, aviation gasoline and benzol from the intermediate naphthas, and aromatic hydrocarbon, benzene, have been tested for oil extraction.[62-71]

### 14.10.4.1.2 Performance of selected hydrocarbon solvents

*Factors affecting extraction*: There is little theoretical basis to be followed for the extraction of oilseeds.[66,89-91] The study of the extraction of oilseeds is complicated by the fact that the total extractible material is variable in quantity and composition.[66,89] Composition of the early extracted material is nearly pure triglycerides. As the extraction progresses, increasing amount of non-glyceride material will be extracted.[66,89] IT is believed that the majority of the oil from oilseed flakes is easily and readily extracted.[66,90] While the thickness of flakes affects extraction rate, the concentration of miscella below 20% does not greatly increase the amount of time to reduce the residual oil in flakes to 1%.[89] Good[91] summarized much of the early effort in soybean extraction: (1) The first oil extracted is superior in quality to the last small fraction; (2) While other solvents have been used in the past, hexane has become the primary solvent due to a combination of properties; (3) Flake thickness is the most important factor in achieving good extraction results; (4) Higher extractor temperatures up to nearly the boiling point, improve extraction results; (5) Moisture control is important throughout the extraction process; (6) Heat treatment affects the total extractibles; and (7) The soaking theory of extraction indicates that weak miscellas are very effective in helping to achieve good extraction results.

Particle size which relates to the surface area available for extraction and is obviously one of the most important factors for extraction study. Coats and Wingard[92] noticed that particle size was more influential when the seed grit was being extracted. When oilseed flakes were being extracted, the flake thickness would be a more important factor instead of size of the flakes. Moisture content in oilseed can affect the extraction results.[93-95] Optimum moisture content of cottonseed meats for extraction was first reported by Reuther et at.[94] to be from 9 to 10%. Work by Arnold and Patel[95] indicated 7 to 10% to be the optimum moisture for cottonseed flakes and very little variation in extraction rate for soybean with moisture content between 8 and 12%.

Wingard and Phillips[96] developed a mathematical model to describe the effect of temperature on extraction rate using a percolation extractor as follows:

$$\log(\mathit{time}, \mathrm{min}) = n\log\left(\mathit{Temp.}, {}^{\circ}F\right) + \log k \quad \mathit{or} \quad \mathit{time} = k(\mathit{Temp.})^{n} \qquad [14.10.1]$$

where time is defined as the number of minutes required to reach 1% residual oil in the oilseed flakes. For all practical purpose, they concluded that the time in minutes required to reduce the oilseed to 1% residual oil content on a dry basis varied inversely with the square of the extraction temperature in degrees Fahrenheit.

*Evaluation methods*: Except for the pilot plant batch or counter-current extraction described by various labs,[54,74,78] most of the solvent extraction evaluation work found in the literature was done in one or several of the lab scale devices. The percolation batch-extraction apparatus of the Soxhlet type has often been used to evaluate the rate of extraction of hydrocarbon solvents such as the one described by Bull and Hopper.[89] Wingard and Shand[97] described a percolation type of extractor and a co-current batch extractor and claimed to be useful to study the factors influencing equipment design and plant operation as well as fundamental studies contributing to a general understanding of extraction. Wan, et al. modified the design of percolation type extractor to closely simulate a single stage counter current miscella extraction conditions as practiced in the factory.[85] Co-current batch extractor with numerous variations was also frequently applied for the extraction properties of selected solvents which were often operated at room temperature.[75,97] Soxhlet extraction[84,85] and Soxtec System HT6 (Perstorp Analytical, Herndon, VA) were also frequently used to evaluate solvents.[98] Soxhlet extractor allows vaporized and condensed pure solvent to percolate through oilseed sample. The temperature of the condensed solvent is normally lower than its boiling point. Depending upon the cooling efficiency of the condenser and the room temperature, the temperature of the condensed solvent and the temperature of the extracting solvent in the extractor largely varied from lab to lab. This extraction temperature variability was minimized with the Soxtec method by refluxing the oilseed sample in the boiling solvent for 15 minutes followed by Soxhlet type of rinsing for 35 minutes. In theory the Soxtec method is more efficient and better reproduced. However, the Soxtec method only utilized a 3 g oilseed sample. The heterogeneity of an oilseed sample could be a significant source of variation.

Flakes of oilseeds were most frequently used for the solvent extraction studies. Sometimes, ground oilseed kernels through a specified sieve size was used.[98] Residual oil content in the extracted flakes after a certain specified extraction condition or oil content in miscella (mixture of oil and solvent) was examined and the percentage of total oil extracted was calculated.[89-97] The total extractable oil of flakes was determined by four hours Soxhlet extraction. Wan et al.[85] used a precision densitometer to determine the miscella concentration (percent of oil in miscella by weight) after a given time of extraction from which the percentage of oil extracted from cottonseed flakes was calculated. From these data, Wan et al.[85] was also able to estimate the initial rate of extraction and final extraction capacity for each solvent as fresh and at selected initial miscella concentrations up to 30%.

Bull and Hopper[89] conducted extraction of soybean flakes in a stainless steel batch-extraction apparatus of the Soxhlet type with petroleum solvents, Skellysolve F (boiling range, 35 to 58°C) at 28°C and Skellysolve B (boiling range, 63 to 70°C) at 40°C. The extraction was carried out to permit the miscella obtained by each flooding of the flakes with solvent to be recovered separately. Their results showed that iodine number decreased and refractive index increased slightly with the extraction time which implied that more saturated fat was extracted during later stage of the extraction. Oils extracted during the later stages of the extraction were found to contain greater amounts of unsaponifiable matter and were rich in phosphatides, as high as 18% of the last fraction. Skellysolve B which is a hexane rich solvent demonstrated a much faster initial rate of extraction than that of Skellysolve F which is a pentane rich solvent and therefore, it took longer to complete the extraction for Skellysolve F. The fatty acid profile of each fraction showed a slight increase of saturated and a slight decrease of unsaturated fatty acid in the later fractions.

Arnold and Choudhury[82] reported results derived from a lab scale extraction of soybean and cottonseed flakes in a tubular percolation extractor at 135-140°F with pure, high purity and commercial hexane, and reagent grade benzene. They claimed that pure hexane extracted soybean slower than high purity and commercial hexane. During the first 60 minutes of extraction, benzene extracted more oil than the hexanes. However, at the end of 80 minutes, benzene extracted only slightly more than pure hexane but definitely less than the commercial hexanes. Similar results were obtained for the four solvents when cottonseed flakes were extracted.

A laboratory extraction study of cottonseed flakes using various hydrocarbon solvents was reported by Ayers and Dooley.[84] Soxhlet extractor and Waring blender were used for these experiments. Among the petroleum hydrocarbon solvents tested were branched, normal and cyclo-paraffins as well as aromatic hydrocarbons with various degrees of purity. They were: pure grade (99 mole percent purity) n-pentane, isopentane, cyclohexane, benzene, and n-heptane; technical grade (95 mole percent purity) neohexane, diisopropyl, 2-methylpentane, 3-methylpentane, n-hexane, and methylcyclopentane; technical grade (90 mole percent purity) cyclopentane; and commercial grade n-heptane, isohexanes, n-hexane, isoheptane and n-heptane. To assess the performance of these solvents, they used the following empirical formula:

$$\begin{aligned}\textit{Quality-Efficiency Rating} &= 0.4\,(\textit{Oil Yield Factor}) + 0.4\,(\textit{Refining Loss Factor})\\ &\quad + 0.2\,(\textit{Refined and Bleached Oil Color Factor})\end{aligned} \qquad [14.10.2]$$

When comparing the oil yield factor alone, 3-methylpentane was rated the best. When comparing the solvents based on the empirical Quality-Efficiency Rating formula, they concluded that methylpentanes (3- and 2-methylpentane) were superior extraction solvents for cottonseed oil. The normal paraffins, highly-branched isohexanes, cycloparaffins, and aromatics were progressively rated as less efficient than methylpentanes. Therefore, they recommended a tailor-made solvent for the extraction of cottonseed should exclude aromatic hydrocarbons, have low limits on cycloparaffin content, and consist largely of normal and isoparaffin hydrocarbons.

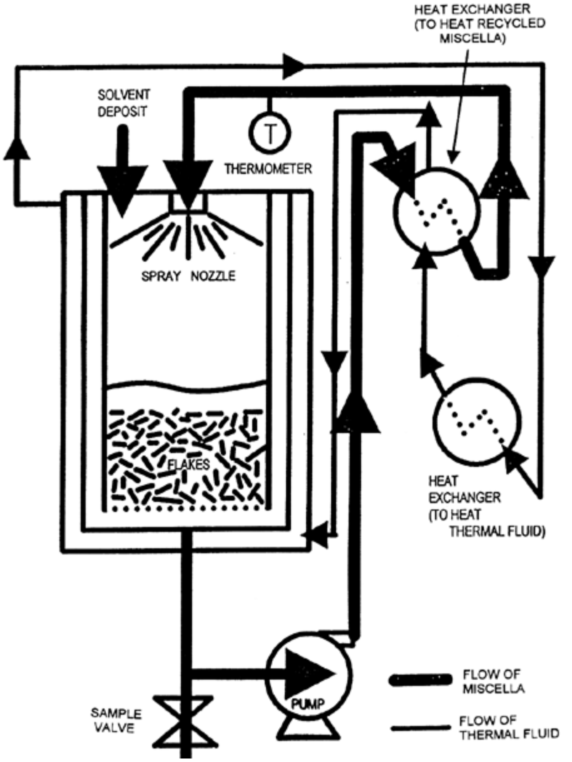

Figure 14.10.3. Schematic of bench-scale dynamic percolation extractor.

A more recent study by Wan et al.[85] using a laboratory scale dynamic percolation type of extractor (Figure 14.10.3) operated at the following conditions such as, temperature (5°C below the boiling point of each solvent) and miscella flow rate (9 gal/min/ft$^2$), similar to those applied in the oil mill practice. Commercial grade hexane, heptane, isohexane, neohexane, cyclohexane, and cyclopentane were used to extract cottonseed flakes which had 5.8% moisture and 31.4% oil. When these solvents were tested near their boiling points, hexane apparently extracted cottonseed oil at a higher initial rate, > 94% oil extracted after 2 minutes, than all other solvents. Both heptane and hexane were able to extract more oil at the end of 10 minutes of extraction. Isohexane demonstrated to have adequate initial extraction rate (80% oil extracted after 2 minutes) and extraction capacity (93% oil extracted after 10 minutes of extraction) but is noticeably less effective than hexane. Similar to findings by Ayers and Dooley,[84] results from the study by Wan et al.[85] also demonstrates that neohexane, cyclohexane and cyclopentane performed distinctly less efficiently than hexane, heptane and isohexane. Conkerton et.al.[98] tested commercial heptane versus hexane in a Soxtec extractor. Under this extraction condition, heptane actually extracted more oil than hexane from ground cottonseed kernel passed through a 20 mesh screen. The oil and meal quality were not appreciably affected by the higher temperature extraction of heptane.

*Plant scale results*: Although hydrocarbon solvents have been used for oilseed extraction since the 1930’s, very little in plant operating data are available. During the spring of 1994, Wan et al.[7] conducted plant trials with commercial heptane and isohexane at a 300 tons/day cottonseed crushing plant which routinely used hexane as the extraction solvent. Test results indicated that heptane performed well as an extraction solvent. However, it required extra energy and time to recover and consequently reduced the throughput rate of cottonseed being processed. Isohexane on the other hand was termed as an “easier” solvent by the plant engineers than hexane to operate. The plant also experienced a 40% steam savings and better than 20% throughput increase when it was operating with isohexane.[7] This encouraging result prompted a second plant trial with commercial isohexane.[45] The second plant trial was carried out at a cottonseed oil mill with a relatively new extraction and miscella refining facility which was constructed in 1988 with a designed capacity of 500 tons/day but operated at only 270 tons/day due to limited delinting capacity. After week long testing with commercial isohexane, this plant experienced more than 20% natural gas usage and easily increased the throughput rate by close to 10% when compared with commercial hexane. This energy savings with commercial isohexane over commercial hexane may be largely attributed to the difference in the amount of water present in their corresponding azeotropes. Isohexane requires an additional step - isomerization to manufacture and will always be priced higher than hexane. But based on the two cottonseed oil mill trials, isohexane can be a cost efficient solvent.[99] One additional benefit, the shorter residence time of the extracted cottonseed marc in the desolventizer/toaster because of the lower boiling range of isohexane will likely preserve more vegetable protein in the final meals which has been observed by both plants during the tests.[7,45] The benefit in improved quality of oils were not obvious in both plant trials but might be realized with extended trials.

*Further evaluation of hydrocarbon solvents*: As indicated in the study conducted by Wan et al.,[85] the commercial cyclic hydrocarbons are the least effective extraction solvent than the branched and linear hydrocarbons. The comparison of extraction efficiency of pure isomers of hexane was conducted with the same single stage extractor as displayed in Figure 14.10.3. This was done to identify any unique structure-function characteristics of these pure components of commercial hexane and provide some guidance to the selection and tailored formulation for future commercial isohexane for the oilseed extraction industry. The extraction results for various pure isomers of six carbon paraffins using the single stage extractor indicated the following: (a) cyclohexane is noticeably less efficient in extracting cottonseed flake than all the other isomers; (b) slightly branched isomers, such as, 2-methyl and 3-methyl pentane, and methyl-cyclopentane are very slightly less efficient than n-hexane; and (c) highly branched isomers, 2,2-dimethyl and 2,3-dimethyl butane, are slightly less efficient than slightly branched isomers in extraction (Unpublished data).

## 14.10.5 FUTURE TRENDS

In the future there most likely will be new demands for highly specialized extraction solvents as newly domesticated species that make useful novel oils[30] and other products and new or altered biological products with enhanced nutritional and industrial properties will be developed through conventional breeding and genetic engineering for use as "functional foods"[31] (e.g., phytosterols to achieve cholesterol lowering); as oils with altered lipid profiles[32] (e.g., for lower saturated fat) or with more vitamin E; new drugs/nutraceuticals, industrial chemicals (e.g., fatty acids for lubricants, as cosmetics, coatings, detergents, surfactants, flavors, polymers, etc.); as sources for specialty chemicals; as value added products; etc.[31-38]

Genetically enhanced (GE) /biotech crops make up a growing share of the agricultural output.[39] Biotechnology is the most powerful tool ever put in the hands of agricultural scientists. The ability to breed desirable traits or eliminate problematic ones can yield potentially spectacular benefits, such as various chemicals of importance including improved fats and oils, and vaccines and medicine, improved nutrition (e.g., in casaba, oilseeds, rice, sweet potatoes), and improved yields with the use of less agricultural chemicals. GE/biotech crops could be increasingly developed as biofactories for a wide range of products, including nutrients pharmaceuticals, and plastics. There is much promise for being able to produce products that would protect millions from disease, starvation, and death. However biotechnology and GM crops have become very controversial, and have run into serious problems in Europe, particularly in the UK.[40] Europe,[41] Japan, Korea, and Australia/New Zealand already have some restrictions and require some labeling. The U.S. is reviewing the issue.[42] Thus even though this technology has great promise for increased use of new and existing solvents for extraction of products from diverse biological materials, there are also many potential problems because of misperceptions and misinformation.

In the U.S. EPA is developing Maximum Available Control Technology (MACT) standards for vegetable oil processing that are likely to be finalized in 2001 (see Section 14.10.2.2.1, Hazardous Air Pollutants), with enforcement three years after promulgation.[16,17] Commercial hexane, which is a HAP and a VOC, is presently the solvent used.[16,17] To meet new and existing CAA requirements it is likely that extraction facilities will become much more efficient chemical engineering operations with upgraded equipment,[43] more computerized monitoring and control for better quality management,[44] and better environmental management/stewardship.[19] In addition it is possible that alternate solvents (e.g., isohexane[3,7,45]) or lower n-hexane content commercial hexane (30-50% vs. 64%) will be used to meet these regulations. It is also possible that solvents like acetone, which is not a HAP or VOC and is not on the TRI list, will be more strongly investigated.[16,17,46]

In Europe trans fatty acid labeling of retail foods is required and in the U.S. FDA has proposed to label trans fats as saturated fat on the nutrition labeling panel required on packaged food sold at retail (64 FR 62,764; Nov. 17, 1999). This regulation if, promulgated as proposed, will result in reformulation of many products that could affect the vegetable oil producing and extracting industries.

It is clear that the future has much uncertainty, while at the same time it offers much promise. It appears that there will be many potential changes that will put new demands on extraction solvents. Solvents that are more environmentally friendly, are nontoxic to plants, workers, and consumers, have specialized properties, have high solvent power at low temperatures (are easy to desolventize), etc., may have wider potential use in conventional extraction as well as specialized niche markets.

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## 14.11 GROUND TRANSPORTATION

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The ground transportation industry in the USA is dominated by truck freight (78.6%). Other methods of transportation include: rail (7.9%), water (5.2%), air (4%), pipeline (2.2%), and other (2.1%). Solvents are used and solvent wastes and emissions are generated during refurbishing and maintenance.

Rail car refurbishing involves stripping and painting. Paint is usually removed by mechanical means (steel grit blast system) but solvents are occasionally used. Solid wastes are generated from latex paint wastes but hazardous wastes are also generated from solvent-based paints and thinners. Parts cleaning is mostly done using mineral spirits. Waste solvents are sent off-site for reclamation.

Truck maintenance work usually requires a parts washer which may involve either a heated or ambient temperature solvent, hot tank, or a spray washer. In the solvent tank washer, solvent (usually mineral spirits, petroleum distillates, and naphtha) is recirculated from solvent tank. Spent solvent is usually replaced monthly. Carburetor cleaning compounds contain dichloromethane. Tanker cleaning often involves a solvent spray.

The ground transportation industry employs a large number of people (more than 2 million in the USA). It is one of the less polluting industries. It generates 0.3% of VOC released by all major industries combined (about half of that of the aerospace industry). Most solvents used are of low toxicity. Good system of collection and reclamation of solvent wastes is done effectively and this is the major reason for the relatively good performance of the industry.

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## 14.12 INORGANIC CHEMICAL INDUSTRY

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This industry has two major sectors: inorganic chemicals and chlor-alkali. Inorganic chemicals are often of mineral origin processed to basic chemicals such as acids, alkalies, salts, oxidizing agents, halogens, etc. The chlor-alkali sector manufactures chlorine, caustic soda, soda ash, sodium bicarbonate, potassium hydroxide and potassium carbonate. The major processes in this industry do not use solvents but there are many specialized auxiliary processes which use solvents. Tables 14.12.1 and 14.12.2 give information on the reported solvent releases and transfers from inorganic chemical industry.

The tables show that the industry, which operates almost 1,500 plants and employs over 110,000 people, has minimal impact on global emission of VOCs. Consequently, the industry does not have any major initiative to deal with solvent emissions or wastes. Future safety improvements concentrate on non-solvent issues.

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**Table 14.12.1. Reported solvent releases from the inorganic chemical plants in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| benzene | 33,000 | hexane | 2,000 |
| carbon tetrachloride | 3,000 | methanol | 574,000 |
| chloromethane | 2,600 | methyl ethyl ketone | 460 |
| dichloromethane | 12,500 | N-methyl-2-pyrrolidone | 180 |
| ethyl benzene | 110 | toluene | 12,000 |
| ethylene glycol | 1,800 | xylene | 1,500 |

**Table 14.12.2. Reported solvent transfers from the inorganic chemical plants in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| benzene | 780 | methyl ethyl ketone | 9,000 |
| carbon tetrachloride | 6,400 | N-methyl-2-pyrrolidone | 8,700 |
| dichloromethane | 5,000 | toluene | 6,000 |
| ethylene glycol | 12,000 | xylene | 96,000 |

## 14.13 IRON AND STEEL INDUSTRY

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With almost 1,400 plants, the US iron and steel industry is very diverse industry having total sales of $100 billion and over 400,000 employees. Figure 14.13.1 is a schematic diagram of the iron and steel making process. Only one stage – finishing – employs solvents. The finishing stage includes processes to remove mill scale, rust, oxides, oil, grease and soil prior

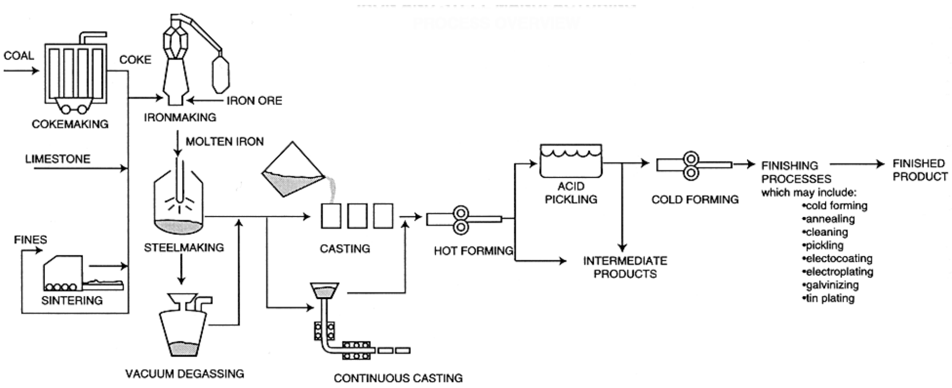

Figure 14.13.1. Schematic diagram of operations in the iron and steel manufacturing process. [Reproduced from EPA Office of Compliance Sector Notebook Project. Reference 1.]

**Table 14.13.1. Reported solvent releases from the iron and steel plants in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| benzene | 321,000 | N-methyl-2-pyrrolidone | 3,600 |
| n-butyl alcohol | 26,000 | polycyclic aromatic compounds | 2,400 |
| cresol | 1,800 | tetrachloroethylene | 91,000 |
| dichloromethane | 318,000 | 1,2,4-trimethylbenzene | 17,000 |
| ethylbenzene | 5,000 | trichloroethylene | 620,000 |
| methanol | 241,000 | toluene | 261,000 |
| methyl ethyl ketone | 358,000 | xylene | 168,000 |

to coating. Methods used include solvent cleaning, pressurized water or air blasting, cleaning with abrasives, and alkaline or acid pickling.

Tables 14.13.1 and 14.13.2 give information on the reported solvent releases and transfers from the iron and steel industries. Not all the solvents listed in the tables are used in processing. Some are by-products of coke manufacture from coal. Benzene and polycyclic aromatics compounds are by-products. Strong solvents such as methyl ethyl ketone, toluene, xylene, and trichloroethylene are typical of those used in cleaning processes. There is no program formulated by the industry to reduce amounts of solvents used.

## REFERENCES

1 EPA Office of Compliance Sector Notebook Project. Profile of the Iron and Steel Industry. Trucking, Railroad, and Pipeline. US Environmental Protection Agency, 1995.
2 EPA Office of Compliance Sector Notebook Project. Sector Notebook Data Refresh - 1997. US Environmental Protection Agency, 1998.

**Table 14.13.2. Reported solvent transfers from the iron and steel plants in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| benzene | 3,000 | N-methyl-2-pyrrolidone | 11,500 |
| n-butyl alcohol | 1,400 | polycyclic aromatic compounds | 3,820,000 |
| cresol | 12 | tetrachloroethylene | 20,000 |
| dichloromethane | 14,500 | 1,2,4-trimethylbenzene | 3,600 |
| ethylene glycol | 197,000 | trichloroethylene | 165,000 |
| ethylbenzene | 550 | toluene | 11,500 |
| methanol | 25 | xylene | 14,000 |
| methyl ethyl ketone | 66,000 | | |

## 14.14 LUMBER AND WOOD PRODUCTS - WOOD PRESERVATION TREATMENT: SIGNIFICANCE OF SOLVENTS

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### 14.14.1 GENERAL ASPECTS

Wood preservation is based on various fundamental principles, e.g., construction aspects such as exposure to humidity, selection of different types of wood products according to their durability, and chemistry of wood preservatives. Important groups of chemical wood preservatives are water-soluble and solvent-based substances.[1]

The main requirements of chemical wood preservatives are:[1]

- Stability, especially chemical stability.
- Resistance to environmental conditions, e.g., light or heat.
- Penetration into the wood products.
- Effectiveness against wood attacking agents (e.g., insects, fungi, bacteria).
- Compatibility with other construction components, e.g., paints, adhesives, and fasteners.
- Construction aspects, e.g., corrosion.
- Minimal environmental impact, e.g., minimum emissions or minimum environmental pollution.
- Ability to work with a range of wood products.
- Case applications, e.g. fundamental differences of indoor and outdoor coatings.
- Having favorable visual aspects, e.g., surface properties, color, uniformity, influence on grain pattern, etc.

All requirements cannot be fulfilled completely by the various wood preservatives. Therefore wood preservatives should be selected according to the particular case.

## 14.14.2 ROLE OF SOLVENTS

### 14.14.2.1 Occurrence

Various solvents are added to wood preservatives. Only a limited number of wood preservatives are authorized by governmental agencies, e.g., in Germany "Institut für Bautechnik (DIBt)".[2] But there is a large grey market for wood preservatives other than the authorized substances. As a result, a large variety of solvents can occur in wood preservatives.

Different systems of classification are used worldwide. In Germany, authorized wood preservative substances are published in an index of wood preservatives ("Holzschutzmittelverzeichnis")[2] which is elaborated by the DIBt and the central German environmental authority ("Umweltbundesamt").

A systematic survey of wood preservatives is shown in Table 14.14.1, including wood preservatives containing solvents. Solvents are normally found in wet systems of wood preservatives. Commonly used solvents are substances which are applied in connection with normally used binders (aldehyde resins, acrylates and polyurethanes). Water or the appropriate solvents are added to binders.

**Table 14.14.1. Systems of wood preservatives**

| Purpose and base | Terms | Active components |
|---|---|---|
| Water-soluble agents as preventive treatment against fungi and insects | "CF-salts" | chromium and fluorine compounds |
| | "CFA-salts" | alkali fluorides, alkali arsenate, and bichromate (no longer permitted) |
| | "SF-salts" | silicofluorides |
| | "HF-salts" | hydrogen fluorides |
| | "B-salts" | inorganic boron compounds |
| | "Single CK-salts" | copper salts, bichromate |
| | "CKA-salts" | copper salts, bichromate with arsenic compounds |
| | "CKB-salts" | copper salts, bichromate with boron compounds |
| | "CKF-salts" | copper salts, bichromate with fluorine compounds |
| | "CFB-salts" | chromium, boron and fluorine compounds |
| | collective group | other compounds, e.g., bis(N-cyclohexyl-diazeniumdioxyl)-copper |
| Oily agents as preventive treatment against fungi and insects | tar oil preparations | distillates of bituminous coal tar (carbolineum) |
| | preparations containing solvents | organic fungicides and insecticides |
| | pigment-free preparations containing binders and solvents | organic fungicides and insecticides |
| | preparations with stained pigments containing solvents | organic fungicides and insecticides |
| | special preparations only used in stationary installations | organic fungicides and insecticides |
| | preparations containing coal tar oil | organic agents, special distillates containing coal tar oil, solvents and pigments |
| Preparations used for special applications | pastes | |
| | wood preservatives used in particle board in manufacturing plants | |
| | agents used as preventive treatment against insects contain organic insecticides | |

Solventborne wood preservatives contain mainly nonpolar, organic solvents apart from other substances such as fungicides and insecticides.[1] These solvents are classified as VOCs.

### 14.14.2.2 Technical and environmental aspects

Solvent-based wood preservatives show several advantages, especially in their application and technical effectiveness.[1] They can be applied repeatedly and do not alter the structure of the wood products. Application is faster and the characteristics of the final product are improved, e.g., visual appearance of surface.

Nevertheless, there are some disadvantages, especially environmental ones. Most solvents are released quickly (VOCs) and can cause severe environmental effects. This is especially true if toxic solvents are employed.

Emissions of solvents from wood products are described under various conditions, e.g. indoor air emissions from furniture or emissions in test chambers.[3,4] Solvents can be emitted as primary or reactive products of the wood product or the coating system; solvents can also be investigated as secondary emission products.[3,5] The emission characteristics depend on solvent properties and surrounding conditions, e.g., air velocity and air exchange rate.[6]

In the indoor air, solvents from wood products follow various pathways. Examples of interactions are possible reactions of solvents (e.g., styrene) with air components (e.g., hydroxy radicals),[3] transport into and through indoor materials[7] or sorption processes.[5] The emitted solvents can be reduced by ventilation processes or they may be absorbed by organisms.

For humans, absorption of the wood preservatives or ingredients (e.g., solvents) can cause various toxic effects. It is often difficult to pinpoint the causative agents (see Chapter 20).

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## 14.15 MEDICAL APPLICATIONS

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Industries manufacturing medical devices use a wide variety of technological processes which most likely take advantage of most of the available solvents. The range of solvent use is so wide that a complete description of each solvent and its application is not possible in this book. It is questionable if such analysis is possible given that many processes are guarded by trade secrets where there is no patent disclosure. Some examples are given, more to show that, although solvents do contribute to pollution, they also help to produce materials which are needed for health and well being.

Polyurethanes are materials which have the required properties and biocompatilibity which makes them good candidate for use in medical devices. Common applications include pacemaker leads, peripheral and central catheters, feeding tubes, balloons, condoms, surgical gloves, instrument and appliance covers, wound dressings, and many other.[1-4] Several methods are used to process polyurethanes. These include injection molding, extrusion, and solution processing. In solution processing film casting and dip molding are the most frequent techniques.

Dimethylacetamine, tetrahydrofuran, dichloromethane, methyl ethyl ketone, N,N-dimethylformamide, N-methylpyrrolidone, cyclopentanone, cyclohexanone, dioxane, and chloroform are the most commonly used solvents. Most of these are hazardous but used because they contribute to highly transparent product which is very desirable in medical devices. Transparent materials can only be made from transparent solutions.[1] These solvents can dissolve polymers well and form clear solutions. Ease of solvent removal from the material is very important in formulation design. Obviously, no traces of solvents should remain in the medical devices since even trace amounts may interfere with the treatment and the patient's health. An inappropriate solvent selection may cause the formation of crust as the solvent escapes. This leads to material discontinuity (e.g., pinholes) which renders the product inferior. This brings a discussion of solvent evaporation, the rheological properties of formulation, and formation of multilayer materials.

Good solvents can be used in lower concentration but they result in viscous solutions which, in dip coating, form thick films which have the potential of blistering on evaporation. If the solution is diluted, film continuity suffers which increases the number of pinholes. Rapid evaporation causes a formation of a crust of gelled solidified polymer which makes solvent removal more difficult and damages the integrity of the layer. Also, material does not have time to adjust and leveling suffers. On the other hand slow evaporation may cause dissolution of the layer below the coating in a multilayered products and bubbling between the layers.

The selection of solvents for dip coating is usually a complex process ultimately requiring multicomponent solvent mixtures which include a good solvent, a poor solvent, and a solvent of lower boiling point (sometime called "blush resistor") to balance viscosity and rate of evaporation.[2] In wound dressings, the solvents selected affect the material microstructure which controls the evaporation of exuded body fluids but prevents bacteria and pathogens from entering the wound.[3] In infection-resistant medical devices, the antimicrobial agent must be uniformly distributed over all areas of the medical device which may come into contact with a patient. Otherwise there is a risk of infection.[4] Not all solvents dissolve antimicrobial agents and swell surface of medical device.

Cleaning of penetrable septa, tubing systems, and infusion and dialysis systems is another application in which solvents are used. The solvents which are suitable for elastomer cleaning are dichloromethane, perchloroethylene, halogenated hydrocarbons, and freons.[5] This cleaning method extracts undesirable organic materials from medical devices which might otherwise be extracted by body fluids. Heat treatment of catheters followed by washing with a polar solvent increase its surface lubricity. Catheter with poor surface lubricity often causes frictional pain upon its insertion into the body cavity and damages the mucosal tissue resulting in cross infection.[6] Film dressings contain two types of solvents: solvents to dissolve the polymer and propellant solvents. These must be selected to achieve technological goals related to solubility and compatibility.[7]

These examples show that the many technological considerations place constraints on in solvent selection. Solvent replacement in complex products and technological processes is a long-term, expensive proposition which usually results in a need for complete reformulation of the material with failure to achieve the objective a very possible outcome.

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## 14.16 METAL CASTING

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The metal casting industry has 3,100 facilities in the USA and employs 250,000 people. Most plants are small and technological processes are very diverse. The processes do share common phases, including pattern making, mold and core preparation, furnace charge and metal melting, mold charging, cooling and finishing. Most steps use solvents. In the mold-making process, a many chemical binding systems are used, some of which contain methanol, benzene, toluene, and cresol. The metal is most often recycled and it typically requires cleaning before it is charged to the furnace. This is accomplished either by precombustion or solvent cleaning. In die casting operations, solvent-based or water-based lubricants are used. Die casters also use die fluxes which contain solvents. Some solvent replacement additives in water-based lubricants contain hazardous solvents. Finishing operations involve casting cleaning to remove scale, rust, oxides, oil, grease, and dirt. Solvents are typically chlorinated solvents, naphtha, toluene, and methanol. Cleaning can also be done by emulsifiers, abrasives, alkaline agents, and acid pickling. The cleaning operation is usually followed by painting which frequently involves solvent-based paints and thinners.

Tables 14.16.1 and 14.16.2 contain information on the reported solvent releases and transfers from metal casting industry. The data show that solvent use is not excessive relative to other industries. The industry plans to further improve its environmental record by developing environmentally improved materials which meet regulations. The solvent cleaning and die lubrication are processes under study.

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1 EPA Office of Compliance Sector Notebook Project. Profile of the Metal Casting Industry. US Environmental Protection Agency, 1998.
2 EPA Office of Compliance Sector Notebook Project. Sector Notebook Data Refresh - 1997. US Environmental Protection Agency, 1998.

**Table 14.16.1. Reported solvent releases from the metal casting industry in 1995 [Data from Ref. 1]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| benzene | 110,000 | methyl ethyl ketone | 22,000 |
| n-butyl alcohol | 15,000 | methyl isobutyl ketone | 22,000 |
| cresol | 20,000 | N-methyl-2-pyrrolidone | 41,000 |
| dichloromethane | 50,000 | tetrachloroethylene | 13,000 |
| ethylbenzene | 10,500 | 1,1,1-trichloroethane | 111,000 |
| ethylene glycol | 64,000 | trichloroethylene | 75,000 |
| hexachloroethane | 16,000 | toluene | 233,000 |
| methanol | 5,860,000 | xylene | 388,000 |

**Table 14.16.2. Reported solvent transfers from the metal casting industry in 1995 [Data from Ref. 1]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| benzene | 115 | N-methyl-2-pyrrolidone | 22,000 |
| ethylbenzene | 340 | 1,1,1-trichloroethane | 500 |
| ethylene glycol | 50,000 | trichloroethylene | 1,000 |
| methanol | 10,000 | toluene | 4,000 |
| methyl ethyl ketone | 8,000 | xylene | 82,000 |

## 14.17 MOTOR VEHICLE ASSEMBLY

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Automotive industry in US alone employs 6.7 million person and it is a large contributor to the gross national product. It uses large quantities of solvents and it is perceived to contribute to pollution by solvents and other materials.[1-6] Solvents are used in a variety of cleaning, preparation, and painting operations. Automotive finishing process may be divided into four main categories: anti-corrosion operations (cleaning, phosphate treatment, and chromic acid treatment), priming operations (electrodeposition of primer, anti-chip coating application, and primer application), joint sealant application, and other finishing operations (color coat, clear coat). These main operations employ many materials which contain solvents.

The cleaning process involves acid/alkaline and solvent cleaning. Typical solvents involved are acetone, xylene, toluene, and 1,1,1-trichloroethylene. The primer bath is water-based but usually some organic solvents are present (5-10%). These solvents are the same as those listed above. After the application of primer, the car body is baked and then undergoes waterproofing with an application of polyvinylchloride sealant which contains a small amount of solvents. Following waterproofing, the automotive body proceeds to the anti-chip booth, where urethane or epoxy solvent-coating systems are applied. This process is followed by application of primer-surfacer coating which is either a polyester or an epoxy ester in a solvent system. The primer-surfacer coating is applied by spraying and provides a durable finish which can be sanded. After the sanding step, the primary color coating is applied also by spraying. These primary color formulations contain about twice as much solvent as the primer-surfacer coating. Solvents are flashed-off (no heating) and a clear coat is applied. Then the entire car body is baked for about 30 min. Solvents used include butanol, isobutanol, methanol, heptane, mineral spirits, butyl acetate ethyl acetate, hexyl acetate, methyl ethyl ketone, acetone, methyl amyl ketone, toluene, and xylene.

Several finishing operations also employ solvents. After baking, a sound-deadener is applied to certain areas of the underbody. It is a solvent based material with a tar-like consistency. A trim is applied with adhesives which contain solvents (see section on adhesives and sealants). After the installation of trim and after the engine is installed, car undergoes an inspection. Some repainting is required in about 2% of the production. If damage is minor then repainting is done by a hand operated spray gun. If the damage is substantial a new body is installed. Equipment cleaning solvents are also used. Spraying equipment is cleaned with a "purge solvent" which may consist of a mixture of dimethylbenzene, 4-methyl-2-pentanone, butyl acetate, naphtha, ethyl benzene, 2-butanone, toluene, and 1-butanol.

Tables 14.17.1 and 14.17.2 contain information on the reported solvent releases and transfers from the motor vehicle assembly industry. The data show that solvent use is very large compared with all industries covered so far in our discussion except for the steel and iron industry. The motor vehicle assembly industry is the sixth largest producer of VOC and also the sixth largest industry in reported emissions and transfers.

The data in Tables 14.17.1 and 14.17.2 are data from 1995 the most recent available. The automotive industry and associated paint companies conduct extensive work on replacement of VOC containing paint systems. These efforts are mainly directed to water-based systems and powder coatings. Until recently, water-based systems were preferred but now attention is shifting to powder coatings which eliminate VOC. There is no status quo. Changes are dynamic and kept protected by trade secrets which makes it difficult to comment on specific progress. Solvent use by the European industry[5] is that the production of one car requires an average of 10 kg of solvents. Solvents use is not the only problem the industry is facing. 16% of the total energy used in car production is required by painting and finishing operations. Both energy conservation and reduction is solvent consumption must be pursued to meet environmental objectives. Not only can these issues be addressed through material reformulation but the design of equipment used in applying and drying the coating can also reduce emission and save energy.

A new trend is apparent as plastics are introduced to automotive production. Plastic parts must also be painted. Paint systems are difficult to select. Chlorinated polyolefins provide good adhesion of paints and reduce VOC but are also under scrutiny because of pres-

**Table 14.17.1. Reported solvent releases from the motor vehicle assembly industry in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| benzene | 13,000 | methyl ethyl ketone | 2,320,000 |
| n-butyl alcohol | 2,260,000 | methyl isobutyl ketone | 3,060,000 |
| sec-butyl alcohol | 86,000 | N-methyl-2-pyrrolidone | 193,000 |
| tert-butyl alcohol | 4,200 | methyl tert-butyl ether | 32,000 |
| cyclohexane | 35,000 | tetrachloroethylene | 140,000 |
| dichloromethane | 380,000 | 1,1,1-trichloroethane | 730,000 |
| ethylbenzene | 1,370,000 | trichloroethylene | 1,300,000 |
| ethylene glycol | 180,000 | 1,2,4-trimethylbenzene | 1,120,000 |
| isopropyl alcohol | 9,000 | toluene | 2,610,000 |
| hexane | 95,000 | xylene | 10,800,000 |
| methanol | 1,550,000 | m-xylene | 25,000 |

**Table 14.17.2. Reported solvent transfers from the motor vehicle assembly industry in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| benzene | 3,400 | methyl ethyl ketone | 2,100,000 |
| n-butyl alcohol | 1,030,000 | methyl isobutyl ketone | 4,700,000 |
| sec-butyl alcohol | 9,000 | N-methyl-2-pyrrolidone | 330,000 |
| tert-butyl alcohol | 1,000 | methyl tert-butyl ether | 2,300 |
| cyclohexane | 670 | tetrachloroethylene | 49,000 |
| dichloromethane | 450,000 | 1,1,1-trichloroethane | 140,000 |
| ethylbenzene | 1,740,000 | trichloroethylene | 480,000 |
| ethylene glycol | 605,000 | 1,2,4-trimethylbenzene | 330,000 |
| isopropyl alcohol | 2,000 | toluene | 2,020,000 |
| hexane | 25,000 | xylene | 9,200,000 |
| methanol | 760,000 | m-xylene | 2,100 |

ence of chlorine. Powder coatings are available[7] but they require a high energy input. These problems are apparent but the solution to them will take several years to implement due, in large part, to the long term testing needed to confirm coating performance (up to 5 years in Florida).

**Table 14.18.1. Reported solvent releases from the organic chemical industry in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| allyl alcohol | 31,000 | ethylbenzene | 370,000 |
| benzene | 690,000 | ethylene glycol | 6,050,000 |
| n-butyl alcohol | 850,000 | hexane | 600,000 |
| sec-butyl alcohol | 63,000 | isopropyl alcohol | 150 |
| tert-butyl alcohol | 430,000 | methanol | 8,750,000 |
| carbon disulfide | 85,000 | methyl ethyl ketone | 260,000 |
| carbon tetrachloride | 10,000 | methyl isobutyl ketone | 520,000 |
| chlorobenzene | 27,000 | N-methyl-2-pyrrolidone | 350,000 |
| chloroform | 7,000 | methyl tert-butyl ether | 64,000 |
| cresol | 280,000 | pyridine | 120,000 |
| m-cresol | 320,000 | tetrachloroethylene | 20,000 |
| o-cresol | 270,000 | toluene | 1,040,000 |
| p-cresol | 162,000 | 1,2,4-trichlorobenzene | 41,000 |
| cyclohexane | 450,000 | 1,1,1-trichloroethane | 130,000 |
| cyclohexanol | 1,100,000 | trichloroethylene | 18,000 |
| dichloroethane | 120,000 | xylene | 350,000 |
| 1,2-dichloroethylene | 70 | m-xylene | 59,000 |
| dichloromethane | 310,000 | o-xylene | 34,000 |
| N,N-dimethylformamide | 25,000 | p-xylene | 660,000 |
| 1,4-dioxane | 12,000 | | |

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**Table 14.18.2. Reported solvent transfers from the organic chemical industry in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| allyl alcohol | 210,000 | ethylbenzene | 980,000 |
| benzene | 420,000 | ethylene glycol | 6,800,000 |
| n-butyl alcohol | 1,500,000 | hexane | 770,000 |
| sec-butyl alcohol | 1,700,000 | isopropyl alcohol | 85,000 |
| tert-butyl alcohol | 12,500,000 | methanol | 23,000,000 |
| carbon disulfide | 96,000 | methyl ethyl ketone | 800,000 |
| carbon tetrachloride | 12,000 | methyl isobutyl ketone | 390,000 |
| chlorobenzene | 130,000 | N-methyl-2-pyrrolidone | 110,000 |
| chloroform | 92,000 | methyl tert-butyl ether | 210,000 |
| cresol | 430,000 | pyridine | 33,000 |
| m-cresol | 720,000 | tetrachloroethylene | 138,000 |
| o-cresol | 57,000 | toluene | 4,400,000 |
| p-cresol | 870,000 | 1,2,4-trichlorobenzene | 8,000 |
| cyclohexane | 900,000 | 1,1,1-trichloroethane | 290,000 |
| cyclohexanol | 3,700 | trichloroethylene | 42,000 |
| dichloroethane | 230,000 | xylene | 4,000,000 |
| 1,2-dichloroethylene | 1,000 | m-xylene | 51,000 |
| dichloromethane | 870,000 | o-xylene | 460,000 |
| N,N-dimethylformamide | 370,000 | p-xylene | 1,700 |

## 14.18 ORGANIC CHEMICAL INDUSTRY

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The chemical industry operates about 1000 plants in the USA with 53 companies producing 50% of the total output of $65 billion in sales and employing 125,000 people. There are point source solvent emissions (e.g., laboratory hoods, distillation units, reactors, storage tanks, vents, etc.), fugitive emissions (e.g., pump valves, flanges, sample collectors, seals, relief devices, tanks), and secondary emissions (waste water treatment units, cooling towers, spills). Organic liquid wastes containing solvent are generated from processes such as equipment washing, surplus chemicals, product purification, product reaction, housekeeping, etc.

Tables 14.18.1 and 14.18.2 give the reported solvent releases and transfers from the organic chemical industry. Large quantities of solvents are involved. The organic chemical industry produced the second largest quantity of VOC and the second largest releases and transfers. The industry is actively working to reduce solvent use because of the high costs (waste treatment, fines, liabilities, etc). There are many efforts under way to reduce environmental emissions and improve safe practices. The initiatives include process modifications such as a reduction in non-reactive materials (e.g., solvents) to improve process efficiency, a reduction in the concentration of chemicals in aqueous solution, and improved R&D and process engineering. Equipment modifications are planned to reduce leaks, prevent equipment breakdown, and improve the efficiency of emission control devices.

## REFERENCES

1 EPA Office of Compliance Sector Notebook Project. Profile of the Organic Chemical Industry. US Environmental Protection Agency, 1995.
2 EPA Office of Compliance Sector Notebook Project. Sector Notebook Data Refresh - 1997. US Environmental Protection Agency, 1998.

## 14.19 PAINTS AND COATINGS

### 14.19.1 ARCHITECTURAL SURFACE COATINGS AND SOLVENTS

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### 14.19.1.1 General aspects

Coating materials and coating techniques can be distinguished and systematized in various ways.

The fundamental principles of common coating systems are:[1]

- *Physical drying*. A solid surface film is formed after the evaporation of water or organic solvents.
- *Physico-chemical drying/curing*. Polycondensation or polyaddition are combined with evaporation of organic solvents.
- *Chemical curing*. Solvents, e.g., styrene or acrylic monomers, react with the curing system.

The actual effects depend on the surrounding conditions and the ingredients of the coating system, e.g., solvents.

Solvents contribute many essential properties to coating systems. Solvents can improve technical factors such as application or surface properties. Solvents also bring negative qualities to coating materials, especially with respect to environmental conditions (e.g., toxic effects of emitted organic solvents).

### 14.19.1.2 Technical aspects and properties of coating materials

Application techniques for coatings can be considered in various ways. The stability and durability of coating is essential. Coatings that have normal wear and tear requirements are mainly based on oils and aldehyde resins. Higher durability or stability can be achieved by the use of one of the following one- or two-component systems.

One-component:
- Bituminous materials
- Chlorinated rubber
- Polyvinyl chloride
- Polyacrylic resin
- Polyethene
- Saturated polyester
- Polyamide

Two-component:
- Epoxy resin
- Polyurethane
- Mixtures of reactive resins and tar

A survey of the performance of different coating materials together with an assessment of various environmental factors is given in Table 14.19.1.1.

**Table 14.19.1.1. Environmental performance of some coating materials**

| Material | Abbreviation | Weathering response | Acid atmosphere | Humidity | Under water | Chemical stress | | Solvent | Temperature <60°C | Mechanical | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | acid | alkali | | | abrasion | scratch |
| plant oil (linseed oil) | OEL | +y,s,f | +/- | +/- | - | - | -s | - | + | - | - |
| alkyd resin | AK | + | +/- | +/- | - | - | -s | - | + | - | - |
| bitumen | B | +/-e,f | + | + | + | +/- | + | - | +/- | - | - |
| chlorinated rubber | RUC | +/-b,c,f | + | + | + | + | + | - | + | +/- | +/- |
| PVC-soft | PVC | +/-e,f | + | +/- | +/- | + | +/- | - | + | +/- | +/- |
| Polyacrylic resin | AY | + | + | + | + | + | + | - | + | + | +/- |
| polyethene | PE | +/-e | + | + | + | + | + | + | + | + | + |
| polyester (saturated) | SP | + | + | +/- | +/- | + | +/-(s) | + | + | + | + |
| epoxy resin | EP | +/-c,g | + | + | + | +/- | + | + | + | + | + |
| polyurethane | PU | + | + | +/- | +/- | + | +/- | +/- | + | + | + |
| epoxy resin tar | EP-T | +/-c,e | + | + | + | +/- | + | +/- | + | + | + |
| polyisobutylene | PLB | +/- | + | + | + | + | + | - | + | + | + |

+ = suitable, +/- = limited suitability, - = unsuitable, () = less distinct; b = bleaching, c = chalking, e = embrittlement, f = acid fragments, g = loss of gloss, s = saponification, y = yellowing

The following are examples of architectural surface coatings.

#### *14.19.1.2.1 Concrete coating materials*

According to DIN 1045 concrete must be protected against aggressive substances if the chemical attack is severe and long-term. These are the requirements:

- Good adhesion
- Waterproof and resistant to aggressive substances and resistant to the alkalinity of the concrete
- Deformable

To realize these requirements, the following technical solutions can be applied:

- The use of paint coatings based on duroplast or thermoplastic substances
- Surface treatment - impregnation

Protective coatings based on polymers are used in construction with and without fillers and with or without reinforcing materials (fibers).

The following techniques are generally used:

- Film forming paint coatings (brushing, rolling, spraying).
- Coating (filling, pouring).

During application, the coating materials are normally liquid and subsequently harden by evaporation of solvents or as a result of chemical reactions.

The common coating systems for concrete are listed in Table 14.19.1.2. Synthetic resins (e.g., chlorinated rubber, styrene resins, acrylic resins) contain normally 40-60% solvents and form a thin film. Several coats must be applied. Reactive resins may require little or no solvent.

**Table 14.19.1.2. Survey of often used coating systems for concrete**

| Film-forming agents | Hotmelts | Film-forming agents dissolved | Film-forming agents emulsified | Reaction resin liquid |
|---|---|---|---|---|
| Bituminous substances | + | + | + | |
| Synthetic resin | | + | + | |
| Reactive resins | | (+) | (+) | + |

#### *14.19.1.2.2 Coating materials for metals*

Wet coating processes are detailed in Table 14.19.1.3.

**Table 14.19.1.3. Wet coatings - coating materials for metals**

| | | Abbreviation | Application | State | Curing method |
|---|---|---|---|---|---|
| Natural substances | oil | OEL | binders for wet coating | liquid | oxidizing |
| | bitumen | B | | | physical |
| | tar | T | | | physical |
| Plastic materials | alkyd resin | AK | binders for wet coating | | oxidizing |
| | polyurethane | PU | | | chemical |
| | epoxy resin | EP | | | chemical |
| | acrylic resin | AY | | | physical |
| | vinyl resin | PVC | | | physical |
| | chlorinated | RUC | | | physical |
| | rubber | | | | |

The chemical properties of binders are not affected by the drying process if coatings are of physically drying type. After solvent has evaporated, the polymer molecules become intermeshed, thus producing the desired coating properties.

In contrast to physical drying, binders based on reactive resins such as epoxy resins, polyurethanes or polyesters consist of two components (liquid resin and curing agent) which are either mixed shortly before the coat is applied, or, in the case of a one component system, one which is applied as slow reacting mixture. The setting reaction occurs at the surface of the coated material. The final products are normally more resistant and more compact than products based on physically drying binders. Pretreatment of substrate is more critical for applications where chemically hardening products are applied. Coatings can be more or less permeable to water vapor and oxygen. Damage to the metal substrate can occur if water and oxygen reach the reactive surface simultaneously. This is normally impossible if the coatings adhere well and the coated surface is continuous. The adhesion of the coating also prevents the penetration by harmful substances via diffusion processes. Adhesion is enhanced by adsorption and chemical bonds.

### *14.19.1.2.3 Other coating materials*

Other aspects of solvents contained in paint coatings and varnishes are given in Chapter 18.3.

The market offers a wide spectrum of coating systems. Examples of common industrial coating materials are listed in Table 14.19.1.4 and relevant aspects concerning application and environmental or health risks are also included.

## Table 14.19.1.4. Examples of coating materials containing hazardous ingredients, especially solvents[3]

| Product group/ compounds | Application | Hazardous ingredients, especially solvents | Relevant health and environmental risks |
|---|---|---|---|
| zinc dust coating based on epoxy resin | corrosion protection/primer, application by brush, spray, airless-spraying | xylene 2,5-25%, ethylbenzene 2,5-10%, solvent naphtha 2,5-10%,1-methoxy-2-propanol 1-2,5% | irritations (respiratory, skin, eyes), neurological (narcotic) effects, absorption (skin), flammable, explosive mixtures |
| reactive PUR-polymers containing solvents | corrosion protection/coating | solvent naphtha 10-20%, diphenylmethane isocyanate 2,5-10% | sensitization (respiratory) irritation (skin, eyes, gastrointestinal tract), neurological effects (narcotic effects, coordination), absorption (skin), flammable, water polluting |
| modified polyamine containing solvents | corrosion protection/coatings/rigid system | 4-tert-butylphenol 10-25%, M-phenylenebis 2,5-10%, trimethylhexane, 1,6-diamine 10-25%, nonylphenol, 10-25% xylene 10-25%, ethylbenzene 2,5-10% | sensitization (skin, respiratory), irritations (skin, eye, respiratory, gastrointestinal tract), neurological (narcotic) effects (coordination), flammable, water polluting |
| modified epoxy resin containing solvents | corrosion protection/coatings/ rigid system | bisphenol A (epichlorohydrin) 25-50% oxirane, mono($C_{12}$ -$C_{14}$-alkyloxy)methyl derivatives 2,5-10%, cyclohexanone 1-2,5%, 2-methylpropane-1-ol 2,5-10%, xylene 10-25%, ethylbenzene 2,5-10%, benzyl alcohol 1-2,5%, 4-methyl-pentane-2-one 1-2,5% | irritations (skin), sensitization (skin, contact), neurological (narcotic) effects, absorption (skin), flammable, water polluting |
| modified epoxy resin containing solvent | corrosion protection/top layer | bisphenol A (epichlorohydrin) 50-100%, 3-amino-3,5,5-trimethyl ethylbenzene 10-25%, xylene 10-25% | irritation (skin, eyes, respiratory), sensitization (skin), flammable, explosive gas/air mixtures, hazardous reactions (with acids, oxidizers), water polluting |
| filled and modified epoxy resin | coatings and corrosion prevention/ pore sealer | bisphenol A (epichlorohydrin) 50-100%, P-tert-butylphenyl-1-(2,3-epoxy)propyl-ether 1-2,5% | irritations, sensitization, water polluting |
| filled and modified epoxy resin | coatings and corrosion prevention/ pore sealer | trimethylhexamethylendiazine-1,6-diamine 10-25%, trimethylhexamethylendiamine -1,6-cyanoethylene 50-100% | irritations, sensitization, water polluting |

| Product group/ compounds | Application | Hazardous ingredients, especially solvents | Relevant health and environmental risks |
|---|---|---|---|
| filled and modified epoxy resin | flooring/mortar screen | bisphenol A (epichlorohydrin) 25-50%, benzyl butyl phthalate 2,5-10%, xylene 2,5-10% | irritation (eye, skin, respiratory), sensitization (contact, skin), explosive gas/ air mixtures (with amines, phenols), water polluting |
| modified polyamine | flooring/mortar screen | benzyl alcohol 10-25%, nonylphenol 25-50%, 4,4´-methylenebis(cyclohexylamine) 10-25%, 3,6,9-triazaundecamethylendiamine 10-25% | irritation (eye, skin, respiratory), sensitization (contact, skin), hazardous reactions (with acids, oxidizers), flammable, water polluting |
| filled and modified epoxy resin | corrosion protection/top layer | naphtha 2,5-10%, 2-methoxy-1-methylethylacetate 2,5-10%, 2-methylpropane-1-ol 1-2,5%, xylene 10-25%, ethylbenzene 2,5-10% | irritation (skin, eyes, respiratory), neurological (narcotic) effects, flammable, explosive, hazardous reactions (with oxidizers), water polluting |
| copolymer dispersion | walls, especially fungicidal properties, good adhesion in damp environment, resistant against condensed water | isothiazolone 1-2,5%, 3-methoxybutylacetate 1-2,5% | irritations (skin, eyes, gastrointestinal tract), water polluting |
| coating of synthetic resin containing solvents | corrosion protection/coating (steel) | solvent naphtha (petroleum) 25-50 %, xylene 2,5-10%, ethylbenzene 1-2,5% | irritations (eyes, skin, respiratory, gastrointestinal tract), neurological (narcotic) effects, flammable, explosive gas/air mixtures, hazardous reactions (with oxidizers), water polluting |
| bituminous emulsion (phenol-free, anionic) | corrosion protection/coating (steel, drinking water tanks) | naphtha (petroleum) 25-50% | irritations (skin, eyes, respiratory), neurological effects (coordination), flammable, water polluting |
| modified, filled anthracene oil and polyamine | corrosion protection/top layer | solvent naphtha 2,5-10%,<br>biphenyl-2-ol 2,5-10%,<br>3-amino-3,5,5-trimethylcyclohexamine 1-2,5%,<br>xylene 1-2,5% | irritations (skin, eyes, respiratory), flammable, water polluting |
| partially neutralized composition of aminoalcohols | sealants and adhesives/elastic products (floor joints, joints) | 2-aminoethanol 2,5-10% | sensitization, irritations, slight water pollution |

| Product group/ compounds | Application | Hazardous ingredients, especially solvents | Relevant health and environmental risks |
|---|---|---|---|
| filled, reactive PUR-polymers | sealants and adhesives/elastic products (floor joints, joints) | 3-isocyanatemethyl-3,5,5-trimethylcyclohexylisocyanate 0,1-1%, N,N-dibenzylidenepolyoxypropylene diamine 1-2,5%, xylene 2,5-10%, ethylbenzene 1-2,5% | sensitization, irritations, hazardous reactions (with amines, alcohols) |
| solvent based composition, based on PVC | coatings and corrosion prevention/impregnation, sealer | solvent naphtha 50-100%, 1-methoxy-2-propanol 2,5-10%, | irritations, flammable, neurological effects |
| acrylate dispersion, water dispersed adhesion, promotor | coatings and corrosion protection/ rigid coat (for concrete and dense mineral substrates) | water-borne so-called solvent-free systems | irritations (long-term contact), slightly water polluting |

## References

1 **Ullmann´s Encyclopedia of Industrial Chemistry**,1998.

2 DIN 1045 (Deutsches Institut für Normung), Concrete and Reinforced Concrete. Beton und Stahlbeton, Beuth Verlag, Berlin (1988), part 1 (1997), part 2 (1999).

3 Sika TechnoBauCD, Sika Chemie GmbH, Stuttgart (2000).

## 14.19.2 RECENT ADVANCES IN COALESCING SOLVENTS FOR WATERBORNE COATINGS

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### 14.19.2.1 Introduction

The role of coalescing solvents in coating formulations, the factors which affect the choice of coalescing solvents, and the recent developments in esters of low volatility, low odor and rapid biodegradability for use in coating formulations are discussed.

The term "paint" is widely used to describe a coating applied to a variety of substrates for protective or decorative purposes. "Paint" also implies a pigmented species, whereas "surface coatings" is a broader term for coating systems with or without pigments used for any coating purpose.

All paint systems may be considered as a combination of a small number of constituents. These are: continuous phase or vehicle (polymer and diluent), discontinuous phase or pigment and extender, and additives.

This paper is not concerned with the detail of paint formulation, but the polymer types most widely encountered are alkyds, polyurethanes and nitrocellulose in solvent based systems, and acrylics, styrene-acrylics, and copolymers of vinyl acetate in water-based coatings.

### 14.19.2.2 Water based coatings

Until recent times, most paints were solvent based. Since many polymers were produced in solution, it was natural that the coating system, derived from these polymers, would use the solvent of reaction as the diluent for the polymer. These were almost invariably organic species. The objections to the use of organic solvents in paint formulations were at first confined to those with strong views regarding the loss of significant quantities of organic species to the environment. Latterly, these opinions have been reinforced by the role of some organic species in damage to the ozone layer, or to the production of smog in the lower atmosphere. This is as a result of the reaction between organic species present catalyzed by sunlight and exacerbated by the presence of other pollutants associated with motor vehicles, etc. Flammability of paints also poses a significant problem in storage and use.

All this tended to reinforce the need to develop aqueous based systems, for which these problems would be eliminated.

### 14.19.2.3 Emulsion polymers

Of course, the manufacture of polymers need not be carried out in solution; emulsion polymerization has a long and honorable tradition in the field of macromolecular chemistry. This polymerization technique is performed using water-insoluble monomers, which are caused to form an emulsion with the aqueous phase by the addition of a surfactant. Polymerization may be effected by the use of a variety of radical generating initiating species, and the molecular weight of the polymer is controlled by the use of chain transfer agents and the concentration of initiator employed. The final polymer dispersion is often described as a latex, named after natural rubber, which is also an emulsion polymer!

This polymerization technique allows for the formation of copolymers in which the addition of relatively small quantities of comonomer may have a significant effect on the final properties of the polymer. This is particularly the case with the glass transition temperature, $T_g$, of the polymer. This is a physical transition, which occurs in the polymer when the amorphous structure of that polymer begins to change from a glassy to a rubbery state. At temperatures below a polymer's $T_g$, it will be relatively brittle, and will be unlikely to form a coherent film.

This effect has a major impact on the use of polymers in aqueous systems. In the case of a polymer in solution, the presence of the solvent plasticizes the polymer during film formation. A polymer with a high $T_g$, i.e., one greater than ambient temperature, can, when in solution be applied at temperatures below its $T_g$. In the case of an emulsion polymer, water is a non-solvent in the system and film formation below the polymer $T_g$ is unlikely. The temperature at which a coherent film may be formed from a solution or emulsion based system is known as the Minimum Film Forming Temperature (MFFT or MFT).

Figures 14.19.2.1-14.19.2.4 describe the formation of a discrete film from an emulsion system.

When the film is applied onto the substrate, discrete polymer particles are dispersed in the aqueous phase. The system is stabilized by the presence of the surfactant at the water-particle interface. The particles are spherical, with an average diameter of 0.1-0.2 μm.

As water is lost from the system, the mutual repulsive forces associated with the surfactants present inhibit the close packing of the particles and a cubic arrangement of the particles is formed.

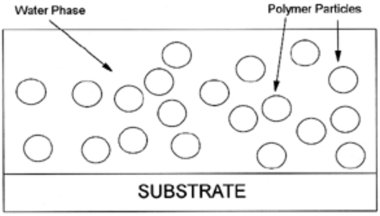

Figure 14.19.2.1. Latex in contact with substrate.

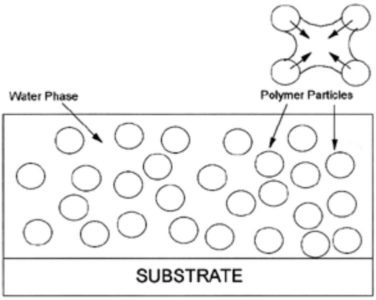

Figure 14.19.2.2. Initial water evaporation and film formation.

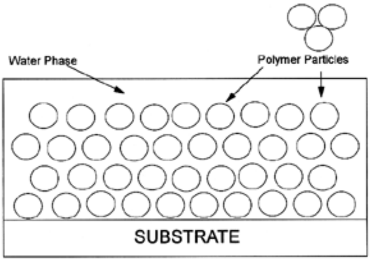

Figure 14.19.2.3. Close packing of latex particles.

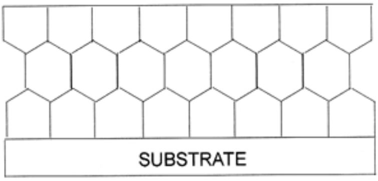

Figure 14.19.2.4. Coalescence to form a polymeric film.

As the water continues to evaporate, the particles become close packed with a solids volume of around 70%. Capillary forces continue to force the particles together.

The final stage is achieved when most of the water is lost from the system. Here, the interparticular repulsive forces are overcome by increasing surface tension and the particles coalesce into a discrete film. This will only occur at temperatures in excess of the MFFT.

### 14.19.2.4 Role of a coalescing solvent

Most coatings based on emulsion polymers are used in environments where they will be expected to form a coherent film at temperatures as low as 0°C. However, other physical properties besides film forming capability are required from the polymer. These include; abrasion resistance, hardness, chemical resistance, impact performance, etc. These can often be impossible to achieve with a polymer of low $T_g$. The polymers, which most clearly meet these criteria are acrylics or copolymers of vinyl acetate or styrene. These would, without additions of coalescing species, be brittle, forming incoherent films with little adhesion to the substrate at normal application temperatures.

Coalescing solvents allow these polymeric systems to form films at ambient or sub-ambient temperatures. The presence of the coalescing solvent has the following effects.

- It reduces the total surface energy of the system by reducing polymer surface area.
- It increases the capillary forces by the controlled evaporation of the water.
- It reduces the repulsive forces between the polymeric particles.
- It allows deformation of the particles in contact with each other by effectively lowering the $T_g$ of the polymer.

An emulsion polymer consists of a dispersion of polymeric particles varying in size from 0.05-1 μm, dispersed in an aqueous environment. The coalescing solvent may be found in several different locations depending on their nature. They are classified according to their preferred location in the aqueous system.

Hydrophobic substances such as hydrocarbons will prefer to be within the polymer particle; these are described as A Group coalescents. These tend to be inefficient coalescing agents. Molecules, which are more hydrophilic than hydrocarbons tend to be preferentially sited at the particle - aqueous interface, along with the surfactant system. These are described as AB Group coalescents. These exhibit the best efficiency as coalescing solvents.

In the third group are the hydrophobic glycol ethers and similar species. These exhibit good coalescing power, but are partitioned between the polymer particle, the boundary layer, and the aqueous phase. More of these are required than AB Group coalescents, they are called ABC Group coalescents. Finally, hydrophilic species such as glycols and the more polar glycol ethers are inefficient coalescing agents, and are more commonly used as freeze thaw stabilizers. These are described as C Group coalescents.

### 14.19.2.5 Properties of coalescing agents

#### *14.19.2.5.1 Hydrolytic stability*

A coalescing agent should have good hydrolytic stability (a high degree of resistance to hydrolysis) so that it can be used successfully in both low and high pH latex systems.

#### *14.19.2.5.2 Water solubility*

It is desirable for a coalescing aid to have low water miscibility for the following reasons:

- When added to a coating formulation, a coalescing aid with low water miscibility partitions into the polymer phase and softens the polymer; this improves pigment binding and polymer fusion.
- There is less tendency for the evaporation of the coalescing aid to be accelerated by evaporation of the water during the early stages of drying.
- The early water resistance of the coating is not adversely affected.
- When a latex coating is applied to a porous substrate, water immiscible coalescing aids are not lost into the porous substrate along with the water; i.e., more coalescing aid will be available to coalesce the coating.

#### *14.19.2.5.3 Freezing point*

The freezing point of a coalescing agent should be low (below -20°C) as materials with a high freezing point may require specialized (therefore more expensive) handling techniques in transport and storage.

#### *14.19.2.5.4 Evaporation rate*

The evaporation rate of a coalescing aid should be slow enough to ensure good film formation of the emulsion coating under a wide range of humidity and temperature conditions; however, it should be fast enough to leave the coating film in a reasonable length of time and not cause excessive film softness. The evaporation rate of the coalescing aid should be less than that of water but not so slow that it remains in the film for an extended period of time causing dirt pickup.

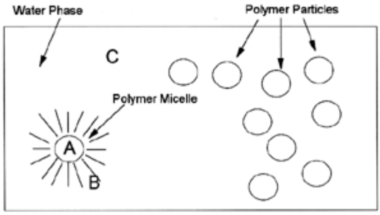

Figure 14.19.2.5. Location of species in aqueous dispersions.

#### *14.19.2.5.5 Odor*

The odor of a coalescing agent should be minimal. This is especially important for interior coatings applications.

#### *14.19.2.5.6 Color*

A coalescing agent should be colorless, to prevent discoloration of the product.

#### *14.19.2.5.7 Coalescing efficiency*

The effectiveness of a coalescing agent is based upon the MFFT test.

#### *14.19.2.5.8 Incorporation*

A good coalescing agent should be capable of addition during any stage of paint manufacture. Any particular coalescing agent may need premixing prior to addition with varying amounts of the water and surfactant used in the paint stage.

#### *14.19.2.5.9 Improvement of physical properties*

A good coalescing agent can provide a significant improvement in scrub resistance, stain resistance, flexibility and weatherability.

#### *14.19.2.5.10 Biodegradability*

A good coalescing agent should exhibit acceptably rapid biodegradation quickly.

#### *14.19.2.5.11 Safety*

The use of the coating system requires that the nature of the coalescing agent should permit use in the domestic environment. The suitability of such a material is therefore obviously dependent on its toxicity, flash point, vapor pressure and VOC classification.

### 14.19.2.6 Comparison of coalescing solvents

From the above, it may readily be seen that AB type coalescing solvents give the best performance in use. These are the high molecular weight esters and ester alcohols. Other species have some of the benefits of these materials but have side effects, which render them less suitable. Minimization of the quantity used tends to be a key financial issue, as well as offering the best environmental option. In virtually all cases, the efficiency of the AB group in application is so marked, that they have become the industry standards. Several other properties, perhaps less important, than efficiency must then be considered when selecting between these.

These products are usually used in enclosed spaces, where product odor will be vital for acceptance to the consumer. The dibasic esters are virtually odor free. For legislative reasons, a solvent not classified as a VOC will be of definite benefit, given the current attitude to organics in consumer products. Again, the dibasic esters have initial boiling points considerably above the VOC threshold of 250°C.

The stability of the product towards hydrolysis is also a significant factor in the selection of the optimum coalescing agent. Effectively, this parameter determines the storage stability of the product. Again, dibasic esters, particularly those produced from higher molecular weight alcohols appear to have advantage.

The efficiency of the AB group of coalescents towards almost all polymer types has already been mentioned. For styrene-acrylics and vinyl acetate - Veova copolymers, the diesters have a significant edge in performance compared with other members of that group. This advantage is shown in the reduction in amount required to attain a particular MFFT or the actual MFFT for a given addition level.

Coasol manufactured by Chemoxy is the blend of di-isobutyl esters of the dibasic acids; adipic, glutaric and succinic. These acids are produced as a by-product in the production of adipic acid in the manufacture of Nylon 6,6. The ratio of the acids is 15-25% adipic, 50-60% glutaric, 20-30% succinic. Esterification using isobutanol is then performed and the product is isolated following distillation. Coasol was introduced in the early part of last decade as a coalescing agent to the aqueous based coatings industry.

Coasol has excellent coalescing properties and is compatible with virtually all paint systems. It has very low vapor pressure at ambient temperature which ensures excellent plasticization throughout the film forming and drying process. Its extremely low odor also significantly improves the general view that aqueous systems have unpleasant odors. This is almost always as a result of the coalescing solvent. Its resistance to hydrolysis allows its use in a wide variety of formulations, including those, which require adjustment of pH to basic conditions.

It rapidly biodegrades, both aerobically and anaerobically, since, as an ester, it is readily attacked by ubiquitous bio-species. Finally, its toxicological profile is virtually benign, so in use it can be handled with confidence in most working environments. Its properties are summarized in Table 14.19.2.1.

**Table 14.19.2.1. Properties of Coasol**

| Physical Characteristic | Coasol | Comments |
|---|---|---|
| Boiling point | > 275°C | Not a VOC |
| Evaporation rate | < 0.01 (Butyl acetate = 1.0) | Slow, allowing excellent coalescence |
| Freezing point | < -55°C | No freeze-thaw issue |
| Water solubility | 600 ppm | |
| Hydrolytic stability | Very Good | No hydrolysis in normal use |
| Color | 5 Hazen units | Imparts no color to coatings |
| Coalescing efficiency | Excellent for most polymer systems | |
| Biodegradability | 80% in 28 days | Biodegradable |
| Odor | None discernible | |
| Toxicology | Oral LD50 (Rat) >16,000 mg/kg | Essentially non toxic |

### 14.19.2.7 RECENT ADVANCES IN DIESTER COALESCING SOLVENTS

We have also prepared the di-isopropyl esters of the higher adipic content stream. This has a vapor pressure similar to that of Coasol, but is slightly more water soluble. Finally, we have manufactured di-isopropyl adipate, which has the highest boiling point, the lowest vapor pressure and the lowest water solubility of all of this range of products. These preparations were undertaken to add to repertoire of products to suit the diverse requirements of the formulators of aqueous based systems.

In virtually all cases, the dibasic esters gave a significant improvement in efficiency in reducing the MFFT for a given quantity of additive. The attempts are made to offer a tailor made solution to each individual polymer system employed in the development of aqueous based systems. The dibasic esters of the AGS acids group offer the opportunity for fine tuning, with the added advantage of low odor, low toxicity and “excellent” VOC status.

### 14.19.2.8 Appendix - Classification of coalescing solvents

| Coalescent Type | Type of Species | Examples | Comments |
|---|---|---|---|
| Type A | Hydrocarbons | White Spirit | |
| Type AB | Diesters | DBE Dimethyl esters<br>DBE Diisobutyl esters<br>Di-isobutyl adipate<br>Di-isopropyl adipate<br>Dibutyl phthalate | Estasol, Du Pont<br>DBE's<br>Coasol, Lusolvan<br>Chemoxy new products |
| Type AB | Ester alcohols | Diol Monoesters | Texanol |
| Type ABC | Glycol esters & Glycol ester ethers | PGDA<br>Butyldiglycol acetate | |
| Type ABC | Ether alcohols & diethers | PnBS<br>2-Butoxyethanol<br>MPG Diethers | Dow Products<br>BASF and others<br>Proglides and glymes |
| Type C | Glycols | DEG<br>DPG<br>TEG | |

## 14.20 PETROLEUM REFINING INDUSTRY

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The US petroleum refining industry generates sales of over \$140 billion with only about 200 plants. It employs 75,000 people. About 90% of the products used in US are fuels of which 43% is gasoline. Figure 14.20.1 illustrates how the products breakdown. The process is described in detail in Chapter 3. Emissions of hydrocarbons to the atmosphere occur at almost every stage of the production process. Solvents are produced in various processes and they are also used to extract aromatics from lube oil feedstock, deasphalting of lubricating base stocks, sulfur recovery from gas stream, production of solvent additives for motor fuels such as methyl tert-butyl ether and tert-amyl methyl ether, and various cleaning operations. Emissions to atmosphere include fugitive emissions of the volatile components of crude oil and its fractions, emissions from incomplete combustion of fuel in heating system, and various refinery processes. Fugitive emissions arise from thousands of valves, pumps, tanks, pressure relief valves, flanges, etc. Individual leaks may be small but their combined quantity results in the petrochemical industry contributing the largest quantity of emissions and transfers.

Tables 14.20.1 and 14.20.2 give solvent releases and transfers data for the petroleum refining industry. Transfers are small fraction of releases which means that most wastes are processed on-site.

In addition to emissions to atmosphere, some plants have caused contamination of ground water by releasing cooling and process water.

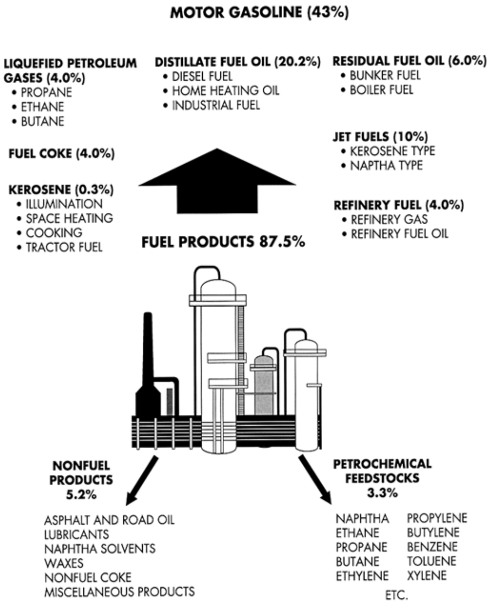

Figure 14.20.1. Diagram of production outputs from refineries. [Reproduced from EPA Office of Compliance Sector Notebook Project. Profile of the Petroleum Refining Industry. US Environmental Protection Agency, 1995.

Toluene, xylenes, and benzene constitute the majority of solvent emissions since they are native components of crude oil. Methyl ethyl ketone is also emitted in large quantities because of its use in lube oil dewaxing.

Pollution prevention will become increasingly important to the petroleum industry as federal, state and municipal regulations become more stringent and waste disposal cost rises. The industry estimates that to comply with 1990 Clean Air Act Amendments it will require investment of $35-40 billion. Actions required to decrease pollution include process equipment modification, waste segregation and separation, recycling, and better training and supervision.

**Table 14.20.1. Reported solvent releases from the petroleum refining industry in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| benzene | 1,750,000 | methyl isobutyl ketone | 110,000 |
| n-butyl alcohol | 23,000 | N-methyl-2-pyrrolidone | 280,000 |
| tert-butyl alcohol | 28,000 | methyl tert-butyl ketone | 1,380,000 |
| carbon tetrachloride | 17,000 | tetrachloroethylene | 21,000 |
| cresol | 75,000 | 1,1,1-trichloroethane | 50,000 |
| cyclohexane | 960,000 | trichloroethylene | 730 |
| dichloromethane | 8,000 | 1,2,4-trimethylbenzene | 420,000 |
| ethylbenzene | 600,000 | toluene | 4,360,000 |
| ethylene glycol | 46,000 | xylene | 2,330,000 |
| hexane | 3,000,000 | m-xylene | 170,000 |
| methanol | 540,000 | o-xylene | 150,000 |
| methyl ethyl ketone | 2,100,000 | p-xylene | 1,000,000 |

**Table 14.20.2. Reported solvent transfers from the petroleum refining industry in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| benzene | 160,000 | N-methyl-2-pyrrolidone | 4,000 |
| tert-butyl alcohol | 900 | methyl tert-butyl ketone | 34,000 |
| carbon tetrachloride | 1,000 | tetrachloroethylene | 900 |
| cresol | 130,000 | 1,1,1-trichloroethane | 6,500 |
| cyclohexane | 10,000 | 1,2,4-trimethylbenzene | 31,000 |
| ethylbenzene | 61,000 | toluene | 270,000 |
| ethylene glycol | 58,000 | xylene | 340,000 |
| hexane | 13,000 | m-xylene | 11,000 |
| methanol | 180,000 | o-xylene | 30,000 |
| methyl ethyl ketone | 30,000 | p-xylene | 7,000 |
| methyl isobutyl ketone | 3,500 | | |

## REFERENCES

1 EPA Office of Compliance Sector Notebook Project. Profile of the Petroleum Refining Industry. US Environmental Protection Agency, 1995.
2 EPA Office of Compliance Sector Notebook Project. Sector Notebook Data Refresh - 1997. US Environmental Protection Agency, 1998.

# 14.21 PHARMACEUTICAL INDUSTRY

## 14.21.1 USE OF SOLVENTS IN THE MANUFACTURE OF DRUG SUBSTANCES (DS) AND DRUG PRODUCTS (DP)

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### 14.21.1.1 Introduction

Today the manufacturing of a pharmaceutical drug is almost totally the responsibility of:

- the chemical industry for the preparation of the drug substance (active principle) and the excipients used for preparing the DP (finished product)
- the pharmaceutical industry for the preparation of the DP itself.

For the reader who is not familiar with the pharmaceutical industry, a reminder of the key points is given below.

One or several active compounds (DS) are prepared by organic synthesis, extracted from vegetable, animals, micro-organisms or obtained by biotechnology. The DS is generally associated in the product with several excipients of chemical, mineral or biological in nature either as monomers or as polymers.

The goal is to formulate a processable DP stable over the time and allowing the active substance to be released in vitro and in vivo. Obviously the formulation is designed in relation to the route of administration:

- oral route solid dosage forms (e.g., tablets, capsules, etc.) drinkable solutions etc.
- ORL route (nasal solutions, spray)
- local route (suppositories, transdermal systems, eye-drop formulation, spray)
- intravenous and intramuscular route (injectable solution, lyophilizate, etc.)

At practically every step of the manufacture of the drug substance and the excipients, solvents including water are utilized. This is equally true for the preparation of the pharmaceutical formulations.

Ideally we would like to have available a universal stable solvent, ultrapure, non-toxic and which does not affect the solutes. This is an old dream of the alchemists who searched for a long time for the “Alkahest” or “Menstruum universal” as it was named by Paracelsus.[1]

The fact that a solvent is not a totally inert species allows it to play an important role in chemical equilibria, rates of chemical reactions, appearance of new crystalline forms, etc. and consequently contributes to the great wealth of compounds which the chemists are able to produce.

But of course, there are drawbacks in using solvents. Because there are not totally inert they may favor the formation of undesirable impurities in the intermediates of synthesis and in the DS. Regarding the manufacture of the DP, the solvents, including water, may induce either polymorphic transformations or formation of solvates (hydrates) which, after drying, could lead to a desolvated solvate with quite different physical properties impacting potentially either positively or negatively on the DP performance.[2]

Another crucial aspect which deserves to be discussed, is the notion of purity. Impurities present in solvents could have an impact on the stability of drugs, for example, or on the crystallization process.

Last, but not least, the toxicological aspects should be taken into account. Numerous solvents show different kinds of toxicity and this should be a matter of concern in relation to the health of workers exposed to them.[3] But ultimately residual solvents still present in the DS and DP have to be assessed and systematically limited.

We are now going to consider several aspects of the use of solvents in the manufacture of drug substances (DS) and drug products (DP) including their quality (purity) and influence on the quality, stability and physico-chemical characteristics of pharmaceutical products.

The issue of residual solvents in pharmaceutical products will be considered in Chapter 16.2 and will focus amongst other things on the corresponding ICH Guideline.[4]

## 14.21.1.2 Where are solvents used in the manufacture of pharmaceutical drugs?

### *14.21.1.2.1 Intermediates of synthesis, DS and excipients*

#### 14.21.1.2.1.1 General points

Raw materials are now produced by the chemical industry and involve the use of solvents at different steps in their production. These materials are usually produced by:

- chemical synthesis
- an extraction process, a fermentation process
- or a biotechnology process

The goal of this chapter is, of course, not to deal with the criteria for selection in relationship to their use in particular chemical reactions or extraction processes but rather to stress that impurities present in solvents could have an impact on the purity of the substances obtained, on their stability and potentially on their safety. These three concepts are of paramount importance in the pharmaceutical field.

A list of solvents which are commonly used in the chemical industry[5] is presented in Table 14.21.1.1.

**Table 14.21.1.1. Solvents commonly used in the chemical industry**

**Alcohols**
Ethanol
Butanol
2-Ethylhexanol
Isobutanol
Isopropanol
Methanol
Propanol
Propyleneglycol

**Amide**
Dimethylformamide

**Amine**
Pyridine

**Aliphatic hydrocarbons**
Cyclohexane
Hexane

**Ketones**
Acetone
Methyl ethyl ketone
Methyl isobutyl ketone
Methyl isopropyl ketone
Mesityl oxide

**Ethers**
1.4-Dioxane
Butyl ether
Ethyl ether
Diisopropyl ether
Tetrahydrofuran
Tert-butyl methyl ether (MTBE)

**Nitriles**
Acetonitrile

**Water**

**Halogenated solvents**
Ethylene bromide
Chloroform
Ethylene chloride
Dichloromethane
Tetrachloroethylene
Carbon tetrachloride
Trichloroethylene

**Sulphur-containing**
Dimethylsulfoxide

**Aromatics hydrocarbons**
Toluene
Xylene

**Esters**
Ethyl acetate

It is generally relatively easy to know for pharmaceutical industry the nature of solvents to be looked for in a DS because it produces itself the active component or because it can have by contract an access to the DS Mater File or because there is a compendial monograph giving occasionally some indications (e.g., search for benzene in carbomers).

As a consequence of the ICH Guideline Q3C[4] dealing with the residual solvents in pharmaceutical products (see Chapter 16.2), the use of solvents of class I (solvents to be avoided) like benzene is no more possible. It is known that carbopol resins (carbomer), used to modify the rheology of polar systems and as a binder in sustained release tablets, were up to now polymerized in benzenic medium. In the current quality of poloxamers it was possible to retrieve up to 1000 ppm of benzene. The ICH limit being 2 ppm, it was impossible to achieve this goal. The manufacturers have consequently developed new polymerization media[6] containing either ethyl acetate alone or a mixture of ethyl acetate and cyclohexane, the first one belonging to class III (no safety concern), the second one belonging to class II (ICH limit 3880 ppm).

#### 14.21.1.2.1.2 Criteria of purity

This is a difficult matter. Purity in chemistry is an ideal concept referring to a situation where a product consists of one type of molecules only. This is a theoretical situation which can only be EXPERIMENTALLY approached more or less closely.[7]

The purity of a product is a relative notion and is dependant on the analytical methods used and their performances. More practically the quality finally chosen for a solvent will depend on the specific use for which this solvent is intended to be utilized.[8]

A solvent is considered sufficiently pure if it does not contain impurities able in nature and in quantity to interfere on the admissible quality of the product in the manufacture of which it participates.[7]

#### 14.21.1.2.1.3 Solvents as reaction medium

In this case the solvents should have a range between the melting point and the boiling point as extended as possible and a good thermal and chemical stability. The purity should be of good degree but could depend on the step considered of the global synthesis.

As an example let us consider the case of the dimethylformamide (DMF).[5] If it is used in reactions evolving in anhydrous media, it will be mandatory to control the level of water at the ppm level. The specification regarding the water content will be of course loosened if the DMF in the chemical step considered is used in conjunction with water as reaction media.

We will see further that solvents contain actually a lot of chemical impurities which could be reactive vis a vis the main molecule undergoing the chemical reaction and leading to additional impurities other than those coming from the mechanism of reaction itself.

#### 14.21.1.2.1.4 Solvents for crystallization

They should be carefully chosen in such a way that they show a high solubility at high temperature and a low solubility at low temperature of the substance to be crystallized or recrystallized.

Of course the solvent should be absolutely inert and of the highest achievable purity for at least two reasons:

- The first one being identical to the one mentioned for solvents as reaction media: possibility to produce other impurities.
- The second one being linked to the crystallization process itself. It is well known that the presence of impurities whatever the origin could have serious effects on the nucleation and growth process. We will tell a little bit more about that further in the text.

14.21.1.2.1.5 Solvents used for extraction and preparative chromatography

As in the precedent cases they have to be absolutely inert (as far as it is possible) and with a high degree of purity for the reasons already evoked. In case of preparative chromatography a special care will be taken concerning the chemical inertia to adsorbate[9] of the solvents constituting the mobile phase and the fact that impurities or additives contained in the solvents in a way not under control could impair significantly the reproducibility of the retention times.

14.21.1.2.1.6 Nature and origin of impurities contained in solvents[10]

It should be reminded here that a solvent used at the industrial level is rarely pure (we mean here no impurity analytically detectable).

Industrial solvents may contain:

- impurities coming from their origin or their manufacturing process
- impurities originating from the container during transportation
- stabilizers
- denaturing agents
- impurities resulting from a transformation of the solvent during the chemical reaction

These impurities or side products should be look for as far as it is possible when assessing the purity of the solvent. In fact they could be less volatile than the main solvent and could finally concentrate in the pharmaceutical product.

We will now review shortly the nature of all these kinds of impurities of the most often used solvents.

14.21.1.2.1.6.1 Impurities coming from the origin or the manufacturing process of the solvent[1,10]

**Table 14.21.1.2. Solvent impurities**

| Class of solvents | Possible impurities (according to the manufacturing process) |
|---|---|
| *Hydrocarbons* | |
| Toluene | Methylthiophene, benzene, paraffinic hydrocarbons |
| Xylene | Mixture of ortho, meta and para isomers, paraffinic hydrocarbons, ethyl benzene, sulfur compounds |
| Cyclohexane | Benzene, paraffinic hydrocarbons, carbonyl compounds |
| *Halogenated compounds* | |
| Dichloromethane | Chloroform, carbon tetrachloride, chloromethane |
| Chloroform | Chlorine, carbonyl chloride (phosgene), dichloromethane, carbon tetrachloride, hydrogen chloride |
| Carbon tetrachloride | Chlorides, chlorine, carbon disulfide |
| *Alcohols* | |
| Methanol | Water, acetone, formaldehyde, ethanol, methyl formate, dimethylether, carbon dioxide, ammonia |

| | |
|---|---|
| Ethanol | Aldehydes, ketones, esters, water, ethyl ether, benzene (if anhydrous ethanol) |
| 2-propanol | Water, peroxides |
| N.B.: Some alcohols obtained by fermentation could contain pesticides. It is necessary to obtain from the purchaser some guaranty in requiring limit contents (expressed in Parathion e.g.). | |
| *Aliphatic ethers/cyclic ethers* | |
| Ethylether/isopropyl ether/monoalkylated ethers/ethylene glycol/diethylene glycol/etc. | Alcohols (from which they are prepared), water, corresponding aldehydes, peroxides |
| Tetrahydrofuran | Water, peroxides |
| Dioxane | Acetaldehyde, water, acetic acid, glycol acetal paraldehyde, crotonaldehyde/peroxides |
| *Ketones* | |
| Acetone | Methanol, acetic acid, water |
| *Esters* | |
| Methyl acetate | Acetic acid, water, methanol |
| Ethyl acetate | Acetic acid, ethanol, water |
| *Amides* | |
| Formamide | Formic acid, ammonium formate, water |
| N,N-Dimethylformamide | N-Methylformamide, formic acid, water |
| *Nitriles* | |
| Acetonitrile | Acetamide, ammonium acetate, ammoniac, water, toluene |
| *Nitro compounds* | |
| Nitrobenzene | Nitrotoluene, dinitrothiophene, dinitrobenzene, aniline |

### 14.21.1.2.1.6.2 Impurities originating from the container during transportation

It relates to contamination coming from tankers or drums not correctly cleaned. These concerns of course solvents of low quality conveyed in industrial quantity. In case of utilization of such solvents, the user has to bear in mind that some incidents or uncommon behavior may find an explanation based on this considerations.

### 14.21.1.2.1.6.3 Stabilizers

It is of course very difficult to know every stabilizer used. There is here an important problem of confidentiality. We quote thereafter some of them which are well known.

**Table 14.21.1.3 Stabilizers used in selected solvents**

| Solvents | Stabilizers |
|---|---|
| Dichloromethane | Ethanol, 2-methyl-but-2-ene |
| Chloroform | Ethanol (1% V/V) for avoiding the phosgene formation, 2-methyl-but-2-ene |
| Diethylether | 2,6-di-tert-butyl-4 methylphenol (BHT) |
| Tetrahydrofuran | BHT, p-cresol, hydroquinone, calcium hydride |

14.21.1.2.1.6.4 Denaturing agents

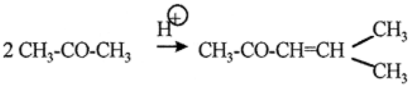
This process is relevant primarily to ethanol. Common denaturing agents are: methanol, isopropanol, ethyl acetate, toluene.

14.21.1.2.1.6.5 Transformation of the solvent during the chemical reaction

Solvents are rarely chemically inert. During the reactions where solvents are involved, they can undergo chemical transformation generating impurities which can be found, for example in the DS.

This is a huge field which cannot be exhaustively covered. We give below a few examples of well-known side reactions.

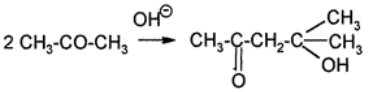
- Acetone in acidic media is easily transformed into mesityl oxide:



$$2\,\mathrm{CH_3\text{-}CO\text{-}CH_3} \xrightarrow{H^{\oplus}} \mathrm{CH_3\text{-}CO\text{-}CH{=}CH}\left\langle\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_3}\end{array}\right.$$

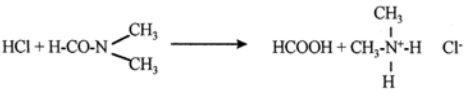
So do not forget to test for it when performing residual solvents analysis on drugs.

- In basic medium the diketone-alcohol is obtained:



$$2\,\mathrm{CH_3\text{-}CO\text{-}CH_3} \xrightarrow{OH^{\ominus}} \mathrm{CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}C}\left\langle\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_3}\\ \mathrm{OH}\end{array}\right.$$

- DMF can be hydrolyzed in presence of hydrochloric acid:

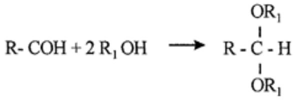


$$\mathrm{HCl + H\text{-}CO\text{-}N}\left\langle\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_3}\end{array}\right. \longrightarrow \mathrm{HCOOH + CH_3\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{N^+}}\text{-}H \quad Cl^-}$$

- Acids undergoing reaction in alcoholic media can be partially transformed into esters
- Transesterification reaction. Take care when, for example, recrystallization has to be performed for a molecule containing an ester group:

$$\mathrm{R\text{-}COOR_1 + R_2\text{-}OH \longrightarrow R\text{-}COOR_2 + R_1\,OH}$$

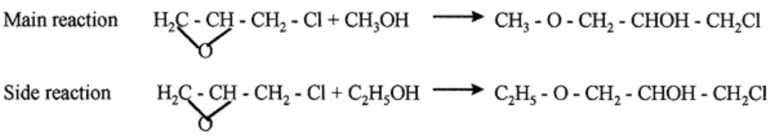
- Aldehydes (even ketones) can be transformed in alcoholic solutions into ketals:



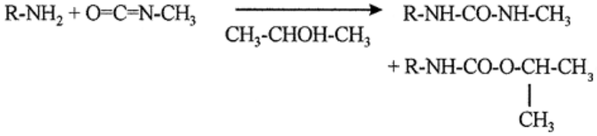
$$R\text{-}COH + 2R_1OH \rightarrow R\text{-}\overset{OR_1}{\underset{OR_1}{C}}\text{-}H$$

- From time to time the solvent can react in lieu of the reagent.

In a synthesis aimed to prepare 3-chloro-1-methoxy-2-propan-2-ol starting from chloromethyloxirane and methanol, traces of ethanol present in methanol gave the corresponding ethoxylated compound:



Another and final example concerns the preparation of a urea derivative using the reaction of an amine and isocyanate in presence of isopropanol:



$$R\text{-}NH_2 + O{=}C{=}N\text{-}CH_3 \xrightarrow[CH_3\text{-}CHOH\text{-}CH_3]{} R\text{-}NH\text{-}CO\text{-}NH\text{-}CH_3 + R\text{-}NH\text{-}CO\text{-}O\text{-}\underset{CH_3}{CH}\text{-}CH_3$$

Other examples could be found. These obvious examples stress the need for close collaboration between chemists and analysts when elaborating chemical syntheses and corresponding quality control monographs.

### *14.21.1.2.2 Drug products*[11,12]

#### 14.21.1.2.2.1 General points

Because ultimately it is the DP which is administered to the patient, it is necessary to have the quality of the solvents potentially used in the design of pharmaceutical formulations under control.

#### 14.21.1.2.2.2 Areas of utilization

Solvents including water are used in different ways in pharmaceutical formulation:

- either as a part of the final drug product:
  injectables,
  drinkable solutions,
  patches, sprays,
  microemulsions
- or used as an intermediary vehicle which is removed at the end of the process:
  granulation
  coating
  sugar coating
  microencapsulation

We have listed in Table 14.21.1.4. the most commonly used solvents.

**Table 14.21.1.4 Solvents used in formulation**

| | |
|---|---|
| Water | Dichloromethane |
| Ethyl acetate | Chloroform |
| Ethyl alcohol (denaturated with butanol and isopropanol) | Hexane |
| Isopropyl alcohol (denaturated with methyl ethyl ketone) | Cyclohexane |
| Methanol | Polyethylene glycol (low molecular weight) |
| Acetone | |

Manufacturers try progressively to replace the formulations using organic solvents such as chloroform, dichloromethane, cyclohexane belonging to the class 2 (ICH classification see Chapter 16.2), for example by developing aqueous coatings.

14.21.1.2.2.3 What should be the quality?

Taking into account the fact that the solvents used in the DP manufacturing process, either as a component of the formulation or as a residual solvent, will be absorbed by the patient, their quality must be of the highest standard. From a regulatory point of view, in almost every country if not all, it is mandatory to use solvents covered by a pharmacopoeial monograph (e.g., European Pharmacopoeia, USP, JP, local Pharmacopoeias). Some examples are given below.

## 14.21.1.3 Impacts of the nature of solvents and their quality on the physicochemical characteristics of raw materials and DP.

### *14.21.1.3.1 Raw materials (intermediates, DS, excipients)*

The impurities contained in the solvents could have several effects on the raw materials:

- When the solvents are removed, non-volatile or less volatile impurities will be concentrated in raw materials.
- They can induce chemical reactions leading to side products.
- They can affect the stability of the raw material considered.
- They can modify substantially the crystallization process.

14.21.1.3.1.1 Concentration of less volatile impurities

Due to the potential concentration of these impurities, they should be tested for in both DS and excipients and even in intermediates of synthesis if the latter constitute the penultimate step of the synthesis and if solvents belong to class 1 or class 2 solvent (see Chapter 16.2).

14.21.1.3.1.2 Side reactions

This case has already been illustrated (see paragraph 14.21.1.2.1.6.5). The skills of the chemist together with those of the analyst are needed to ensure that the presence of unexpected impurities can be detected. By way of example, the reactions involving the keto-enol tautomerism deserve to be mentioned. The equilibrium is very sensitive to the solvent so that the presence of other solvents as impurities in the main solvent can modify the keto-enol ratio leading to irreproducibility in the chemical process.[13,14]

14.21.1.3.1.3 Consequences for stability

Some solvents, as mentioned in the paragraph 14.21.1.2.1.5, can contain very active entities such as aldehydes and peroxides. For example, if the raw material contains primary or secondary amines and/or is susceptible to oxidation or hydrolysis, it is likely that degradants will be formed over the time, reducing potentially the retest date of the raw material. The same situation could affect the DP and therefore two examples are given in paragraph 14.21.1.3.2.

### 14.21.1.3.1.4 Solvent purity and crystallization

This issue is may be less known except for chemists working in this specialized area. Because the consequences can be important for the processability, stability and occasionally bioavailability of the drug substance in its formulation, it is relevant to comment on this subject.

#### 14.21.1.3.1.4.1 Role of the nature and the quality of solvent on crystallization

Most of the drugs on the market are obtained as a defined crystalline structure and formulated as solid dosage forms. It is well known that a molecule can crystallize to give different crystalline structures displaying what is called polymorphism. The crystal structures may be anhydrous or may contain a stoichiometric number of solvent molecules leading to the formation of solvates (hydrates in case of water molecules). Pseudopolymorphism is the term used to describe this phenomenon.

Another characteristic which plays a major role in the overall processability of the DS for DP manufacture is the "crystal habit". This term is used[15,16] to describe the overall shape of crystals, in other words, the differing external appearance of solid particles which have the same internal crystalline structure.

Both structures (internal, external) are under the control of different parameters including the nature of the solvent used and its quality. The role of the solvent itself in the overall crystallization process, including the determination of the crystal structure and the crystal habit is well known.[17] But it is equally worth noting that impurities coming from:

- the product to be crystallized
- the solvent used
- the environment

can selectively affect the nucleation process and the growth rates of different crystal faces.[17-21] They can be selectively adsorbed to certain faces of the polymorphs thereby inhibiting their nucleation or retarding their growth to the advantage of others. Crystal shape (habit) can also be modified by a solvent without polymorphic change. Additives or impurities can block, for a defined polymorph, the growth rate of certain faces leading e.g. to needles or plates. It is possible to introduce deliberately additives to "steer" the crystallization process. An interesting example of this crystal engineering strategy have been published for e.g., adipic acid[22] or acetaminophen.[23]

#### 14.21.1.3.1.4.2 Solvent-solid association/overview

After the crystallization of the product, solvents must be removed in order to obtain the minimum amount of residual solvents compatible with safety considerations and/or physicochemical considerations including stability, processability and occasionally microbiological quality (see Chapter 16.2). Different situations can be encountered.

##### 14.21.1.3.1.4.2.1 Solvent outside the crystal

The solvent remains outside the crystals at the time of crystal formation. It is adsorbed on the surface or in the crystal planes. In the first case, the solvent is easily removed. But in the second case, if a cleavage plane exists, the drying process can be very difficult. Two methods can be used to try to remove this type of residual solvent almost completely.

- Displacement by water vapor in an oven, keeping in mind that this method may introduce some degradation leading to processability problems.[11,24]
- Extraction by supercritical $CO_2$[25,26] but the extraction power of $CO_2$ is basically limited to slightly polar solvents.

#### 14.21.1.3.1.4.2.2 Solvent inside the crystal

The solvent remains inside the crystalline structure. Three situations can arise.

##### 14.21.1.3.1.4.2.2.1 Occluded solvents

During rapid crystallization, some degree of disorder (amorphous phases, crystalline defects) can arise, creating pockets where residual solvent can be occluded. Through a process of dissolution/recrystallization this "hole" moves towards the external faces of the crystal releasing the solvent at the end. This phenomenon is more frequent for large crystals (500 μm/600 μm) but rare for smaller crystals (1 - 100 μm). The solvent odor which is detected when opening a drum or a bag containing a substance which was dried in the normal way can be explained by this mechanism.

##### 14.21.1.3.1.4.2.2.2 Solvates

At the end of the crystallization process, the substance can be isolated as a solvate (hydrate), i.e., as a pseudopolymorph. The solvates generally have quite different physicochemical properties from the anhydrous form. Their stability can be questionable and in any case deserves to be investigated. In some cases it is possible to remove the solvent from the crystal without changing the structure of the lattice leading to an isomorphic desolvate which displays a similar X-ray diffraction pattern to that of the parent compound.[2,27] The lattice of the desolvated solvate is in a high energy state relative to the original solvate structure. A better dissolution rate and compressability can be expected,[28] but the drawbacks are hygroscopicity and physico-chemical instability. The lattice could undergo a relaxation process over time which increases the packing efficiency of the substance by reducing the unit cell volume.

When developing a new chemical entity all these aspects have to be considered to avoid unpleasant surprises during development or once the drug is on the market. Due to the need for process scale-up and of making the manufacturing process more industrial, changes are introduced especially in the crystallization and the drying processes, (e.g., change from static drying to dynamic drying). Because the drying is a particularly disturbing process for the integrity of the lattice, defects and/or amorphous phases may be created favoring subsequent polymorphic or pseudopolymorphic transformations of the crystalline form developed so far, if it is not the most stable one.

##### 14.21.1.3.1.4.2.2.3 Clathrates

In contrast to solvates, clathrates do not show any stoichiometric relationship between the number of molecules of the substance and the number of molecules of solvent. Clathrates actually correspond to a physical capture of solvent molecules inside the crystal lattice without any strong bonds including hydrogen bonds. Molecules of one or several solvents can be trapped within the crystalline structure as long as the crystallization has been performed with a pure solvent or a mixture. The case of the sodium salt of warfarin giving "mixed" clathrates with water and isopropyl alcohol is well known and the existence of 8/4/0 or 8/2/2 proportions has been shown.[11]

It is fairly obvious that some powder properties like wettability can be modified by the formation of clathrates. Because their formation is not easy to control, some batch to batch inconsistency may be expected in this situation.

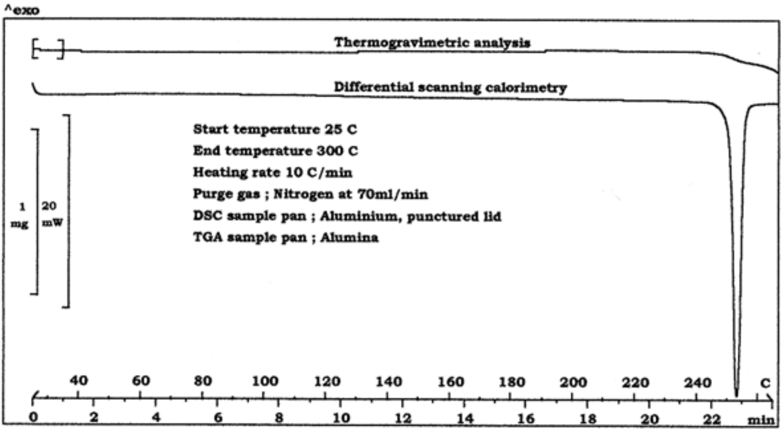


Figure 14.21.1.1. DSC and TG patterns.

In order to demonstrate the internal character of the clathrate relative to the crystal lattice, the example of a molecule developed in the laboratory of one of the authors is given below.

Figure 14.21.1.1 shows the DSC pattern of a molecule with the melting event at 254°C and the corresponding TG pattern obtained at the same temperature scanning rate. At the time the melting occurs, a *loss of weight is observed* corresponding to the loss of 0.2 % of isopropanol. The nature and the amount of the solvent have been confirmed by GC after dissolving the substance.

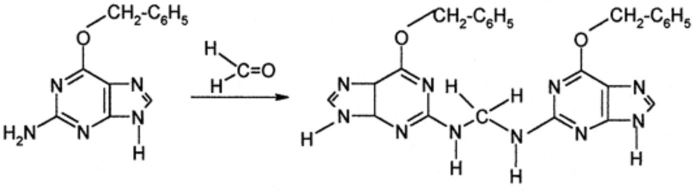
### 14.21.1.3.2 Drug product

As for the DS, the solvents used for DP manufacture can produce some negative effects by themselves or through their own impurities.

For liquid or semi liquid formulations, the formulator has to ensure that the solvents themselves do not display chemical interactions with the DS or the excipients. Everything which has been said in paragraphs 14.21.1.2.1.5 and 14.21.1.3.1 remains true here.

14.21.1.3.2.1 Interaction of impurities contained in the solvent

As said in paragraph 14.21.1.3.1 with the DS, impurities contained in the solvent especially if they are strongly reactive, like aldehydes or peroxides, can promote formation of degradants. Regarding aldehydes, the publication of Bindra and all[29] should be mentioned. It relates to the degradation of the o-benzylguanine in an aqueous solution containing polyethylene glycol 400 (PEG 400). This type of solvent very often contains formaldehyde, which can lead to the formation of a precipitate over time:



PEG can also contain peroxides which can initiate over time, the formation of degradants via an oxidation process. Several publications have dealt with this phenomenon.[30,31]

14.21.1.3.2.2 Interaction with the container

When the formulation is a solution which is prepared from water and different organic solvents, it is mandatory to investigate possible interactions between the medium and the container especially if the latter is of polymeric nature (PVC-PVDC, polyethylene, etc.) with or without elastomeric stoppers. A thorough investigation is necessary including:

- an examination of the solution for plasticizers, antioxidants, monomers and oligomers, mineral impurities, potentially extracted from the container,
- the evaluation of the absorption by the container of components (DS, excipients) contained in the solution.

In the first case, the migration of impurities into the solution could initiate physicochemical instability and possibly some potential toxicity.

In the second case, a decrease in the content of the DS and/or some excipient (e.g., organic solvents added to promote the solubility) could lead to some loss of therapeutic efficacy and in some case to physical instability (precipitation).

14.21.1.3.2.3 Solvates formation during the solid dosage form manufacture

During the granulation process it is possible that the DS (occasionally the excipient) could transform into a solvated crystalline structure (solvate, hydrate). During the drying process, different situations can occur:

- The solvate is poorly stable and the solvent is easily removed leading to either the original polymorphic form but creating a certain degree of disorder in the crystalline structure or to what is called a "desolvate solvate" form. In this last case, also named "isomorphic desolvate", the desolvated solvate retains the structure of its parent solvated form. The X-ray diffraction patterns look similar between the parent and the daughter forms. In this situation we have the creation of a molecular vacuum which could substantially impact on the stability, hygroscopicity and mechanical characteristics of the DS and finally of the DP.
- The solvate is stable within the formulation: we then have in a sense a new chemical entity. The properties of the solvate could be entirely different (solubility, kinetics of dissolution, stability, processability, etc.) and the consequence could be either positive or negative. The case where the kinetics of dissolution are affected by the formation of solvates should always be investigated. Papers on this subject have been published for molecules such as lorazepam,[32] hydrocortisone,[33] cephalexin,[32] etc.
- Obviously, as in the case of raw materials (14.21.1.3.1.4.2.2.3) clathrate formation should be considered in order to explain possible batch to batch inconsistency.

### *14.21.1.3.3 Conclusions*

We have seen that the solvent, far from being inert, plays a key role by itself and occasionally via its own impurities in different ways which are important for pharmaceutical development. We will now discuss how to set up sound specifications for solvents in relation to their field of use.

## 14.21.1.4 Setting specifications for solvents

### *14.21.1.4.1 Solvents used for the raw material manufacture*

For the raw materials we should distinguish between solvents:

- used during the synthesis
- and those used for the last step of the manufacture corresponding very often to the crystallization process.

**Table 14.21.1.5. Examples of monographs**

| *Solvents used during the synthesis (of well controlled origin)* |
|---|
| Character/Appearance |
| Identification (IR, GC or $n_D^{20}$) |
| Purity GC (generally not less than 98%) |

**Table 14.21.1.6. Examples of monographs**

| *Final crystallization solvents (of well controlled origin)* |
|---|
| Character/Appearance |
| Identification (IR, GC or $n_D^{20}$) |
| Tests |
| Water content (0.1 to 0.5 depending on solvent type) |
| Residue on evaporation: not more than 0.01 per cent |
| Purity GC not less than 99 % (examine for denaturing agents and other potential impurities) |

As a rule of thumb, the specifications set for solvents used for the crystallization step will be more stringent than those used during the synthesis.

For the intermediates of synthesis, if the origin of the solvent is under control (e.g., existence of contracts/Quality Assurance audits) a simplified monograph is completely adequate (see Table 14.21.1.5) as long as the supplier provides a detailed certificate of analysis where impurities (including solvents) are properly specified with acceptable limits. If the same solvent is used for the crystallization step additional purity tests are necessary (Table 14.21.1.6).

For economic reasons, it may be necessary to recycle solvents. If so, the containers should be fully identified in terms of storage:

- If solvents can be efficiently purified (e.g., by redistillation) they must comply with the same specifications as those of fresh solvents and consequently can be used in any synthesis.
- If they still contain volatile impurities resulting from the reaction they come from, they can be recycled only for this reaction. In this case, the impurities should be identified and their possible impact on the reaction evaluated. In Tables 14.21.1.7 and 14.21.1.8 we have summarized possible specifications for a fresh batch of ethyl acetate used for a defined chemical reaction and those for the recycled solvent.

We recommend working with reliable solvent suppliers who can give every assurance on the quality of solvents provided to avoid any “unpleasant surprises”.

Water should be mentioned separately. If it is used during the synthesis of intermediates the quality “drinking water” can be used without any problems. But if water is used during the last step of the process, its quality must be in compliance with the requirements of purified water as they are described in several pharmacopoeias. In Table 14.21.1.9 the requirements for the Ph. Eur and USP are given as examples. Purified water is generally obtained from the drinking water. It undergoes demineralization by either distillation or an ion-exchange process. Particular attention has to be paid to microbiological quality.

**Table 14.21.1.7. Example of monograph applied to new solvent: Ethyl acetate**

**Specifications**

| Controls | Standards |
|---|---|
| Characters | Clear liquid, colorless |
| *Identification* | |
| A - Infrared spectrum | Complies |
| or | |
| B - Refractive index | 1.370 to 1.373 |
| or | |
| C - Gas chromatography | Complies |
| *Assay* | |
| Ethyl acetate (purity) | Not less than 99.5% |

**Table 14.21.1.8. Example of monograph applied to recycled solvent: Ethyl acetate**

**Specifications**

| Controls | Standards |
|---|---|
| Characters | Clear liquid, colorless |
| *Identification* | |
| Gas chromatography | Complies |
| *Tests* | |
| Water content | Not more than 2.0% |
| Related substances | |
| Methanol | Not more than 1.0% |
| Ethanol | Not more than 2.0% |
| Ethyl chloride | Not more than 2.0% |
| Others impurities (sum) | Not more than 2.0% |
| *Assay* | |
| Ethyl acetate (purity) | Not less than 99.5% |

### *14.21.1.4.2 Solvents used for the DP manufacture*

There is no other choice than to use the quality of solvents defined by a Pharmacopoeia. It is true that there are still discrepancies between the pharmacopoeias of different countries. It is hoped that the ICH process dealing with the harmonization of quality, safety and efficacy amongst three main zones of the world (EU, USA, Japan) will progressively reduce the remaining differences in dossiers submitted to Regulatory Authorities and the way the data are evaluated.

As examples, Tables 14.21.1.10, 14.21.1.11, and 14.21.1.12 summarize specifications for acetone, ethanol and isopropanol given by the Ph. Eur. and USP. As can be seen only the Ph. Eur. monograph makes reference to volatile impurities to be tested for by GC.

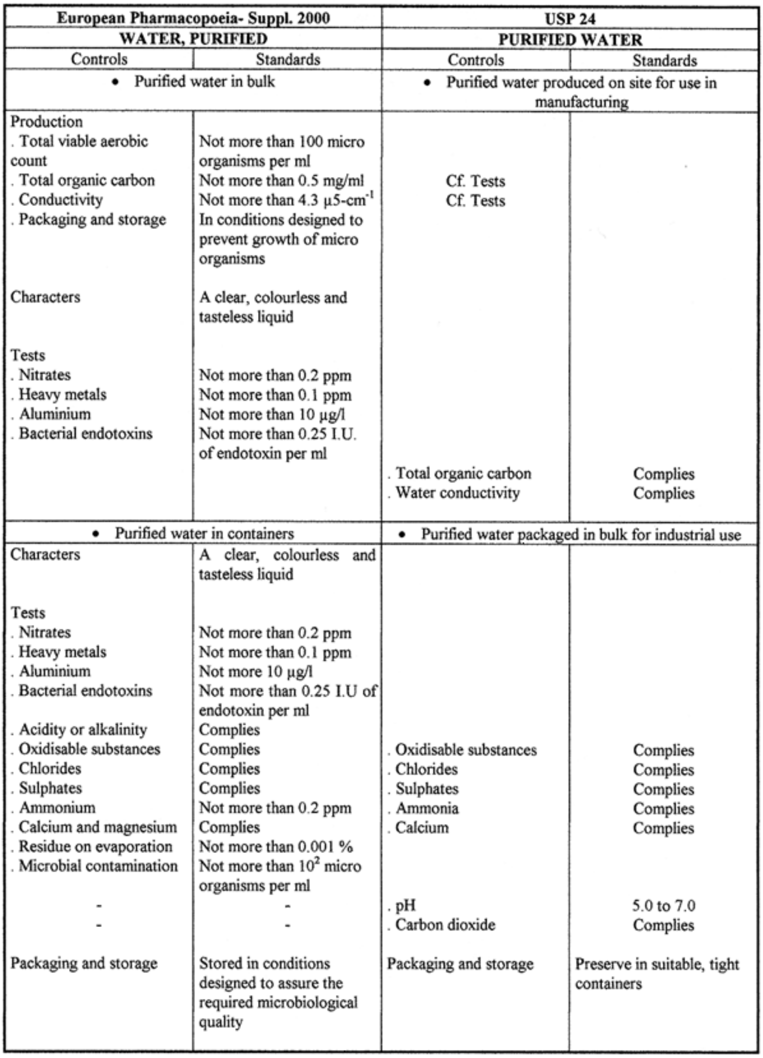
## 14.21.1.5 Quality of solvents and analysis

The solvents, including water, are used in almost every area of analytical sciences: spectroscopy, chromatography, potentiometry, electrochemistry. They should be characterized by a set of properties making them suitable for use for their intended purpose.

### *14.21.1.5.1 Quality of solvents used in spectroscopy*

As a general requirement, the solvents used in spectroscopy should be transparent and stable towards the relevant range of wavelengths. They should be able to dissolve the substance to be examined and not contain impurities affecting the stability of the substance or the validity of the method (selectivity, repeatability, limit of detection, analytical response). Theoretically the solvent chosen should have minimal interaction with the solute. But what could be seen as a disadvantage could also be an important source of structural information. What is called the solvent effect can help in UV, IR and NMR spectroscopies[34] e.g. in struc-

**Table 14.21.1.9. Water quality**

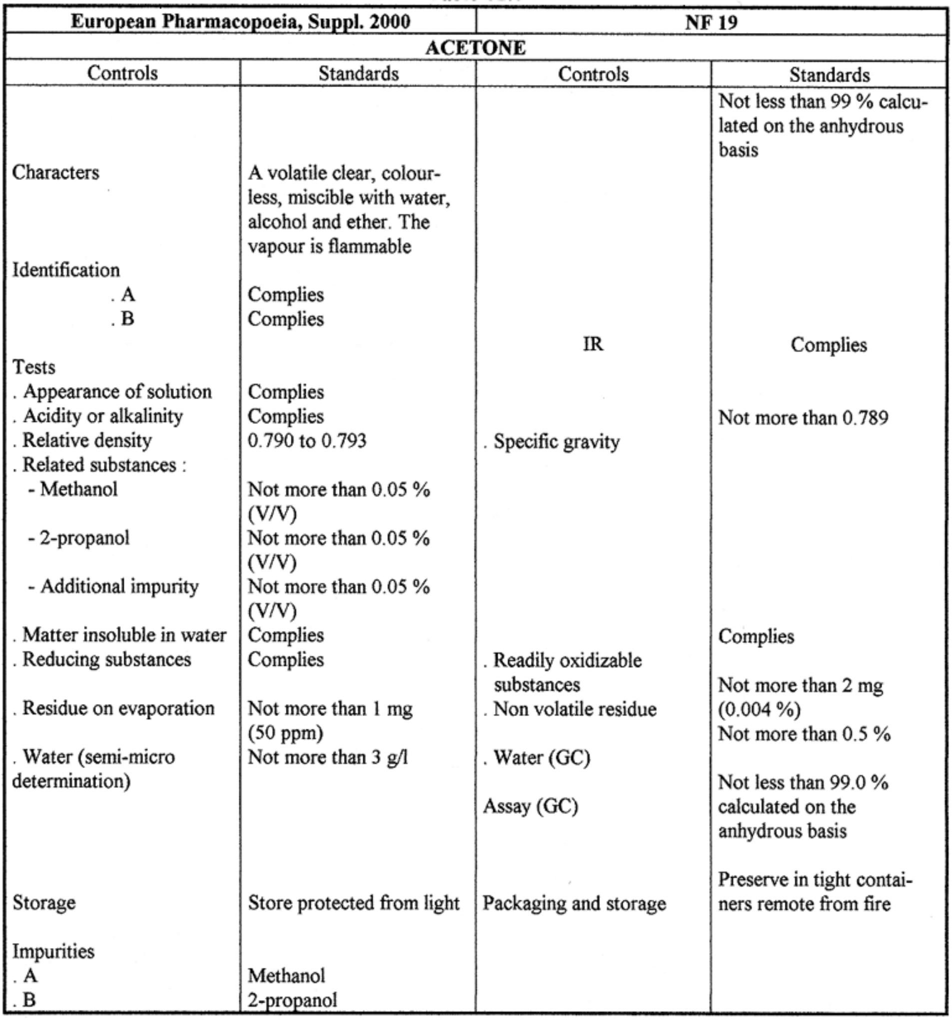


| European Pharmacopoeia- Suppl. 2000 | | USP 24 | |
|---|---|---|---|
| WATER, PURIFIED | | PURIFIED WATER | |
| Controls | Standards | Controls | Standards |
| • Purified water in bulk | | • Purified water produced on site for use in manufacturing | |
| Production | | | |
| . Total viable aerobic count | Not more than 100 micro organisms per ml | | |
| . Total organic carbon | Not more than 0.5 mg/ml | Cf. Tests | |
| . Conductivity | Not more than 4.3 µ5-cm$^{-1}$ | Cf. Tests | |
| . Packaging and storage | In conditions designed to prevent growth of micro organisms | | |
| Characters | A clear, colourless and tasteless liquid | | |
| Tests | | | |
| . Nitrates | Not more than 0.2 ppm | | |
| . Heavy metals | Not more than 0.1 ppm | | |
| . Aluminium | Not more than 10 µg/l | | |
| . Bacterial endotoxins | Not more than 0.25 I.U. of endotoxin per ml | | |
| | | . Total organic carbon | Complies |
| | | . Water conductivity | Complies |
| • Purified water in containers | | • Purified water packaged in bulk for industrial use | |
| Characters | A clear, colourless and tasteless liquid | | |
| Tests | | | |
| . Nitrates | Not more than 0.2 ppm | | |
| . Heavy metals | Not more than 0.1 ppm | | |
| . Aluminium | Not more 10 µg/l | | |
| . Bacterial endotoxins | Not more than 0.25 I.U of endotoxin per ml | | |
| . Acidity or alkalinity | Complies | | |
| . Oxidisable substances | Complies | . Oxidisable substances | Complies |
| . Chlorides | Complies | . Chlorides | Complies |
| . Sulphates | Complies | . Sulphates | Complies |
| . Ammonium | Not more than 0.2 ppm | . Ammonia | Complies |
| . Calcium and magnesium | Complies | . Calcium | Complies |
| . Residue on evaporation | Not more than 0.001 % | | |
| . Microbial contamination | Not more than $10^2$ micro organisms per ml | | |
| - | - | . pH | 5.0 to 7.0 |
| - | - | . Carbon dioxide | Complies |
| Packaging and storage | Stored in conditions designed to assure the required microbiological quality | Packaging and storage | Preserve in suitable, tight containers |

ture elucidation. In the book by Reichardt,[1] data regarding the cut-off points of solvents commonly used in UV/visible spectroscopy are provided. The cut-off point is defined as the wavelength in the ultraviolet region at which the absorbance approaches 1.0 using a 1-cm cell path with water as the reference. In the same way the range of transparency for IR-solvents are given. Complete IR-spectra of organic solvents can be found in the "Stadler IR spectra handbook of common organic solvents" . The solvents suppliers usually provide catalogues including a "spectroscopic grade" allowing the user to make a sound choice.

In the case of the NMR spectroscopy problems arise with the residual protonated part of deuterated solvents ($^1$H-NMR) and the $^{13}$C-NMR absorption bands of compounds used as solvents. References can be found[1] where detailed data are given regarding these points.

**Table 14.21.1.10. Specification for acetone**



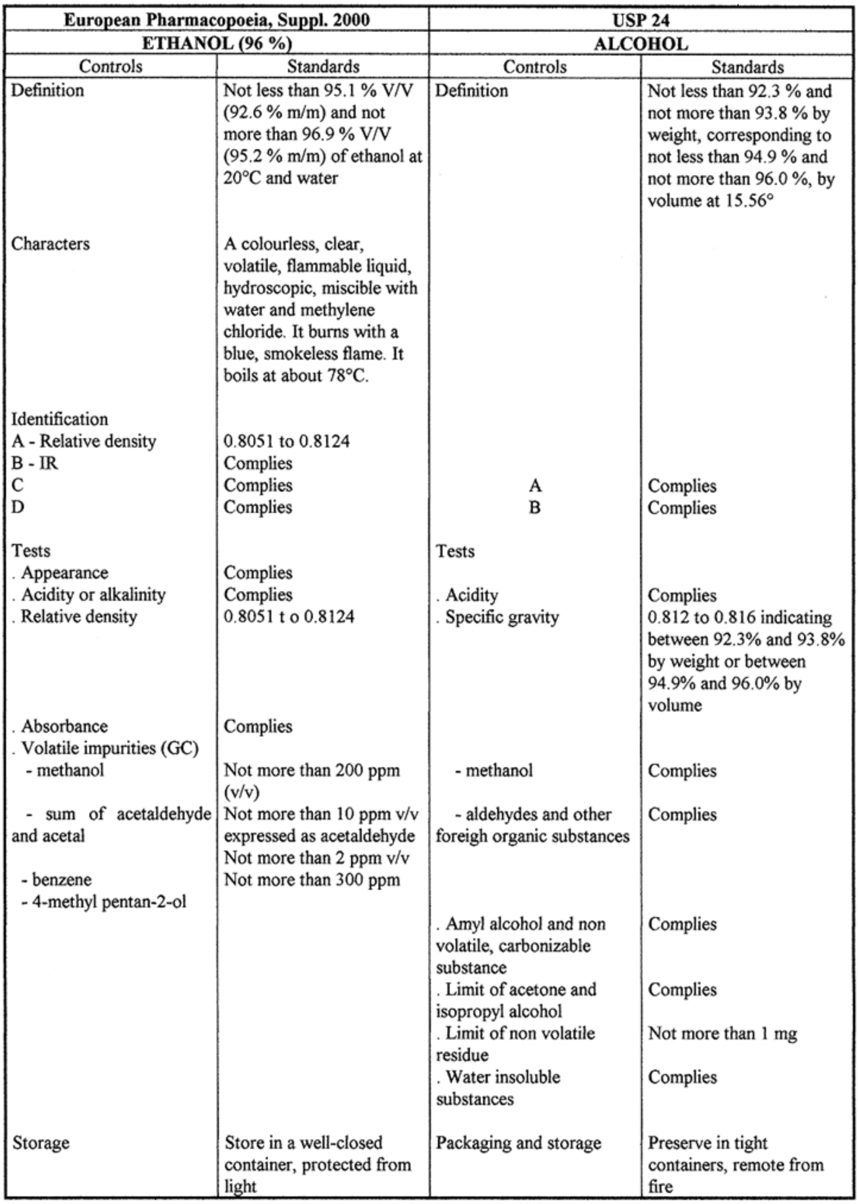
| European Pharmacopoeia, Suppl. 2000 | | NF 19 | |
|---|---|---|---|
| ACETONE | | | |
| Controls | Standards | Controls | Standards |
| | | | Not less than 99 % calculated on the anhydrous basis |
| Characters | A volatile clear, colourless, miscible with water, alcohol and ether. The vapour is flammable | | |
| Identification | | | |
| . A | Complies | | |
| . B | Complies | | |
| | | IR | Complies |
| Tests | | | |
| . Appearance of solution | Complies | | |
| . Acidity or alkalinity | Complies | | Not more than 0.789 |
| . Relative density | 0.790 to 0.793 | . Specific gravity | |
| . Related substances : | | | |
| - Methanol | Not more than 0.05 % (V/V) | | |
| - 2-propanol | Not more than 0.05 % (V/V) | | |
| - Additional impurity | Not more than 0.05 % (V/V) | | |
| . Matter insoluble in water | Complies | | Complies |
| . Reducing substances | Complies | . Readily oxidizable substances | Not more than 2 mg (0.004 %) |
| . Residue on evaporation | Not more than 1 mg (50 ppm) | . Non volatile residue | Not more than 0.5 % |
| . Water (semi-micro determination) | Not more than 3 g/l | . Water (GC) | |
| | | Assay (GC) | Not less than 99.0 % calculated on the anhydrous basis |
| Storage | Store protected from light | Packaging and storage | Preserve in tight containers remote from fire |
| Impurities | | | |
| . A | Methanol | | |
| . B | 2-propanol | | |

A common problem which can be met regularly in chemistry is the identification of signals from common contaminants in solvents of medium quality (see paragraph 14.21.1.2.1.6.1). Gottlieb and Col[35] have published data on NMR chemical shifts of trace impurities contained in common laboratory solvents, making NMR spectroscopy the instrument of choice as a tool for routine quality control.

### *14.21.1.5.2 Quality of solvents used in chromatography*

The aim of this paragraph is not to focus on strategies for solvent selection in order to achieve extraction or liquid chromatography. A detailed literature review has been published by Barwick[36] on this matter allowing the user to design relevant methodology in any

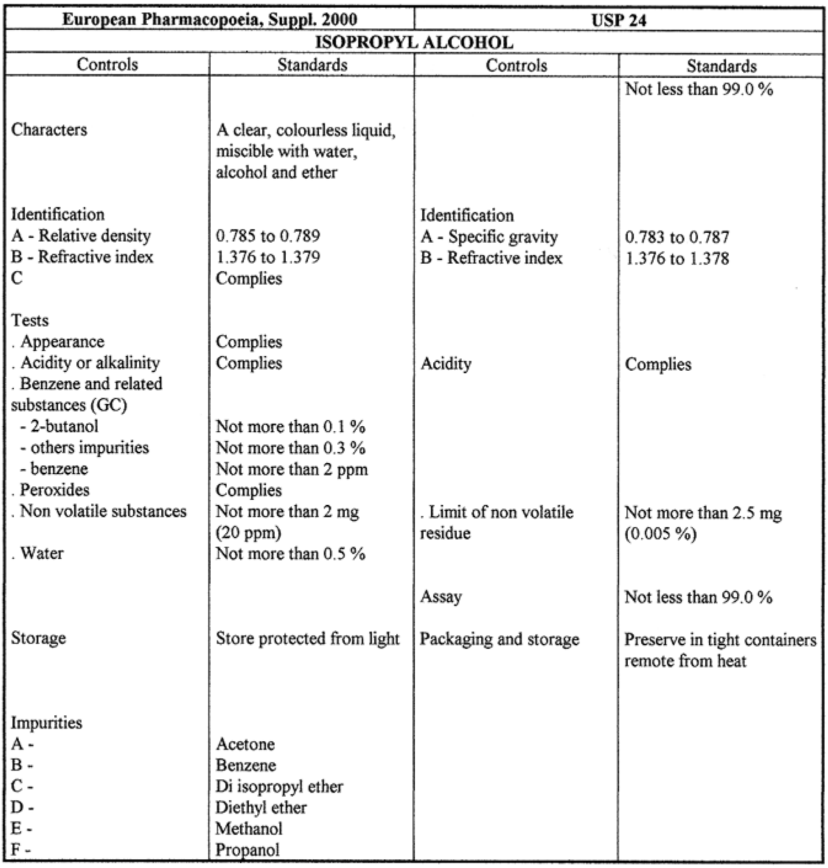
### Table 14.21.1.11. Specification for ethanol



| European Pharmacopoeia, Suppl. 2000 | | USP 24 | |
|---|---|---|---|
| ETHANOL (96 %) | | ALCOHOL | |
| Controls | Standards | Controls | Standards |
| Definition | Not less than 95.1 % V/V (92.6 % m/m) and not more than 96.9 % V/V (95.2 % m/m) of ethanol at 20°C and water | Definition | Not less than 92.3 % and not more than 93.8 % by weight, corresponding to not less than 94.9 % and not more than 96.0 %, by volume at 15.56° |
| Characters | A colourless, clear, volatile, flammable liquid, hydroscopic, miscible with water and methylene chloride. It burns with a blue, smokeless flame. It boils at about 78°C. | | |
| Identification | | | |
| A - Relative density | 0.8051 to 0.8124 | | |
| B - IR | Complies | | |
| C | Complies | A | Complies |
| D | Complies | B | Complies |
| Tests | | Tests | |
| . Appearance | Complies | | |
| . Acidity or alkalinity | Complies | . Acidity | Complies |
| . Relative density | 0.8051 t o 0.8124 | . Specific gravity | 0.812 to 0.816 indicating between 92.3% and 93.8% by weight or between 94.9% and 96.0% by volume |
| . Absorbance | Complies | | |
| . Volatile impurities (GC) | | | |
| - methanol | Not more than 200 ppm (v/v) | - methanol | Complies |
| - sum of acetaldehyde and acetal | Not more than 10 ppm v/v expressed as acetaldehyde<br>Not more than 2 ppm v/v | - aldehydes and other foreign organic substances | Complies |
| - benzene | Not more than 300 ppm | | |
| - 4-methyl pentan-2-ol | | | |
| | | . Amyl alcohol and non volatile, carbonizable substance | Complies |
| | | . Limit of acetone and isopropyl alcohol | Complies |
| | | . Limit of non volatile residue | Not more than 1 mg |
| | | . Water insoluble substances | Complies |
| Storage | Store in a well-closed container, protected from light | Packaging and storage | Preserve in tight containers, remote from fire |

Impurities as per European Pharmacopoeia, Supplement 2000:
A - 1,1-diethoxyrethane (acetal); B - Acetaldehyde; C - Acetone; D - Benzene; E - Cyclohexane; F - Methanol; G - Butan-2-one (methyl ethyl ketone); H - 4-methylpentan-2-one (methyl isobutyl ketone); I - Propanol; J - Propan-2-ol; K - Butanol; L - Butan-2-ol; M - 2-methylpropanol (isobutanol); N - Furan-2-carbaldehyde (furfural); O - 2-methylpropan-2-ol (1,1-dimethyl alcohol); P - 2-methylbutan-2-ol; Q - Pentan-2-ol; R - Pentanol; S - Hexanol; T - Heptan-2-ol; U - Hexan-2-ol; V - Hexan-3-ol

**Table 14.21.1.12. Specification for isopropanol**



| European Pharmacopoeia, Suppl. 2000 | | USP 24 | |
|---|---|---|---|
| ISOPROPYL ALCOHOL | | | |
| Controls | Standards | Controls | Standards |
| | | | Not less than 99.0 % |
| Characters | A clear, colourless liquid, miscible with water, alcohol and ether | | |
| Identification | | Identification | |
| A - Relative density | 0.785 to 0.789 | A - Specific gravity | 0.783 to 0.787 |
| B - Refractive index | 1.376 to 1.379 | B - Refractive index | 1.376 to 1.378 |
| C | Complies | | |
| Tests | | | |
| . Appearance | Complies | | |
| . Acidity or alkalinity | Complies | Acidity | Complies |
| . Benzene and related substances (GC) | | | |
| - 2-butanol | Not more than 0.1 % | | |
| - others impurities | Not more than 0.3 % | | |
| - benzene | Not more than 2 ppm | | |
| . Peroxides | Complies | | |
| . Non volatile substances | Not more than 2 mg (20 ppm) | . Limit of non volatile residue | Not more than 2.5 mg (0.005 %) |
| . Water | Not more than 0.5 % | | |
| | | Assay | Not less than 99.0 % |
| Storage | Store protected from light | Packaging and storage | Preserve in tight containers remote from heat |
| Impurities | | | |
| A - | Acetone | | |
| B - | Benzene | | |
| C - | Di isopropyl ether | | |
| D - | Diethyl ether | | |
| E - | Methanol | | |
| F - | Propanol | | |

particular case. It is preferable to focus on the impact of impurities present in the solvent on the chromatographic performances.

Impurities in and additives to solvents can cause several problems and artifacts in liquid and gas chromatography.[37-39] Primarily they can be the origin of irreproducible separations, enhanced UV-background and even of mechanical problems. De Schutter and Col[37] have investigated this problem in purity of solvents used in high-performance thin-layer chromatography.

A way to improve the stability of the chromatographic system by minimizing the role of solvent impurities is to add deliberately a controlled amount of organic modifier. For example, Lauren and Col[40] have applied this technique, using decanol for improving the stability of the LC used for analyzing carotenoids. Middleditch and Zlatkis[41] have listed an impressive range of stabilizers and additives which can be found in solvents which may help the chromatographer in explaining the occurrence of artifacts in chromatography. Zelvensky and Col[38] have determined by gas chromatography the most common impurities contained in solvents for liquid chromatography. The series of solvents investigated include acetonitrile, methanol, ethanol, dichloromethane, formic acid, dimethylformamide, pyridine, tetrahydrofuran and dimethyl sulphoxide. Parsons and Col[39] have performed a search for trace impurities in solvents commonly used for gas chromatographic analysis of environmental samples.

### *14.21.1.5.3 Quality of solvents used in titrimetry*

For titrimetric determinations performed in an aqueous medium it is highly recommended to use distilled water and to perform a blank determination if necessary.

For determinations performed in non aqueous media, the solvents should be as anhydrous as possible and, of course, inert to the titrant and the substance. Their purity should be such that they do not contain impurities which could react with the substance to be analyzed. A blank titration should be performed if necessary.

## 14.21.1.6 Conclusions

Far from being inert and not affecting the molecules dissolved in it, the solvent can affect the behavior of the solute in different ways. This chapter has aimed to support the idea that it is important for the chemist and the pharmacist to control the quality of the solvents used in the different areas of pharmaceutical activity. As we have tried to show, many pitfalls can be avoided during the development of a drug if a thorough investigation of the quality of the solvents used is carried out.

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## 14.21.2 PREDICTING COSOLVENCY FOR PHARMACEUTICAL AND ENVIRONMENTAL APPLICATIONS

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### 14.21.2.1 Introduction

Cosolvency refers to the effects of adding one or more solvents (cosolvents), which are different from the existing solvent in a solution, on the properties of the solution or behavior of the solute. Cosolvency has found its applications in numerous engineering and scientific disciplines. The discussion in this section will be limited to aqueous phase cosolvency (the primary solvent is water), and cosolvents will include only pure organic solvents which are miscible with water either completely (in any proportion) or partially (in only certain proportions). The extent of cosolvency will be quantitatively described by the difference in solute solubilities in pure water and in a mixture of water and cosolvent(s).

Cosolvency has been studied for decades. However, it remains a poorly understood phenomenon due in large measure to our limited awareness of the liquid structure and the intermolecular forces. At present, practical approaches to predicting cosolvency are to develop models based on established theories and to make use of correlation between experimental observations and properties of the substances involved. As with all modeling efforts, it is essential to make judicious simplifications at various levels. The efforts to date have given rise to several models, including the extended regular solution theory[1-3] and its modification,[4] excess free energy model,[5-7] the phenomenological model,[8,9] modified Wilson model,[10,11] the combined nearly ideal binary solvent (NIBS) model,[12] the mixture response surface model,[13] and others. Many of these models, however, are considered to be more descriptive than predictive, because they inevitably involve one or more model parameters which are usually specific to a particular solute/solvent/cosolvent(s) system, and must be estimated from experimental data of solubility obtained for that system. On the other hand, purely empirical models, e.g., the double-log exponential equation,[14] aim at satisfying mathematical descriptions of measured data, and often offer little insight to the process. Comparisons among cosolvency models have been made in several published papers.[15-19]

This discussion is intended to provide an easy approach for predicting the effect of cosolvents, which are frequently involved in pharmaceutical and environmental applications, on the solubility of organic chemicals. The starting point is the widely used log-linear model.

### 14.21.2.2 Applications of cosolvency in pharmaceutical sciences and industry

Although many drugs are formulated and administrated in solid, vapor, powder, or other forms, using solutions as drug delivery vehicle has significant advantages. Most parenterally administered medicines are in the form of liquid solution, and for intravenous injection, liquid form dosage is the only possible form. However, drugs are usually designed with little concern about their level of solubility in solution. It is the task of pharmaceutical formulators to find appropriate forms for the drug to be effectively delivered into biological systems.

The phenomena of cosolvency have been studied for more than a century by pharmaceutical scientists. Numerous experimental data are published in the literature, and most of the models mentioned in the introduction section have been developed from pharmaceutical research. In addition to the need of solubilizing drugs which are poorly water-soluble, controlling the dissolution of drugs administered as solids to optimize therapeutic activity also demands an improved understanding of drug solubilization. Approaches that may be pursued to enhance drug solubility in a liquid dosage formulation include adjusting pH, adding surfactants, cosolvents, or complexation agents. Choice of these techniques depends primarily on the drug's chemical structure and physicochemical properties. For example, control of pH is applicable only when the drug is an electrolyte. To solubilize nonelectrolyte drugs, the use of cosolvents outweighs surfactants and complexing agents.[20]

Cosolvents that are routinely used in drug formulation include ethanol, propylene glycol, polyethylene glycol, and glycerin. Examples of pharmaceutical products containing these cosolvents are summarized in Table 14.21.2.1.

**Table 14.21.2.1. Selected pharmaceutical products containing cosolvents**

| Trade Name | Cosolvent | vol% | Manufacturer | Type |
|---|---|---|---|---|
| Aclovate cream | Propylene glycol | | Schering | Topical |
| Alurate elixir | Ethanol | 20 | Roche | Oral liquid |
| Amidate | Propylene glycol | 35 | Abbott | Parenteral |
| Amphojel | Glycerin | | Wyeth-Ayerst | Oral |
| Apresoline | Propylene glycol | 10 | Ciba | Parenteral |
| Aristocort cream | Propylene glycol | | Fujisawa | Topical |
| Ativan | Polyethylene glycol<br>Propylene glycol | 20<br>80 | Wyeth-Ayerst | Parenteral |
| Bentyl syrup | Propylene glycol | | Lakeside | Oral |
| Brevibioc | Ethanol | 25 | DuPont | Parenteral |
| Cleocin T lotion | Glycerin | | Upjohn | Topical |

| Trade Name | Cosolvent | vol% | Manufacturer | Type |
|---|---|---|---|---|
| Comtrex cough | Ethanol | 20 | Bristol | Oral liquid |
| Cyclocort lotion | Polyethylene glycol | | Lederle | Topical |
| Delsym | Propylene glycol | | McNeil Consumer | Oral |
| Depo-Medrol | Polyethylene glycol | | Upjohn | Parenteral |
| Dilantin | Ethanol<br>Propylene glycol | 10<br>40 | Parke-Davis | Parenteral |
| Dramamine | Propylene glycol | 50 | Searle | Parenteral |
| Elocon lotion | Propylene glycol | | Schering | Topical |
| Entex liquid | Glycerin | | Norwich-Eaton | Oral |
| Fluonid solution | Propylene glycol | | Herbert | Topical |
| Halog cream | Propylene glycol | | Westwood-Squibb | Topical |
| Halog ointment | Polyethylene glycol | | Westwood-Squibb | Topical |
| Kwell cream | Glycerin | | Reed & Carnrick | Topical |
| Lanoxin | Ethanol<br>Propylene glycol | 10<br>40 | Burroughs Wellcome | Parenteral |
| Librium | Propylene glycol | 20 | Roche | Parenteral |
| Lidex | Propylene glycol | | Syntex | Topical |
| Luminal Sod | Propylene glycol | 67.8 | Winthrop | Parenteral |
| MVI-12 | Propylene glycol | 30 | Armour | Parenteral |
| Nembutal | Ethanol<br>Propylene glycol | 10<br>40 | Abbott | Parenteral |
| Neoloid | Propylene glycol | | Lederle | Oral |
| Nitro-BID IV | Ethanol | 70 | Marion | Parenteral |
| Novahistine DH | Glycerin | | Lakeside | Oral |
| Paradione | Ethanol | 65 | Abbott | Oral liquid |
| Pentuss | Propylene glycol | | Fisons | Oral |
| Psorcon ointment | Propylene glycol | | Dermik | Topical |
| Rondec DM | Glycerin | | Ross | Oral |
| S-T Forte syrup | Ethanol | 5 | Scot-Tussin | Oral liquid |
| Sulfoxyl lotion | Propylene glycol | | Stiefel | Topical |
| Tinactin | Polyethylene glycol | | Schering | Topical |
| Trideslon cream | Glycerin | | Miles | Topical |
| Tussar | Propylene glycol | | Rorer | Oral |
| Tussionex | Propylene glycol | | Fisons | Oral |

| Trade Name | Cosolvent | vol% | Manufacturer | Type |
|---|---|---|---|---|
| Tylenol | Propylene glycol | | McNeil Consumer | Oral |
| Valium | Ethanol<br>Propylene glycol | 10<br>40 | Roche | Parenteral |
| Vepesid | Ethanol | 30.5 | Bristol-Myers | Parenteral |

(Data are from reference 21)

### 14.21.2.3 Applications of cosolvency in environmental sciences and engineering

The significance of cosolvency research in environmental sciences stems from the need for accurately modeling the distribution and movement of organic pollutants, and cleaning up polluted soils and sediments. Since the late 1970s, environmental research on the effect of cosolvents has grown steadily.

Most published research papers have focused on the effects of adding cosolvents on the aqueous solubility[18,22-31] and soil sorption[28,32-44] of pollutants of interest. A few researchers have also examined cosolvent effects on liquid phase partitioning.[45,46] In the cases of industrial waste discharges, liquid fuel and paint spills, storage tank leakage, landfill leaching, and illegal dumping, various organic solvents may find their way into the natural environment. These solvents may not only act as pollutants themselves, but also bring substantial changes on the distribution, movement, and fate of other environmental pollutants with high concern. In environmental cosolvency studies, the majority of the solutes are hydrophobic organic compounds (HOCs), including benzene and its derivatives, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and furans (PCDDs and PCDFs), and various pesticides. These chemicals are toxic, and many of them are mutagenic and carcinogenic. The 1990 Clean Air Act Amendment has stimulated research on gasoline additives such as methyl t-butyl ether (MTBE) and formulated fuels like gasohol. Their cosolvent effects on the solubility and sorption of a few pollutant groups have also been examined.[25,47]

Meanwhile, environmental engineers have put cosolvents to work in cleaning up contaminated sites. As a consequence of the failure of using traditional pump-and-treat remediation for soils contaminated with organic pollutants, a few new approaches have been experimented since the late 1980s. Among those involving cosolvents, *Ex situ* solvent extraction was developed to treat excavated soils, sediment, or sludge. A typical one is the basic extractive sludge treatment (B.E.S.T.) process certified by USEPA.[48,49] Triethylamine was selected as the extracting solvent due mainly to its inverse miscibility property - it is completely miscible with water below 60°F but separates from water above 90°F. This property makes it easier to recycle the solvents after separating the treated solids from liquids containing the solvent, pollutants, and water. For PCBs in various soils, it is typical to achieve an extraction efficiency higher than 99% using the B.E.S.T technique.

More attractive are *in situ* remediation approaches, which often cost less. Cosolvents promote the mobilization of organic chemicals in soils, thus accelerating the cleanup of contaminated site. Cosolvent flushing has been developed using the same principles as those used in solvent flooding, a technique to enhance petroleum recovery in oil fields. It involves injecting a solvent mixture, mostly water plus a miscible cosolvent, into the vadose or saturated zone upgradient of the contaminated area. The solvent with the removed contaminants is then extracted downgradient and treated above ground. Precise formulations for the water/cosolvent mixture need to be determined by laboratory and pilot studies in order to achieve the desired removal.[50-53]

A few field-scale evaluations of this technique were carried out at Hill Air Force Base, Utah, where the aquifer had been severely contaminated by jet fuel, chlorinated solvents, and pesticides during 1940s and 1950s. These contaminants had formed a complex non-aqueous phase liquid (NAPL) containing more than 200 constituents, which covered the surfaces of soil particles and was trapped in pores and capillaries over the years. One of the evaluations consisted of pumping ternary cosolvent mixture (70% ethanol, 12% n-pentanol, and 18% water) through a hydraulically isolated test cell over a period of 10 days, followed by flushing with water for another 20 days.[54,55] The removal efficiency varied from 90-99% at the top zone to 70-80% at the bottom near a confining clay layer. Similar removal efficiencies were obtained from another test cell using a combination of cosolvent n-pentanol and a surfactant at a total of 5.5 wt % of the flushing solution.[56] In order to remove gasoline residuals at a US Coast Guard base in Traverse City, Michigan, it was demonstrated that the contaminants were mobilized when cosolvent 2-propanol was used at 50% concentration, while methanol at either 20% or 50% showed little effect.[57] Cosolvent flushing was also proven to be effective in treating NAPLs which were denser than water. Methanol, isopropanol, and t-butanol were used in treating soils contaminated with tri- and tetra-chlorinated ethylenes.[58]

The applicability of solvent flushing, however, is often limited by the characteristics of the soil, especially the particle size distribution. While sandy soils may result in uncontrolled fluid migration, clayey soils with particles size less than 60 μm are often considered unsuitable for *in situ* solvent flushing due to low soil permeability. In an attempt to remove PAHs from poorly permeable soils, Li, et al.[59] investigated the possibility of combining cosolvent flushing with the electrokinetic technique. Electrokinetic remediation involves application of a low direct electrical current to electrodes that are inserted into the ground. As water is continuously replenished at anodes, dissolved contaminants are flushed toward the cathode due to electroosmosis, where they can be extracted and further treated by various conventional wastewater treatment methods. Their column experiment of removing phenanthrene from soil was moderately successful with the assistance of cosolvent n-butylamine at 20%(v). Retardation factor (ratio of the water linear velocity to that of the chemical) of phenanthrene was reduced from 753 in pure water to 11 by the presence of n-butylamine, and 43% of the phenanthrene was removed after 127 days or 9 pore volumes. However, significant removal of phenanthrene was not attained in their experiments with acetone and hydrofuran as cosolvents.

### 14.21.2.4 Experimental observations

Numerous experimental data exist in the literature on the solubility of organic solutes, including both drugs and environmental pollutants, in various mixtures of water and cosolvents. Experimental observations are often illustrated by plotting the logarithm of solubility of the solute versus the volume fraction of cosolvent in the solvent mixture. A few examples of solubilization curves are shown in Figure 14.21.2.1, which shows three typical situations for solutes of different hydrophobicity in the mixture of water and ethanol.

The classification of solute/cosolvent/water systems based on their relative polarity was suggested by Yalkowsky and Roseman.[61] Solutes which are less polar than both water

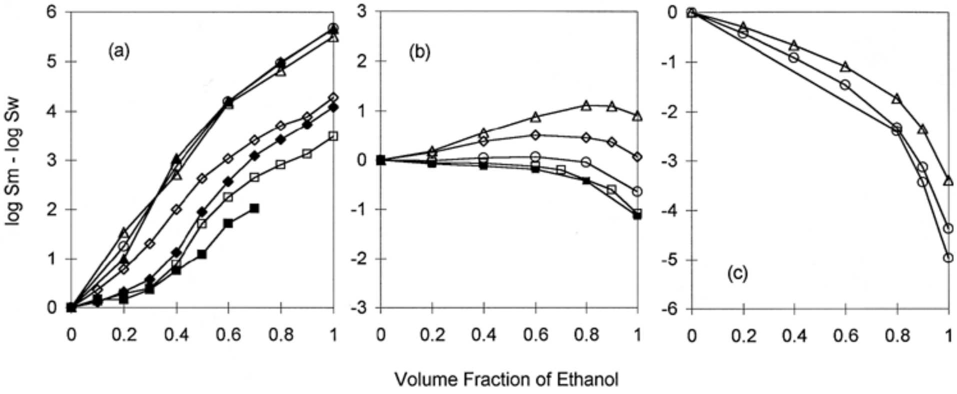

Figure 14.21.2.1. Effects of ethanol on the solubilities of selected organic compounds. (a): ■ benzene, □ naphthalene, ◆ biphenyl, ◇ anthracene, ▲ benzo(a)pyrene, △ perylene, ○ chrysene; (b) ■ hydantoic acid, □ hydantoin, ○ methyl hydantoic acic, ◇ 5-ethyl hydantoin, △ 5-isobutyl hydantoin; (c) □ triglycine, ○ diglycine, △ glycine [Adapted, by permission, from Li and Yalkovsky, *J. Pharm. Sci.*, **83**, 1735 (1994).]

and the cosolvent are considered as "nonpolar", those which have a polarity between those of water and the cosolvent as "semipolar", and those which are more polar than both water and cosolvent as "polar". Figure 14.21.2.1-a illustrates the behavior of relatively hydrophobic compounds, which tend to have monatonically increasing solubilization curves. The solubility enhancement is greater for the more hydrophobic solutes. Curves with opposite trends were mostly observed for polar solutes. The monatonical desolubilization is greater for more hydrophilic solutes, as evidenced by the curves in Figure 14.21.2.1-c. In-between are semipolar solutes with slightly parabolic curves shown in 14.21.2.1-b. The impact of adding cosolvents is much less profound for the semipolars than for the other two groups. On a linear solubility scale, the parabola tends to be more obvious than on the log scale. The same general trends were seen for the cosolvents glycerine[61] and propylene glycol[61,62] and presumably many other water-miscible cosolvents.

It is more difficult to evaluate the effects of cosolvents which have limited miscibility with water. In the literature, such organic solvents have been termed as both cosolvents and cosolutes, and there is no clear criteria for the distinction. Cosolvent is usually miscible with water, or to be used in an attempt to increase the aqueous solubility of the solute. Cosolute, on the other hand, may be organic chemicals which have a similar chemical structure or behave similarly with the solute when they exist in water alone. The effects of cosolutes have been examined in a limited number of published papers.[63-73]

Partially water-miscible organic solvents (PMOSs) may act as either cosolvents or cosolutes, and the research in the past has shown the complexity of their effects.[23,27-30,73-75] It was demonstrated that in order to exert effects on solubility or sorption of HOCs, PMOSs must exist as a component of the solvent mixture in an appreciable amount: Munz and Roberts[23] suggested a mole fraction of greater than 0.005 and Rao and coworkers[27,28] proposed a volume percent of 1% or a concentration above $10^4$ mg/L. Cosolvents with relatively high water solubility are likely to demonstrate observable effects on the solubilities of solutes, up to their solubility limits, in a similar manner to cosolvents of complete miscibility with water. A few experimental examples of the effects of PMOSs include 1-butanol and

1-pentanol acting on PCB congeners[30] and naphthalene.[26] and butanone on anthracene and fluoranthene.[75]

Even more hydrophobic organic solvents produce little or even negative influence on the solubility of HOCs. For instance, the presence of benzene does not increase the aqueous solubility of PCBs up to their saturation concentration.[29] Solubility of a few PCB congeners in water were found to be depressed by dissolved dichloromethane and chloroform.[73] On the other hand, PCB solubility showed little change when cosolvent benzyl alcohol, 1-hexanol, 1-heptanol, or 1-octanol was present.[29,30] Similar "no change" observations were made for naphthalene with cosolvents dichloromethane and chloroform,[73] and for solutes benzene and hexane with cosolvent MTBE.[25] Much of the complexity with hydrophobic cosolvents, or rather, cosolutes, can be explained by the fact that these cosolvents may partition into the solute phase, thus the physical state of the solute is no longer the same as is in pure water. Instead of a basically pure crystalline or liquid phase of solute, the solute and the cosolvent form an organic mixture, and the composition and ideality of this mixture will very much determine the concentrations of its components in the aqueous phase. Such a situation may be better investigated along the line of phase partitioning, where Raoult's law defines an ideal system.

### 14.21.2.5 Predicting cosolvency in homogeneous liquid systems

The log-linear model

Yalkowsky and Roseman introduced the log-linear model in 1984 to describe the phenomenon of the exponential increase in aqueous solubility for nonpolar organic compounds as the cosolvent concentration is increased.[61] They showed that

$$\log S_m^i = f \log S_c + (1-f)\log S_w \qquad [14.21.2.1]$$

Rearranging equation [14.21.2.1] results in

$$\log\left(S_m^i / S_w\right) = f \log(S_c / S_w) = \sigma f \qquad [14.21.2.2]$$

The left side of equation [14.21.2.2] reflects the extent of solubilization; f defines how much cosolvent is required to reach the desired solubilization. The constant σ is the end-to-end slope of the solubilization curve and defined by:

$$\sigma = \log S_c - \log S_w = \log(S_c / S_w) \qquad [14.21.2.3]$$

The model can be extended to systems containing a number of cosolvents:

$$\log\left(S_m^i / S_w\right) = \sum \sigma_i f_i \qquad [14.21.2.4]$$

where the subscribe i denotes the ith component of the solvent mixture.

Two measured solubilities will define the value of σ that is specific to a solute/cosolvent pair. The value of σ is also dependent of the solubility unit selected and on whether 10-based or *e*-based logarithm is used. The magnitude of σ reflects the difference in molecular interactions between solute/cosolvent and solute/water. When applied to describe cosolvency, σ is like a microscopic partition coefficient if water and cosolvent are thought of as two independent entities. There had been other definitions of σ, such as the partial derivative $\partial(\log S_m)/\partial f$,[76] or the regressional (not end-to-end) slope of the solubilization curve.[77] The $\sigma$ defined in these ways will depend on the range of f and on the accuracy of all data points over the entire range of f. These definitions are not desirable because they make $\sigma$ difficult to predict and interpret in light of the concept of ideal solvent mixture on which the log-linear model is based. Note also that $\sigma$ is not related to the crystalline structure of the solute, since the contributions from the free energy of melting to the two solubilities cancel out. However, it may change if the solute exists in pure cosolvent with a chemical identity different from that in water, as in the cases where solute degradation, solvation, or solvent-mediated polymorphic transitions occur in either solvent.

### Estimation of $\sigma$

Laboratory measurements of $S_w$ and $S_c$ can be costly and difficult. Various methods, including group contribution technique and quantitative structure (or property) property relationships (QSPRs or QPPRs),[78] are available to estimate $S_w$ and $S_c$, from which $\sigma$ values can be derived. A direct approach of predicting $\sigma$ has also been established based on the dependence of cosolvency on solute hydrophobicity. Among a number of polarity indices, octanol/water partition coefficient, $K_{ow}$, was initially chosen by Yalkowsky and Roseman[61] for correlation with $\sigma$, due mainly to the abundance of available experimental $K_{ow}$ data and the wide acceptance of the Hansch-Leo fragment method[79] for its estimation. $K_{ow}$ is a macroscopic property which does not necessarily correlate with micro-scale polarity indices such as dipole moment, and only in a rank order correlates with other macroscopic polarity indicators such as surface tension, dielectric constant, and solubility parameter.

Correlation between $\sigma$ and solute $K_{ow}$ takes the form:

$$\sigma = a + b\log K_{ow} \qquad [14.21.2.5]$$

where a and b are constants that are specific for the cosolvent but independent of solutes. Their values have been reported for various cosolvents and are summarized in Table 14.21.2.2.

From Table 14.21.2.2, the slopes of equation [14.21.2.5], b, are generally close to unity, with few below 0.6 or above 1.2. Most of the intercepts a are less than one, with a few negative values. In searching for the physical implications of the regression constants a and b, Li and Yalkowsky[80] derived equation [14.21.2.6]:

$$\sigma = \log K_{ow} + \log\left(\gamma_0^{\infty *} / \gamma_c\right) + \log\left(\gamma_w / \gamma_w^{\infty *}\right) + \log\left(V_0^{*} / V_c\right) \qquad [14.21.2.6]$$

According to this equation, $\sigma$~log $K_{ow}$ correlation will indeed have a slope of one and a predictable intercept of log ($V_o$*/$V_c$) if both $\gamma_0^{\infty *}/\gamma_c$ and $\gamma_w/\gamma_w^{\infty *}$ terms equal unity. $V_o^* = 0.119$ L mol$^{-1}$ based on a solubility of water in octanol of 2.3 mol L$^{-1}$, and $V_c$ ranges from 0.04 to 0.10 L$^3$ mol$^{-1}$, thus log ($V_o$*/$V_c$) is in the range of 0.08 to 0.47, for the solvents included in Table 14.21.2.2 with the exclusion of PEG400. However, both $\gamma_0^{\infty *}/\gamma_c$ and $\gamma_w/\gamma_w^{\infty *}$ are not likely to be unity, and their accurate values are difficult to estimate for many solutes. The ratio $\gamma_0^{\infty *}/\gamma_c$ compares the solute behavior in water-saturated octanol under dilute conditions and in pure cosolvent at saturation, while the $\gamma_w/\gamma_w^{\infty *}$ term reflects both the effect of dissolved octanol on the aqueous activity coefficient and the variation of the activity coefficient with concentration. Furthermore, the magnitudes of both terms will vary from one solute to another, making it unlikely that a unique regression intercept will be observed over a wide range of solutes. Indeed, both a and b were found to be dependent on the range of the solute log $K_{ow}$ used in the regression. For instance, for solutes with log $K_{ow} \leq 0$, 0.01 to 2.99, and $\geq 3$, the correlation of $\sigma$ versus log $K_{ow}$ for cosolvent ethanol have slopes of 0.84, 0.79, and 0.69, respectively, and the corresponding intercepts increase accordingly; the slope of the overall correlation, however, is 0.95. Much of the scattering on the $\sigma$~log $K_{ow}$ regression resides on the region of relatively hydrophilic solutes. Most polar solutes dissociate to some extent in aqueous solutions, and their experimental log $K_{ow}$ values are less reliable. Even less certain is the extent of specific interactions between these polar solutes and the solvent components.

According to equation [14.21.2.6], $\sigma$ may not be a linear function of solute log $K_{ow}$ on a theoretical basis. However, despite the complexities caused by the activity coefficients, quality of the regression of $\sigma$ against log $K_{ow}$ is generally high, as evidenced by the satisfactory $R^2$ values in Table 14.21.2.2. This can be explained by the fact that changes in both $\gamma$ ratios are much less significant compared with the variations of $K_{ow}$ for different solutes. In addition, the two $\gamma$ terms may cancel each other to some degree for many solutes, further reducing their effects on the correlation between $\sigma$ and log $K_{ow}$. It is convenient and reliable to estimate $\sigma$ from known log $K_{ow}$ of the solute of interest, especially when the log $K_{ow}$ of the solute of interest falls within the range used in obtaining the values of a and b.

Dependence of $\sigma$ on the properties of cosolvents has been less investigated than those of solutes. While hundreds of solutes are involved, only about a dozen organic solvents have been investigated for their cosolvency potentials. A few researchers examined the correlations between $\sigma$ and physicochemical properties of cosolvents for specific solutes, for instance, Li et al. for naphthelene,[31] and Rubino and Yalkowsky for drugs benzocaine, diazepam, and phenytoin.[81] In both studies, hydrogen bond donor density (HBD), which is the volume normalized number of proton donor groups of a pure cosolvent, is best for comparing cosolvents and predicting $\sigma$. Second to HBD are the solubility parameter and interfacial tension (as well as log viscosity and $E_T$-30 for naphthalene systems), while log $K_{ow}$, dielectric constant, and surface tension, correlate poorly with $\sigma$. The HBD of a solvent can be readily calculated from the density and molecular mass with the knowledge of the chemical structure using equation [14.21.2.7]. The disadvantage of using HBD is that it cannot distinguish among aprotic solvents which have the same HBD value of zero.

$$HBD = (\textit{number of proton donor groups})(\textit{density})/(\textit{molecular mass}) \qquad [14.21.2.7]$$

In an attempt to generalize over solutes, Li and Yalkowsky[82] investigated the possible correlations between cosolvent properties and slope of the $\sigma$~log $K_{ow}$ regressions (b). Among the properties tested as a single regression variable, octanol-water partition coefficient, interfacial tension, and solubility parameter, are superior to others in correlating with b. Results of multiple linear regression show that the combination of log $K_{ow}$ and HDB of the cosolvent is best (equation [14.21.2.8]). Adding another variable such as solubility parameter does not improve the quality of regression.

$$b = 0.2513 \log K_{ow} - 0.0054\, HBD + 1.1645 \qquad [14.21.2.8]$$

$$(N = 13,\ R^2 = 0.942,\ SE = 0.060,\ F = 81.65)$$

where log $K_{ow}$ (range: -7.6 ~ 0.29) and HBD (range: 0 ~ 41) are those of the cosolvent.

Equation [14.21.2.8] can be helpful to obtain the b values for cosolvents not listed in Table 14.21.2.2. In order to estimate cosolvency for such cosolvents, values of the intercept a are also needed. However, values of a can be found in Table 14.21.2.2 for only about a dozen cosolvents, and there is no reliable method for its estimation. To obtain a for a cosolvent, a reasonable starting value can be log ($V_o$*/$V_c$), or -(0.92 + log $V_c$). The average absolute difference between a values listed in Table 14.21.2.2 and log ($V_o$*/$V_c$) is 0.18 (N=7) for alcohols and glycols, 0.59 (N = 6) for aprotic cosolvents, and > 1 for n-butylamine and PEG400.[82]

**Table 14.21.2.2. Summary of regression results for relationship between σ and solute log $K_{ow}$**

| Cosolvent | N | a | b | $R^2$ | log $K_{ow}$ range | Ref. |
|---|---|---|---|---|---|---|
| Methanol | 79 | 0.36±0.07 | 0.89±0.02 | 0.96 | -4.53 ~ 7.31 | 80 |
| Methanol | 16 | 1.09 | 0.57 | 0.83 | 2.0 ~ 7.2 | 29 |
| Methanol | 16 | 1.07 | 0.68 | 0.84 | n.a. | 24 |
| Ethanol | 197 | 0.30±0.04 | 0.95±0.02 | 0.95 | -4.90 ~ 8.23 | 80 |
| Ethanol | 107 | 0.40±0.06 | 0.90±0.02 | 0.96 | -4.9 ~ 6.1 | 60 |
| Ethanol | 11 | 0.81 | 0.85 | 0.94 | n.a. | 24 |
| 1-Propanol | 17 | 0.01±0.13 | 1.09±0.05 | 0.97 | -3.73 ~ 7.31 | 80 |
| 2-Propanol | 20 | -0.50±0.18 | 1.11±0.07 | 0.94 | -3.73 ~ 4.49 | 80 |
| 2-Propanol | 9 | 0.63 | 0.89 | 0.85 | n.a. | 24 |
| Acetone | 22 | -0.10±0.24 | 1.14±0.07 | 0.92 | -1.38 ~ 5.66 | 80 |
| Acetone | 14 | 0.48 | 1.00 | 0.93 | 0.6 ~ 5.6* | 24 |
| Acetonitrile | 10 | -0.49±0.42 | 1.16±0.16 | 0.86 | -0.06 ~ 4.49 | 80 |
| Acetonitrile | 8 | 0.35 | 1.03 | 0.90 | n.a. | 24 |
| Dioxane | 23 | 0.40±0.16 | 1.08±0.07 | 0.91 | -4.90 ~ 4.49 | 80 |
| Dimethylacetamide | 11 | 0.75±0.30 | 0.96±0.12 | 0.87 | 0.66 ~ 4.49 | 80 |
| Dimethylacetamide | 7 | 0.89 | 0.86 | 0.95 | n.a. | 24 |
| Dimethylformamide | 11 | 0.92±0.41 | 0.83±0.17 | 0.73 | 0.66 ~ 3.32 | 80 |
| Dimethylformamide | 7 | 0.87 | 0.87 | 0.94 | n.a. | 24 |
| Dimethylsulfoxide | 12 | 0.95±0.43 | 0.79±0.17 | 0.68 | 0.66 ~ 4.49 | 80 |
| Dimethylsulfoxide | 7 | 0.89 | 0.87 | 0.95 | n.a. | 24 |
| Glycerol | 21 | 0.28±0.15 | 0.35±0.05 | 0.72 | -3.28 ~ 4.75 | 80 |
| Ethylene glycol | 13 | 0.37±0.13 | 0.68±0.05 | 0.95 | -3.73 ~ 4.04 | 80 |
| Ethylene glycol | 7 | 1.04 | 0.36 | 0.75 | n.a. | 24 |
| Propylene glycol | 62 | 0.37±0.11 | 0.78±0.04 | 0.89 | -7.91 ~ 7.21 | 80 |

| Cosolvent | N | a | b | $R^2$ | log $K_{ow}$ range | Ref. |
|---|---|---|---|---|---|---|
| Propylene glycol | 47 | 0.03 | 0.89 | 0.99 | -5 ~ 7 | 61 |
| Propylene glycol | 8 | 0.77 | 0.62 | 0.96 | n.a. | 24 |
| PEG400 | 10 | 0.68±0.43 | 0.88±0.16 | 0.79 | -0.10 ~ 4.18 | 80 |
| Butylamine | 4 | 1.86±0.30 | 0.64±0.10 | 0.96 | -1.69 ~ 4.49 | 80 |

*estimated from Figure 3 in Reference 24.
n.a. = not available.

This empirical approach using equations [14.21.2.8], [14.21.2.5], and [14.21.2.2] can produce acceptable estimates of log ($S_m/S_w$) only if the solubilization exhibits a roughly log-linear pattern, such as in some HOC/water/methanol systems. In addition, it is important to limit the use of equations [14.21.2.5] and [14.21.2.8] within the ranges of log $K_{ow}$ used in obtaining the corresponding parameters.

## 14.21.2.6 Predicting cosolvency in non-ideal liquid mixtures

Deviations from the log-linear model

Most solubilization curves, as shown in Figure 14.21.2.1, exhibit significant curvatures which are not accounted for by the log-linear model. A closer look at the solubilization curves in Figure 14.21.2.1 reveals that the deviation can be concave, sigmoidal, or convex. In many cases, especially with amphiprotic cosolvents, a negative deviation from the end-to-end log-linear line is often observed at low cosolvent concentrations, followed by a more significant positive deviation as cosolvent fraction increases.

The extent of the deviation from the log-linear pattern, or the excess solubility, is measured by the difference between the measured and the log-linearly predicted log $S_m$ values:

$$\log\left(S_m / S_m^i\right) = \log S_m - \left(\log S_w + \sum \sigma_i f_i\right) \quad [14.21.2.9]$$

The values of log ($S_m/S_m^i$) for naphthalene, benzocaine, and benzoic acid in selected binary solvent mixtures are presented in Figures 14.21.2.2-a, -b, and -c, respectively.

The log-linear model is based on the presumed ideality of the mixtures of water and cosolvent. The log-linear relationship between log ($S_m/S_w$) and f is exact only if the cosolvent is identical to water, which cannot be the case in reality. Deviation is fortified as any degradation, solvation, dissociation, or solvent mediated polymorphic transitions of the solute occur. The problem is further compounded if the solute dissolves in an amount large enough to exert significant influence on the activity of solvent components. Due to the complexity of the problem, efforts to quantitatively describe the deviations have achieved only limited success.

A generally accepted viewpoint is that the deviation from the log-linear solubilization is mainly caused by the non-ideality of the solvent mixture. This is supported by the similarities in the patterns of observed log $S_m$ and activities of the cosolvent in solvent mixture, when they are graphically presented as functions of f. Based on the supposition that solvent non-ideality is the primary cause for the deviation, Rubino and Yalkowsky[87] examined the correlations between the extent of deviation and various physical properties of solvent mix-

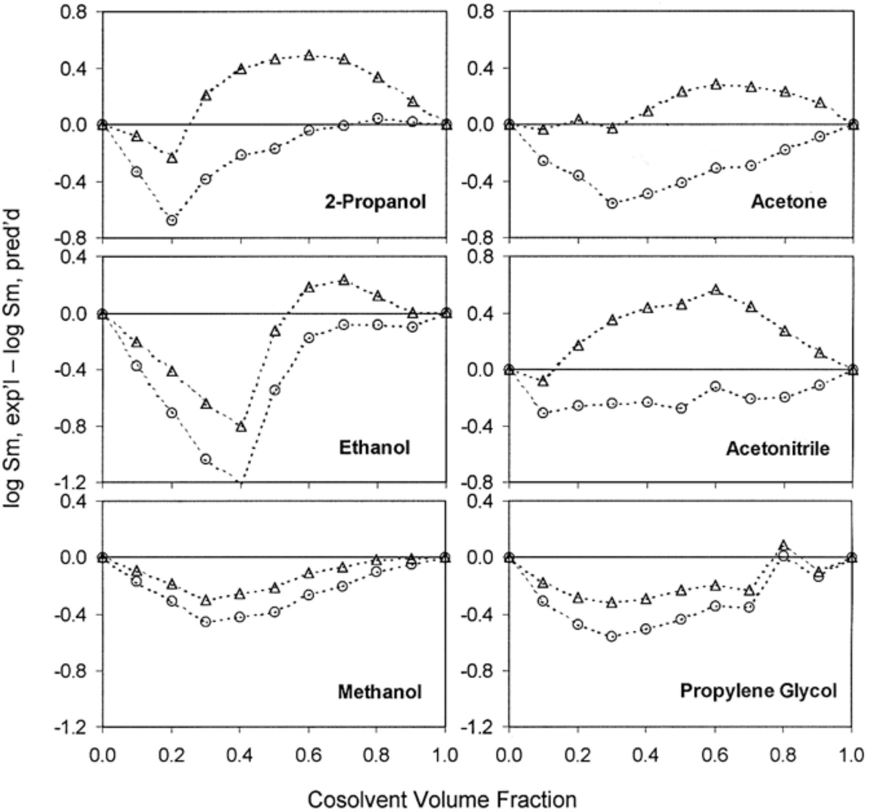

Figure 14.21.2.2a. Deviations from log-linear model (equation [14.21.2.2], triangle) and the extended log-linear model (equation [14.21.2.10], circle) for solute naphthalene in various water cosolvent systems. Experimental data are from Ref. 83.

tures. However, none of the properties consistently predicted the extrema of the deviation, although density corresponded in several cases.

Non-ideality of a mixture is quantitatively measured by the excess free energy of mixing. From this standpoint, Pinal et al.[75] proposed that a term $\Sigma(f_i \ln \gamma_i)$ be added to equation [14.21.2.4] to account for the effect of the non-ideality of solvent mixture:

$$\log\left(S_m^{ii} / S_w\right) = \sum \sigma_i f_i + 2.303 \sum f_i \log \gamma_i \qquad [14.21.2.10]$$

where $\gamma_i$ is the activity coefficient of solvent component i in solute-free solvent mixture. Values of $\gamma$'s can be calculated by UNIFAC, a group contribution method for the prediction of activity coefficients in nonelectrolyte, nonpolymeric liquid mixtures.[88] UNIFAC derived activity coefficients are listed in Table 14.21.2.3 for selected cosolvent-water mixtures. They are calculated with UNIFAC group interaction parameters derived from vapor-liquid equilibrium data.[89,90]

The difference between the experimental log $S_m$ and that predicted by the extended log-linear model, i.e., equation [14.21.2.10], is

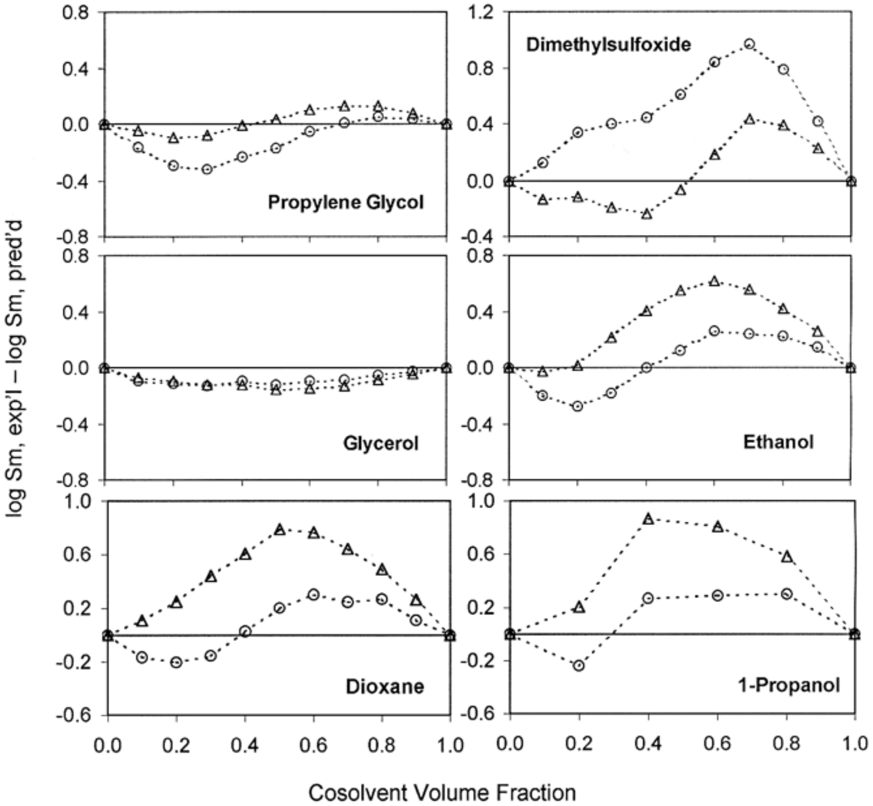

Figure 14.21.2.2b. Deviations from log-linear model (equation [14.21.2.2], triangle) and the extended log-linear model (equation [14.21.2.10], circle) for solute benzocaine in various water cosolvent systems. Experimental data are from Refs. 84 and 85.

$$\log\left(S_m / S_m^{ii}\right) = \log S_m - \left(\log S_w + \sum \sigma_i f_i + 2.303 \sum f_i \log \gamma_i\right) \quad [14.21.2.11]$$

Results of equation [14.21.2.11] for naphthalene, benzocaine, and benzoic acid in selected binary solvent mixtures are also included in Figure 14.21.2.2. A few other examples can be found in Pinal et al.[75]

The extended log-linear model outperforms the log-linear model in more than half of the cases tested for the three solutes in Figure 14.21.2.2. The improvement occurs mostly in regions with relatively high f values. In the low f regions, negative deviations of solubilities from the log-linear pattern are often observed as discussed above, but are not accounted for by the extended log-linear model as presented by equation [14.21.2.10]. In some cases, such as naphthalene in methanol and propylene glycol, and benzoic acid in ethylene glycol, the negative deviations occur over the entire f range of 0~1. In these cases, the extended log-linear model does not offer better estimates than the original log-linear model. With the activity coefficients listed in Table 14.21.2.3, the extended log-linear model generates worse estimates of log ($S_m/S_w$) than the log-linear model for systems containing dimethylacetamide, dimethylsulfoxide, or dimethylformamide. There is a possibility that

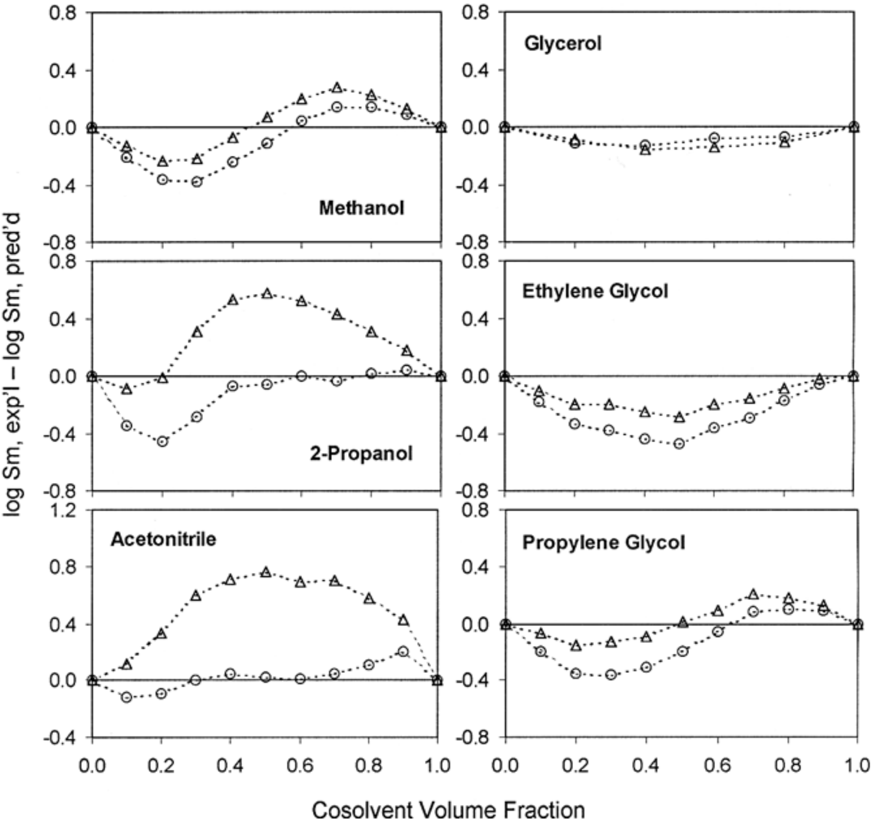

Figure 14.21.2.2c. Deviations from log-linear model (equation [14.21.2.2], triangle) and the extended log-linear model (equation [14.21.2.10], circle) for solute benzoic acid in various water cosolvent systems. Experimental data are from Refs. 61 and 86.

the UNIFAC group interaction parameters involved in these systems are incorrect. With all the systems tested in this study with solute naphthalene, benzocaine, or benzoic acid, it is also found that replacing $f_i$ in the last term of equation [14.21.2.11] with mole fraction $x_i$ offers slight improvement in only a few cases. Dropping the logarithm conversion constant 2.303 results in larger estimation errors for most systems.

An apparent limitation of this modification is the exclusion of any active role the solute may play on the observed deviation. Little understanding of the influence of solute structure and properties on deviations from the log-linear equation has been obtained. Although the patterns of deviations tend to be similar among solutes, as mentioned above, the extent of deviation is solute-dependent. For instance, $C_1$~$C_4$ alkyl esters of p-hydroxybenzoates and p-aminobenzoates demonstrated similar characteristics of solubilization by propylene glycol, with a negative deviation from the log-linear pattern occurring when f is low, followed by a positive one when f increases.[91] The magnitude of the negative deviation, however, was found to be related to the length of the solute alkyl chain in each group, while that of the positive deviation to the type of the polar groups attached.[91]

Both the hydrophobicity and hydrogen bonding property of the solutes seem to be important in influencing the extent of the deviation from the ideal log-linear pattern.

Additional deviations related to the solute's behavior may occur. For organic electrolytes, the acid dissociation constant $K_a$ may decrease as cosolvent fraction f increases.[40,75,92] This, in turn, will affect the patterns of solubilization by cosolvents. Furthermore, a high concentration of solutes may invalidate the log-linear model, which presumes negligible volume fraction of solute and no solute-solute interactions. For solid solutes, solvent induced polymorphism may also bring additional changes in their solubilization profile.

Another approach to quantitatively address the deviations of solubilization from the log-linear model makes use of an empirical parameter β:

$$\beta = \log(S_m / S_w) / \log(S_m^i / S_w) \qquad [14.21.2.12]$$

The modified log-linear equation then takes the form:

$$\log(S_m / S_w) = \beta \sum \sigma_i f_i \qquad [14.21.2.13]$$

**Table 14.21.2.3. UNIFAC derived activity coefficients for selected binary water-cosolvent systems**

| f | 0.1 | 0.2 | 0.4 | 0.6 | 0.8 | 0.9 |
|---|---|---|---|---|---|---|
| **Methanol** | MW = 32.04 | | | Density = 0.7914 | | |
| mol/L | 2.4700 | 4.9401 | 9.8801 | 14.8202 | 19.7603 | 22.2303 |
| x | 0.0471 | 0.1000 | 0.2286 | 0.4001 | 0.6401 | 0.8001 |
| γ, cosolvent | 1.972 | 1.748 | 1.413 | 1.189 | 1.052 | 1.014 |
| γ, water | 1.003 | 1.013 | 1.055 | 1.14 | 1.298 | 1.424 |
| **Ethanol** | MW = 46.07 | | | Density = 0.7893 | | |
| mol/L | 1.7133 | 3.4265 | 6.8530 | 10.2796 | 13.7061 | 15.4194 |
| x | 0.0331 | 0.0716 | 0.1705 | 0.3163 | 0.5523 | 0.7351 |
| γ, cosolvent | 5.550 | 4.119 | 2.416 | 1.564 | 1.152 | 1.050 |
| γ, water | 1.005 | 1.022 | 1.097 | 1.256 | 1.57 | 1.854 |
| **1-Propanol** | MW = 60.1 | | | Density = 0.8053 | | |
| mol/L | 1.3399 | 2.6799 | 5.3597 | 8.0396 | 10.7195 | 12.0594 |
| x | 0.0261 | 0.0569 | 0.1385 | 0.2657 | 0.4910 | 0.6846 |
| γ, cosolvent | 12.77 | 8.323 | 3.827 | 2.001 | 1.248 | 1.077 |
| γ, water | 1.006 | 1.024 | 1.111 | 1.301 | 1.706 | 2.093 |
| **2-Propanol** | MW = 60.1 | | | Density = 0.7848 | | |
| mol/L | 1.3058 | 2.6116 | 5.2233 | 7.8349 | 10.4466 | 11.7524 |

| f | 0.1 | 0.2 | 0.4 | 0.6 | 0.8 | 0.9 |
|---|---|---|---|---|---|---|
| x | 0.0255 | 0.0555 | 0.1355 | 0.2607 | 0.4846 | 0.6790 |
| γ, cosolvent | 12.93 | 8.488 | 3.921 | 2.040 | 1.258 | 1.080 |
| γ, water | 1.006 | 1.023 | 1.107 | 1.294 | 1.695 | 2.084 |
| **Acetone** | MW = 58.08 | | | Density = 0.7899 | | |
| mol/L | 1.3600 | 2.7200 | 5.4401 | 8.1601 | 10.8802 | 12.2402 |
| x | 0.0265 | 0.0577 | 0.1403 | 0.2686 | 0.4947 | 0.6878 |
| γ, cosolvent | 8.786 | 6.724 | 3.952 | 2.370 | 1.484 | 1.196 |
| γ, water | 1.004 | 1.015 | 1.075 | 1.222 | 1.616 | 2.211 |
| **Acetonitrile** | MW = 41.05 | | | Density = 0.7857 | | |
| mol/L | 1.9140 | 3.8280 | 7.6560 | 11.4840 | 15.3121 | 17.2261 |
| x | 0.0369 | 0.0793 | 0.1868 | 0.3407 | 0.5795 | 0.7561 |
| γ, cosolvent | 10.26 | 7.906 | 4.550 | 2.536 | 1.501 | 1.126 |
| γ, water | 1.005 | 1.021 | 1.11 | 1.366 | 2.076 | 3.571 |
| **Dioxane** | MW = 88.11 | | | Density = 1.0329 | | |
| mol/L | 1.1723 | 2.3446 | 4.6891 | 7.0337 | 9.3783 | 10.5506 |
| x | 0.0229 | 0.0501 | 0.1233 | 0.2404 | 0.4577 | 0.6551 |
| γ, cosolvent | 14.71 | 8.743 | 3.616 | 1.833 | 1.171 | 1.124 |
| γ, water | 1.006 | 1.026 | 1.112 | 1.284 | 1.604 | 1.666 |
| **DMA** | MW = 87.12 | | | Density = 0.9429 | | |
| mol/L | 1.0823 | 2.1646 | 4.3292 | 6.4938 | 8.6584 | 9.7407 |
| x | 0.0212 | 0.0464 | 0.1149 | 0.2261 | 0.4380 | 0.6368 |
| γ, cosolvent | 0.121 | 0.141 | 0.204 | 0.330 | 0.602 | 0.826 |
| γ, water | 0.999 | 0.994 | 0.962 | 0.872 | 0.651 | 0.453 |
| **DMF** | MW = 73.1 | | | Density = 0.9445 | | |
| mol/L | 1.2921 | 2.5841 | 5.1683 | 7.7524 | 10.3365 | 11.6286 |
| x | 0.0252 | 0.0549 | 0.1342 | 0.2586 | 0.4819 | 0.6767 |
| γ, cosolvent | 0.833 | 0.873 | 0.930 | 0.962 | 0.983 | 0.985 |
| γ, water | 0.999 | 0.997 | 0.991 | 0.984 | 0.972 | 0.969 |
| **DMSO** | MW = 78.13 | | | Density = 1.10 | | |
| mol/L | 1.4079 | 2.8158 | 5.6316 | 8.4475 | 11.2633 | 12.6712 |
| x | 0.0274 | 0.0596 | 0.1445 | 0.2754 | 0.5034 | 0.6952 |
| γ, cosolvent | 0.07956 | 0.110 | 0.211 | 0.399 | 0.715 | 0.899 |
| γ, water | 0.996 | 0.981 | 0.913 | 0.774 | 0.540 | 0.386 |

| **f** | **0.1** | **0.2** | **0.4** | **0.6** | **0.8** | **0.9** |
|---|---|---|---|---|---|---|
| **Glycerol** | | MW = 92.1 | | Density = 1.2611 | | |
| mol/L | 1.3693 | 2.7385 | 5.4771 | 8.2156 | 10.9542 | 12.3235 |
| x | 0.0267 | 0.0580 | 0.1411 | 0.2699 | 0.4964 | 0.6893 |
| $\gamma$, cosolvent | 1.257 | 1.066 | 0.903 | 0.899 | 0.969 | 0.996 |
| $\gamma$, water | 1.003 | 1.010 | 1.027 | 1.025 | 0.979 | 0.942 |
| **Ethylene glycol** | | MW = 62.07 | | Density = 1.1088 | | |
| mol/L | 1.7864 | 3.5727 | 7.1455 | 10.7182 | 14.2910 | 16.0773 |
| x | 0.0345 | 0.0744 | 0.1765 | 0.3254 | 0.5626 | 0.7432 |
| $\gamma$, cosolvent | 2.208 | 1.923 | 1.494 | 1.214 | 1.053 | 1.013 |
| $\gamma$, water | 1.002 | 1.01 | 1.047 | 1.12 | 1.247 | 1.338 |
| **Propylene glycol** | | MW = 76.09 | | Density = 1.0361 | | |
| mol/L | 1.3617 | 2.7234 | 5.4467 | 8.1701 | 10.8934 | 12.2551 |
| x | 0.0265 | 0.0577 | 0.1405 | 0.2688 | 0.4951 | 0.6881 |
| $\gamma$, cosolvent | 3.392 | 2.498 | 1.567 | 1.177 | 1.044 | 1.019 |
| $\gamma$, water | 1.005 | 1.018 | 1.069 | 1.145 | 1.224 | 1.267 |
| **Butylamine** | | MW = 73.14 | | Density = 0.7414 | | |
| mol/L | 1.0137 | 2.0273 | 4.0547 | 6.0820 | 8.1094 | 9.1231 |
| x | 0.0199 | 0.0436 | 0.1084 | 0.2149 | 0.4219 | 0.6215 |
| $\gamma$, cosolvent | 6.532 | 4.498 | 2.318 | 1.391 | 1.042 | 0.998 |
| $\gamma$, water | 1.004 | 1.016 | 1.071 | 1.175 | 1.326 | 1.384 |

Under the assumptions that the solute is chemically stable and has little influence on the activity of solvent component, $\beta$ reflects the extent of deviation caused by the nonideality of the solvent mixture, as suggested by Rao et al.[28] However, since $\beta$ itself is a complicated function of f, equation [14.21.2.13] does not provide additional aid for predicting cosolvency.

### 14.21.2.7 Summary

Applications of cosolvency in pharmaceutical and environmental research and industries are briefly summarized. Using ethanol as an example, the effects of adding a cosolvent on the solubilities of various organic solutes are presented in Figure 14.21.2.1. The log-linear solubilization model, equation [14.21.2.2] or [14.21.2.4], is the simplest theory of cosolvency developed so far. It discovers general trends and major determinant factors of cosolvency, thus providing guidelines for predicting solubility of organic chemicals in mixed solvents. The cosolvency power of a specific cosolvent towards a solute of interest, $\sigma$, can be estimated with equation [14.21.2.5] with the knowledge of the solute octanol-water partition coefficient $K_{ow}$. Sources of error associated with this estimation method are discussed based on equation [14.21.2.6]. The slope of the $\sigma$~log $K_{ow}$ regression, b, can be estimated from the log $K_{ow}$ and hydrogen bond donor density of the cosolvent, as presented by equation [14.21.2.8]. One of the previously published modifications to the log-linear model, equation [14.21.2.10], is evaluated. The difference between the measured log $S_m$ and those predicted by the log-linear and the extended log-linear model are presented in Figure 14.21.2.2 for solutes naphthalene, benzocaine, and benzoic acids in selected water and cosolvent mixtures.

## Notations

| | |
|---|---|
| a | intercept of $\sigma \sim \log K_{ow}$ regression |
| b | slope of $\sigma \sim \log K_{ow}$ regression |
| f | volume fraction of cosolvent in mixed solvent with water. |
| $K_{ow}$ | n-octanol water partition coefficient |
| $S_c$ | solubility in pure cosolvent |
| $S_m$ | solubility in the mixture of water and cosolvent |
| $S^i_m$ | solubility in the mixture of water and cosolvent, predicted by the log-linear model (Eq. [14.21.2.2]) |
| $S^{ii}_m$ | solubility in the mixture of water and cosolvent, predicted by the extended log-linear model (Eq. [14.21.2.10]) |
| $S_w$ | solubility in pure water |
| $V_o$* | molar volume of 1-octanol saturated with water, 0.119 L $mol^{-1}$ (based on a solubility of water in octanol of 2.3 mol $L^{-1}$) |
| $V_c$ | molar volume of cosolvent |
| $V_w$* | molar volume of water saturated with 1-octanol, ≈ 0.018 L $mol^{-1}$ |
| $V_w$ | molar volume of water, 0.018 L $mol^{-1}$ |
| $\beta$ | empirically obtained water-cosolvent interaction parameter |
| $\sigma$ | cosolvency power, $\sigma = \log (S_c/S_w)$ |
| $\gamma_0^{\infty*}$ | infinite dilution activity coefficient of solute in 1-octanol saturated with water |
| $\gamma_c$ | activity coefficient of solute in cosolvent |
| $\gamma_w$ | activity coefficient of solute in water |
| $\gamma_w^{\infty*}$ | infinite dilution activity coefficient of solute in water saturated with 1-octanol |

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## 14.22 POLYMERS AND MAN-MADE FIBERS

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The resin production industry has over 450 plants in the USA with total sales of $33 billion/year and about 60,000 employees. The man-made fiber industry has over 90 plants. It employs about 45,000 people and it has sales of $13 billion/year.

In the polymer manufacture industry, production processes are diverse both in technology and equipment design. They have common steps which include preparation of reactants, polymerization, polymer recovery, polymer extrusion (if in pelletized form), and supporting operations. In some preparation operations, solvents are used to dissolve or dilute monomer and reactants. Solvent are also used to facilitate the transportation of the reaction mixture throughout the plant, to improve heat dissipation during the reaction, and to promote uniform mixing. Solvent selection is optimized to increase monomer ratio and to reduce polymerization costs and emissions. The final polymer may or may not be soluble in the solvent. These combinations of polymers and solvents are commonly used: HDPE - isobutane and hexane, LDPE - hydrocarbons, LLDPE - octene, butene, or hexene, polypropylene - hexane, heptane or liquid propylene, polystyrene - styrene or ethylbenzene, acrylic - dimethylacetamide or aqueous inorganic salt solutions. These examples show that there are options available. Excess monomer may replace solvent or water can be used as the solvent. During polymer recovery unreacted monomer and solvents are separated from polymer (monomers and solvents are flashed off by lowering the pressure and sometimes degassing under vacuum), liquids and solids are separated (the polymer may be washed to remove sol-

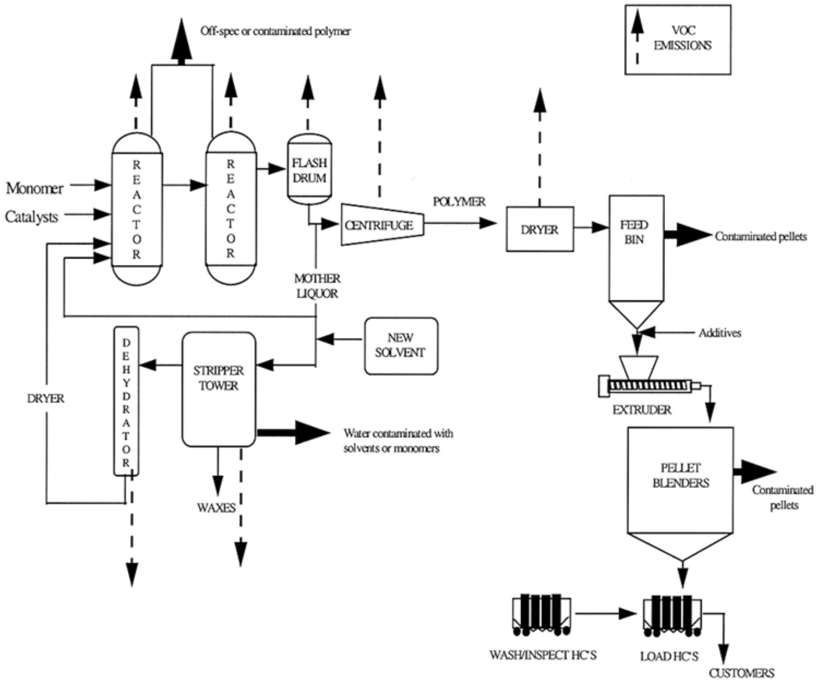

Figure 14.22.1. Schematic diagram of emissions from the polymer manufacturing industry. [Reproduced from EPA Office of Compliance Sector Notebook Project. Profile of the Petroleum Refining Industry. US Environmental Protection Agency, 1995.]

vent), and residual water and solvent are purged during polymer drying. Residual solvents are removed by further drying and extrusion. Solvents are also used in equipment cleaning. Solvents are often stored under a nitrogen blanket to minimize oxidation and contamination. When these systems are vented solvent losses occur. Figure 14.22.1 shows a schematic diagram of potential emissions during polymer manufacture.

Manufacture of man-made fibers involves polymerization (usually the core part of the process), preparation of the solution, spinning, washing and coagulation, drying and other operations. Fibers are formed by forcing the viscous liquid through small-bore orifices. A suitable viscosity can be achieved either by heating or dissolution. The rheological properties of the solution are governed to a large degree by the solvents selected. Wastes generated during the spinning operation include evaporated solvent and wastewater contaminated by solvent. The typical solvents used in the production of fibers are dimethylacetamide (acrylic), acetone or chlorinated hydrocarbon (cellulose acetate), and carbon disulfide (rayon). In the dry spinning process a solution of polymer is first prepared. The solution is then heated above the boiling temperature of the solvent and the solution is extruded through spinneret. The solvent evaporates into the gas stream. With wet spinning the fiber is directly extruded into a coagulation bath where solvent diffuses into the bath liquid and the coagulant diffuses into the fiber. The fiber is washed free of solvent by passing it through an additional bath. Each process step generates emissions or wastewater. Solvents used in production are normally recovered by distillation. Figure 14.22.2 is a schematic diagram of fiber production showing that almost all stages of production generate emissions.

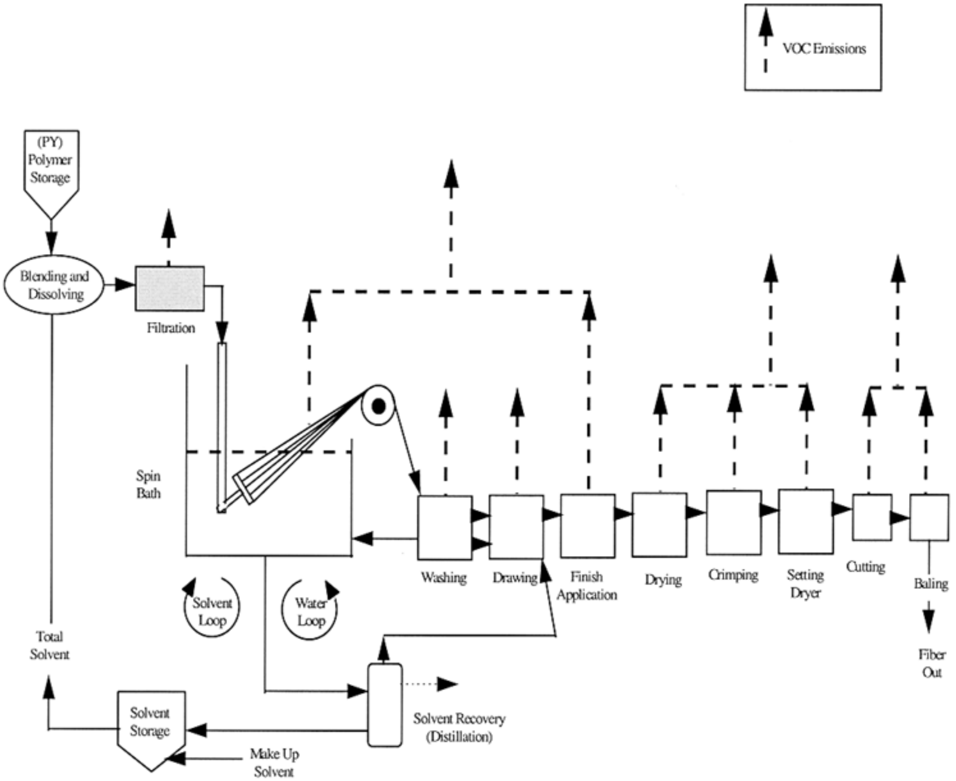

Figure 14.22.2. Schematic diagram of emissions from the man-made fiber manufacturing industry. [Reproduced from EPA Office of Compliance Sector Notebook Project. Profile of the Petroleum Refining Industry. US Environmental Protection Agency, 1995.]

Tables 14.22.1 and 14.22.2 provide data on releases and transfers from both polymer manufacturing and man-made fiber production in the USA. Carbon disulfide, methanol, xylene, and ethylene glycol are used in the largest quantities. Carbon disulfide is used in manufacture of regenerated cellulose and rayon. Ethylene glycol is used in the manufacture of polyethylene terephthalate, the manufacture of alkyd resins, and as cosolvent for cellulose ethers and esters. Methanol is used in several processes, the largest being in the production of polyester. This industry is the 10th largest contributor of VOC and 7th largest in releases and transfers.

There have been many initiatives to reduce emissions and usage of solvents. Man-made fiber manufacturing no longer uses benzene. DuPont eliminated o-xylene and reduced methanol and ethylene glycol use in its Wilmington operation. This change resulted in annual savings of $1 million. Process modification in a polymer processing plant resulted in a decrease in total emissions of 74% and a reduction in the release of cyclohexane by 96%. Monitoring of thousands of valves in Eastman Texas plant resulted in a program of valve replacement which eliminated 99% of the emissions. Plant in Florida eliminated solvents from cleaning and degreasing. These examples show that in many cases pollution can be reduced by better equipment, organization, and care.

**Table 14.22.1 Reported solvent releases from the polymer and man-made fiber industry in 1995 [Data from Ref. 1]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| allyl alcohol | 29,000 | 1,4-dioxane | 10,000 |
| benzene | 60,000 | ethylbenzene | 130,000 |
| n-butyl alcohol | 480,000 | ethylene glycol | 1,400,000 |
| sec-butyl alcohol | 25,000 | hexane | 880,000 |
| tert-butyl alcohol | 16,000 | methanol | 3,600,000 |
| carbon disulfide | 27,500,000 | methyl ethyl ketone | 260,000 |
| carbon tetrachloride | 100 | methyl isobutyl ketone | 98,000 |
| chlorobenzene | 19,000 | pyridine | 67,000 |
| chloroform | 14,000 | tetrachloroethylene | 4,000 |
| cresol | 4,000 | 1,1,1-trichloroethane | 120,000 |
| cyclohexane | 98,000 | trichloroethylene | 39,000 |
| 1,2-dichloroethane | 98,000 | 1,2,4-trimethylbenzene | 12,000 |
| dichloromethane | 1,300,000 | toluene | 900,000 |
| N,N-dimethylformamide | 19,000 | xylene | 460,000 |

**Table 14.22.2. Reported solvent transfers from the polymer and man-made fiber industry in 1995 [Data from Ref. 1]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| allyl alcohol | 120,000 | ethylbenzene | 880,000 |
| benzene | 160,000 | ethylene glycol | 49,000,000 |
| n-butyl alcohol | 330,000 | hexane | 8,000,000 |
| sec-butyl alcohol | 12,000 | methanol | 5,600,000 |
| tert-butyl alcohol | 160,000 | methyl ethyl ketone | 460,000 |
| carbon disulfide | 14,000 | methyl isobutyl ketone | 43,000 |
| carbon tetrachloride | 200,000 | N-methyl-2-pyrrolidone | 780,000 |
| chlorobenzene | 570,000 | pyridine | 70,000 |
| chloroform | 59,000 | tetrachloroethylene | 330,000 |
| cresol | 20,000 | 1,1,1-trichloroethane | 21,000 |
| cyclohexane | 420,000 | trichloroethylene | 76,000 |
| dichloromethane | 250,000 | 1,2,4-trimethylbenzene | 98,000 |
| N,N-dimethylformamide | 300,000 | toluene | 2,800,000 |
| 1,4-dioxane | 11,000 | xylene | 7,800,000 |

New technology is emerging to reduce solvent use. Recent inventions disclose that, in addition to reducing solvents, the stability of ethylene polymers can be improved with the new developed process.[3] A proper selection of solvent improved a stripping operation and contributed to the better quality of cyclic esters used as monomers.[4] Solvent was used for the recovery of fine particles of polymer which were contaminating water.[5] A new process for producing fiber for cigarette filters uses reduced amounts of solvent.[6] Optical fibers are manufactured by radiation curing which eliminates solvents.[7] A new electrospinning process has been developed which produces unique fibers by the dry spinning method, providing a simpler separation and regeneration of the solvent.[8]

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## 14.23 PRINTING INDUSTRY

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The number of printing and publishing operations in the US is estimated at over 100,000. 1.5 million people are employed. The value of shipments is over $135 billion. 97% of printing is done by lithography, gravure, flexography, letterpress, and screen printing on substrates such as paper, plastic metal, and ceramic. Although, these processes differ, the common feature is the use of cleaning solvents in imaging, platemaking, printing, and finishing operation. Most inks contain solvents and many of the adhesives used in finishing operations also contain solvents. Many processes use the so-called fountain solutions which are applied to enable the non-image area of the printing plate to repel ink. These solutions contain primarily isopropyl alcohol. But the printing operation is, by itself, the largest contributor of VOCs. Each printing process requires inks which differ drastically in rheology. For example, gravure printing requires low viscosity inks which contain a higher solvent concentrations.

Tables 14.23.1 and 14.23.2 provide data on the reported releases and transfers of solvents by the US printing industry. These data show that there are fewer solvents and relatively low releases and transfers compared with other industries. In terms of VOC contribution, the printing industry is 5th and 10th in the total emissions and transfers.

Current literature shows that there is extensive activity within and outside industry to limit VOCs and reduce emissions. Cleaning operations are the major influence on emissions. Shell has developed a new cleaning formulations containing no aromatic or chlorinated hydrocarbons.[3] An additional requirement was to optimize the solvent mixture to prevent swelling of the rubber in blanket cylinders and rollers. It is predicted that the European industry will increase rate of the introduction of radiation-cured inks and eliminate isopropanol from fountain solutions.[4] It is expected that radiation-cured flexographic inks will grow by 30%/year in the next five years.[5] In Germany, 70-80% of emissions or 47,000 ton/year will have to be eliminated by the year 2007.[6] Beginning in 1999, the UK industry must keep VOC concentration below 5 tonnes/year per plant.[7] VOC concentration in outside atmosphere must not exceed 150 mg/m$^3$ (50 mg/m$^3$ if there is more than 5% aromatic solvents). Reactive hot melts are being used in book binding.[8] This will eliminate emissions from currently used solvent adhesives.

Solvent replacements are not the only solution at hand. Solvent-containing systems often give better quality than replacement systems, therefore methods have been developed to make the solvent based materials more acceptable. A soil bed biofiltration system was tested in California with excellent results.[9] This biofilter is a bed of soil impregnated with microorganisms which use VOC as their food. Present California regulations require that such a treatment system has a 67% capture and VOC destruction efficiency. The new method was proven to have 95.8% efficiency. In addition to environmental issues with solvents, the printing industry has addressed the source of their raw materials. Present systems are based on petroleum products which are not considered renewable resources. Terpenes are natural products which are now finding applications in the print industry.[10] In Denmark, of 70% cleaning solvents are vegetable oil based. These and other such innovations will continue to be applied to reduce solvent use and emissions. It is also reported[10] that water-based system replaces fountain solutions.

Other factors are driving changes. Odors in packaging materials and the migration of solvent to foods are unacceptable. Most odors in packaging materials are associated with process and coalescing solvents.[11] Foods which do not contain fat are more susceptible to the retaining the taste of solvents. Printing inks which may be acceptable for foods containing fat may not be suitable for fat-free applications (see more on this subject in Chapter 16.1).[12]

Many recent inventions have also been directed at solving the current environmental problems of printing industry.[13-21] The solvent in gravure printing inks not only contribute to pollution but also to the cost of solvent recovery and/or degradation. A new technology is proposed in which a solvent free ink with a low melting point can be processed in liquid state and then be solidified on cooling.[13] A non-volatile solvent for printing inks was developed based on a cyclic keto-enol tautomer and a drying oil.[14] An alcohol soluble polyamide for rotary letterpress printing inks was developed[15] and subsequently adapted to flexographic/gravure inks.[18] A polyamide was also used in a rotary letterpress ink which enabled low alcohols to be used as the solvent with some addition of an ester.[16] This new ink is compatible with water-based primers and adhesives which could not be used with solvent-based inks. Inks for jet printers are water sensitive. One solvent-based technology was developed using esters and glycols[17] and the other using low alcohols.[20] Another recent invention describes aqueous ink containing some low alcohols.[19] UV and electron beam cured ink concentrates were also developed.[21]

This information from open and patent literature clearly indicates that industry is actively working on the development of new technological processes to reduce emissions of solvents.

**Table 14.23.1. Reported solvent releases from the printing and publishing industry in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| n-butyl alcohol | 43,000 | methyl isobutyl ketone | 170,000 |
| dichloromethane | 59,000 | N-methyl-2-pyrrolidone | 31,000 |
| 1,4-dioxane | 8,000 | tetrachloroethylene | 34,000 |
| ethylene glycol | 46,000 | 1,1,1-trichloroethane | 180,000 |
| ethylbenzene | 23,000 | trichloroethylene | 13,000 |
| hexane | 50,000 | 1,2,4-trimethylbenzene | 36,000 |
| isopropyl alcohol | 27,000 | toluene | 12,200,000 |
| methanol | 170,000 | xylene | 700,000 |
| methyl ethyl ketone | 960,000 | | |

**Table 14.23.2. Reported solvent transfers from the printing and publishing industry in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| n-butyl alcohol | 7,000 | methyl isobutyl ketone | 63,000 |
| dichloromethane | 43,000 | N-methyl-2-pyrrolidone | 28,000 |
| 1,4-dioxane | 340 | tetrachloroethylene | 27,000 |
| ethylene glycol | 16,000 | 1,1,1-trichloroethane | 39,000 |
| ethylbenzene | 9,200 | trichloroethylene | 4,000 |
| hexane | 12,000 | 1,2,4-trimethylbenzene | 33,000 |
| isopropyl alcohol | 12,000 | toluene | 2,800,000 |
| methanol | 17,000 | xylene | 240,000 |
| methyl ethyl ketone | 700,000 | | |

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## 14.24 PULP AND PAPER

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The US pulp and paper industry operates over 550 facilities which employ over 200,000 people. Total shipments are $60 billion with an additional $80 billion in converted products. Several processes contribute to the emission of solvents. These include chemical pulping kraft process (terpenes, alcohols, methanol, acetone, chloroform), bleaching (acetone, dichloromethane, chloroform, methyl ethyl ketone, carbon disulfide, chloromethane, and trichloroethane), wastewater treatment (terpenes, alcohols, methanol, acetone, chloroform and methyl ethyl ketone), and evaporators in chemical recovery systems (alcohols and terpenes).

**Table 14.24.1. Reported solvent releases from the pulp and paper industry in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| benzene | 320,000 | methanol | 63,000,000 |
| n-butyl alcohol | 46,000 | methyl ethyl ketone | 700,000 |
| chloroform | 4,500,000 | methyl isobutyl ketone | 10,000 |
| chloromethane | 260,000 | 1,2,4-trimethylbenzene | 17,000 |
| cresol | 410,000 | toluene | 580,000 |
| ethylbenzene | 22,000 | xylene | 49,000 |
| ethylene glycol | 37,000 | o-xylene | 260 |
| hexane | 150,000 | | |

**Table 14.24.2. Reported solvent transfers from the pulp and paper industry in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| benzene | 24,000 | hexane | 8,600 |
| n-butyl alcohol | 16,000 | methanol | 23,000,000 |
| chloroform | 150,000 | methyl ethyl ketone | 36,000 |
| chloromethane | 120 | 1,2,4-trimethylbenzene | 1,400 |
| cresol | 3,600 | toluene | 23,000 |
| ethylene glycol | 190,000 | xylene | 4,000 |

**Table 14.25.1. Reported solvent releases from the rubber and plastics industry in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| benzene | 5,800 | ethylene glycol | 120,000 |
| n-butyl alcohol | 380,000 | hexane | 1,700,000 |
| sec-butyl alcohol | 17,000 | isopropyl alcohol | 28,000 |
| tert-butyl alcohol | 240 | methanol | 4,000,000 |
| carbon disulfide | 5,500,000 | methyl ethyl ketone | 5,500,000 |
| chlorobenzene | 5,000 | methyl isobutyl ketone | 1,100,000 |
| chloroform | 46,000 | N-methyl-2-pyrrolidone | 32,000 |
| chloromethane | 47,000 | tetrachloroethylene | 160,000 |
| cresol | 9,000 | 1,1,1-trichloroethane | 3,000,000 |
| cyclohexane | 480,000 | trichloroethylene | 660,000 |
| dichloromethane | 11,700,000 | 1,2,4-trimethylbenzene | 260,000 |
| N,N-dimethylformamide | 350,000 | toluene | 7,600,000 |
| 1,4-dioxane | 2,600 | xylene | 2,200,000 |
| ethylbenzene | 210,000 | m-xylene | 6,000 |

Tables 14.24.1 and 14.24.2 give the reported releases and transfers of solvent data for the US pulp and paper industry. If not for the emissions of methanol and chloroform the industry would be a much less serious polluter. It is 7th in VOC contributions and 8th in total releases and transfers.

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2 EPA Office of Compliance Sector Notebook Project. Sector Notebook Data Refresh - 1997. US Environmental Protection Agency, 1998.

**Table 14.25.2. Reported solvent transfers from the rubber and plastics industry in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| benzene | 15,000 | hexane | 50,000 |
| n-butyl alcohol | 370,000 | isopropyl alcohol | 14,000 |
| sec-butyl alcohol | 1,100 | methanol | 1,400,000 |
| tert-butyl alcohol | 85,000 | methyl ethyl ketone | 3,500,000 |
| carbon disulfide | 150,000 | methyl isobutyl ketone | 450,000 |
| chloroform | 1,200 | N-methyl-2-pyrrolidone | 120,000 |
| chloromethane | 330 | tetrachloroethylene | 47,000 |
| cresol | 3,000 | 1,1,1-trichloroethane | 160,000 |
| cyclohexane | 350,000 | trichloroethylene | 170,000 |
| dichloromethane | 900,000 | 1,2,4-trimethylbenzene | 14,000 |
| N,N-dimethylformamide | 570,000 | toluene | 2,200,000 |
| 1,4-dioxane | 49,000 | xylene | 940,000 |
| ethylbenzene | 350,000 | m-xylene | 5,700 |
| ethylene glycol | 15,300,000 | | |

## 14.25 RUBBER AND PLASTICS

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The US rubber and plastics industry employs over 800,000 people and operates over 12,000 plants. Its total production output is estimated at over $90 billion. The industry produces a wide diversity of products some of which do not contain solvents but many of which require the use of process solvents. Solvents are contained in adhesives used in finishing operations. Large quantities of solvents are used for surface cleaning and cleaning of equipment.

Tables 14.25.1 and 14.25.2 provide data on the reported releases and transfers of solvents by the US rubber and plastics industry. These industries contribute small amounts of VOC which are in the range of 0.00001-0.00005 kg VOC/kg of processed rubber. It was the ninth largest contributor to releases and transfers of all US industries. Dichloromethane, toluene, carbon disulfide, methyl ethyl ketone, methanol, 1,1,1-trichloroethane, hexane, methyl isobutyl ketone, and xylene are emitted in very large quantities.

## REFERENCES

1 EPA Office of Compliance Sector Notebook Project. Profile of the Rubber and Plastics Industry. US Environmental Protection Agency, 1995.
2 EPA Office of Compliance Sector Notebook Project. Sector Notebook Data Refresh - 1997. US Environmental Protection Agency, 1998.

## 14.26 USE OF SOLVENTS IN THE SHIPBUILDING AND SHIP REPAIR INDUSTRY

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### 14.26.1 INTRODUCTION

The focus of this chapter will be on the use of solvents in the shipbuilding and ship repair industry. This industrial sector is involved in building, repairing, repainting, converting, or alteration of marine and fresh water vessels. These vessels include self-propelled vessels, those propelled by other vessels (barges), military and Coast Guard vessels, commercial cargo and passenger vessels, patrol and pilot boats, and dredges. The industry sector is also involved in repairing and coating navigational aids such as buoys. This chapter begins with an overview of operations in a typical shipbuilding and/or ship repair facility (shipyard), to identify those operations that generate significant volatile organic compound (VOC) emissions and/or hazardous air pollutant (HAP) emissions from the use of organic solvents. Organic solvents that are VOCs contribute to formation of ozone in the troposphere. Other organic solvents such as chlorinated fluorocarbons (CFCs) cause depletion of the ozone layer in the stratosphere. Therefore, VOCs and other air toxics, such as those compounds listed as HAPs, are both indirectly and directly detrimental to the general public's health. Because many solvents are VOCs and often contain large amounts of HAPs, many state agencies[1,2] and the United States Environmental Protection Agency (U.S. EPA) have issued regulations to limit their content in materials used for surface coating and cleaning operations at shipyards.[3-7]

### 14.26.2 SHIPBUILDING AND SHIP REPAIR OPERATIONS

Most facilities engaged in shipbuilding or ship repair activities (shipyards) have several manufacturing areas in common, each including one or more "unit operations". These areas include: (a) surface preparation of primarily steel surfaces, which may include cleaning with multiple organic solvents; (b) assembly operations, which involve assembly of blocks that were constructed from sub-assembled parts (this step involves steel cutting and material movement using heavy equipment such as cranes); (c) cleaning operations (other than surface preparation) such as equipment and parts cleaning; and (d) coating operations.[8,9] There are secondary operations such as chrome plating, asbestos removal, fuel combustion, carpentry, and, to various degrees, polyester lay-up operations (composite materials construction activities). We will next discuss those operations that involve the use of organic cleaning solvents.

### 14.26.3 COATING OPERATIONS

Marine coatings can be applied by the use of spraying equipment, brushes, or rollers. Coating operations at shipyards are typically conducted at two primary locations: (1) outdoor work areas or (2) indoor spray booths. The outdoor work areas can include ship exteriors and interiors. Most shipyards report that typically only a small percentage (10%) of the coating operations are done indoors. However, in large construction yards a larger proportion (up to 30 %) of the coatings are applied indoors.[10] Coating and cleaning operations constitute the major source of VOC and HAP emissions from shipyards. If the metal surface is not well prepared before a coating is applied or if the coating is applied at the wrong ambient conditions, the coating system may fail and the work may have to be redone. The amount of cleaning necessary will depend on the type and extent of the problem and the coating system that is being used.

## 14.26.4 CLEANING OPERATIONS USING ORGANIC SOLVENTS

In most industrial applications involving metal substrates, organic cleaning solvents are used to remove contaminants or undesirable materials from surfaces before a coating is applied to clean equipment and parts utilized to apply the coating or soiled during that operation. Solvents are used for general maintenance of equipment parts. These surfaces are typically made of steel. However, vessels may also be made from natural materials such as wood and synthetic materials such as fiberglass. Therefore, a solvent must be selected that will not attack the substrate being cleaned.

For material accounting purposes, we can classify cleaning (unit) operations as follows:[11,12]

1. Surface preparation of large manufactured components (stage before a coating is applied).
2. Surface preparation of small manufactured components (stage before a coating is applied).
3. Line cleaning (includes piping network and any associated tanks).
4. Gun cleaning (manually or in a machine).
5. Spray booth cleaning (walls and floor).
6. Tank cleaning (mostly inner tank surfaces and any associated pipes).
7. Parts (machine) cleaning (simple dip tanks and large machines).
8. Cleaning of equipment and other items (e.g., bearings, buckets, brushes, contact switches).
9. Floor cleaning (organic solvents are no longer used).

These categories are similar to those found in other industries involved in the application of surface coating. However, the number of cleaning categories varies from one industry to another. For example, the automotive manufacturing industry (SIC code 3711) and the furniture industry are involved to various degrees in all nine types of cleaning operations. On the other hand, the photographic supplies (chemicals) industry will not include the first three listed cleaning operations.[11]

### 14.26.4.1 Surface preparation and initial corrosion protection

Large manufactured ship components are often cleaned with an organic solvent as the first of a number of cleaning steps that are required before a coating is applied. The method of surface preparation is selected to work with a chosen coating system. Surface preparation may include application of chemicals such as etching agents, organic solvents cleaners, and alkaline cleaners. Organic solvents such as mineral spirits, chlorinated solvents, and coal tar solvents are used to remove unwanted materials such as oil and grease.[13] If a ship is being repaired, existing coatings usually need to be removed. Solvents such as dichloromethane are commonly used for removing (stripping off) old or damaged coatings. However, aqueous systems involving caustic compounds are now being used more frequently for such purposes.[14] Pressure washing and hydro blasting are other cleaning techniques used. But, the predominant method is still particulate blasting (using abrasive media), which is used to remove mil scale, extra weld material, rust, and old coatings.

The angle at which the surface is blasted is chosen to generate the desired peaks and valleys on the substrate, that will accommodate the viscosity, chemistry (polar groups) of the primer coating. The surface profiling will also help the primer coating adhere mechanically to the substrate, contributing to the longevity of the coating system.[15] Pre-construction primers are sometimes used immediately following surface preparation (blasting) to prevent steel from oxidizing (rusting). This primer is removed by particulate blasting, before the protective coating system (one or more coatings) is applied to the assembled parts or blocks. Removal of such primers (when they cannot be welded-through) can result in emissions of VOCs and HAPs.

### 14.26.4.2 Cleaning operations after coatings are applied

Surface coating operations at shipyards use predominantly solvent-based coatings. Hence, relatively large amounts of organic solvents are used for cleaning and thinning activities. Table 14.26.1 shows the most common organic solvents used for thinning and cleaning, based on 1992 data.[16] Table 14.26.2 gives examples of solvent products that can be used for both thinning coatings and for cleaning surfaces after coatings are applied and for maintenance cleaning. The solvent products are listed in decreasing order of evaporative rate. Acetone, a ketone solvent is commonly used for cleaning and thinning polyester resins and gel coats. However, it is also used in formulating low-VOC and low-HAP products. Methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) are fast evaporative solvents that are used for thinning and cleaning vinyl coatings, epoxy coatings, and many other high performance coatings. Fast evaporative coatings that can improve application properties for a good finish may also be formulated by blending different solvents. Examples are shown in Table 14.26.2. The fast evaporative mix includes solvents varying in polarity and solubility parameters. They include an oxygenated solvent (MIBK), aromatic hydrocarbon solvents that contain less than 10 percent (by mass) HAPs, and aromatic hydrocarbons like xylene that are 100 percent HAPs as will be shown later. Together they produce the correct solvency for the polymer (resin).

**Table 14.26.1. Predominant solvents used in marine coatings [from ref. 16 ] and EPA regulatory classifications**

| Organic solvent | VOC | HAP, Sec. 112 (d) | Toxic chemicals, Sec. 313 |
|---|---|---|---|
| ALCOHOLS | | | |
| Butyl alcohol | Y | Y | Y |
| Ethyl alcohol | Y | N | N |
| Isopropyl alcohol | Y | N | Y[a] |
| AROMATICS | | | |
| Xylene | Y | Y | Y |
| Toluene | Y | Y | Y |
| Ethyl benzene | Y | Y | Y |

| Organic solvent | VOC | HAP, Sec. 112 (d) | Toxic chemicals, Sec. 313 |
|---|---|---|---|
| ETHERS | | | |
| Ethylene glycol ethers | Y | Y | Y |
| Propylene glycol ethers | Y | N | N |
| KETONES | | | |
| Acetone | N | N | Y |
| Methyl ethyl ketone | Y | Y | Y |
| Methyl isobutyl ketone | Y | Y | Y |
| Methyl amyl ketone | Y | N | N |
| PARAFFINIC | | | |
| Mineral spirits | Y | Y[b] | N |
| High-flash naphtha | Y | Y[b] | Y |
| n-Hexane | Y | Y | N |

VOC = volatile organic compound; HAP = Hazardous air pollutant; Sec 313 of the Emergency Right-to-know Act (EPCRA), also known as Title III of the Superfund Amendments and Reauthorization Act of 1986 (40 CFR Part 372). [a]Use of strong acid process, no supplier notification. [b]Ligroine (light naphtha), VM&P naphtha, Stoddard solvent, and certain paint thinners are also commonly referred to as mineral spirits. These distillation fractions contain less than 10 % by mass HAPs (see Table 14.26.4).

## Table 14.26.2. Selected products that are used as both solvent thinners and solvent cleaners

| Thinner & cleaning solvents | Typical coating | Compound, wt% | Solubility parameter, $(cal/cm^3)^{1/2}$ | Relative rate, nBUOAc =1.0 | Vapor press., mmHg @ 20°C | B.P., °C @ 760 mmHg | Surface tension, dynes/cm 20°C | Av. sp. gr, @ 25°C | Viscosity, cP @ 25°C |
|---|---|---|---|---|---|---|---|---|---|
| Acetone | Polyester | Acetone, 100% (approx.) | 9.8 | 6.1 | 186 | 56 | 27.1 | 0.787 | 0.31 |
| MEK* | Vinyl | MEK, 100 % (approx.) | 9.3 | 4.0 | 70 | 80 | 24.2 | 0.806 | 0.43 |
| Spraying thinner & solvent cleaner (fast)[b] | Epoxy | MIBK**, 24 % | 8.58 | 1.7 | 28 | 116 | 23.3 | 0.796 | 0.54 |
| | | N-butyl alc., 24% | 11.6 | 0.44 | 5.5 | 118 | 23.4 | 0.806 | 2.62 |
| | | Toluene, 52% | 8.93 | 2.0 | 22 | 111 | 28.2 | 0.863 | 0.57 |
| Brushing thinner & solvent cleaner (medium)[b] | Epoxy | MIBK, 23 % | 8.58 | 1.7 | 28 | 116 | 23.3 | 0.796 | 0.54 |
| | | EGBE***, 26% | 10.2 | 0.072 | 0.6 | >169 | 26.9 | 0.899 | 3.0 |
| | | AHC****, 30% | 7.7 | 0.16 | 2.0 | >160 | 23.4 | 0.775 | 0.88 |
| | | 1,2,4-Trimethylbenzene, 16% | 8.9 | 19 | 2.1 | 168 | 30.2 | 0.871 | 0.94 |
| | | Xylene (mixed), 2% | 9.9 | 0.77 | 6.0 | >135 | 27.6 | 0.856 | 0.63 |

| Thinner & cleaning solvents | Typical coating | Compound, wt% | Solubility parameter, (cal/cm$^3$)$^{1/2}$ | Relative rate, nBUOAc=1.0 | Vapor press., mmHg @ 20°C | B.P., °C @ 760 mmHg | Surface tension, dynes/cm 20°C | Av. sp. gr, @ 25°C | Viscosity, cP @25°C |
|---|---|---|---|---|---|---|---|---|---|
| Lacquer retarder (thinner) & cleaner (slow)[b] | Lacquer | EGBE, 51% | 10.2 | 0.072 | 0.6 | >169 | 26.9 | 0.899 | 3.0 |
| | | AHC, 30% | 7.7 | 0.16 | 2.0 | >160 | 23.4 | 0.775 | 0.88 |
| | | 1,2,4-Trimethylbenzene, 16% | 8.9 | 19 | 2.1 | 168 | 30.2 | 0.871 | 0.94 |
| | | Xylene (mixed), 1% | 9.9 | 0.77 | 6.0 | >135 | 27.6 | 0.856 | 0.63 |

*MEK=methyl ethyl ketone, **MIBK=methyl isobutyl ketone, ***EGBE=ethylene glycol monobutyl ether, ****AHC=aromatic hydrocarbon solvent; [a]Physical properties mainly from Industrial Solvents Handbook, 110 -114. [b]Material Safety Data Sheet (Mobile Paint Co. Alabama)

The lower specific gravity of ketones (see Table 14.26.2) than other materials such as glycol ethers helps reduce total mass of VOCs (or HAPs) per volume of nonvolatiles (solids) in a container of coating. Glycol ethers are good solvents for epoxies and acrylics. They also have good coupling abilities in blends of poorly miscible solvents[17] and have low evaporative rates. The properties of a solvent product are dependent on the chemical structure and distillation range of the solvent mix in the product. The latter will affect the evaporative rate from a coating or cleaner, affecting the solubility of the resin in the coating and viscosity of the coating and solvent cleaner. Therefore, the viscosity of the solvent product must be close to that of the resin in a coating.[18] The surface tension of a solvent provides a measure of the penetrability of a cleaning solvent. A low surface tension also means the solvent spreads more readily, which is an important property for a cleaning product. However, several properties in Table 14.26.2 come into play in determining the effectiveness of a cleaning solvent.

Most coating operations, due to the size and accessibility of ships, occur in open air in drydocks, graving docks, railway, or other locations throughout a facility. Because of the size of ships, the predominant application method is airless spray guns. The thickness of the coating will determine if the application equipment needs to be cleaned during application of the coating or after the job is completed. The lines from the supply tanks to the spray gun may in some instances exceed 46 m (150 ft) in length. The ensemble of equipment and items that have to do with the application of the coating or "unit operation system (UOS)" is shown schematically in Figure 14.26.1. The representation depicts a layout for outdoor application of coatings. It includes the container used to hold the coating, attached feed pump, line transferring the coating to the spray gun, the spray gun itself, and any other item soiled with a coating that will need to be cleaned with organic solvent before it can be reused.

The need and frequency for cleaning will depend on the individual facility or company cleanliness standard (i.e., requirements) and the number of coating formulation or color changes. Cleaning of spray guns, internal transfer lines, and associated tanks account for a large part of organic solvent usage. At most shipyards, a small percentage of the coatings are applied indoors, in spray-booths. The walls and floors of these booths are cleaned by wiping with a solvent laden cloth. The coating application equipment UOS for most facilities will look very similar to that shown in Figure 14.26.1, except that the coating transfer lines will be shorter if the coating storage tanks are positioned close to the spray booths. The transfer lines, that will need to be cleaned with solvent, will be longer if the coating tanks are located away from the application area. When this is the case, the transfer lines typically run underground at the facility and another representation than the one shown in Figure 14.26.1 will need to be used, to clearly identify the emission points and waste streams for properly quantifying solvent losses. The latter may include a unit for recycling or reclaiming solvents.

Spray gun cleaning procedures may be a once-through type with collection of spent solvent in a container for disposal or reuse. Some facilities use commercial gun washers. Because gun washers are enclosed and recirculate solvent, they can reduce the amount of solvent lost by evaporation. In either case, the emissions are calculated as the difference between the amount used and the amount recovered.

To calculate the emissions associated with cleaning a spray gun it is recommended that a material balance around a “unit operation system” be considered. Several examples are provided in the Alternative Control Techniques (ACT) document on industrial cleaning solvents.[19]

Several types of part cleaners are used at shipbuilding and ship repair facilities. The types used in such facilities vary from the more simple sink and spray systems[20] to more elaborate parts (machine) cleaners of the cold or vapor types.[4] Most of the parts cleaners in shipyards are small — around 1.5 m x 1 m and 1 m deep - usually located in the machine shops, not the paint rooms. Most of the parts are small components being cleaned prior to being joined to other small parts into assemblies and sub-assemblies or being cleaned as part of some type of repair operation. Most of parts cleaners used were basket-type design with the parts loaded into a basket and dropped through the vapor zone several times to clean off the oils and dirt. Some shipyards use contractors to come in and change out the solvent on a routine schedule.

### 14.26.4.3 Maintenance cleaning of equipment items and components

Shipyards also undertake scheduled maintenance cleaning of many ship components such as contacts and switches and equipment items such as bearings and packaging machines. This is mostly done by hand-wiping the parts with organic solvents. These operations will generally consume a relatively small amount of the overall volume of organic solvents used for cleaning in shipyards. Solvents are also used in machine shop areas and thus contribute to the waste stream.

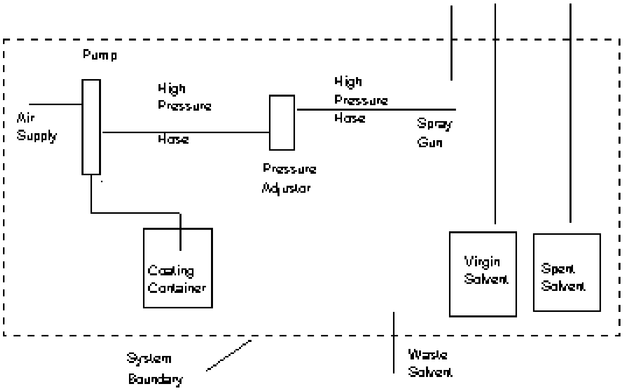

Figure 14.26.1 Schematic diagram of marine coating application equipment.

### 14.26.5 MARINE COATINGS

There are several categories of marine coatings that are used to protect the surface of a ship from the aggressive marine environment and for other performance requirements such as preventing corrosion and fouling; protecting cargoes from contamination; providing safety warnings and informational markings; providing cosmetic and camouflage colors; preventing slipping and sliding on walking surfaces; reducing fire hazards; and providing cathodic protection.[21] The coating systems of marine coatings are selected to meet:

- the type of marine environment to which a vessel will be exposed
- the time a vessel is to remain operational before it needs to be reworked.

General areas of a ship include: (1) underwater hull, (2)superstructures and freeboard, (3) interior habitability areas, (4) exterior deck areas, and (5) fuel, water ballast and cargo tank.[22] The freeboard is the area above water hull. These areas have different characteristics and operational requirements. Table 14.26.3[23] shows the predominant resin and solvent types used on ships based on a 1991/1992 survey of the industry obtained as part of the shipbuilding and ship repair regulation was being developed. The summary table also gives average VOC and HAP content for the various coating category types. Epoxy coatings constitute a large percentage of the coatings used. The epoxy films are strongly resistant to most chemicals and are very good anti-corrosion coatings, and require little surface preparation.

**Table 14.26.3. Summary of marine coating usage (by coating type)[23]**

| Coating types | Average usage in U.S. shipyards, % | Average VOC content, g/L (lb/gal) | Average HAP content, g/L (lb/gal) |
|---|---|---|---|
| *General use types* | | | |
| alkyd based | 10 | 474 (3.95) | 355 (2.98) |
| epoxy based | 59 | 350 (2.92) | 56 (0.47) |
| *Speciality types* | | | |
| antifouling (multiple resins)[1] | 11 | 388 (3.23) | 268 (2.25) |
| inorganic zinc based | 10 | 545 (4.54) | 274 (2.30) |
| other speciality categories | 10 | 400 (3.33) | 144 (1.20) |
| TOTAL | 100 | | |

[1] resins: epoxy, polyurethane, vinyl, and chlorinated rubber

The coating system used will depend on service requirements. Maximum protection at an economical price can be achieved when the user understands the protection needed and the functions performed by the coatings. Coatings are designed for spray viscosity, drying time, pot-life, and cure profile; all of these parameters affect shelf stability.[24] The physical parameters and properties of a coating are affected by the volatile constituents (mainly organic solvents) in a coating, some of which are VOCs, HAPs, ozone depleters, and SARA 313 toxic chemicals that need to be reported.[25]

## 14.26.6 THINNING OF MARINE COATINGS

The sprayability of a coating is determined by its viscosity at application. The viscosity is a measure of the ability of a material to resist flow and is an important formulation design parameter. Application viscosity is affected by the ambient conditions and by the degree of mixing that occurs within the applicator. The thinner is often the same material as the cleaner (as indicated in Table 14.26.2). The solvent material is often a blend of miscible materials. Together they will dissolve a dry resin that needs to be removed or give the coating certain needed properties such as reduced/increased viscosity or shorter drying times.

Standard spraying equipment will apply coatings up to some maximum viscosity. Above that maximum value, thinning solvents are required. Thinning solvent is sometimes added to enhance brushability or sprayability of a coating. The appropriate viscosity is provided by the coating manufacturer or supplier; it will depend on the solvent content of the coating and temperature at the point of application.[26] Since most coatings are applied outdoors, extreme weather conditions may require adding thinning solvents to the coating. Organic thinning solvents are added to coatings to alter their flowing properties. However, the flow properties of a coating may be altered by using special heaters or a combination of solvent and heat. The effect of a heater on the viscosity of a coating depends on the physical properties of the coating and on the flow rate in the in-line heater. Under cold weather conditions, in-line heaters may provide good viscosity control, but may not be able to solve all application problems that are encountered in the field. Under extremely low temperatures, the substrate surface can act as a heat sink, which may inhibit the setting or curing of the coating. In-line heaters which are used for low volume coatings are not suitable for large volume coatings. As a result, thinning solvents are still needed to transfer the fluid from storage to pumps and hoses.

Under hot and humid weather conditions, certain coatings (e.g., lacquers) can rapidly lose organic solvent prior to and during application. Often under these situations a facility will add solvent blends to make up for the reduction in viscosity and to overcome condensation on the surface (blushing).[27] Evaporative losses can be minimized by adopting good work practices and by using formulations that contain organic solvents with low vapor pressures.

## 14.26.7 SOLVENT EMISSIONS

Several states with their own rules regulating marine coatings have separate rules addressing solvent cleaning operations. While marine coating rules typically address VOC contents and types of application equipment, the cleaning solvent rules are more generic and address cleaning solvents used at any and all metal-related manufacturing operations.

Many types of solvents are used in marine coatings and in their associated cleaning materials as shown in Table 14.26.1. Almost all solvents used at shipyards are VOC and approximately one in three solvents contain HAPs. Of the HAPs reported, several are included on the list of 17 high priority chemicals targeted by U.S. EPA for the 33/50 program.[28] These included xylene (commercial), toluene, and the ketones. Commercial grade xylene represents the major portion of the volatile HAPs reported.

Many of the commonly known solvents are actually petroleum distillation fractions and are composed of a number of compounds (e.g., mineral spirits and naphthas). There are two general types of solvents derived from petroleum, aliphatics or aromatics. Aromatics are stronger solvents than aliphatics since they dissolve a wider variety of resins. Most major solvent suppliers (chemical manufacturers) produce several types and variations of these solvents and the associated HAP contents can vary significantly from manufacturer to manufacturer and from batch to batch. These types of solvents are used extensively and are present in the majority of marine coatings. Table 14.26.4 provides a summary of common petroleum distillate solvents and solvent blends and their associated HAP content. For any solvent or solvent blend that is not listed as specified in Table 14.26.4, another table (Table 14.26.5) was developed to provide solvent groupings and associated HAP component/content values. The HAP values for Tables 14.26.4 and 14.26.5 were adapted from estimates provided in 1998 by the Chemical Manufacturer Association's Solvent's Council.

**Table 14.26.4. HAP content of single solvents and solvent blends. [Adapted, by permission from Chemical Manufacturer Association's Solvent's Council]**

| Solvent/solvent blend | CAS No. | HAP content range, wt% | Average HAP content, wt% | Typical HAP, wt% |
|---|---|---|---|---|
| Toluene | 108-88-3 | 100 | 100 | toluene |
| Xylene(s) | 1330-20-7 | 100 | 100 | xylenes, ethylbenzene[a] |
| Hexane | 110-54-3 | 49-55 | 50 | n-hexane[b] |
| Ethylbenzene | 100-41-4 | 100 | 100 | ethylbenzene |
| Aliphatic 140 | | 0 | 0 | none |
| Aromatic 100 | | <5 | 2 | 1% xylene, 1% cumene |
| Aromatic 150 | | <10 | 9 | naphthalene |
| Aromatic naphtha | 64742-95-6 | <5 | 2 | 1% xylene, 1% cumene |
| Aromatic solvent | 64742-94-5 | <10 | 10 | naphthalene |
| Exempt mineral spirits | 8032-32-4 | 0 | 0 | none |
| Ligroines (VM & P) | 8032-32-4 | 0 | 0 | none |
| VM & P | 8032-32-4 | 0 | 0 | none |
| Lactol spirits | 64742-89-6 | 12-20 | 15 | toluene |
| Low aromatic white spirit | 64742-82-1 | 0 | 0 | none |
| Mineral spirits | 64742-88-7 | <2 | 1 | xylenes |
| Hydrotreated naphtha | 64742-48-9 | <0.01 | 0 | none |
| Hydrotreated light distillate | 64742-47-8 | <0.1 | 0.1 | toluene |
| Stoddard solvent | 8052-41-3 | 1-2 | 1 | xylenes |
| Super high-flash naphtha | 64742-95-6 | 0-6 | 5 | xylenes |
| Varsol® solvent | 8052-49-3 | <1.1 | 1 | 0.5% xylenes,<br>0.5% ethylbenzene |
| VM & P naphtha | 64742-89-8 | 5-10 | 6 | 3% toluene, 3% xylene |
| Petroleum distillate mixture | 68477-31-6 | 4-9 | 8 | 4% naphthalene,<br>4% biphenyl |

**Table 14.26.5. Petroleum solvent groups and associated HAP contents. [Adapted, by permission from Chemical Manufacturer Association's Solvent's Council]**

| Solvent Type | Solvent Name | HAP Component | HAP Concentration, wt% |
|---|---|---|---|
| Aliphatic | Mineral spirits 135<br>Mineral spirits 150 EC<br>Naphtha<br>Mixed hydrocarbon<br>Aliphatic hydrocarbon<br>Naphthol spirits<br>Petroleum spirits<br>Petroleum oil<br>Petroleum naphtha<br>Solvent naphtha<br>Solvent blend | Xylene<br>Toluene<br>Ethylbenzene | 1<br>1<br>1 |
| Estimated total HAP for each solvent type | | | 3 |
| Aromatic | Medium-flash naphtha<br>High-flash naphtha<br>Aromatic naphtha<br>Light aromatic naphtha<br>Light aromatic hydrocarbons<br>Aromatic hydrocarbons<br>Light aromatic solvent | Xylene<br>Toluene<br>Ethylbenzene | 4<br>1<br>1 |
| Estimated total HAP for each solvent type | | | 6 |

The percentage of solvent used that evaporates during cleaning operations will depend on the volatility of the solvent and on the type cleaning operation. Any materials such as rags or sponges that come into contact with the solvent must also be considered part of the solvent cleaning system and disposed of properly.

Since marine coatings are mostly air dried, it is generally impractical to capture air emissions from coating operations and until recently, to duct air emissions into abatement devices such as incinerators or adsorbers. The use of low solvent (VOC or HAP) containing coatings and high performance coatings provide a suitable means of achieving lower volatile emissions from coating of ships. Such coatings will lead to lower life cycle costs and emissions, since the ship will require less rework. EPA has recently approved the use of technology for capturing and destroying air pollutant emissions from the application of coatings to the hull of a ship.[29]

## 14.26.8 SOLVENT WASTE

The waste cleaning solvent is handled differently by different shipyards. Facilities that use different type solvents for cleaning and thinning, or utilize multiple cleaners may select disposal rather than recycling for re-use. This decision is typically based on cost. Other facilities will first mix their waste solvents with unused coating. Incineration is generally selected as the disposal method when it is determined to be less expensive than recycling.

The type of solvent waste generated from shipbuilding and ship repair facilities does not vary much. Surface preparation and cleaning operations following application of coatings does not represent the most significant part of the organic solvent waste. Certain coatings, such as antifouling coatings, contain toxic pigments (metals) such as chromium, lead, and tributyltin. The waste will likely be hazardous waste if the waste material contained coating residues or other materials that are toxic. Solvents used in cleaning are often mixed with other waste fuels such as hydraulic fluids, waste fuels, and other maintenance by-products. Some of the larger shipyards segregate the solvent waste or recycle it for re-use.

### 14.26.9 REDUCING SOLVENT USAGE, EMISSIONS, AND WASTE

The amount of organic solvent usage for cleaning operations makes up about 20 percent of the total solvent usage in cleaning operations and coating operations at shipyards. The waste from solvent cleaning represents a major portion of the waste in a plant that has surface coating operations. Line cleaning, gun cleaning, and tank cleaning are three operations that utilize most of the cleaning solvents. There are many steps that a facility can undertake to reduce the use of solvent for cleaning. It can reuse some of the solvent, scrape off the paint left on the inside of a mix tank, or modify existing cleaning practices and procedures.[5,30] Some shipyards have modified their coating operations to use less solvent. For planning purposes, a facility needs to know where the major solvent usage, emissions, and waste occur in the facility. This may be achieved by:

- Developing a solvent accounting system for tracking the usage, fate, and costs of organic solvents in coating operations and cleaning operations;
- Identifying actions management will take to reduce solvent content in coatings and reduce usage of cleaning materials containing organic solvents.[5,31]

The steps are not mutually independent and require full management support and financial backing. Obtaining reliable data is one of the major problems that a manager or supervisor involved in pollution reduction faces. Any program adopted should be one that can identify accurate and specific material usage, emission data, and waste data that will be useful for evaluating pollution cost and risk.[32] The “unit operation system” (UOS) approach was used to categorize the universe of cleaning into nine main categories equivalent to those identified here in the section discussing cleaning operations. The concept of a UOS provides the foundation for a standardized material accounting method that provides transportable data, that a secondary user can understand, for setting up a material balance, for comparing alternatives, or evaluating risk. The visual representation of a set up, as was done in Figure 14.26.1, is an essential component of this approach.

When facility managers and operators are able to identify with some confidence, at the source, final solvent disposition and cost of cleaning, they are in a better position to make informed decisions and take the necessary actions for reducing solvent usage. Facilities have the added incentive to reduce worker exposure to toxics contained in solvents because of OSHA requirements.[33] The facility owners and operators also have to abide by state, local, and federal regulations that limit the amount of VOCs and HAPs emitted to the air and water streams. Facilities that generate large amounts of solvent waste streams will have to deal with RCRA hazardous waste regulations.[34]

## 14.26.10 REGULATIONS AND GUIDELINES FOR CLEANING SOLVENTS

The U.S. EPA developed a guideline document to help state and local agencies reduce VOC emissions for the use of cleaning solvents. The document does not provide emission limits, but instead recommends the use of a management system for tracking usage, emissions, and waste from the use of organic solvents and provides a list of definitions that should be used for that purpose.[35] Less than 20 states had regulated VOC emissions from the use of organic cleaning solvents by 1997.[36] Many states only had minimal record-keeping requirements. Some regulations are driving facilities to use solvents with lower vapor pressures. These low vapor pressure solvents evaporate more slowly at ambient temperatures. However, the emission benefits cannot be guaranteed to last forever. An organic solvent should eventually all evaporate unless it is reused, recycled, or sealed in a container.

Many of the cleaning solvents used, such as 1,1,1-trichloroethane, are not considered VOC in the United States. Those solvents are regulated as HAPs and are being phased out because of the Montreal Protocol which aims to reduce ozone depleters. Alternative cleaners are now being used and further developed. To meet regulatory requirements, a facility will often replace or substitute a cleaning product containing HAP material(s) with one or more products containing no HAP solvents (but may contain VOC solvents or vice versa). Acetone, once the preferred solvent for fiberglass boat manufacturers, was replaced starting in 1992 with other solvents such as diacetone alcohol.[37] The latter solvent is as effective as acetone, but has a much lower vapor pressure (0.80 mm Hg at 20°C) and flash point (52°C) to reduce the amount of VOC emitted and hazardous reportable releases. Acetone was recently determined not to have significant photochemical reactivity and is no longer considered a VOC in the United States. As a result, acetone is now making a comeback in cleaners and in some coatings. HCFCs are now being used instead of CFCs, but will soon need to be replaced because of the Montreal Protocol. There are many articles in the literature that discuss alternatives that will reduce VOC and HAP emissions.[38-42] The use of waterborne materials or other material(s) containing no HAPs or VOCs is the ideal solution, when such coatings or cleaners will do the job. Software and internet sites also exist to help in the selection of the appropriate solvent cleaner or method of cleaning.

## Disclaimer

The views expressed in this chapter are those of the authors and do not necessarily reflect those of their affiliation. Mentioning the names of organizations does not constitute an endorsement.

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## 14.27 STONE, CLAY, GLASS, AND CONCRETE

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This is a very diverse industry segment which manufactures glass, glassware, cement, concrete, clay products pottery, gypsum, and plaster products. In the USA the industry employs about 500,000 people and operates over 16,000 facilities. There is a broad range of

**Table 14.27.1. Reported solvent releases from the stone, clay, glass, and concrete industry in 1995 [Data from Ref. 2]**

| Solvent | Amount. kg/year | Solvent | Amount. kg/year |
|---|---|---|---|
| benzene | 4,000 | ethylene glycol | 42,000 |
| n-butyl alcohol | 74,000 | hexane | 12,000 |
| sec-butyl alcohol | 1,700 | isopropyl alcohol | 300 |
| tert-butyl alcohol | 4,000 | methanol | 560,000 |
| carbon disulfide | 5 | methyl ethyl ketone | 700,000 |
| carbon tetrachloride | 14 | methyl isobutyl ketone | 25,000 |
| chlorobenzene | 14 | tetrachloroethylene | 44,000 |
| chloroform | 14,000 | 1,2,4-trichlorobenzene | 46,000 |
| cresol | 610 | 1,1,1-trichloroethane | 330,000 |
| cyclohexane | 77,000 | trichloroethylene | 110,000 |
| 1,4-dichlorobenzene | 14,000 | toluene | 890,000 |
| 1,2-dichloroethane | 17 | xylene | 500,000 |
| dichloromethane | 120,000 | m-xylene | 450 |
| 1,4-dioxane | 230 | o-xylene | 540 |
| ethylbenzene | 60,000 | p-xylene | 110 |

**Table 14.27.2. Reported solvent transfers from the stone, clay, glass, and concrete industry in 1995 [Data from Ref. 2]**

| Solvent | Amount. kg/year | Solvent | Amount. kg/year |
|---|---|---|---|
| benzene | 6,000 | ethylene glycol | 29,000 |
| n-butyl alcohol | 44,000 | hexane | 15,000 |
| sec-butyl alcohol | 600 | isopropyl alcohol | 2,500 |
| tert-butyl alcohol | 2,000 | methanol | 300,000 |
| carbon disulfide | 5 | methyl ethyl ketone | 760,000 |
| carbon tetrachloride | 5,000 | methyl isobutyl ketone | 92,000 |
| chlorobenzene | 4,000 | tetrachloroethylene | 26,000 |
| chloroform | 20,000 | 1,2,4-trichlorobenzene | 10,000 |
| cresol | 7,000 | 1,1,1-trichloroethane | 60,000 |
| cyclohexane | 12,000 | trichloroethylene | 54,000 |
| 1,4-dichlorobenzene | 3,000 | toluene | 800,000 |
| 1,2-dichloroethane | 3,000 | xylene | 470,000 |
| dichloromethane | 20,000 | m-xylene | 600 |
| N,N-dimethylformamide | 5,000 | o-xylene | 1,200 |
| ethylbenzene | 67,000 | p-xylene | 340 |

processes involved which use a wide variety of chemicals. Solvents are used for cleaning and are components of product decoration materials.

Tables 14.27.1 and 14.27.2 give data on the reported releases and transfers of solvents by the US stone, clay, glass, and concrete industry. Numerous solvents are used but most are used in small quantities the only high volume ones being toluene, xylene, methanol, 1,1,1-trichloroethane, and methyl ethyl ketone. Although the industry does not release large quantities of solvents, their total VOC contribution puts them second among the US industries. Total releases and transfers are one of the smallest of all industries.

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# 14.28 TEXTILE INDUSTRY

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The US textile industry operates over 5,500 plants, employs over 600,000 people and has shipments exceeding $70 billion. In addition to conventional methods of processing and finishing, this industry also produces coated fabrics, tire cord and fabrics, and cordage and twine. Numerous operations are employed by the textile manufacturing and finishing but only a few of these operations involve the use of solvents. These include printing (volatile solvents and xylenes), finishing (e.g., methanol), scouring (glycol ethers and mineral spirits), cleaning knit goods, desizing (glycol ethers and methanol in PVA desizing), and coating (methyl ethyl ketone and toluene).

Tables 14.28.1 and 14.28.2 provide data on the reported releases and transfers of solvents by the US textile industry. Methyl ethyl ketone, toluene, and methanol are emitted in the greatest quantities. The total number of solvents used is low. The textile industry is among the lowest contributors to VOC and is the second smallest (after shipbuilding industry) in the amount of emitted and transferred solvents.

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**Table 14.28.1. Reported solvent releases from the textile industry in 1995 [Data from Ref. 1]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| n-butyl alcohol | 900 | methyl isobutyl ketone | 190,000 |
| 1,4-dichlorobenzene | 700 | N-methyl-2-pyrrolidone | 180,000 |
| 1,2-dichloroethane | 4,000 | tetrachloroethylene | 29,000 |
| dichloromethane | 230,000 | 1,2,4-trichlorobenzene | 21,000 |
| N,N-dimethylformamide | 53,000 | 1,1,1-trichloroethane | 150,000 |
| ethylene glycol | 66,000 | trichloroethylene | 130,000 |
| hexane | 59,000 | 1,2,4-trimethylbenzene | 24,000 |
| isopropyl alcohol | 11,000 | toluene | 1,600,000 |
| methanol | 1,300,000 | xylene | 380,000 |
| methyl ethyl ketone | 2,200,000 | | |

**Table 14.28.2. Reported solvent transfers from the textile industry in 1995 [Data from Ref. 1]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| 1,2-dichloroethane | 3,500 | tetrachloroethylene | 26,000 |
| dichloromethane | 9,000 | 1,2,4-trichlorobenzene | 51,000 |
| N,N-dimethylformamide | 52,000 | 1,1,1-trichloroethane | 2,000 |
| ethylene glycol | 210,00 | trichloroethylene | 170,000 |
| methanol | 120,000 | 1,2,4-trimethylbenzene | 20,000 |
| methyl ethyl ketone | 640,000 | toluene | 330,000 |
| methyl isobutyl ketone | 61,000 | xylene | 67,000 |
| N-methyl-2-pyrrolidone | 83,000 | | |

## 14.29 TRANSPORTATION EQUIPMENT CLEANING

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Transportation equipment cleaning includes cleaning of interior of trucks, rail cars, barges, intermodal tank containers, intermediate tank containers, tank interiors, and the exterior of aircraft. These operations rarely involve solvents. Transportation equipment is also cleaned before refurbishing which includes old paint removal, surface cleaning, and painting. These processes usually do require solvents. Aircraft deicing is done using a mixture containing ethylene glycol. There is no data available on the amount of solvents used and emitted from these processes.

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## 14.30 WATER TRANSPORTATION

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Water transportation equipment is divided into self-propelled vessels and barges. The US industry is composed of over 13,000 establishments employing over 150,000 people operating about 40,000 vessels. Solvents are used in maintenance for paint removal, painting, degreasing engines, and cleaning carburetors. There is no information available regarding solvent use by the industry.

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## 14.31 WOOD FURNITURE

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The US wood furniture industry operates over 11,000 manufacturing facilities which employ over 250,000 people. Total sales are over $22 billion. Several operations use solvents, including veneer application (adhesives), derosination (certain types of wood contain rosin which may interfere with the effectiveness of certain finishes; rosin is removed by application of a mixture of acetone and ammonia), pretreatment (coating contains coalescing solvent (slow evaporating) and diluent (fast evaporating), a new UNICARB® technology uses carbon dioxide in the mixture with a coalescing solvent which eliminates the need for a diluent), several finishing operations (stains, paints, fillers, inks used to print simulated wood grain on plywood, topcoat, and cleaning liquids). Nitrocellulose lacquers are commonly used in the USA; polyurethane and unsaturated polyester finishes are still rarity. Solvents and thinners used in paints include toluene and xylene. Adhesives usually contain solvents such as methyl isobutyl ketone, methyl ethyl ketone, xylene, toluene, and 1,1,1-trichloroethane. Table 14.31.1 shows the relative amounts of VOC emissions from different finishing components depending on furniture type and type of process used. The long process consists of applications of 3 or more coats of stain, a washcoat, a filler, a sealer, a highlight, and two to three topcoat applications. In the short-sequence process two stain coats are applied, followed by a washcoat, a sealer, and two top coat applications. Office furniture uses only one application of a stain, a sealer, and a topcoat.

Tables 14.31.2 and 14.31.3 provide data on the reported releases and transfers of solvents by the US furniture and fixtures industry. Toluene, xylene, methanol, and methyl ethyl ketone are released in the largest quantities. The furniture and fixtures industry is one of lesser contributors of VOCs releases and transfers among the US manufacturing industries.

Several alternative technologies are under development and some are at the field trial stage.[3-12] Waterborne clear varnishes are being used increasingly but the market is still dominated by solvent-based varnishes. One reason may be that waterborne varnishes are 2-3 times more expensive than solvent-based products.[3] It is also not clear if waterborne varnishes have lower odor and can be applied at the same rate as solvent-based products. Waterborne varnishes have one important advantage in clear coatings for they have no color therefore the natural wood color is more vivid. Two-component water-based polyurethane coatings have been introduced recently.[4] They have a very low VOC content and have very good drying speed, gloss, and potlife. The drying rate and potlife are controlled by the ratio of isocyanate and hydroxyl components. Increasing this ratio increases drying speed but decreases potlife. However, at 4 hours, potlife is acceptable. Polyurethane dispersions are used in furniture adhesive applications, and are especially useful in the lamination of kitchen tables.[5]

**Table 14.31.1. Relative VOC emissions. [Reproduced from EPA draft Guidelines for the Control of Volatile Compound Emissions from Wood Furniture Coating Operations]**

| Operation | Percentage of total emissions | | |
|---|---|---|---|
| | Long process | Short process | Office furniture |
| Stain | 26 | 28 | 32 |
| Washcoat | 4 | 4 | - |
| Filler | 3 | - | - |
| Wiping stain/glaze | 8 | - | - |
| Sealer | 18 | 32 | 32 |
| Highlight | 1 | - | - |
| Topcoat | 40 | 36 | 36 |

**Table 14.31.2. Reported solvent releases from the furniture and fixtures industry in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| n-butyl alcohol | 940,000 | methyl isobutyl ketone | 590,000 |
| cyclohexane | 10 | tetrachloroethylene | 7,300 |
| dichloromethane | 180,000 | 1,2,4-trichlorobenzene | 90 |
| ethylbenzene | 360,000 | 1,1,1-trichloroethane | 160,000 |
| ethylene glycol | 30 | trichloroethylene | 29,000 |
| hexane | 25,000 | 1,2,4-trimethylbenzene | 140,000 |
| isopropanol | 105,000 | toluene | 5,300,000 |
| methanol | 3,600,000 | xylene | 3,300,000 |
| methyl ethyl ketone | 1,900,000 | | |

One problem related to all water-base coatings is the degree to which they penetrate into wood grain. Waterborne coatings are composed of relatively large emulsified particles which are frequently the size of the pit openings. After the emulsion droplets dry out they become very viscous and penetration becomes even more difficult. The penetration of alkyd waterborne coatings was tested by microautoradiography.[6] The results indicate that the penetration rate is controlled by the viscosity and form of the material (solution vs. emulsion) is less important.

UV curable coatings have also problems in application to wood finishing. These finishes need to have low viscosity but it is difficult to formulate 100% solids curable coatings which have a sufficiently low application viscosity.[7] It possible to formulate waterborne UV curable coatings but their performance is still an issue.

**Table 14.31.3. Reported solvent transfers from the furniture and fixtures industry in 1995 [Data from Ref. 2]**

| Solvent | Amount, kg/year | Solvent | Amount, kg/year |
|---|---|---|---|
| n-butyl alcohol | 53,000 | methyl isobutyl ketone | 145,000 |
| cyclohexane | 110 | 1,2,4-trichlorobenzene | 110 |
| dichloromethane | 28,000 | 1,1,1-trichloroethane | 5,700 |
| ethylbenzene | 340,000 | trichloroethylene | 300 |
| hexane | 16,000 | 1,2,4-trimethylbenzene | 160,000 |
| isopropanol | 11,000 | toluene | 1,030,000 |
| methanol | 570,000 | xylene | 1,700,000 |
| methyl ethyl ketone | 380,000 | | |

Dunlop developed a two-part water-based adhesive which performed well in lamination of wood and foam.[8] Also, a new reactive hot-melt system for attaching moldings in furniture assembly is in use.[9] A water reducible coating for wood finishing has been developed based on copolymer which can be cured by crosslinking.[11] Another solvent-free material was developed to cover scratches and other damage of finished wood articles.[12] Replacement of solvent based adhesives is essential if this industry, which uses 12% of all adhesives, is to significantly reduce its solvent usage.[10]

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## 14.32 SUMMARY

The data from the US industry given in the various sections of this chapter allow analysis of releases and transfers of the various solvents and helps us to understand the patterns of solvent use. Also industries can be ranked based on the amounts of solvents released. This information is provided in Tables 14.32.1, 14.32.2, 14.32.3, 14.32.4, 14.32.5, and 14.32.6 which contain total release of solvents from all reporting industries, the total transfers of solvents from all reporting industries, the sum of releases and transfers from these industries and the total release of solvents by each industry, the total transfers of solvents by each in-

**Table 14.32.1. Reported solvent releases from all industries in 1995 [Data from EPA Office of Compliance Sector Notebooks]**

| Solvent | Amount, ton/year | Solvent | Amount, ton/year |
|---|---|---|---|
| acetone | 870 | 2-ethoxyethanol | 19 |
| allyl alcohol | 60 | ethylbenzene | 3,810 |
| benzene | 3,378 | ethylene glycol | 8,122 |
| n-butyl alcohol | 5,640 | hexachloroethane | 16 |
| sec-butyl alcohol | 216 | hexane | 6,571 |
| tert-butyl alcohol | 482 | isopropyl alcohol | 205 |
| carbon disulfide | <u>33,085</u> | methanol | **93,965** |
| carbon tetrachloride | 30 | 2-methoxyethanol | 23 |
| chlorobenzene | 181 | methyl ethyl ketone | 23,315 |
| chloroform | 458 | methyl isobutyl ketone | 6,876 |
| chloromethane | 310 | N-methyl-2-pyrrolidone | 1,111 |
| cresol | 800 | methyl tert-butyl ether | 1,477 |
| m-cresol | 320 | pyridine | 187 |
| o-cresol | 270 | tetrachloroethylene | 1,692 |
| p-cresol | 162 | toluene | *41,015* |
| cyclohexane | 3,001 | 1,2,4-trichlorobenzene | 1,245 |
| cyclohexanone | 303 | 1,1,1-trichloroethane | 8,631 |
| cyclohexanol | 1,100 | trichloroethylene | 6,611 |
| 1,2-dichlorobenzene | 15 | trichlorofluoromethane | 84 |
| 1,4-dichlorobenzene | 15 | 1,2,4-trimethylbenzene | 2,308 |
| 1,2-dichloroethane | 222 | xylene | 26,544 |
| dichloromethane | 16,332 | m-xylene | 269 |
| N,N-dimethylformamide | 447 | o-xylene | 82 |
| 1,4-dioxane | 33 | p-xylene | 1,660 |

dustry, and the total release and transfer of solvents by each industry, respectively. The three highest entries in the tables (either amount, release, or transfer) are marked by **bold** (first), *italic* (second), or <u>underlining</u> (third).

Methanol, ethylene glycol, toluene, xylene, and carbon disulfide occupy the highest places in Tables 14.32.1-14.32.3, followed by methyl ethyl ketone, dichloromethane, 1,1,1-trichloroethane, tert-butyl alcohol, hexane, and methyl isobutyl ketone. These eleven solvents constitute 86% of all 550,738 tons of solvents released and transferred per year. Methanol alone constitutes over a quarter (27.1%) of the released and transferred solvents.

**Table 14.32.2. Reported solvent transfers from all industries in 1995 [Data from EPA Office of Compliance Sector Notebooks]**

| Solvent | Amount, ton/year | Solvent | Amount, ton/year |
|---|---|---|---|
| acetone | 767 | 2-ethoxyethanol | 2 |
| allyl alcohol | 330 | ethylbenzene | 4,691 |
| benzene | 792 | ethylene glycol | **72,549** |
| n-butyl alcohol | 3,636 | hexane | 8,910 |
| sec-butyl alcohol | 1,723 | isopropyl alcohol | 168 |
| tert-butyl alcohol | 12,749 | methanol | *55,287* |
| carbon disulfide | 260 | 2-methoxyethanol | 8 |
| carbon tetrachloride | 224 | methyl ethyl ketone | 15,119 |
| chlorobenzene | 704 | methyl isobutyl ketone | 6,811 |
| chloroform | 322 | N-methyl-2-pyrrolidone | 1,497 |
| chloromethane | 0.5 | methyl tert-butyl ether | 246 |
| cresol | 594 | pyridine | 103 |
| m-cresol | 720 | tetrachloroethylene | 1,189 |
| o-cresol | 57 | toluene | 18,717 |
| p-cresol | 870 | 1,2,4-trichlorobenzene | 69 |
| cyclohexane | 1,711 | 1,1,1-trichloroethane | 1,778 |
| cyclohexanone | 1 | trichloroethylene | 1,967 |
| cyclohexanol | 4 | trichlorofluoromethane | 4 |
| 1,2-dichlorobenzene | 4 | 1,2,4-trimethylbenzene | 729 |
| 1,4-dichlorobenzene | 3 | xylene | 27,000 |
| 1,2-dichloroethane | 3 | m-xylene | 98 |
| dichloromethane | 2,895 | o-xylene | 491 |
| N,N-dimethylformamide | 1,298 | p-xylene | 9 |
| 1,4-dioxane | 60 | | |

Methanol + xylene + toluene constitute over half (52.6%) of all released and transferred solvents by the analyzed industries. This is in fact good news because neither of the five most frequently released and transferred solvents is considered to have carcinogenic effect. But four (methanol, xylene, ethylene glycol, and toluene) contribute to the pollution of lower atmosphere and xylene and toluene cause formation of ozone in lower atmosphere by which it may affect the respiratory system. Carbon disulfide causes formation of hydroxyl radicals which have relatively long half-life (a few days) and thus participate in a variety of photochemical processes. All five solvents are relatively easy to biodegrade.

**Table 14.32.3. Reported solvent releases and transfers from all industries in 1995 [Data from EPA Office of Compliance Sector Notebooks]**

| Solvent | Amount, ton/year | Solvent | Amount, ton/year |
|---|---|---|---|
| acetone | 1,637 | 2-ethoxyethanol | 21 |
| allyl alcohol | 390 | ethylbenzene | 8,501 |
| benzene | 4,170 | ethylene glycol | *80,671* |
| n-butyl alcohol | 9,276 | hexachloroethane | 16 |
| sec-butyl alcohol | 1,939 | hexane | 15,481 |
| tert-butyl alcohol | 13,231 | isopropyl alcohol | 373 |
| carbon disulfide | 33,345 | methanol | **149,252** |
| carbon tetrachloride | 254 | 2-methoxyethanol | 31 |
| chlorobenzene | 885 | methyl ethyl ketone | 38,434 |
| chloroform | 780 | methyl isobutyl ketone | 13,687 |
| chloromethane | 311 | N-methyl-2-pyrrolidone | 2,608 |
| cresol | 1,394 | methyl tert-butyl ether | 1,723 |
| m-cresol | 1,040 | pyridine | 290 |
| o-cresol | 327 | tetrachloroethylene | 2,881 |
| p-cresol | 1,032 | toluene | 59,732 |
| cyclohexane | 4,712 | 1,2,4-trichlorobenzene | 1,314 |
| cyclohexanone | 304 | 1,1,1-trichloroethane | 10,409 |
| cyclohexanol | 1,104 | trichloroethylene | 8,578 |
| 1,2-dichlorobenzene | 19 | trichlorofluoromethane | 88 |
| 1,4-dichlorobenzene | 18 | 1,2,4-trimethylbenzene | 3,037 |
| 1,2-dichloroethane | 225 | xylene | 53,544 |
| dichloromethane | 19,227 | m-xylene | 367 |
| N,N-dimethylformamide | 1,745 | o-xylene | 573 |
| 1,4-dioxane | 93 | p-xylene | 1,669 |

The largest releases and transfers of methanol are from the pulp and paper (57.7%), organic chemical (21.3%), and the polymer and man-made fibers industry (6.2%) which contribute 85.2% of the total methanol releases and transfers. Ethylene glycol releases and transfers are mostly from the polymer and fiber industry (62.5%), the rubber and plastics (19.1%), and the organic chemical industry (15.9%). These three industries contribute 97.5% of all releases and transfers of ethylene glycol from the reporting industries. Toluene and xylene are typical paint, ink, cleaning and process solvents. The largest source of these

**Table 14.32.4. Total releases from different industries in the USA in 1995. [Data from EPA Office of Compliance Sector Notebooks]**

| Industry | Release ton/year | Percent total % | Release/employee kg/year | Release/$1000 of shipment, g |
|---|---|---|---|---|
| Aerospace | 3,483 | 1.1 | 4.3 | 48 |
| Metal fabrication | 24,310 | 7.9 | 221 | **2455** |
| Inorganic chemicals | 643 | 0.2 | 5.8 | 21 |
| Iron and steel | 2,434 | 0.8 | 6.1 | 24 |
| Metal casting | 7,051 | 2.3 | 28 | 237 |
| Motor vehicle | 30,675 | 10.0 | 77 | 153 |
| Organic chemicals | 24,678 | 8.0 | 197 | 380 |
| Petroleum | 19,419 | 6.3 | 259 | 139 |
| Polymer & fiber | 37,646 | 12.3 | **358** | 818 |
| Printing | 14,750 | 4.8 | 9.8 | 109 |
| Pulp & paper | 70,101 | **22.8** | *351* | *876* |
| Rubber & plastics | 45,119 | *14.7* | 56 | 501 |
| Stone, clay, ... | 3,630 | 1.2 | 7.3 | - |
| Textile | 6,629 | 2.2 | 11 | 95 |
| Wood furniture | 16,636 | 5.4 | 67 | 756 |
| **Total** | **307,204** | **100** | **Average = 111** | **Average = 472** |

is from the motor vehicle assembly industry (20%), the printing industry (13.7%), the rubber and plastics industry (11.4%), and the metal fabrication industry (10.7%). In total, these industries contribute over half of all releases and transfers of toluene and xylene (55.8%). The majority of carbon disulfide (82.5%) is contributed by the man-made fiber industry from rayon production.

The solvents ranked below the top five in the releases and transfers are mostly used in the paint and surface cleaning. The majority of emitted methyl ethyl ketone comes from the metal fabricating industry (25.2%), the rubber and plastics industry (23.4%), and the vehicle assembly industry (11.5%) which jointly contribute 60.1% of the total releases and transfers. 1,1,1-trichloroethane is released and transferred from the metal fabricating industry (36.6%), the rubber and plastics industry (30.4%), and the motor vehicle assembly industry (8.4%), totals 75.4% of all releases and transfers of this solvent. Tert-butyl alcohol is almost solely contributed by the organic chemical industry (94.6%). Hexane comes from polymer and fiber (57.4%), petroleum (19.5%), and rubber and plastics industry (11.3%) which together give 88.2% of all releases and transfers. Methyl isobutyl ketone is mostly contributed by the motor vehicle industry (56.7%) but metal fabricating (13%) and rubber and plastics industry (11.3%) also release and transfer large amounts of this solvent. Together all three industries account for 81% of its total release and transfer. Dichloromethane

**Table 14.32.5. Total transfers from different industries in the USA in 1995. [Data from EPA Office of Compliance Sector Notebooks]**

| **Industry** | **Transfer ton/year** | **Percent total %** | **Transfer/employee kg/year** | **Transfer/$1000 of shipment, g** |
|---|---|---|---|---|
| Aerospace | 1,080 | 0.4 | 1.3 | 15 |
| Metal fabrication | 13,164 | 5.3 | *120* | *1330* |
| Inorganic chemicals | 324 | 0.1 | 2.9 | 11 |
| Iron and steel | 4,328 | 1.7 | 10.8 | 43 |
| Metal casting | 178 | 0.1 | 0.7 | 6 |
| Motor vehicle | 23,980 | 9.6 | 60 | 60 |
| Organic chemicals | 63,680 | *25.3* | *509* | 980 |
| Petroleum | 1,382 | 0.6 | 18 | 10 |
| Polymer & fiber | 78,584 | **31.4** | **748** | **1708** |
| Printing | 4,051 | 1.6 | 2.7 | 30 |
| Pulp & paper | 23,457 | 9.4 | 117 | 293 |
| Rubber & plastics | 27,215 | 10.9 | 34 | 302 |
| Stone, clay, ... | 2,736 | 1.1 | 5.5 | - |
| Textile | 1,845 | 0.7 | 3.1 | 26 |
| Wood furniture | 4,439 | 1.8 | 18 | 202 |
| **Total** | **250,443** | **100** | **Average = 110** | **Average = 358** |

comes from rubber and plastics (65.5%), metal fabricating (24.8%), and polymer and fibers industry (8.1%) totals 98.4% of dichloromethane.

The second tier solvents are more harmful to health and environment than the first five most frequently released and transferred solvents. Ketones are suspected carcinogens by some sources. Dichloromethane is a probable human carcinogen. 1,1,1-trichloroethane is an ozone depleter. Because of their volatility, these solvents reside mostly in the lower atmosphere causing pollution and participating in radical processes.

Five industries are the largest contributors to the second tier solvents: rubber and plastics (23.8%), metal fabricating (18.1%), motor vehicle assembly (11.8%), organic chemicals (11.7%), and polymer and fiber (9.4%). Their joint contribution accounts for 74.8% of the releases and transfers of these solvents.

Two pertinent observations can be concluded from the above data

- tight controls and applications of new technology in the top three industries using a particular solvent can make big difference
- most releases and transfers stem from the use of paints and coatings.

Tables 14.32.4-14.32.6 analyze releases from different industries. The polymer & fiber, pulp & paper, organic chemicals, rubber & plastics industries pollute the most from the point of view of releases and transfers of solvents.

**Table 14.32.6. Total releases and transfers from different industries in the USA in 1995. [Data from EPA Office of Compliance Sector Notebooks]**

| **Industry** | **Total ton/year** | **Percent %** | **Total/employee kg/year** | **Total/$1000 of shipment, g** |
|---|---|---|---|---|
| Aerospace | 4,563 | 0.8 | 5.7 | 63 |
| Metal fabrication | 37,474 | 6.7 | 341 | **3785** |
| Inorganic chemicals | 967 | 0.2 | 8.8 | 32 |
| Iron and steel | 6,762 | 1.2 | 16.9 | 68 |
| Metal casting | 7,229 | 1.3 | 28.9 | 243 |
| Motor vehicle | 54,355 | 9.8 | 136 | 271 |
| Organic chemicals | 88,358 | 15.8 | *707* | 1359 |
| Petroleum | 20,801 | 3.7 | 277 | 158 |
| Polymer & fiber | 116,230 | **20.9** | **1107** | *2527* |
| Printing | 18,801 | 3.4 | 12.5 | 139 |
| Pulp & paper | 93,558 | *16.8* | 467 | 1169 |
| Rubber & plastics | 72,334 | 13.0 | 90 | 803 |
| Stone, clay, ... | 6,366 | 1.1 | 12.7 | - |
| Textile | 8,474 | 1.5 | 14.1 | 121 |
| Wood furniture | 21,075 | 3.8 | 84 | 958 |
| **Total** | **557,347** | **100** | **Average = 230** | **Average = 835** |

It can be speculated from the release data per employee that workers in pulp & paper, rubber & plastics, and polymer & fiber are the most exposed to solvents. Some technologies cost taxpayers more than others. Metal fabrication is one example. In order to produce goods valued at $1,000, the industry releases and transfers almost 3.8 kg of solvents. The cost in health and cleanup may exceed the value of goods manufactured.

It is characteristic that traditional industries which maintain older plants (metal fabrications, polymer & fiber, rubber & plastics, wood furniture, organic chemicals) contribute more to releases and transfers of solvents (as measured by releases plus transfers per $1000 sales), than industries which invest capital in the improvement of equipment, safety, and research and development (e.g., printing, motor vehicle assembly). This suggests that the avoidance of cost of the required investment is one reason for pollution. This reason was illustrated in the discussion of the petroleum industry where one manufacturer almost eliminated pollution by fixing leaking valves.

Industries consisting of smaller individual companies have fewer resources to develop new, non-polluting technologies (or even enforce safe practices). For example, the metal fabrication industry is composed of smaller plants using older technology which do not have the resources to make environmental improvements and remain competitive.

The traditional chemical industries (pulp & paper, rubber & plastics, and polymer & fiber) will hopefully apply their knowledge and chemical know-how to eliminate most of their contribution to pollution. In the future this will become an increasingly important requirement in competing by decreasing the social cost of applied technology. Perhaps more plastics could replace metals if the polymer, rubber, and plastics industries could demonstrate that their cost of pollution per dollar of output is much smaller than that of the metal industry.