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# SUBSTITUTION ANALYSIS: A CASE STUDY OF SOLVENTS

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## Summary

This paper presents an example of a substitution analysis, an approach often required in dealing with issues of exposure to toxic substances. CFC-113, a chlorofluorocarbon-based solvent is suspected of depleting the ozone layer. This study examines potential alternatives to pure CFC-113, specifically in defluxing applications. The results suggest that none of the potential substitutes is ideal in terms of cleaning capability. Certain CFC-113/alcohol blends or the CFC-113/methylene chloride azeotrope could be substituted in some applications but, because they still contain CFC-113, the threat of ozone depletion would only be reduced, not eliminated. Water is probably the safest possible substitute, but it poses regulatory and technical problems.

## I. Introduction and background

In recent years, we have become increasingly aware that many of the chemicals and chemical products used in our industrial society are hazardous. There are some 60,000 chemicals of industrial importance in commerce today, and about 1,000 new substances are introduced into the market each year. Many of these chemicals have never been tested, and some will turn out to be extremely dangerous to the workers who produce them, to the consumers who use them, and to those living near the disposal sites where they are ultimately dumped.

Not only can hazardous chemicals lead to localized exposure, but they can have global effects as well. One such global issue that scientists are becoming more concerned about is ozone layer depletion. The chemicals thought to contribute most strongly to depletion are a family of chemicals called chlorofluorocarbons (CFCs) [1—3]. Early research suggested that depletion from release of the CFCs could be significant, perhaps 15 to 18 percent; later work estimated depletion would be lower, between 5 and 7 percent. A recent study places potential depletion even lower, at 2 to 4 percent [4]. While these results indicate that the problem may not be as severe as was once thought, the depletion estimates remain highly uncertain. This uncertainty, together with the fact that the potential consequences of depletion could be extremely serious, suggest that research should continue. Analysis of methods for reducing CFC emissions therefore remains important, in case the U.S. Environmental Protection Agency (EPA) eventually decides to regulate.

In this paper, we focus on reducing emissions of one of the CFCs, CFC-113, which is used widely as a solvent. About 35 million pounds of the chemical were used in U.S. defluxing applications by the electronics industry in 1979 [5]. Virtually all of it was emitted to the atmosphere. Since then, the electronics industry has continued to grow rapidly all over the world, and the future use and emissions of CFC-113 could ultimately contribute significantly to ozone depletion.

A promising method for reducing the threat of a particular chemical that is currently receiving more attention is substitution of other chemicals or products that are less dangerous. The effects of substitution are complex and can be unexpected since possible alternatives to a hazardous chemical may themselves be hazardous but in a different way, and there may be no valid way to compare them. For example, it is not obvious how to compare a chemical that causes liver cancer in mice to one that causes photochemical smog, which endangers the lives of infirm, older people. In spite of these limitations, substitution analysis is likely to become an important tool for reducing future risk.

In principal, an ideal substitution analysis would consider all possible substitutes and compare them along three dimensions. The first dimension is technical suitability. All candidates would be compared in terms of their capability to accomplish a specific task. The second dimension is economic. The cost of using each candidate would be evaluated; a complete analysis would include the costs of such things as associated equipment, process changes, regulatory requirements, and disposal. The third dimension is health implications. The possible consequences of producing, using, and disposing of each candidate would be determined. Human health impacts based on epidemiological and toxicological data for each substance would be necessary. Some metric for comparing the health consequences for each chemical would have to be used. In practice, this kind of thorough analysis would require huge resources, and the data limitations would be so severe that the results would not be especially meaningful.

In this paper, we illustrate that substitution of one chemical for another involves a complex set of trade-offs. In the simplest case, an alternative chemical would have physical and chemical properties so close to the compound being replaced, that it could be substituted in existing equipment with little or no change. This is seldom possible, and consequently substitution often forces moderately complicated changes of equipment. For example, in the case of defluxing printed circuit boards (PC boards), we consider chemicals that replace the CFC-113 in vapor phase degreasers without major changes in equipment design. In more complicated substitution cases, the change of chemical may also force a shift to an entirely new technology. For instance, in the cleaning of PC boards, we consider a change from CFC-based to water-based defluxants, which requires new equipment. Such changes must allow detergent composition to be monitored, the use of high velocity air knives, and more extensive drying procedures.

In what follows, we present a substitution analysis for CFC-113 solvent in printed circuit board defluxing operations. We limit our treatment to the dimension of technical suitability; the other two dimensions, cost and health effects, are beyond the scope of the analysis. In Section II, we identify the materials used to make the boards and specify the contaminants that require removal. In Section III, we discuss the characteristics alternative solvents must possess to meet reasonable standards in cleaning and drying. We identify a number of substitution candidates and rank them according to certain important criteria. We then consider an alternate technology, water with a detergent additive, as a potential substitute for CFC-113 solvent technology. In Section IV, we summarize the results.

## II. Specification of substrates and contaminants

The primary use of solvents in the electronics industry is to clean and dry various items of equipment like printed circuits, microcircuitry, capacitors, resistors, connectors, and ferrite computer cores. In these applications, the solvent is commonly placed in a tank called a degreaser in which the solvent is heated for better cleaning action. The item to be cleaned is placed in the tank, and removed to the vapor phase region where cleaning is achieved by condensing and flowing solvent over the surface. These electronic items are made from a large variety of substrate classes including plastics, elastomers, metals, ceramics, and semiconductor materials, and each class has many individual substrate members. Each of these substrates can be expected to interact with a given solvent in a different way. The ceramics and semiconductor classes are less sensitive to the differential action of solvents.

The contaminants on these substrates are varied but principally consist of greases and oils (including fingerprints), salt, rosin flux, plating salts, waxes, water, dust, and machined substrate fragments. They may be grouped into the generic classes of polar, nonpolar, and particulate contaminants. The greases (not including their surfactants), oils, rosin, and waxes are generally composed of long-chain hydrocarbons or molecules with long hydrocarbon side chains; they make up the nonpolar group. Rosin flux activators and their residues, sodium chloride, and soldering and plating salts make up the polar group. Dust and machining fragments make up the particulate group.

## III. Considerations in selecting an alternative solvent

In selecting an alternative solvent for cleaning and drying a particular item, several technical factors must be taken into account simultaneously. These factors are somewhat different depending on the class of substitute solvent. For one class, the volatile organics, the requirements are that they will:

(1) remove all contaminants rapidly while not attacking the materials of construction (the substrate materials);
(2) provide a rapid rate of evaporation of excess solvent (so that remaining solvent will not interfere with following manufacturing steps);
(3) provide a minimal risk to workers (low flammability and toxicity);
(4) require a low expenditure of energy;
(5) be compatible with existing or slightly modified degreaser designs, and
(6) be a minimal threat to the ozone layer.

For another class, the water-based solvents, the specific solvent must allow the use of a hot air knife technology to ensure a rapid rate of evaporation, and, if detergents are used, a method for efficient removal of these surfactants must be found.

The requirement that a solvent remove all contaminants while leaving the substrate unharmed is complicated. As we have noted, the contaminants consist of polar, nonpolar, and particulate residues whereas, in general, a solvent that removes one of these residue types is poor at removing the others. Hence a compromise must be achieved that balances the solubilities of the polar and nonpolar contaminants in the solvent and the ability of the solvent to wet and detach particulates from the substrate surface. For volatile organic solvents, this is achieved by determining the relative ranking of solvents with respect to evaporation rates and certain contaminant removal capabilities. Solvents appearing high in all the solvency rankings are considered potential substitutes. Toxicity, energy use, and special problems are then considered separately to rank each solvent on a final list of possible substitutes. Note that operating costs of the various solvents in degreasers are not calculated, but rather that energy usage (as measured by the energy of vaporization) is used as a surrogate to establish a relative cost ranking.

Water-based defluxants must generally be treated separately, on an *ad hoc* basis. Pure water, as will be seen, is very poor at removing rosin fluxes and must either be used with water-soluble fluxes or combined with saponifying agents to attack rosin fluxes. The procedure for rank ordering the organic solvents assumes that all solvents are dissolving the same flux residues, that all solvent components are volatile, and that dissolution, not chemical reaction, is the primary mode of action. Both the water-soluble flux system and the water—saponification—rosin flux system violate this set of requirements, making an *ad hoc* treatment necessary.

In the next section, we present a formal procedure for rank ordering and selecting good alternative volatile organic defluxants. In the following section, we deal with water-based systems separately, comparing their defluxant capabilities with those of the most common CFC-113/alcohol systems.

### *Alternative volatile organic solvents*

A selected list of cleaning solvents has been gathered in Table 1 along with the values of several parameters that bear on their contaminant removal capabilities. Solvents have been selected from the CFC, chlorocarbon, and alcohol groups. Pure water has been included to represent the far polar end of the solvent spectrum. Most CFC mixtures and all nonflammable chlorocarbons have been included except tetrachloroethane (sym), which is highly toxic (TLV = 5 ppm).* CFC-11 is excluded from consideration because its ozone depletion factor is greater than that of the CFC-113 it would replace. Two alcohols (ethanol and 2-propanol) have been included because they are components of some of the CFC-113 blends and azeotropes and because the electronics industry knows they are capable of removing many rosin flux residues. In this section, the primary contaminants are presumed to be rosin, flux activators, salts, solder oxides, and related residues.

The evaporation rate of each solvent relative to carbon tetrachloride, set at 100, is tabulated in the first column. The second column gives the boiling point of each solvent. This is important because the relative volatility of a solvent is expected to be given by the ordering of inverse boiling points. The next two columns give measures of the solvent's capacity for forming solutions with a nonpolar constituent and a polar constituent; both types are present following use of conventional rosin fluxes, particularly if exposure to oils occurs. We have limited our consideration here to a long-chain hydrocarbon, n-hexadecane, and to water. Chain lengths of the order of hexadecane are found in several oils and in the sidechain of the major natural rosin component. n-Hexadecane may therefore be considered as representative of these contaminant classes. Water has been selected as the representative polar constituent partly because it has a large dipole and partly because actual solubility data were available for the solvents listed in Table 1.

The solubility values for water in the various solvents are given as the weight percent at 77°F. The values given in the n-hexadecane column are not solubilities but are measures of its tendency to form miscible solutions with the various solvents. These miscibility figures have been calculated from the solubility parameters, $\delta$, defined by Ref. [6], and are equal to the square of the difference in solubility parameter values between n-hexadecane and each of the solvents.**

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*TLV is the maximum allowable time-weighted average concentration to which a human may be exposed over an eight-hour working day, 40-hour work week. Generally, the more toxic the chemical, the lower the TLV. CFC-113 has a TLV of 1,000, the highest value assigned.

**Use of these parameters and regular solution theory assumes that all (binary) solutions being considered mix without volume change, have no excess entropy of mixing, and that the energy of interaction of dissimilar molecules is given by the geometric mean of those for the two pairs of similar molecules. For the polar molecules (and even CFC-113) in Table 1, the latter assumption is poor and the use of solubility parameters does not yield quantitative results. However, as long as one considers mixtures of polar and nonpolar substances and the specific directional forces are relatively small, solubility parameters may still be used empirically to estimate qualitative solubility relations. These parameters may be related to several thermodynamic variables, but the simplest method is to identify them with the square root of the ratio of the molar energy of vaporization to the molar volume of the fluid.

TABLE 1

Selected parameter values of various solvents

| Solvent | Evaporation rate[a] | Boiling point (°F) | Miscibility[b] | Solubility (wt. % of $H_2O$ at 77°F) | Wetting index $\left(\frac{1000\rho}{\eta\gamma}\right)$ |
|---|---|---|---|---|---|
| CFC-113 | 280 | 118 | 0.64 | 0.01 | 126 |
| CFC-113/5.7% methanol[c,d] | – | 103 | (0.14) | 0.27 | 121 |
| CFC-113/3.8% ethanol[c,d] | – | 112 | (0.08) | 0.28 | 120 |
| CFC-113/49.5% methylene chloride[c] | – | 97 | (0.55) | 0.09 | 116 |
| CFC-113/35% ethanol | – | 119 | (2.66) | 6.3 | 68 |
| CFC-113/35% 2-propanol | – | 120 | (0.24) | 9.1 | 43 |
| CFC-112/14.5% n-propanol[c] | - | 196[e] | – | – | – |
| 1,1,1-Trichlorethane | 139 | 165 | 0.16 | – | 65 |
| 1,1,2-Trichlorethane | 21 | 235 | 1.40 | 0.05 | 36 |
| Perchlorethylene | 27 | 252 | 2.89 | 0.01 | 57 |
| Trichlorethylene | 69 | 189 | 1.69 | 0.02 | 87 |
| Chloroform | 118 | 142 | 1.21 | 0.07 | 98 |
| Methylene chloride | 147 | 105 | 2.25 | 0.15 | 108 |
| Carbon tetrachloride | 100 | 171 | 0.36 | 0.01 | 62 |
| Ethanol | 37[f] | 173 | 22.1 | ∞ | 30 |
| 2-Propanol | 34 | 180 | 12.2 | ∞ | 15 |
| Water | – | 212 | 237 | ∞ | 14 |

[a] Based on American Society for Testing and Materials D-1901-67 where possible; relative to $CCl_4$ (= 100); source is Ref. [7].

[b] $(\delta_{\text{solvent}} - \delta_{n\text{-}C_{16}H_{34}})^2$ where $\delta$ is a solubility parameter at 298 K [6]. Numerical values of $\delta$ were supplied by DuPont except 1,1,2-trichloroethane, which was calculated from latent heat of vaporization and molar volume ($\delta_{1,1,2\text{-tri}} = 9.1$). For reference, $\delta_{n\text{-}C_{16}H_{34}} = 8.0$.

[c] Azeotrope.

[d] Stabilized with nitromethane.

[e] Estimated; must be below the boiling point of either component for azeotrope formation (boiling point of CFC-112 = 199°F; boiling point of n-propanol = 207°F).

[f] 95 Percent ethanol.

In the theory of regular solutions, the highest temperature at which two immiscible liquid phases of the components exist, the upper consolute temperature, is proportional to the square of the difference in solubility parameters. The closer this square is to zero, the further the region of immiscibility will be from the operating temperature of the solvent (its boiling point) in a degreaser, and the greater the tendency of the solvent to take up the contaminant fluid.*

The solubility parameters we use have all been referred to 298 K and most were obtained from an extensive table [8] or from Table A5.1 of Reference [6]. Exceptions are 1,1,2-trichloroethane and the CFC-113 azeotropes and blends; we estimated their solubility parameters from experimental heats of vaporization and average molar volumes.

The sixth column in Table 1 presents the wettability index of each solvent. It is the solvent density (g/cm$^3$) divided by the product of the viscosity (in cP) and the surface tension (dyne/cm). The density is related to a solvent's ability to float off debris, while the viscosity and surface tension indicate the ease with which a solvent may penetrate blind spaces in a part. This parameter is especially useful in estimating whether a particulate contaminant can be wetted and removed from the surface of a substrate.

Table 2 shows the relative ranking of our selected solvents for the four criteria in Table 1. We have also placed numbers next to some of the solvents giving the amount of conductive salts (in micrograms of NaCl equivalents per square centimeter) remaining on a printed circuit board after these solvents have been used to remove activated rosin flux residue.** The important thing to notice is that, within experimental error, the amount of ionic residue remaining on the surface falls off as a direct function of the solubility of water in the solvent. For the special application of defluxing, it is therefore apparent that any substitute solvent should have a high polar content.

In Table 3 we present a crude overall ranking of a solvent's cleaning potential based on the contaminant removal criteria of Table 2. We have assumed that for a solvent to be superior, it must better satisfy the four criteria of rapid evaporation rate, good polar solubility, good nonpolar solubility, and good wettability. Hence the rank of the worst quality in Table 2 has been used to achieve the ordering in Table 3. This procedure formalizes the assumption that a solvent is only as good as its worst property. For example, a solvent with a high evaporation rate but poor solubility characteristics is no better than a solvent that is poor in both qualities. This approach is incomplete in that it does not weight each cleaning criterion in proportion to its effect on cost, but it does provide some idea of the ability of one solvent to substitute for another.

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*In some liquid–liquid pairs, the upper consolute temperature may never actually be reached before gas–liquid phase changes are encountered. Nonetheless, the "virtual" consolute point implied by $(\delta_1 - \delta_2)^2$ remains a useful concept.

**The defluxing method employed is outlined in Ref. [9].

TABLE 2

Relative selected properties of various solvents[a]

| Rank | Evaporation rate[b] | Nonpolar solubility[c] | Polar solubility[d] // Post deflux ionic contamination[e] | Wettability[f] |
|---|---|---|---|---|
| 1 | 113/MC[g] | 113/3.8% EtOH[g] | (Water | 113 |
| 2 | 113/MeOH[g] | 113/MeOH[g] | EtOH[i] | 113/MeOH[g] |
| 3 | MC | TRI | IPA[i])[h] | 113/3.8% EtOH[g] |
| 4 | 113/3.8% EtOH[g] | 113/35% IPA | 113/35% IPA | 113/MC[g] |
| 5 | 113 | $CCl_4$ | 113/35% EtOH/ /7.5 ± 0.6 | MC |
| 6 | 113/35% EtOH | 113/MC[g] | (113/MeOH[g]/ /8.3 ± 0.8 | $CHCl_3$ |
| 7 | 113/35% IPA | 113 | 113/3.8% EtOH[g]/ /11.3 ± 1.4)[h] | TCE |
| 8 | $CHCl_3$ | $CHCl_3$ | MC | 113/35% EtOH |
| 9 | TRI | 2-TRI | 113/MC[g]/ /10.2 ± 0.79 | TRI |
| 10 | $CCl_4$ | TCE | $CHCl_3$ | $CCl_4$ |
| 11 | EtOH[i] | MC | 2-TRI | PERC |
| 12 | IPA[i] | 113/35% EtOH | (TCE | 113/35% IPA |
| 13 | TCE[j] | PERC | TRI//15.6 ± 2.19)[h] | 2-TRI |
| 14 | Water | IPA[i] | (PERC | EtOH[i] |
| 15 | 2-TRI | EtOH[i] | $CCl_4$ | IPA[i] |
| 16 | PERC | Water | 113)[h] | Water |

[a] Abbreviations: methylene chloride, MC; methanol, MeOH; ethanol, EtOH; n-propanol, NPA; 2-propanol, IPA; 1,1,1-trichloroethane, TRI; 1,1,2-trichloroethane, 2-TRI; trichloroethylene, TCE; perchloroethylene, PERC; CFC-113, 113; CFC-112, 112.

[b] Based on inverse boiling point; decreasing order.

[c] Based on solvent/n-hexadecane solubility parameters; decreasing order.

[d] Based on solubility of water in solvent; decreasing order.

[e] Micrograms NaCl equivalents per square centimeter of printed circuit board (see text).

[f] Based on wettability index; decreasing order.

[g] Azeotrope.

[h] Brackets group solvents with nearly identical solubilities of water; ordering within brackets is based on solubility parameters with $\delta_{H_2O} = 23.4$.

[i] Flammable.

[j] 112/NPA falls between TCE and water.

The ordering in Table 3 suggests that the CFC-113 azeotropes are the best solvents for simultaneously dissolving both oil-chain-length hydrocarbons and highly polar compounds. They are excellent at mixing with the hydrocarbon and quite good at mixing with the polar species. Chloroform and methylene chloride appear next on the list, since they both have intermediate rankings of both hydrocarbon miscibility and water solubility.

The next entries must be considered in groups, since minor changes in weighting the cleaning characteristics could lead to upward or downward shifts of two or more positions. The CFC-113/alcohol blends appear below chloroform and methylene chloride, principally because their wetting capabilities are slightly poorer and, in the case of CFC-113/EtOH, because it is also somewhat poorer at forming solutions with hydrocarbons. Trichloroethylene and 1,1,1-trichloroethane appear next, largely because of their poorer polar solubility characteristics. Of the remaining solvents, 1,1,2-trichloroethane and perchloroethylene appear low on the list primarily because of poor evaporation rates; the alcohols, CFC-113, and carbon tetrachloride rank lower because of either poor nonpolar or polar solute miscibility; pure water has a low ranking because of unfavorable values of all parameters except polar solubility.

TABLE 3

Relative cleaning capabilities of various solvents[a]

| Based on n-$C_{16}H_{34}$—$H_2O$ solubility, wetting, evaporation[b] |
|---|
| 113/MeOH[c] |
| 113/3.8% EtOH[c] |
| 113/MC[c] |
| $CHCl_3$ |
| MC |
| 113/35% EtOH<br>113/35% IPA |
| TRI<br>TCE |
| $CCl_4$<br>EtOH<br>IPA<br>2-TRI |
| 113<br>PERC<br>Water |

[a] Abbreviations are the same as in Table 2.

[b] Ordered according to the row in Table 2 above which all four solvent cleaning properties are satisfied.

[c] Azeotropes.

The flammability and toxicity characteristics of the various solvents are shown in Table 4. Except ethanol and 2-propanol, none of these solvents is flammable, reflecting our original selection. However, several of the solvents have TLVs at or below 100 ppm, a level at which environmental control often becomes difficult. Included in this group are chloroform, with a TLV of 10 ppm; trichloroethylene, with a TLV of 100 ppm but on the list for change to 50 ppm, and methylene chloride, with a TLV of 100 ppm. Although a low TLV is not sufficient to rule out future use of a particular solvent, it will encourage users to employ less toxic alternative solvents (including methylene chloride blends) or force them to enhance their environmental control equipment, raising their costs.

Those solvents ranked highest in Table 3 for their cleaning capabilities that have a TLV above 100 ppm include the CFC-113/methanol, /ethanol, and /methylene chloride azeotropes; the CFC-113/ethanol and /2-propanol blends; and 1,1,1-trichloroethane. The CFC-113/alcohol blends can become flammable during use when the alcohol component is concentrated if boil-down occurs. 1,1,1-Trichloroethane, like CFC-113, is a suspected ozone depleter. We are therefore faced with a choice between potentially flammable blends, and possible ozone depleters. If we are willing to include solvents with lower TLVs, we might consider chloroform, methylene chloride, and

TABLE 4

Flammability and toxicity characteristics of various solvents

| Solvent | Flash point (°F) | Toxicity (TLV in ppm) |
|---|---|---|
| CFC-113 | none | 1,000 |
| CFC-113/5.7% methanol[a] | none | 475[b] |
| CFC-113/3.8% ethanol[a] | none | 750[b,c] |
| CFC-113/methylene chloride | none | 270 |
| CFC-113/35% ethanol | none[d] | 1,000[b] |
| CFC-113/35% 2-propanol | none[d] | 700[b] |
| CFC-112/14.5% n-propanol | none | – |
| 1,1,1-Trichloroethane | none | 350 |
| 1,1,2-Trichloroethane | none | 10 |
| Perchloroethylene | none | 100 |
| Trichloroethylene | none | 100[e] |
| Chloroform | none | 10 |
| Methylene chloride | none | 100 |
| Carbon tetrachloride | none | 10 |
| Ethanol | 57 | 1,000 |
| 2-Propanol | 56 | 400 |
| Water | none | – |

[a] Stabilized with nitromethane.

[b] Calculated by OSHA procedure for gaseous mixtures.

[c] Nitromethane stabilizer leads to this value; if only CFC-113 and ethanol are considered, it is 1,000 ppm.

[d] At stated concentrations of alcohol. However, because these are blends, boil-down will concentrate the flammable component to the flash point.

[e] Proposed for change to 50 ppm.

trichloroethylene. All, however, have problems. Methylene chloride is mutagenic; chloroform and trichloroethylene are both mutagenic and carcinogenic. This exercise illustrates how difficult the choices among alternatives can be.

In Table 5 we show the energy requirements of the various solvents when used in vapor phase degreasers. The figures in the second column give the energy required only to raise the solvent to its boiling point and then to vaporize it. The figures in the third column are the annual energy costs per gallon of machine capacity for a metal cleaning process [9]. The values represent total energy consumption, including the energy to boil the solvent, condense it, pump it, and make up for radiative heat losses. A comparison of the figures in the two columns shows that the energy to vaporize a solvent provides a good measure of its overall relative energy cost. The exception in the table is trichloroethylene. This is partly because the trichloroethylene-containing degreaser considered in Ref. [9] was not insulated, even though this compound has a high boiling point and potentially high conductive and radiative losses. On the other hand, the other high boiler in this series, per-

TABLE 5

Energy usage of various cleaning solvents

| Solvent | Energy to vaporize solvent[a] (Btu/gal) | Annual energy cost per gallon capacity[b] (US$) |
|---|---|---|
| CFC-113 | 943 | 27.10 |
| CFC-113/3.8% ethanol[c,d] | 1,062 | 29.80 |
| CFC-113/5.7% methanol[c,d] | 1,157 | 32.80 |
| CFC-113/35% 2-propanol | 1,298 | – |
| CFC-113/methylene chloride[c] | 1,301 | 35.10 |
| 1,1,1-Trichloroethane | 1,383 | 42.10 |
| Carbon tetrachloride | 1,385 | – |
| Chloroform | 1,509 | – |
| Trichloroethylene | 1,579 | 49.30 |
| Methylene chloride | 1,654 | 44.40 |
| CFC-113/35% ethanol | 1,655 | – |
| Perchloroethylene | 1,723 | 47.70[e] |
| 1,1,2-Trichloroethane | 1,832 | – |
| 2-Propanol | 2,293 | – |
| Ethanol | 2,754 | – |
| Water | 9,484 | – |
| CFC-112/14.5% n-propanol | – | – |

[a] Energy required to raise solvent from 75°F to its boiling point and then vaporize it.

[b] Based on a DuPont laboratory model of a metal cleaning process operating 4 hours a week, and with electricity priced at US$0.043/kWh in 1977 dollars. Seven separate energy use factors (unspecified) were considered.

[c] Azeotrope.

[d] Stabilized with nitromethane.

[e] Considered to be contained in an insulated tank.

chloroethylene, was considered to be contained in an insulated unit. This difference in design configuration could lead to substantially different energy requirements.

Once again, the CFC-113 azeotropes and the CFC-113/propanol blend have the most favorable energy requirements. Next come carbon tetrachloride and 1,1,1-trichloroethene followed by chloroform, trichloroethylene, methylene chloride, CFC-113/ethanol, and perchloroethylene. The solvents with good contaminant removal properties and favorable flammable and toxicity qualities can be ranked as follows: CFC-113/3.8 percent ethanol, CFC-113/5.7 percent methanol, CFC-113/35 percent 2-propanol, CFC-113/49.5 percent methylene chloride, 1,1,1-trichloroethane, methylene chloride and CFC-113/35 percent ethanol. Solvent-related CFC emissions could be substantially reduced by substituting those solvents containing less CFC-113 for those containing more. The energy cost for these substitutes can be determined from the figures in Table 5.

### *Other considerations*

The four principal chlorocarbon solvents (methylene chloride, 1,1,1-trichloroethane, trichloroethylene, and perchloroethylene) all have their problems as electronic cleaning agents. Printed circuit board components containing aluminum, zinc, or magnesium react with most chlorocarbon solvents, although this can be restrained by the addition of stabilizers. However, in the case of 1,1,1-trichloroethane, for example, a problem can arise if the degreaser is operated at a temperature below the dew point (−60°F). Around this temperature, water can form on the degreaser condensing coils. The stabilizer which is water-soluble, can be extracted. The solvent may then damage some materials.

One degreaser manufacturer claims that flexible mylar-like materials, which are used to join rigid circuit boards, are incompatible with all presently used solvents except CFC-113/alcohol mixtures. Epoxy, which is often joined to the mylar-like polymers, is attacked by methylene chloride and trichloroethylene on long exposure. Electrolytic capacitors, which are often cold-cleaned, are also incompatible with methylene chloride and trichloroethylene. Many elastomers are swollen by the chlorocarbons. Ceramic components are compatible with all the solvents.

Because chlorocarbon solvents are incompatible with substrates on many printed circuit boards, the CFC-113/ethanol and /2-propanol blends appear better suited for cleaning such items. Even the modest ability of the ethanol blend to mix with long-chain nonpolar contaminants (see Table 2, column 3) is not a serious problem here; the substance that must be removed, rosin, is composed primarily of abietic acid ($C_{19}H_{29}COOH$), which has at least one fragment with polar character. Furthermore, flux activators and residues are quite polar and could easily be handled by the CFC-113/ethanol blend. The ability of such blends to remove activated rosin flux residues has been demonstrated [9,10].

The difficulty with the use of alcohol-rich CFC-113 blends is the increased risk of flammability. Because the alcohol has the higher boiling point, it tends to be left behind in the degreaser or on the surface of a quickly withdrawn part as the more volatile CFC-113 escapes. Control measures could reduce this risk. The degreaser could be modified so that both the temperature of the boil sump and liquid level were monitored [10]. The solvent vapor could be kept below the flammability range by automating the addition of make-up CFC-113/alcohol blend. This guards against ignition in the degreaser. It does not prevent ignition on the surface of a part withdrawn from the degreaser before solvent evaporation is complete, or on the floor following a spill, however. Only careful operating practices can minimize this risk.

### *Water as an alternative solvent*

While we have addressed some of the difficulties in using pure water for (rosin) defluxing of printed circuit boards, we have not yet discussed two other options. In the first, water is combined with alkaline detergents to clear rosin-based fluxes; in the second, pure water is used to clean water-soluble fluxes. The choice and proper use of such defluxants is crucial to the well-being of the electronics industry. In what follows, we present some of the details of those processes and, as discussed above, their technical limitations on an *ad hoc* basis. A close focus on water is beneficial since it is the only potential substitute that posed no major health or safety problems.

In the first option, warm water may be combined with inorganic detergents and amine detergents such as monoethanolamine to form a cleaning solution capable of emulsifying nonpolar soils and saponifying the organic acid (primarily abietic acid) components of rosin. The saponification reaction yields a soap that can be floated off in the aqueous phase. The soaps that are formed carry over to the next phase, the water rinse, and may cause foaming if antifoaming agents are not employed. The small amount of contaminated rinse water that remains on the surface of the part can be removed with a hot air knife. This is a jet of high velocity air that blows off the fluid before the water has a chance to evaporate and concentrate the higher molecular weight impurities on the surface. Finally, the circuit board is heat dried.

There are several difficulties with this process. First, reactive metals on the board (e.g., Al, Zn, Cu) are subject to corrosive attack by the defluxant, and tin and lead ions may be precipitated as insoluble hydroxides [11,12]. Second, because rosin is a nonhomogeneous, natural substance subject to undesirable polymerization, not all of it can be saponified and flux residues may remain on the board after cleaning. Indeed the residue may be as high as ten percent of the rosin present. Third, the residue left behind may lead to insulation failure, particularly for boards later used in high humidity environments. Fourth, it is difficult to rinse off all the alkaline soap [11].

The detergents can also be quite difficult to remove from printed circuit boards when there are entrapment sites like surface-mounted chips or lead wires with insulating sleeves. The detergent solutions may flow into these sites but the pure rinse water will not, due to its much higher surface tension. In this case, the flux residue contaminants may be exchanged for detergent contaminants. Occasionally a CFC rinse has been used to remove the remaining surfactants but, from a CFC emission viewpoint, this would negate the reason for seeking a water solvent alternative.

In the second defluxant option, water-soluble fluxes are used. They are then dissolved in tap, deionized, or acidified water, depending on the particular cleaning requirements [11,13]. As with the detergent removal of rosin flux, a good system should use a hot air knife to blow off the contaminated water remaining on the surface after defluxing; this is called flash drying. In some aqueous cleaning applications like certain military and communication items, high resistance ($10^{10}$–$10^{12}\Omega$) is required on the finished circuit board. In such cases, very low volume conductivity water of 6 to 8 M$\Omega$-cm is used [13]. In most applications, the ultra-pure deionized water is recirculated and reprocessed to achieve the most economical use. Further efficiency can be attained through the use of shut-off valves to prevent recirculation when the cleaning machine is not in use.

This option can also cause difficulties. First, the components of some polyglycol-based fluxes are quite hostile and may react with epoxy or polyimide materials on printed circuit boards. Degradations of up to three orders of magnitude of substrate resistance can occur. However, less harsh fluxes like mildly activated, water-soluble organic flux are often available [13]. Second, high molecular weight polyglycol fluxes can soften boards polymers or the buttercoat adhesives between polymer and copper laminate. The use of lower molecular weight polyglycols such as glycerin may alleviate this difficulty [13]. Third, it is difficult to remove entrapped rinse water from the circuit board, particularly at high component densities. For small or moderate densities, however, flash drying helps considerably [13]; this technique is probably the most critical factor for cost-effective aqueous cleaning. Water-soluble fluxes may require a highly acid wash (pH about 2) to avoid tin and lead hydroxide deposition. Thus any of this rinse water remaining on the surface may corrode solder fillets or attack the laminate surface [13]. Fourth, insulation failure may occur at high relative humidities if any tin or lead oxides are left on the surface [11].

Because of the difficulties in the rosin saponification and aqueous soluble flux techniques, they may not always be used in place of CFC solvent cleaning. Uncleanable (many entrapment sites) boards – those with insulating sleeves or with components lying flat against the surface -- may be best cleaned with CFC solvents [13]. "Organic-acid-flux water cleaning has been very successful for cleaning products that are free from entrapment sites" [13].

Drawing on experience, especially at Motorola, the author of Ref. [13] has stated that for many of these applications, both the CFC- and water-based technologies "are acceptable and equally efficient as to cost and product reliability when the newer technology is properly used." He claims, for example, that relatively complex 6 × 8 inch circuit boards being processed at the rate of 240 boards an hour can be cleaned to current military specification requirements by a closed loop CFC/rosin system for US$0.061 per board; by a closed loop heated deionized water/water soluble flux system for US$0.063 per board; or by a closed loop deionized water plus detergent/rosin system for US$0.084 per board.

The new technologies that would be used with the water systems include flash drying and the use of new highly soluble fluxes and leveling and soldering fluids. With water-soluble flux technology, it is also critical to reduce the level of ionic contamination left on bare boards during earlier plating and etching steps. This is because the water-soluble fluxes, unlike the rosin fluxes, do not encapsulate the impurities, allowing them to be removed during the later cleaning phase. In the event of imperfect cleaning, they do not provide a hydrophobic surface that prevents moisture absorption and electromigration. On the other hand, the more costly rosin saponification technique will have these features.

Environmental problems posed by the disposal of aqueous cleaning wastes has also been noted as a possible barrier to widespread use of water cleaning [11]. Indeed, testing performed at the Alpha Metals Co., where rosin saponification and two versions of water-soluble flux cleaning were investigated, has demonstrated that effluents discharged into the sewage system from a nonrecycling cleaning system will exceed the federal and many municipal standards for lead, pH, Biochemical Oxygen Demand, and Chemical Oxygen Demand. At increased water and energy expense, a closed system, employing ion exchange or precipitating agents, can eliminate this problem by converting the waste to a sludge. The cleaning cost per board figures quoted above [13] included waste disposal costs of US$ 100 per drum of waste for the CFC system, but did not include these costs for the aqueous system. If we assume that the monthly volume of aqueous process waste did not exceed that of the CFC process, the costs for the water systems would increase by no more than eight percent, from US$ 0.063 per board to US$ 0.068 per board.

Aqueous cleaning systems are a viable alternative to CFC systems for low- to moderate-density printed circuit boards with very few entrapment sites. However, we must recognize that the trend in the electronics industry is toward still more dense boards. Indeed component spacings of a few mils and more than 80 solder joints per square inch will be common by 1986. If this trend continues, an increasing number of circuit boards will be too dense to allow flash drying, and water cleaning may lose ground to the CFC system for purely technical reasons.

## IV. Conclusions

The choices among alternative solvents in defluxing applications are complex. Based upon the properties of evaporation rate, contaminant solubilities of non-water-soluble rosins, wettability, and TLV-related toxicity, we have identified CFC-113/35% ethane, CFC-113/35% 2-propanol, and CFC-113/49.5% methylene chloride as potential substitutes for presently used CFC-113 azeotrope defluxants which are characterized by high ozone depletion factors. However, the alcohol blends require the introduction of new vapor phase degreasers modified to guard against the concentration of alcohol content and creation of a flammability risk. The CFC-113/methylene chloride azeotrope is capable of removing contaminants but has the drawback of being incompatible with many substrate materials, thus restricting its use. Other organic solvents we examined do not have the right combination of physical and chemical properties to efficiently remove conventional flux residue contaminants or are associated with more extreme health or fire risks.

Water combined with inorganic and amine detergents is another alternative for removing conventional rosin fluxes that has already found acceptance. Likewise pure or acidified water may be substituted for CFC solvents, but water-soluble fluxes must be introduced. Unfortunately, both water technologies appear to be limited in their ability to clean densely packed circuit boards and may not offer an alternative to CFC technology in the future if the trend to more dense boards continues.

We may therefore conclude that water (and its associated technology) may be substituted for CFC solvents in the short run. In the long run, this option may exist only for moderate- to low-density boards, and CFC-113 alcohol blends may be the substitute of choice. If the increased flammability risk of these blends were found unacceptable by industry, then solvent substitution might not be practical and the industry would have to fall back on improved containment procedures.

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