

After CFCs

Option: Semi-aqueous Non-volatile Solvents*

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ABSTRACT—The demise of the CFC-113/alcohol azeotropic solvent for de-fluxing circuit assemblies after soldering has led, in recent years, to the electronics assembly industry being offered other cleaning technologies, some new and some new to this industry. In terms of uptake, one of the most successful will be semi-aqueous cleaning involving the use of an organic solvent of low volatility to dissolve the contamination followed by an aqueous rinsing process. Two families of solvent have evolved based on natural products (terpenes) and synthetic hydrocarbon chemicals. This paper reviews the possible semi-aqueous processes and the development of the solvents that has taken place. The cleaning performance is considered as well as the potential for effluent control and fully closed-loop systems.

INTRODUCTION

A semi-aqueous cleaning process is one in which the soil (rosin flux residue, contamination, etc.) is first dissolved from the workpiece (the soldered PCB) using a non-volatile solvent and the solvent-soil mixture then rinsed from the surface using water. The workpiece is then dried by some means.

Probably the most familiar semi-aqueous cleaning process is that used commonly in the home as well as in the factory for removing engineering greases and oils from hands. Soap and hot water is quite ineffective for removing engineering soils from the skin since it lacks the organic solvency. A semi-aqueous solvent dissolves the grease and oil but is too non-volatile to evaporate from the hands. The solvent contains a surfactant that allows the mixture to be rinsed away with water.

Semi-aqueous cleaning techniques have been used widely for many years in various industrial manufacturing sectors, but generally for cleaning machined or relatively smooth surfaces that allow some mechanical brushing to assist dissolution. Underbrush cleaning of the bottom side of wave soldered plated-through-hole electronics assemblies has, for many years, commonly used a semi-aqueous process. For cleaning under and around electronic components on a circuit assembly, brushing is not viable and, although immersion in the liquid solvent may be adequate, a spray of the solvent is better, especially for surface mounted assemblies.

SEMI-AQUEOUS CLEANING PRINCIPLES

The use of a low-volatility, non-halogenated, hydrocarbon solvent to dissolve rosin-based solder flux residues from electronics assemblies without mechanical brushing, followed by water rinsing to remove the solvent and the soils, was described first only a few years ago.¹ Since then, a lot of work has been done evaluating the efficiency of such semi-aqueous systems and demonstrating their technical feasibility for this particular application.²⁻⁵ Advances continue to be made in process design with regard to both the solvent and the water rinsing stages. These will be concomitant with improvements in solvent formulations.

In a semi-aqueous cleaning process, the workpiece is usually first immersed in, or sprayed with, concentrated solvent which may be mixed with a surfactant. The solvent is chosen principally for its dissolving power for the particular contaminants, in this case rosin flux and flux residues. The solvent also has to have other suitable properties such as compatibility with the workpiece materials, low toxicity and environmental benignity. The surfactant is added to give the solvent mixture satisfactory wetting, emulsification and rinsing properties. Typically, a solvent/surfactant composition ratio might be 9:1.

The solvent/surfactant washing step ensures that the workpiece surfaces are wet and the non-ionic surface contaminants such as the rosin flux, oils and greases are dissolved in the solvent and emulsified by the surfactant.

The second cleaning step uses water as the solvent. The water rinses off the solvent containing the dissolved flux residues. Furthermore, water is an excellent solvent for ionic residues such as the flux reaction products and plating salts. The basic stages of a semi-aqueous cleaning process are shown in Figure 1.

TERPENE SOLVENTS

Semi-aqueous cleaning of electronics assemblies has been pioneered by the use of a terpene as the solvent.¹ The range of terpenes with suitable properties is large and several commercial terpene blends are available. Equipment suitable for the use of terpenes for semi-aqueous cleaning of soldered electronics assemblies is available from several commercial sources.

The effectiveness of terpenes for cleaning has been known for a very long time. The most common method of their production is steam

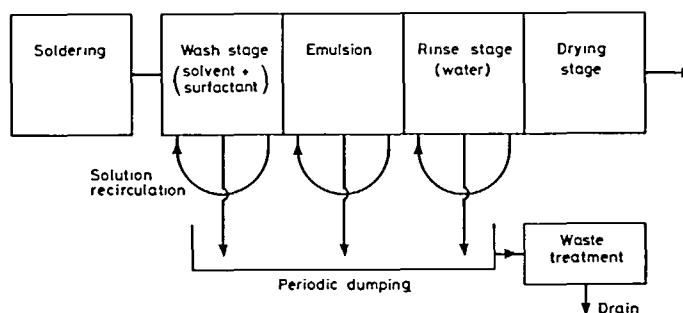


Fig. 1 The configuration of a hydrocarbon/surfactant-based semi-aqueous cleaning process.

distillation of pine tree stumps to produce turpentine oil, whose chief constituents are the terpenes pinene, terpineol, camphene, limonene and terpinene. Also, in the 1930s commercial quantities of the solvent di-limonene were produced from the peel of citrus fruits. The primary source of both these terpene solvents, namely tree stumps and citrus fruit peel, are waste products from other industries. However, there has been relatively little commercial interest, for critical cleaning operations, because of the availability at very low cost of halogenated solvents and petroleum distillates. The re-awakening of interest in terpene solvents has resulted from the increasing concern about halogenated solvents and their potentially detrimental effects on human health and the environment.

The interest in terpene solvents has generated suggestions regarding other non-volatile solvents suitable for semi-aqueous cleaning processes. It is likely that more non-volatile solvent systems will be identified and recommended by their specific advantageous characteristics.

The terpene or terpenoid family is the most numerous and varied class of organic chemicals found in nature. The metabolic processes of the various organisms on Earth are varied and complex, but the end products of metabolism are readily isolatable organic compounds grouped broadly as 'natural products'. Some, such as fats, carbohydrates, proteins and nucleic acids, have obvious rôles and occur in nearly all organisms. A second group, not necessarily less important to the functioning of the organism, are more species-specific. The main examples are the families of terpenes, of steroids and of alkaloids.

The terpenes generally stimulate the olfactory organs of animals and are responsible for many of nature's smells. The fragrance of a pine forest and the aroma of oranges, and indeed the characteristic smells of all flowers and fruits, are examples of terpenes being released naturally into the atmosphere. Terpenes are produced by nearly all living plants and by some animals which attract or warn by their smell. Many terpenes find use as perfumes and flavourings while others are important as antibiotics. Most terpenes are low in toxicity to animals and many are permitted as food additives, being classified in consumer products as 'generally recognised as safe'.

Terpenes are readily obtained by distilling plants with steam. The oil that separates from the distillate usually has a highly characteristic odour. Over 10,000 terpene compounds have been isolated and defined chemically and physically. A few well-known terpenes are shown with their molecular structure in Figure 2. The terpene family thus covers a wide range of properties and the selection of a terpene or a terpene blend is the key to obtaining superior performance for a particular application. Thus, for the

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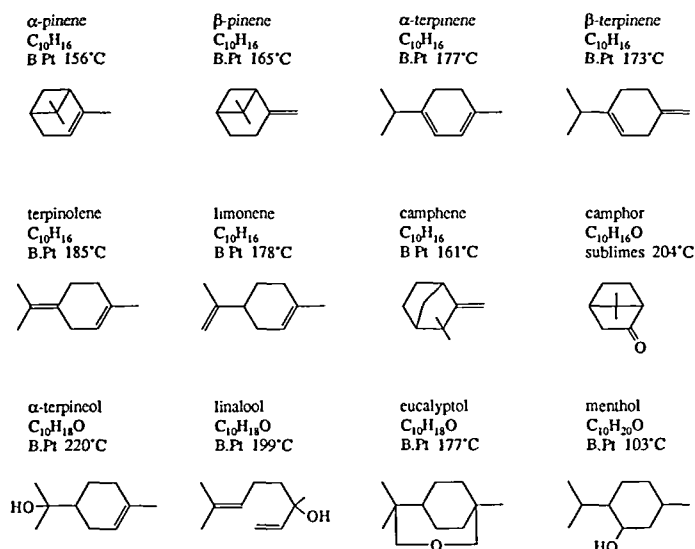


Fig. 2 The molecular structure and some properties of common terpenes.

removal of rosin flux residues, several different commercial terpene-based solvents are available, each having better or worse characteristics with regard to rosin solubility, boiling point, post-cleaning surface electrical resistivity, odour and cost.

Sources of Terpenes

The principal commercial large-scale sources of terpenes are wood and citrus products because of the availability of sources of waste from other industries in the form of tree stumps and orange peel. Some terpenes are used as extracted but most are refined.

The terpene distilled from orange peel is mainly limonene. The solvent blend distilled from wood is turpentine, which is mainly α -pinene and β -pinene. The composition of turpentine depends very strongly on the source of wood, for example from slash pine (*Pinus elliotii*) it typically contains 63% α -pinene, 21% β -pinene plus a range of other terpenes, whereas from white spruce (*Picea glauca*) it contains 37% α -pinene, 29% β -pinene and 15% limonene. For specialised cleaning, such as for defluxing soldered circuit boards, the separate terpenes are distilled, modified and rebled, for example using α -terpinene and γ -terpinene which are derivatives of α -pinene.

The amount of extracted terpenes used commercially as solvents, fragrances and flavourings is large, around 1 megatonne a year, world-wide. This quantity is, however, insignificant compared with the amount released naturally into the atmosphere. It is estimated that about 440 megatonnes per year of terpenes are released by plants into the atmosphere.⁶ Once in the air, the terpenes are photochemically decomposed as part of the natural cycle.

The Properties of Terpenes

Terpenes are naturally-derived chemicals originating in plants. As such, they are molecularly similar to rosin, itself a naturally-derived product from pine trees. The general principle that 'like dissolves like' explains why these terpene-based solvents have an exceptionally good solubility for rosin-based fluxes.

The dissolution of rosin in terpenes takes place rapidly even at room temperature. It is not normally necessary to heat terpene cleaning baths to more than 40–50°C. Terpenes are non-volatile and evaporation is minimal at operating temperatures as a result of their relatively high boiling points. Kauri butanol (K_b) values of solubility are not wholly relevant to rosin dissolution but continue to be used in commercial specifications. K_b values of most commercially available terpenes are intermediate between those of commonly used halogenated solvents as shown in Table 1. Some terpenes, however, exhibit K_b values which are much higher, indicative of extremely effective solvency, at least for Kauri gum resin.

Whilst K_b values may offer guidance regarding solvent effectiveness, solubility parameters are more firmly based on general chemical principles and offer a more significant indicator of ability to dissolve rosin fluxes and flux residues. While solubility parameters for semi-aqueous solvents have been determined, they are not, to the author's knowledge, published openly because of their commercial sensitivity, being dependent on the blend of terpenes or hydrocarbons used. Nevertheless the theory does predict that solubility increases as the molecular kinship of solvent and solute becomes

closer, confirming the observation that terpenes are naturally good solvents for rosin.

Table 1
Kauri Butanol (K_b) Values of Some Solvents⁷

	K_b Value
Trichlorotrifluoroethane (CFC-113)	31
α -Pinene	60
β -Pinene	66
Limonene	67
1,1,1-Trichloroethane	124
Methylene chloride	136
α -Terpineol	>500

Terpenes have a low viscosity, allowing convenient application by spraying or agitated immersion. When necessary, if a high-viscosity cleaning composition is required, it is possible to thicken with rheology-controlling additives.

Terpenes generally have flashpoints between 35 and 70°C. Commercial terpene products, suitable for defluxing soldered circuit assemblies, have flashpoints around 50°C, thereby being Class II compounds. The implication of this is that, as combustible liquids, when used in a spray application, the equipment should be inerted with nitrogen.

In concentrated liquid form, terpenes do not usually foam, although care must be exercised in selecting the emulsifier components of the solvent blend if low foaming is to be assured when diluted with water.

The use of terpene solvents is of course dependent upon the compatibility of the materials that are being cleaned, in particular the circuit board, the component package and its markings. The solvents will swell and soften most rubber compounds and, to some degree, many plastic materials after extended exposure of hundreds of hours' immersion. All the plastics and polymer materials normally used in electronics assemblies can be cleaned with no measurable incompatibility effect.⁸ However, care must be exercised as to the choice of materials for the construction of cleaning equipment and some, such as silicone polymers and synthetic rubber materials like polychloroprenes, avoided.

NON-TERPENE SOLVENTS

While terpenes have pioneered the semi-aqueous cleaning of electronics assemblies, so much interest has been generated that other semi-aqueous process solvents have appeared. These include hydrocarbon-based synthetic terpene-like solvents, *n*-methyl pyrrolidone and propylene glycol ethers.

Terpene solvents are generally produced by steam distillation of plants. Non-volatile solvents based on a similar chemistry and hence used in a similar way have been synthesised and are available commercially. It is argued that a synthesised product can have more batch-to-batch control and therefore better process control than one derived directly from natural materials.⁹ Synthetic solvents of this type need not have the strong smell of the terpenes. The chemistry of synthetic solvents for semi-aqueous cleaning is proprietary, but operating properties are similar to those of terpenes, characterised by high boiling point (~150°C) and low vapour pressure (~0.3 mbar at 25°C). However, synthetic solvents have been formulated with significantly higher flashpoints than terpene solvents, and this has implications regarding the allowable volumes and safety precautions necessary when transporting, storing and disposing of the solvents. Synthetic hydrocarbon semi-aqueous solvents are available with flashpoints compatible with Class IIIA (60–93°C) and Class IIIB (>93°C) combustible liquids. Such solvents can be used in the type of commercial equipment available for terpene use, and the same precautions regarding combustion apply when using a spray because fine mists of these solvents can be ignited.

Propylene glycol ethers have been evaluated as potential semi-aqueous solvents for cleaning soldered circuit assemblies¹⁰ and found to yield very good cleanliness results. The particular product most suitable has a flashpoint of 79°C. A range of propylene glycol ethers exists, with different viscosities and flashpoints, which, in principle, all possess good cleaning power by a dissolution mechanism. The molecular structure of these compounds comprises a combination of a non-polar aliphatic chain and a weakly polar ether group.

SEMI-AQUEOUS CLEANING PROCESSES

The conventional semi-aqueous process is one in which the workpiece soils are dissolved with a non-volatile solvent and the solvent/soil mixture then rinsed away with water, leaving the workpiece to be dried. Depending on the cleaning application, the concentration of the solvent solution will vary. Underbrush cleaning of insertion printed circuit assemblies involves

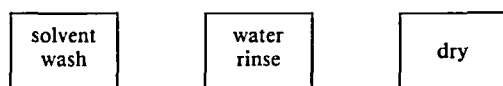
an emulsion of solvent and water at about 40°C with rotating brush cleaners to facilitate dissolution and removal of the contaminants. This method removes flux on the soldered side of the circuit sufficiently to permit contact for bed-of-nails electrical testing. Underbrush cleaning does not clean or remove flux from the component side, so its use is limited to applications where this is permissible. For general post-soldering cleaning of assemblies the solvent must be used neat and, for surface mounting assemblies in particular, it should be sprayed or the process enhanced by ultrasonics.

The conventional semi-aqueous cleaning process is two-stage: flux residue dissolution in the solvent by product immersion, by solvent spray or by ultrasonics, followed by a water wash to emulsify the solvent and remove it from the assembly. The solvent wash process in semi-aqueous cleaning is essentially the pretreatment step prior to water cleaning. The water cleaning stage can be a combination of immersion and spray, followed by an air knife to remove surface water plus a hot air drying station or a non-CFC immersion de-watering bath with evaporative drying.

Different semi-aqueous products require somewhat different process steps. The commercially available solvents can be divided into three categories:

- terpene-based, blended with a surfactant
- terpene-based, without a surfactant
- non-halogenated hydrocarbon blend.

The process for surfactant-containing terpene-based products is:



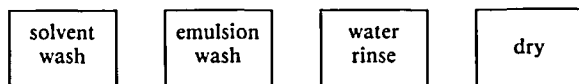
This is very similar to the process used for aqueous cleaning. The wash section can contain mechanical agitation from sprays, spray-under-immersion or ultrasonics. The surfactant in the terpene solvent enables it to be washed from the product using warm water.

The process for non-surfactant terpene-based products uses steam or boiling water to remove the solvent and soil from the product: terpenes are readily steam-distilled. The steam can be used to both rinse and dry the product:



An advantage of this process is the potential to eliminate the drying step. There is also the possibility of converting an existing two-sump vapour cleaning tank for use in this manner. A major advantage is the ease of design of a fully closed loop recycling system since the terpene is not contaminated with surfactant and the steam and the pure distilled terpene can be recycled. A possible disadvantage is that some electronics components may be incompatible with immersion in steam or boiling water, although this is not a general problem.

Equipment for synthetic hydrocarbon products normally includes an extra washing step using an emulsion of the solvent with water to improve the cleaning, to reduce contamination of the rinse water, and to enable spraying (of the emulsion) without inerting with nitrogen:



The advantages of this process result from the incorporation of the emulsion stage, which reduces the amount of waste water contamination and also allows alternative mechanical agitation processes in the emulsion tank.

Steady-state Operation of the Solvent

Equipment design can incorporate an air knife after the solvent wash stage to remove excess solvent-soil mixture from the workpiece, to limit the contamination introduced into subsequent process baths. In some semi-aqueous cleaning systems it is possible to reduce the effectiveness of the air knife in a controlled way in order to operate the solvent bath in a steady state of constant flux residue contamination. With a fully efficient air knife, more contamination is introduced into the solvent bath than is removed and the concentration of flux residues will rise, so that the bath will become too contaminated to perform effectively. Furthermore, the cleaning performance will depend on the point reached in the bath life-cycle. It has been found that the cleaning efficiency of these non-volatile solvents rises

initially, up to concentrations of 10% of rosin flux residues, but then, as the concentration of flux builds up to 40–50%, the cleaning efficiency begins to fall.¹¹ Hence, the effective cleaning performance of a new bath of solvent will rise, equilibrate and then fall substantially. In practice, therefore, the flux concentration in the bath would require monitoring so that the cleaning time could be adjusted appropriately, and the bath solvent would have to be replaced periodically. The cleaning performance of such a system is depicted in Figure 3(a).

The preferred situation is to reduce the effectiveness of the air knife in a controlled manner so that the drag-out of solvent is such that the amount of flux being dragged out of the solvent stage is equal to that being introduced on the workpiece. With this situation, the composition of the bath is in a steady state, having a flux concentration where the cleaning power of the solvent is at a maximum. A continuous small trickle of new solvent into the bath can compensate for that lost by drag-out. Figure 3(b) illustrates the time-dependent cleaning efficiency established in this way.¹¹ All the solvents available for semi-aqueous cleaning of soldered assemblies have a high solubility for flux residues and hence in principle it is possible to operate indefinitely in this way without ever changing the solvent sump.

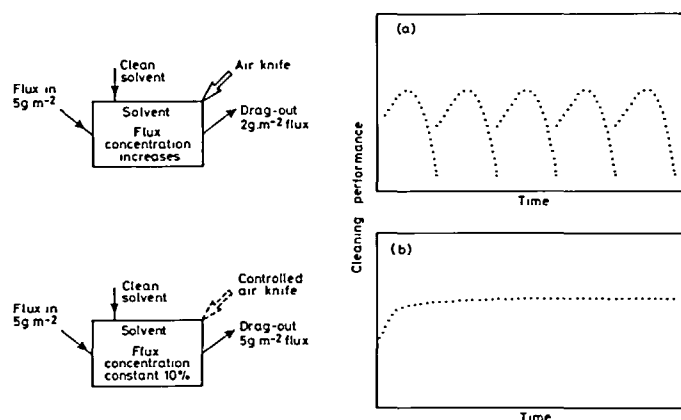


Fig. 3 An air knife can be used to control drag-out from the solvent bath. However, (a) if the air knife is too efficient, the flux concentration in the solvent will build up causing the cleaning performance of the solvent to improve at first but then fall, until the solvent must be replaced. If the effectiveness of the air knife is reduced, (b) the drag-out can be controlled so that the contamination of the solvent remains constant, as does its cleaning performance.¹⁰

Controlling Organics in the Effluent

If the efficiency of the air knife, after the solvent stage, is reduced as described above, more solvent, together with its dissolved flux residue, is transferred into the water cleaning stage. However, instead of pouring this contaminated water straight down the drain, there is the possibility of separating the solvent from the water. With the reduced efficiency of the air knife, an emulsion can be established in the first water bath, the overflow from which can be allowed to settle and then be decanted to separation. A process of this type is illustrated in Figure 4.

Alternatively, the rinse water can simply be filtered through a filter of small pore size: less than one micrometre. This fractionates the liquid into two parts: the flux residue contaminants generated in the soldering process, and the white aqueous effluent that is the water together with extracted surfactant from the cleaning agent. The former contaminants can be burned or reconstituted while the contaminated water can be treated or recycled. This is an important distinction from aqueous cleaning of rosin fluxes where all the soldering flux residues and saponifiers are together and closed-loop recycling is difficult. The solution normally has to be flushed down the drain.

The decanting separator process works because the solvent with its flux residue solute (it is insoluble in water) is present in the water stream in the form of tiny suspended droplets. These droplets separate from the more dense water simply because of gravity. The separated water can then be dumped or, if required for recycling, cleaned up using an activated carbon filter adsorption process or an ion exchange system, which would not be possible if the major part of the contamination had not been removed by decantation.

It should be recognised that the flux residue contaminants have to be disposed of, as do the filter cartridges and spent carbon. The major contaminant in the water extractable part of the spent liquids is surfactant. It is possible to match the particular solvent to enable efficient removal by the activated carbon.

This possibility of recycling the water from semi-aqueous cleaning

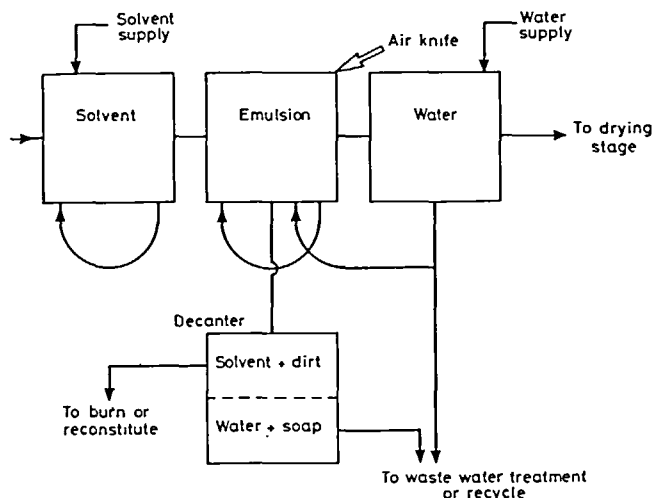


Fig. 4 With semi-aqueous systems the solvent carried over into the water can largely be separated by decanting and filtration to allow the water to be recycled or treated before disposal down the drain.

processes may prove to be very advantageous in these times of increasing requirement for efficient management of natural resources and for cutting environmental pollution. In some localities the discharge of industrial waste water is prohibited or severely regulated.

The final rinse water effluent is contaminated with a mixture of solvent, surfactant and dissolved flux residues, present together in the water in the form of an emulsion. The contamination level is usually in the range 1000–2000 ppm and can at present, if necessary, be put into the drain. This is only possible, however, if neither the solvent/surfactant mixture itself nor any contamination which it dissolves from the workpiece during the cleaning process poses any sewage treatment problems. Furthermore, any regulatory control of contamination levels in aqueous effluent can only become stricter in future years.

The level of contamination in the rinse water is determined by the ratio of drag-out to rinse water flow. A typical drag-out rate of the solvent/surfactant concentrate from a system operating in the steady state is around 50 grams per square metre of board area,¹² corresponding to about 500 grams per hour for a typical cleaning line. The mixture is emulsified into the rinse water. If the rinse water is being supplied at, typically, 10 litres/minute, the concentration of terpene/surfactant/flux residue mixture in the water is less than 1000 ppm.

Flammability Issues

Most commercially available terpene mixtures have flashpoints in the range 38–60°C and are thus often termed Class II liquids, described as combustible, rather than flammable, substances. Other, synthetic semi-aqueous solvents can have flashpoints up to 100°C. (By comparison, isopropyl alcohol has a flashpoint of 15°C and is a Class I flammable liquid.) Whilst ventilation of terpene cleaning equipment is of prime importance to prevent accumulation of combustible gases, the problem is no greater than, for instance, in a wave soldering system in which there are high-temperature components in the same location as alcohol liquid and vapour from the flux. For the cleaning of electronics assemblies the main problem is that, particularly for cleaning under surface mounted components, the terpene solvent must be sprayed. It is essential that a dense fog of solvent droplets be avoided, a situation that would be metastable and prone to spontaneous combustion. This problem is addressed either by spraying under the liquid surface or by inerting the space above the liquid with nitrogen.

If the cleaning equipment incorporates a drying stage, its temperature may well be higher than the flashpoint of the solvent. Normally, no solvent should be on the product at that stage but nevertheless care must be taken over the equipment design to ensure that flammability hazards are minimised.

EQUIPMENT DESIGN

Any equipment designed for use with semi-aqueous solvents must address several issues that arise with all the products:

- flammability and combustibility
- VOC
- waste water contamination
- waste disposal.

Many different techniques have been used.^{12,13}

Reduction of flammability/combustibility hazard

- inert the atmosphere in contact with the solvent
- install fire suppression equipment
- eliminate mist generation
- use solvent in an emulsion form.

Reduction of VOC emissions

- elimination or capture of mist
- careful design of enclosures and covers
- carbon adsorption
- temperature control.

Waste water contamination

- decanter separators
- emulsions
- closed-loop recycling
- solvent rinse.

Waste disposal

- biodegradability
- fuel blending
- collection of waste for central disposal.

Cleaning with semi-aqueous processes requires equipment similar to that used for aqueous cleaning, the principal difference being that a stage or cycle providing for contact of the solvent/surfactant mixture with the soldered assembly must be provided before the water cleaning. If the solvent mixture is required to be sprayed, perhaps for adequate flux residue removal from beneath surface mounted components, consideration must be given to the combustibility of the solvent aerosol produced over the bath. Both batch and in-line semi-aqueous systems are available, which can be inerted with a nitrogen atmosphere if the solvent is to be sprayed.

The optimisation of in-line systems using air knives has already been discussed. Ultrasonics can be fitted to the solvent wash tank and also the water wash tank. Spraying of the solvent can be performed under the liquid but is more effective as a separate stage. If this is incorporated, the atmosphere should be inerted with nitrogen.

Batch cleaning has some advantages over in-line systems, in that it is more economical especially in relatively small production runs. The process is more versatile in terms of process times and, in well designed systems, batch processes can be monitored very closely and accurately controlled. Terpene solvent aerosols and vapours can be combustible and the prevention of accumulations of combustible gases is of prime importance. A minimum venting rate must be specified, established and maintained, and safety controls must be included to signal a ventilation system fault. Nitrogen can be used to dispense the solvent into the sump, which precludes the need for pumps. Nitrogen is also used to purge the cleaning chamber before the cycle begins. Furthermore, sensors are used to ensure that the temperature in the chamber and in the sump are well below the flashpoint of the solvent. The general layout of a batch system for semi-aqueous cleaning is shown in Figure 5.

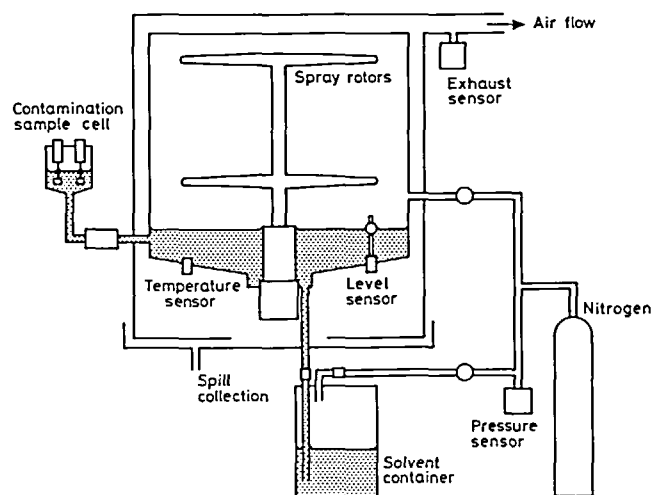


Fig. 5 The configuration of a nitrogen-inerted batch cleaner suitable for a semi-aqueous cleaning cycle.¹²

The best method for monitoring the contamination level of the solvent is by the variation of its specific gravity.¹⁴ The density of the solvent/solute varies with temperature and so a sample must be drawn off from the sump

and held at a given temperature for the measurement to be made. A semi-aqueous solvent typically has a specific gravity of about 0.850. As rosin is dissolved, the density increases and the specific gravity can rise in excess of 0.900 at about 30% by weight of rosin. The cleaning capacity of a semi-aqueous solvent is not normally impaired until rosin concentrations well in excess of 30% are achieved. Since specific gravity can be readily monitored to an accuracy of 0.001, this is a good means of process control. The monitoring and alarm systems can be fully automated.

TREATMENT OF WASTE

A semi-aqueous cleaning process gives rise to two waste stream sources—spent solvent/surfactant concentrate, and the rinse liquid from the water wash.

Appropriate choice of solvent enables the amount of solvent/surfactant concentrate to be minimised. If the solvent is capable of dissolving a sufficiently large quantity of flux residue, addition of new concentrate mixture to compensate for that dragged out on the workpiece assemblies will maintain the flux concentration in the solvent at a constant level below its solubility limit. Solvents with high capability for dissolving the contaminants (flux residues) allow for extremely long bath lives and, in principle, with suitable process control and adjustment of the air knife as already described, it should be possible to operate indefinitely without changing the sump. Terpenes are especially attractive in this regard, with their very high solubility for flux residue.¹⁵

The waste produced in a semi-aqueous cleaning process consists largely of the rinse water. This water is contaminated with low levels, typically up to 1000 ppm in a commercial equipment, of a mixture of solvent, surfactant and dissolved flux residue. These are present in the water in the form of an emulsion.

There does not appear to be any unacceptable problem with heavy metal contamination of the rinse water when using semi-aqueous cleaning, even within the harsh regime of underbrush cleaning. Concentrations of Pb, Sn, Cu and Zn in the disposed rinse water have been measured as consistently below 0.04 ppm.¹⁶ Nevertheless, it is advisable to monitor continuously heavy metal concentrations in the rinse water to ensure that higher concentrations are not inadvertently expended to a sanitary drain.

It has been reported¹⁶ that the effluent from a semi-aqueous facility has been monitored for a range of 129 priority pollutants, none of which has approached concentrations that would give rise to concern when compared with present regulatory control levels.

Because terpenes occur naturally they are harmlessly degradable but they do have a high biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The effluent should be readily treatable biologically and work has been done on bacterial strains able to utilise terpenes and hence find application for this type of effluent in commercial waste treatment plant.¹⁷

Semi-aqueous cleaning readily lends itself to in-house effluent treatment and closed loop processing.¹⁸ This is because the solvent and the rinse water separate as previously described and can therefore be decanted and recycled. Alternatively, if a steam rinse process is used, the solvent can be directly distilled. A possible closed loop for a semi-aqueous batch cleaning system is shown in Figure 6. Not only does such a technology avoid problems of external water treatment and disposal regulations, there is also the possibility of the solid waste being sold for fuel; some semi-aqueous solvents have a heating value that is as high as a good-grade heating oil.

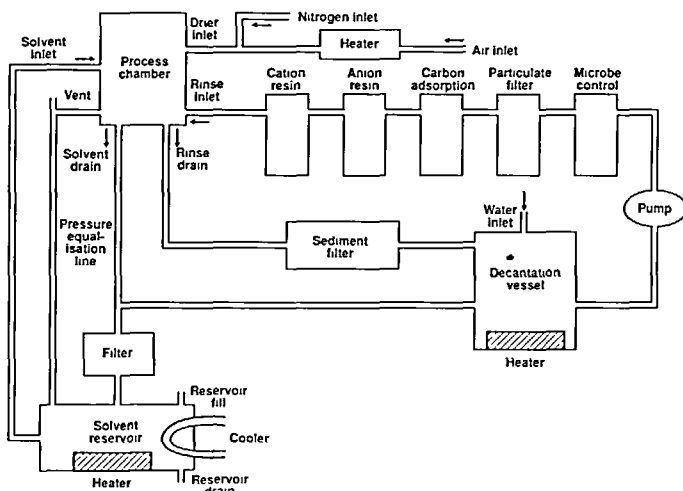


Fig. 6 A possible design for a closed-loop semi-aqueous cleaning equipment.¹⁸

ADVANTAGES OF SEMI-AQUEOUS CLEANING

Cleaning Performance

An advantage of semi-aqueous cleaning processes is their higher level of performance, compared with halogenated solvents, in removing soldering flux residues while retaining compatibility with the materials that are being cleaned. The cleaning performance is so good because of the chemical similarity of the solvents used and the rosin contaminant being removed. Examples of the compatibility of the commercially available semi-aqueous solvents are that ink component markings are not removed and the solvent is not significantly absorbed by the plastic components or the circuit board.

Waste

Semi-aqueous processes offer opportunities for minimising waste. Appropriate choice of solvent allows reduction of solvent/surfactant concentrate to a minimum since the solvent will be capable of cleaning without reduced effectiveness even when contaminated with substantial amounts of flux residue. By suitable process control it is possible to virtually eliminate spent-bath disposal.

Atmospheric Emissions

The solvents suitable for semi-aqueous processes are low in volatility, so that solvent emissions to the atmosphere from such processes are low. These solvents in general have low toxicity and, as a chemical group, huge amounts are emitted naturally into the atmosphere by plants.

DISADVANTAGES OF SEMI-AQUEOUS CLEANING

VOC Regulations

A disadvantage of semi-aqueous cleaning processes is that all the suitable solvents proposed to date are classified as volatile organic compounds, and are therefore subject in some countries and states to restrictions on their use. These regulatory controls seem somewhat ironic in this situation, where the emissions are often in the form of natural substances. Furthermore, the volume of VOC lost in a semi-aqueous process will normally be less than the VOC lost when cleaning with other organic solvent processes.

Combustibility

None of the solvents available for use in semi-aqueous cleaning processes is flammable. Generally they have flashpoints (Tag closed cup) in the range 35–70°C for natural terpenes or up to 100°C for synthetic solvents, classifying them as combustible. Combustibility is a concern in the use of semi-aqueous solvents but is by no means an insurmountable difficulty.

Finely divided spray of these solvents can be ignited (unlike CFC-113 but similar to 1,1,1-trichloroethane). Most of the currently available cleaning equipment for semi-aqueous processes uses a spray of the solvent concentrate in order to achieve adequate penetration and solvent flow beneath components. High-pressure spraying beneath the liquid solvent circumvents the problem to a large extent, avoiding any accumulation of solvent aerosol over the liquid. Other systems are available with the atmosphere in which the spraying takes place inerted by using nitrogen.

Odour

One of the most controversial points about terpenes is their smell. It must be remembered that the noses of animals (including humans) have evolved to be especially sensitive and discerning to nature's smells. Bearing in mind that the perceived odour level is very subjective, terpenes, dictated by their natural origins, have odour thresholds to the human nose between 1 and 1000 parts per billion. Normal threshold detectabilities of chlorinated solvents are between a thousand and a million times greater (~1000 parts per million). Thus, the nose is no measure of the atmospheric concentration of a species, and certainly not of its harmfulness to health.

The human perception of the unacceptability of a terpene smell can, to some extent, be alleviated by blending several together. There seems to be a desensitising mechanism whereby it is common for the slight nausea experienced by some people when using strong-smelling terpene solvents to disappear with continued exposure so that the smell becomes barely discernible.

An attempt to judge the comparative safety of an atmospheric solvent vapour is the Inhalation Hazard Index (IHI), whose value is the ratio of the saturated vapour pressure of the substance and its toxicity. Clearly the ideal situation is for the IHI to have a value less than one. This is not the case for solvents and hence cleaning equipment must be properly designed so that the concentration of solvent vapour in the operator environment is much less than the saturated vapour pressure of the solvent. The IHI value gives an indication of the difficulty of achieving this situation, without extracting excessive solvent vapour into the outside atmosphere by strong

ventilation of the equipment. For example, the IHI at 25°C of CFC-113 is 440, of 1,1,1-trichloroethane about 380, of trichloroethylene about 740, and of methylene chloride about 4600, whereas for terpene solvents it is generally in the range 10–20¹⁹, and for synthetic semi-aqueous hydrocarbon solvents it can be close to 1.

Component Compatibility

While semi-aqueous solvents are fully compatible with virtually all materials used for components and printed circuit boards, the same criteria as have been considered for aqueous cleaning must be met, namely that ingress of the solvent and the water must be eliminated. This requires a more careful design of those components with moving parts (e.g., variable capacitors, potentiometers) and of those with the possibility of capillary ingress (e.g., coils).

REFERENCES

- 1 Hayes, M. E., Hood, C. C., Miller, R. E. and Sharpe, R., 'Method for Printed Circuit Board and/or Printed Wiring Board Cleaning', US Patent 4640719 (1987).
- 2 Hayes, M. E., 'High Performance Cleaning with Terpene/Surfactant Mixtures', Proceedings, Surface Mount '88, Marlborough, Massachusetts (1988).
- 3 Dickinson, D. A., Guth, L. A. and Wenger, G. M., 'Advances in Cleaning of Surface Mount Assemblies', Proceedings, Nepcon West '89, Anaheim, California (1989).
- 4 Hamblett, G. W. and Larsson, G. A., 'Terpene/Aqueous Cleaning', Proceedings, Nepcon West '90, Anaheim, California (1990).
- 5 Osvalder, B., 'Terpene vs CFC Defluxing in Hybrid Circuits Manufacturing', *Hybrid Circuits*, No. 23, pp. 18–21 (1990).
- 6 Rasmussen, R. A. and Went, F. W., 'Volatile Organic Material of Plant Origin in the Atmosphere', Proceedings, National Academy of Sciences USA, Vol. 53, pp. 215–220 (1965).
- 7 Hayes, M. E., 'Terpenes—A Viable Alternative to CFCs', *Electronics Manufacture and Test*, pp. 17–21, June (1989).
- 8 Hayes, M. E., 'Naturally Derived Biodegradable Cleaning Agents', Proceedings, HAZ-MAT West '88, Long Beach, California (1988).
- 9 Merchant, A. and Wolff, M. C., 'Screening and Development of Ozone/Greenhouse Compatible Cleaning Agents', Proceedings, Nepcon West '89, Anaheim, California (1989).
- 10 van Gerven, J., van Horssen, L. and van Veen, N., 'Propylene Glycol Ethers—an Alternative to CFC-113 for the Cleaning of Printed Circuit Boards', *Circuit World*, Vol. 17, No. 1, pp. 15–19, 55, October (1990).
- 11 Dishart, K. T. and Wolff, M. C., 'Circuit Assemblers Can Have a Reliable Future with Adoption of New Cleaning Technologies', Proceedings, Electronics Manufacturing and the Environment '90, Bournemouth (1990).
- 12 Hayes, M. E., 'Semi-Aqueous Assembly Cleaning: The Best Choice for SMT Cleaning', Proceedings, 'Defeating the Ozone Problem' Conference, Teddington, UK (1989).
- 13 Harman, J., 'Equipment Design Considerations for Semi-aqueous Cleaning', Proceedings, Nepcon West '91, Anaheim, California (1991).
- 14 Breunsbach, R., 'Batch Cleaner Design for Terpene Solvent', *Electronics Manufacture and Test*, pp. 35–36, July/August (1989).
- 15 Hayes, M. E., 'Waste Minimisation and High Performance Cleaning Using Semi-Aqueous Processes', Proceedings, Nepcon East '89, Boston, Massachusetts (1989).
- 16 Wenger, G. M., Guth, L. A. and Dickinson, D. A., 'Advances in Cleaning of Surface Mount Assemblies', Proceedings, 'Defeating the Ozone Problem' Conference, Teddington, UK (1989).
- 17 Vandenbergh, P. A. and Cole, R. L., 'Plasmid Involvement in Linalool Metabolism by *Pseudomonas Fluorescens*', *Applied and Environmental Microbiology*, Vol. 52, No. 4, pp. 939–940 (1986).
- 18 King, R., 'Zero Discharge Semi-aqueous Centrifugal Cleaning', Proceedings, Nepcon West '91, Anaheim, California (1991).
- 19 Keyser, G. E., 'Terpenes as Replacement Solvents', Proceedings, Electronics Manufacturing and the Environment '90, Bournemouth, UK (1990).