

Cleaning

Introduction of fluorocarbon solvents

Rosin flux residues require cleaning, especially when activated fluxes have been used, and cleaning was very commonly carried out, especially throughout Europe and the USA, driven by a perception held by military customers that all flux residues are potentially harmful. The original approach used a variety of solvents but these gave problems:

- Organic solvents often have low flash points and present fire hazards
- Chlorinated solvents can be too aggressive.

Some solvents present health hazards and/or have low TLV limits.

Fluorocarbons had been developed during the 1930s as refrigerants, and in the late 1960s were introduced for the cleaning of electronic assemblies. The particular compound most commonly used was 'CFC-113', 1,1,2-trichloro-1,2,2-trifluoroethane¹. This material:

- is inherently non-toxic (TLV 1,000 ppm)
- is non-flammable
- can be mixed with other solvents (such as isopropanol) to give a range of cleaning properties – even with a small percentage of additive, cleaning is effective
- allows cleaning to be carried out at low temperature (typically less than 70°C)

- when formulated with other suitable solvents, can be used for cleaning by immersion, by vapour phase, or by hand after repair or rework

For these reasons, fluorocarbons rapidly became the preferred means of cleaning, despite their expense. The solvents were marketed under a variety of trade-names, of which Arklone and Freon were the best-known in the UK.

¹ The numbering system used for CFCs and similar compounds is confusing, but there is an explanation at <http://www.epa.gov/ozone/geninfo/numbers.html>.

Ozone depletion

Following scientific evidence of the damaging effect on the stratospheric ozone layer, which protects us from the harmful effect of the sun's radiation, over 100 countries agreed, in the Montreal Protocol of September 1987 (amended in London, June 1990 and at Copenhagen, November 1992), to phase out man-made ozone-depleting chemicals as quickly as possible. Not only was CFC-113 affected, but another of the common chlorinated solvents (1,1,1-trichloroethane, or methyl chloroform, and sold as Genklene or Chlorothene) was also covered by the resulting European-wide regulations, where phase-out was scheduled by the mid-1990s. The Protocol and its associated EC regulations imposed control on the supply to the market of the substances rather than their use as such, but the effect is the same, to force electronic companies to seek different ways of approaching the problem, and these materials have now essentially become unavailable.

The Ozone Depletion Potential (ODP) is the ratio of the impact on ozone of a chemical compared to the impact of a similar mass of CFC-11, and

indicates the relative ability of substances to damage the Earth's ozone layer. There are two groups of chemicals, classified according to ODP:

- **Class I substances**² have an ozone-depletion potential of 0.2 or higher. They include chlorofluorocarbons (CFCs), halons, carbon tetrachloride, and methyl chloroform:
 - CFCs were commonly used as refrigerants, solvents, and foam blowing agents.
 - Halons were used as fire extinguishing agents, both in built-in systems and in handheld portable fire extinguishers.
 - Carbon tetrachloride was widely used as a raw material in many industrial uses, including the production of CFCs, and as a solvent. Solvent use ended when it was discovered to be carcinogenic.
 - Methyl chloroform was used as an industrial solvent.

- **Class II substances** have an ozone-depletion potential of less than 0.2.
 - Hydrochlorofluorocarbons (HCFCs) contain chlorine and thus deplete stratospheric ozone, but to a much lesser extent than CFCs, with ODP values ranging from 0.01 to 0.1.

- Hydrofluorocarbons (HFCs) contain only hydrogen, fluorine, and carbon, and do not deplete the ozone layer. However, some HFCs have high Global Warming Potential (see later)

Class I materials, those with significant ODP, have already been phased out. HCFCs and other halogenated materials with some ODP are subject to increasing restrictions and will also be phased out, those with the highest ODP values first. For example, the commonly used HCFC-141b ceased production on 1 January 2003.

If you are interested in researching this in more detail, a good starting point in the US Environmental Protection Agency website at <http://www.epa.gov/docs/ozone/>.

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For a complete listing, see <http://www.epa.gov/ozone/ods.html> (Class I) and <http://www.epa.gov/ozone/ods2.html> (Class II).

Other issues

The list of environmental issues involved with cleaning materials is in fact much more extensive than mere ozone-depletion, although it is that aspect which has been nearest the headlines. A fuller list includes:

- **Global Warming Potential (GWP):** Carbon dioxide induces atmospheric warming as a result of the 'greenhouse effect', by absorbing the infrared radiation emitted from the Earth's surface. How much materials contribute depends on both the emission level and their 'GWP', the ratio of the warming caused by a substance to the warming caused by a similar mass of carbon dioxide. The seriousness also depends on the length of their persistence in the upper atmosphere.

All solvents³ have substantially greater global warming impact per molecule than does carbon dioxide. HCFCs and HFCs have GWP values ranging from 93 to 12,100, the value being generally lower than with CFCs (CFC-12 has a GWP of 8,500; CFC-11 has a GWP of 5,000). Their GWP also degrades more quickly with time, whereas CFCs are effective for over 500 years. Water, a substitute in numerous end-uses, has a GWP of 0.

- **Photochemical Ozone Creation Potential (POCP):** Many solvents are able, in the presence of light, to assist in the formation of ozone at ground level. This 'photo-chemical smog' is a damaging pollutant at high concentrations, which can adversely affect human health, plant growth and building materials. Whilst there are no agreed regulatory values, many of the alcohols and substitutes have significant POCP.
- **Ground water contamination:** Many industrial chemicals are not degraded on disposal, and survive land-fill operations to pollute the water table. The philosophy now embodied in legislation is, in essence, that the person who creates the problem has to clear it up! This has led to the emergence of a whole new industry of licensed disposal operations, with the effect that the cost of disposing of all kinds of waste has increased.
- **Waste water:** This has a number of problem areas, including its acidity or alkalinity (pH), the heavy metal content (lead, copper, nickel, tin) and biodegradability. The significance is that waste water needs to be both neutralised and treated before

discharging to remove heavy metals, and be assessed in terms of the impact it makes on the dissolved oxygen in water within the environment - an essential for aquatic life.

The Environmental Protection Act 1990 controls emission from large cleaning operations (the trigger levels for which are constantly reducing) and, through Water Authority consents, is also affecting the ability of a company to discharge even treated effluent. Legislation in the EPA and elsewhere, regulates how many materials, including spent solvents, may be carried, transferred, stored, treated and disposed of. These regulations are likely to get tighter and involve higher costs in the future.

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Probably the most unfriendly material from the GWP perspective is sulphur hexafluoride. Used as a cover gas in magnesium production and casting, as a dielectric gas and insulator in electric power equipment, as a fire suppression discharge agent in military systems, and formerly as an aerosol propellant, this has a GWP of 22,200 and a life of 3,200 years!

Hazards in cleaning

Almost all cleaning options have some potential to harm operators if not properly controlled to minimise risk. Precautions taken have to be reasonably practical but also to take into account technical, cost and environmental issues. Three aspects of Health and Safety hazard are generally considered:

- **Toxicity** - the main risk is inhalation of vapours, and the more volatile the solvent, and/or the higher the temperature, the higher the risk. Exposure must be kept within operational exposure limits. Some solvents are suspected of being carcinogens, for which no safe level of exposure is allowed.

- **Skin and eye hazards** - solvents designed to dissolve oil, grease and dirt will probably be very good at removing natural oils and greases from the skin, and most cleaning chemicals have the potential to cause skin irritation, sensitivity or dermatitis. Direct skin contact should be avoided as far as it is practicable. Many of the cleaning substances may also be harmful to the eyes if splashed, and suitable eye protection may be required.
- **Flammability** - the ozone-depleting solvents that are being phased out are non-flammable, but most of the alternative hydrocarbon solvents will burn. The flash-point is the lowest temperature at which a solvent will emit sufficient vapour to form a flammable vapour-air mixture which will flash when ignited momentarily by application of a flame. Its value only indicates the hazard, which is increased if the solvent is sprayed, atomised or strongly agitated, for example, using ultrasonics. Normally one recommends a margin of safety of at least 15°C between the operating temperature and the material's flash-point, otherwise stringent precautions are necessary.

Alternatives to CFCs

As with the replacement for tin-lead solder, there is no immediate drop-in replacement for the CFCs used in cleaning. The nearest to such a material, n-propyl bromide, was developed too late in the day, and its use has been somewhat controversial. Although it has an ODP rating of zero, is relatively cheap, non-flammable and fits a range of applications, it is somewhat toxic, with an OEL of 50 ppm, and some concern that this will

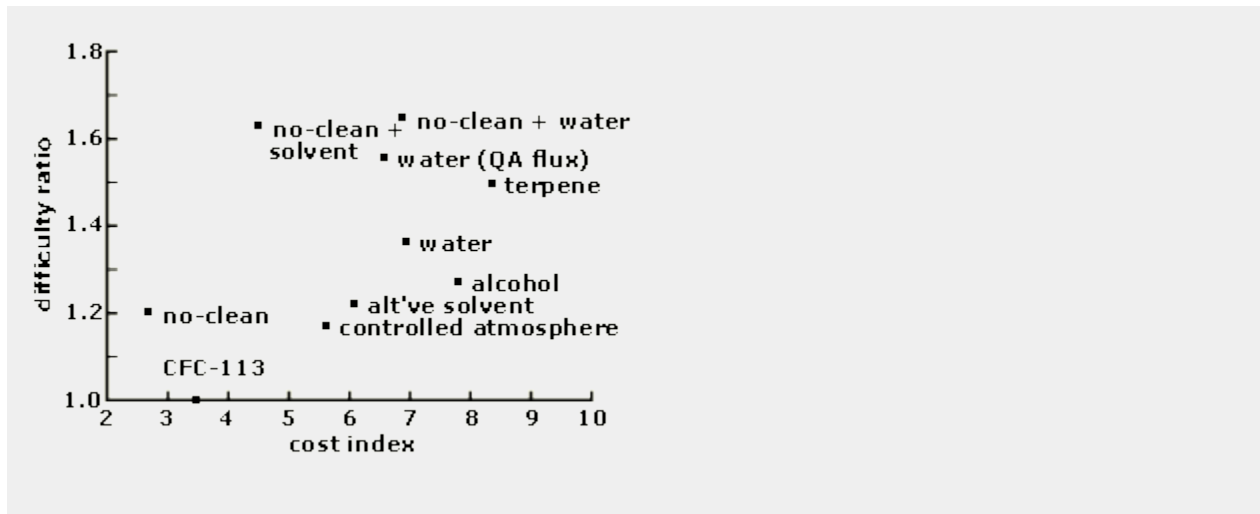
reduce. In consequence, there has been no change to the four basic approaches to the withdrawal of CFCs that were proposed at the outset:

1. Use a volatile organic solvent in a process similar to CFC vapour cleaning using either non-flammable HCFC solvents or flammable solvents with a lower global warming potential.
2. Use an organic solvent with a high boiling point, either evaporating the solvent at elevated temperature or choosing a water-miscible material which can be rinsed with water and dried once the solvent has completed its task of removing the 'soil' - this is referred to as a 'semi-aqueous' process.
3. Use water as a solvent, either in combination with detergent to remove rosin flux residues or in conjunction with water soluble fluxes. Some components are not compatible with water or are difficult to clean because of fluid entrapment in small crevices. Water-soluble fluxes are more active than rosin fluxes, providing a larger process window, but even traces need to be removed because they are acid.
4. Use a no-clean process.

A somewhat unexpected problem with a number of the processes, especially those based on water/saponifier combinations, is that the lead from solder will actually *dissolve* in the solvent, whereas this was not a problem with CFCs. This points out the need to consider every aspect of the process when evaluating a proposed change!

With no 'drop-in replacement' for CFCs available, much attention has inevitably been focussed on removing the need for cleaning. Figure 1 gives an example of a review carried out by a user of the cost and difficulty of alternative cleaning approaches, from which the no-clean option can clearly be seen to be desirable, if less easy than using CFCs.

Figure 1: Difficulty : cost ratio for different cleaning methods, Source: Nortel



No-clean processes

No-clean processes are *not* the same as not cleaning! In the latter case there will be flux residues, and they may or may not be deleterious to the long term reliability of the end product. A no-clean process involves selecting flux materials which will be effective in use but whose residues are:

- Electrically insulating.
- 'Pin testable' (in other words, the pins on test fixtures are able easily to penetrate the coating on test lands and solderable areas).
- Chemically inert, and will not react with any of the materials on the assembly during extended life (which may include elevated temperature and humidity).
- Cosmetically acceptable. This is particularly important where a non-technical end-user gets sight of a board which is less than

critically clean. Would you want to eat with dirty cutlery, even if the deposits were shown to be sterile?!

Of these, the major issues in recent years have been associated with pin testability and cosmetic acceptability, and work continues on solder ball elimination and maximising the process window.

No-clean systems

No-clean systems have been formulated for both wave-soldering and reflow soldering. The basis for both is a flux which has a higher proportion of either solvent (for wave soldering) or rheology modifiers (for reflow soldering) and a lower concentration of both flux base and activator. Moreover both flux base and activators are chosen so that their decomposition products are not harmful.

The ultimate of no clean is 'no residue', where the flux is expended entirely during the process of producing the solder joint. This also presents the ultimate challenge for the user! The issues with all no-clean/no residue processes relate to process control, so that solderability is achieved and, the joint satisfactorily wetted, before the protective qualities of the flux are dissipated.

Source : http://www.ami.ac.uk/courses/topics/0105_clng/index.html