Alternatives to Chlorinated Solvents in Cleaning Applications

FINAL REPORT

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University of California, Riverside Extension
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Prepared by:
The Institute for Research and Technical Assistance

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PREFACE

This document was produced under Contract Number 92-T0131 with the California Department of Toxic Substances Control for the University of California, Riverside Extension. It presents a cross-media analysis of the alternatives to chlorinated solvents in cleaning applications including vapor degreasing, cold cleaning, wipe cleaning and printed circuit board defluxing. Production of two of the chlorinated solvents that are used today in cleaning is slated to be banned on January 1, 1996 because the chemicals contribute to stratospheric ozone depletion. The other three chlorinated solvents are suspect carcinogens and the air, waste, water and worker exposure regulations governing their use are becoming more stringent. The analysis should be of interest to regulatory agencies and industry. Firms who are seeking alternatives to these solvents should find the information in the document useful. This compendium is supplemented by a simplified guidance document which should prove valuable for implementing alternatives at the plant level.

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SECTION 1:
INTRODUCTION

Since World War II, chlorinated solvents have been employed in a variety of end uses. Their characteristics made them useful in cleaning, dry cleaning, paint stripping, adhesives and coatings. Their major use today is in cleaning applications where the solvents are used to remove a range of contaminants from all kinds of parts and assemblies of various types.

The chlorinated solvents have gradually come under increasing scrutiny because of the health and environmental problems they pose. Two of the solvents contribute to stratospheric ozone depletion, a problem of worldwide significance. The major world nations have agreed that production of the two solvents will be banned worldwide on January 1, 1996. The three other chlorinated solvents are suspect carcinogens and they are gradually being more heavily regulated because of their toxicity. All of the chlorinated solvents are persistent in the environment. Because of improper usage and disposal practices, they are now found as contaminants of the soil and groundwater across the nation.

Because of the problems posed by the chlorinated solvents and the bans and stringent regulations, there is an increasing need for substitutes, particularly in cleaning applications. Chemical and process alternatives of all kinds are available or are still emerging and the transition away from the solvents is well underway. There are literally hundreds of different solvent formulations and water-based cleaners being marketed by vendors. Users are confused by the sheer number of alternatives and often, they test numerous formulations in their attempt to select an appropriate alternative.

Many of the alternatives to chlorinated solvents are known to be dangerous and many are new to the market and relatively unscrutinized. Because these chemicals and processes are new, they are relatively unregulated and if they achieve widespread use, they could eventually pose problems of their own. It is important to discourage the adoption of unsafe alternatives and to encourage implementation of the alternatives that best minimize the damage to human health and the environment.

The air, water, waste and workplace regulations are complex and often confusing to firms attempting to identify suitable alternatives. In California, in particular, the regulations are more stringent than they are in other parts of the country. In particular, the air regulations in industrial areas of California are especially restrictive and they govern the pattern of chemical use. A good knowledge of all of the regulations is essential for making judgements about whether or not a particular alternative is appropriate in a specific cleaning use.

This document reviews the potential alternatives to chlorinated solvents in a number of different cleaning applications. It summarizes the air, water, waste and workplace regulations that must be taken into account in their evaluation. It describes a systems approach to screening alternatives that makes it unnecessary to test hundreds of different potential candidates. A method of judging which are the "best" alternatives in a particular application is presented. This approach is intended to simplify the process of identifying, testing and implementing alternatives.

The findings of the analysis conducted here indicate that all of the chemical alternatives can be classified into generic chemical classes. If the class into which a chemical fits is known, much is also known about its properties, the processes for which it might be suitable and its environmental effects. This provides the basis for rejecting the chemical altogether because its characteristics and environmental effects are unacceptable. It also provides the basis for making a decision to use the chemical with the proper controls to minimize the problems it poses.

The conclusions of the analysis suggest a hierarchical scheme for selecting the "best" alternative in a particular operation. The most attractive alternative and the first one to be considered is the no-clean option. In some cases, it may not be necessary to clean at all; in other cases, the processes can be changed so the parts do not become contaminated in the first place. The next set of options to consider are the use of water or water formulations and the use of various other non-chemical processes. Water-based cleaning has wide applicability and water formulations can replace chlorinated solvents in many operations. In some operations, a non-chemical process will be suitable as an alternative. The last option to consider is use of a chemical alternative. This option is the least attractive and only after determining that the other options cannot be used should the chemical option be investigated.

Another conclusion of the analysis is that alternatives must be considered on a case-by-case basis. Although there may be similarities across process types, every operation is unique. The optimal solution for one plant may be entirely inappropriate in another plant with different characteristics even if their processes are similar. Variables that must be considered include technical feasibility, cost, equipment/process requirements, cleanliness standards, regulatory constraints and worker sophistication. These factors must be taken into account during the evaluation phase and when an alternative is selected.

Section 2 of this document provides background information on the chlorinated solvents. It discusses the production and use in cleaning applications of the five most widely used solvents. It summarizes the historical trends and briefly touches on the regulations that prevent or discourage the continued use of the solvents.

Section 3 reviews the regulations that govern the use, releases and disposal of the chlorinated solvents. Many of these regulations also apply to the potential alternatives. The section includes a detailed summary of the Federal, state and local air, waste, water and worker exposure regulations.

In Section 4, the generic scheme for classifying chemical alternatives is proposed. The generic chemical classes are identified and their technical characteristics, environmental problems, advantages and disadvantages are summarized.

Virtually all the chemical alternatives pose at least one problem and this must be taken into account in the selection procedure.

Section 5 identifies the non-chemical process alternatives to the chlorinated solvents. Again, each of the processes is described and the situations for which they are suitable are discussed.

Section 6 focuses on water-based cleaning alternatives to the chlorinated solvents. A method for evaluating formulations based on a material safety data sheet and conversations with vendors is described. Water-based cleaning formulations are likely to be appropriate for a large percentage of the cleaning operations that today employ chlorinated solvents.

A hierarchical method of evaluating alternatives is described in Section 7. Three case studies of substitution are presented in this section. These case studies are meant to illustrate the approach that can be used to evaluate alternatives.

The last section of the document -- Section 8 -- provides a general review of the advantages and disadvantages of the chemical and process alternatives to chlorinated solvents. It summarizes the results of the analysis and draws some conclusions about the procedure for deciding on the "best" alternatives.

SECTION 2:
CHLORINATED SOLVENTS: THE NEED FOR ALTERNATIVES

There are five major chlorinated solvents that have been used widely in commerce for a number of years; they include trichloroethylene (TCE), perchloroethylene (PERC), methylene chloride (METH), 1,1,1-trichloroethane (TCA) and 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113). These solvents have proven to be extremely versatile and they have been employed in a variety of applications. The primary use of the solvents has been in cleaning. Cleaning uses of the solvents include vapor degreasing, cold cleaning and electronics. The solvents are listed, together with their chemical formulas and names, in Table 2-1.

2.1 Chlorinated Solvent Production

Table 2-2 shows the U.S. production of the five solvents for 1988 and 1991. In 1988, combined production of the solvents amounted to 943 thousand metric tons (tmt). By 1991, the production had declined by about 29 percent, to 671 tmt. Over the period, the solvents have come under increasing regulatory scrutiny and production is expected to decline even further in the years to come.

2.2 Chlorinated Solvent Health and Environmental Effects

In Section 3 of this document, many of the regulations and the government agencies responsible for developing and implementing the regulations are described in detail. A brief summary of some of the health and environmental problems posed by the chlorinated solvents is presented in Table 2-3. It is because of these problems that alternatives to the chlorinated solvents are being investigated widely today.

The first column of Table 2-3 shows the Permissible Exposure Level (PEL) for each solvent. The PEL is the worker exposure level set by the Federal Occupational Safety and Health Administration (OSHA). The lower the PEL, the more dangerous the chemical is considered to be. TCE has a PEL of 50 ppm, a fairly low value. OSHA lowered the PEL for PERC to 25 ppm in 1989, but the value was later remanded and it reverted to the previous PEL of 100 ppm. Congress has stated that it intends to strengthen the powers of OSHA and it is likely that the value for PERC will again be decreased in the future to 25 ppm. The legal PEL for METH is currently 500 ppm; OSHA has proposed lowering the value substantially, to 25 ppm. TCA has a reasonably high PEL of 350 ppm. CFC-113 has been assigned a PEL of 1000 ppm, the highest value assigned to chemicals; this high value reflects the low toxicity of the chemical.

The second column indicates whether the chemical is classified as a volatile organic compound (VOC) under the Clean Air Act (CAA). Chemicals that are so classified form precursors that contribute to photochemical smog. TCE and PERC are presently classified as VOCs. In 1992, the Halogenated Solvents Industry Alliance (HSIA) petitioned the EPA to exempt PERC from smog regulations since it

Table 2-1 Major Chlorinated Solvents

Solvent	Chemical Formula	Other Names and Synonyms
TCE	Cl_2CCHCl	Trichloroethylene, Tri 1,1,2-trichloroethylene,trichloroethene
PERC	Cl_2CCCl_2	Perchloroethylene, per, PCE, tetrachloroethylene, tetrachloroethene,
METH	$CHCl_2$	Methylene chloride, dichloromethane
TCA	Cl_3CCH_3	1,1,1-trichloroethane, methyl chloroform
CFC-113	$HCl_2CCH_2Cl_2$	1,1,2-trichloro-1, 2, 2-trifluoroethane, trichlorotrifluoroethane, F-113, FC-113, Freon® 113

Table 2-2 U.S Production of Chlorinated Solvents
(thousand metric tons)

Solvent	1988	1991
TCE	82	57
PERC	226	109
METH	229	177
TCA	328	292
CFC-113	78	36
Total	**943**	**671**

Sources: U.S. ITC, 1991; DOW, 1994; Dupont, 1994; Wolf, et. al. 1991

Table 2-3 Health and Environmental Effects of Chlorinated Solvents

Solvent	PEL[a] (ppm)	VOC[b]	HAP[c]	ODP[d]	GWP[e]	TOX[f]
TCE	50	Yes	Yes	--	--	s
PERC	100(25)	Yes	Yes	--	--	s
METH	500(25)	--	Yes	--	--	s
TCA	350	--	Yes	0.1	0.026	--
CFC-113	1000	--	--	0.8	1.4	--

[a] PEL = permissable exposure level (the lower the PEL, the more dangerous the chemical is considered to be)
[b] VOC = volatile organic compound
[c] HAP = hazardous air pollutant
[d] ODP = ozone depletion potential
[e] GWP = global warming potential
[f] TOX = toxicity; s=suspect carcinogen
( ) Value most likely to be set in future by OSHA

Source: Wolf, 1993/1994

had been known for many years that the chemical is not a VOC. The Agency has not yet acted. METH, TCA and CFC-113 are not VOCs and are exempt under the CAA.

The third column indicates whether the chemical is classified as a hazardous air pollutant (HAP) under the CAA amendments. In general, this list includes chemicals that have been widely used for many years and for which there is an indication that they could cause human health problems. Four of the chlorinated solvents -- all except CFC-113 -- are so classified.

The fourth column provides the ozone depletion potential (ODP) of the chemical. The ODP is the potential for a chemical to deplete stratospheric ozone relative to the potential for one of CFC-11 to deplete ozone. The ODP of CFC-11 is defined as 1.00 and the ODP of other chemicals is a relative value. The values of Table 2-3 show that two of the chlorinated solvents, TCA and CFC-113, contribute to ozone depletion. CFC-113 has a high ODP of 0.8, whereas TCA has a much lower ODP of 0.1.

Many chemicals have short atmospheric lifetimes and they break down readily through attack of the hydroxyl radical in the troposphere. These chemicals are VOCs and they contribute to smog. Other chemicals have much longer atmospheric lifetimes. They do not break down in the lower atmosphere but survive for many years. Eventually they make their way from the lower atmosphere or troposphere to the upper atmosphere or stratosphere. Once there, ultraviolet light impinges upon them, decomposing them. The chlorine they contain is liberated and it catalytically reacts with the ozone, depleting the protective ozone layer. Virtually all organic chemicals are either VOCs because they have short atmospheric lifetimes or are ozone depleters because they have long atmospheric lifetimes. An exception is METH; note that in Table 2-3, the chemical is not classified as a VOC and it has no ozone depletion potential.

The fifth column shows the global warming potential (GWP) of the chemical. The GWP, like the ODP, is a relative value. Long-lived chemicals containing chlorine remain in the atmosphere for many years. During that time, they absorb light and emit it toward the earth at a different frequency. The energy heats the earth and causes the so-called Greenhouse Effect. The two chemicals with long atmospheric lifetimes, TCA and CFC-113, contribute to global warming.

The sixth column in Table 2-3 provides a toxicity rating (TOX) for the chemicals. TCE, PERC and METH are considered to be suspect carcinogens.

All five of the chemicals are listed hazardous wastes under the Resource Conservation and Recovery Act (RCRA). They are also listed under the Superfund Amendments and Reauthorization Act (SARA) Title III and their releases are subject to reporting by certain firms manufacturing and using them. Four of the chemicals, all except CFC-113, are on the EPA's 33/50 list of 17 chemicals; many firms have pledged to EPA that they will reduce their use of the 17 substances.

2.3 Solvent Use in Cleaning Applications

Table 2-4 presents estimates of the demand and use of the chlorinated solvents in various types of cleaning applications. Production of PERC, METH and TCA is reported in the U.S. International Trade Commission Reports annually. Production levels for TCE and CFC-113 are not reported because, in each case, there are only two U.S. producers. IRTA obtained the production data in private conversations with the producers. Demand values were estimated from the Chemical Marketing Reporter "Chemical Profiles" for the chemicals and, for CFC-113, from conversations with the producers. Estimates of the use in the various types of cleaning were made by IRTA or obtained from the Chemical Marketing Reporter or from the producers.

Total U.S. demand for the solvents, after accounting for exports and imports, represents 81 percent of production. Demand for cleaning use is 212.9 tmt, 39 percent of total demand for the solvents. Of the cleaning demand, vapor degreasing accounts for 59 percent, cold cleaning for 24 percent and electronics for 17 percent. TCA is the solvent used most heavily in cleaning, primarily in vapor degreasing and cold cleaning. CFC-113 is largely used in electronics.

Table 2-4 shows only the three major cleaning uses of the chlorinated solvents. There are actually many more cleaning applications that are subsets of the three major ones. These cleaning applications are discussed below and, to facilitate the discussion, Table 2-5 summarizes certain of the physical properties of the solvents.

2.3.1 Vapor Degreasing The chlorinated solvents are especially suited for vapor degreasing because they have no flash points. In vapor degreasing, the solvent is heated to its boiling point in a vapor degreaser. The vapor degreaser is a tank, generally made of stainless steel, with a heater in the bottom and a cooling coil around the inside perimeter. The solvent is liquid in the tank and the cooling coils define a vapor zone where the solvent is in the vapor form above the liquid. The coils cause the solvent to condense, and act as a barrier to emissions. Parts generally are placed in a basket and lowered into the vapor zone. The warm solvent condenses on the colder part, solubilizes the contaminants which fall into the liquid bath. The vapor zone, where the cleaning is performed, is always cleaner than the liquid solvent which contains the contaminants.

There are many types of vapor degreasers ranging from conveyorized equipment to batch equipment. Other features are frequently added to enhance cleaning, depending on the application. For instance, ultrasonic agitation or spray systems or spray wands for directing the solvent are commonly used. Some degreasers are designed to minimize emissions. They may include refrigerated freeboard chillers, which is a second set of cooling coils above the primary chiller, to further reduce evaporation and a higher freeboard, which is the distance between the primary coil and the top of the degreaser. Other models are almost entirely enclosed to reduce losses.

Vapor degreasing with the chlorinated solvents is an especially convenient way of cleaning metal and plastic parts of all kinds. The parts are simply immersed in a

Table 2-4 U.S. Production, Demand, and Cleaning Use of Chlorinated Solvents -- 1991

(thousand metric tons)

Solvent	Production	Demand	Vapor Degreasing	Cold Cleaning	Electronics
TCE	57	25.9	20.4	2.3	--
PERC	109	120.4	14.1	1.6	--
METH	177	121.2	10.0	3.3	4.8
TCA	292	238.4	73.9	42.9	7.2
CFC-113	36.0	36.0	6.5	1.6	24.3
TOTAL	**671**	**541.9**	**124.9**	**51.7**	**36.3**

Sources: U.S. ITC, 1991; DOW, 1994; Dupont, 1994; CMR, 1992a; CMR. 1992b, CMR, 1992c; CMR, 1992d; IRTA estimates

Table 2-5 Properties of Chlorinated Solvents

Solvent	Boiling Point (°F)	Latent Heat of Vaporization (Btu/lb)	Evaporation Rate[a]	Kauri Butanol Value[b]
TCE	188	103	6.39	130
PERC	250	90	2.59	90
METH	104	142	14.50	136
TCA	165	102	6.00	124
CFC-113	118	63	21.00	30

[a] Relative to butyl acetate which has been assigned a value of 1.
[b] Relative value of solvent strength for removing Kauri gum

Sources: Wolf, 1993/94; ASTM, 1989; Texaco, undated; Dupont, 1994.

vapor degreaser for a short time and when they are removed they are not only clean but dry as well. The chlorinated solvents have high vapor pressures which makes them volatile; as a consequence, they evaporate from the parts readily.

Table 2-5 shows that METH and CFC-113 have relatively low boiling points. In vapor degreasing, where the solvent is heated to the boiling point, this is an advantage. A low boiling point combined with a low latent heat of vaporization will lead to lower energy requirements for operating the degreaser. CFC-113, with its low boiling point and latent heat of vaporization has low energy requirements in vapor degreasing. PERC has a relatively high boiling point and it is this feature that makes it attractive for removing waxes and buffing compounds which have high melting points.

A high evaporation rate is advantageous for obtaining a dry part quickly. It is a drawback, however, because solvent losses will be higher. Equipment for use with CFC-113 and METH, which have the highest evaporation rates, must be designed to minimize emissions.

The Kauri Butanol (KB) value is one measure of the solvent strength. The figures of Table 2-5 demonstrate that CFC-113 has relatively low KB value, indicating poor solvent strength. Indeed, this chemical is the one most widely used for particulate removal, water displacement and for applications where precision cleanliness is required. CFC-113 would not be a good solvent for parts that are heavily contaminated. TCE, for many years, was the preferred solvent for metal cleaning. When it was found to be photochemically reactive, its use was restricted and TCA largely replaced it as the most widely used vapor degreasing solvent.

2.3.2 Cold Cleaning Cold bath cleaning operations generally take place in small or large tanks which contain one of the chlorinated solvents at room temperature. The part is dipped into the liquid which dissolves the contaminants, removing them from the part. The disadvantage of cold cleaning is that the contaminants remain in the bath. In contrast, in vapor degreasing, the solvent vapor is always clean. METH and TCA are often used cold in bath cleaning operations.

Other cold cleaning activities involve handwipe, flushing or touch-up operations. In these operations, solvent is placed on a rag or cotton swab which is used to remove contaminants from parts through wiping. Solvent might also be used with special fixturing to flush parts or to wipe the part down prior to shipment. Of the chlorinated solvents, TCA and CFC-113 are most widely used in handwipe operations, largely because they are safer than the other three solvents for workers.

2.3.3 Electronics These applications include removing flux from printed circuit boards, rework of printed circuit boards, semiconductor manufacture and handwipe of electronic components. CFC-113 is the major solvent used in electronics, because it is a gentle solvent and is safe for workers.

2.4 Current and Future Regulations on Chlorinated Solvents

Production of two of the five chlorinated solvents, TCA and CFC-113, is slated to be banned worldwide on January 1, 1996. The U.S., in fulfilling the international agreement, the Montreal Protocol, has set forth a schedule for a production phasedown. The interim schedule requires that production of TCA decline to 50 percent of the 1989 level on January 1, 1994 and to 15 percent of that level on January 1, 1995. Production of CFC-113 is required to be reduced to 25 percent of the 1986 level on January 1, 1994 and will remain at that level until it is phased out altogether on January 1, 1996.

In fact, many firms have already moved away from TCA and particularly CFC-113. EPA has implemented a labeling law that requires parts made with the ozone depleting solvents to be labeled. Congressionally mandated taxes have also been placed on the chemicals to discourage their use. The taxes are proportional to the ozone depletion potential of the chemical. As a consequence, the price of CFC-113 is extremely high. Many users have adopted alternatives and demand, according to one producer, is running well below the allowable 25 percent production level. Firms are also rapidly moving away from TCA and, again, demand is well below the 50 percent production level in place today.

TCE, PERC and METH are suspect carcinogens and TCE and PERC are classified as VOCs. According to the figures of Table 2-2, production of the three chemicals has declined substantially over the period 1988 through 1991. Although there are some new applications for the solvents emerging, these are largely intermediate rather than dispersive uses. TCE and PERC have been found in soil and groundwater near sites where they were used; cleanups of these sites are in progress and more will occur over the next several years. Although there might be some movement from TCA and CFC-113 into TCE, PERC and METH as the ban becomes effective, this movement should be offset by the transition away from the solvents because of their health and environmental effects.

2.5 Historical Perspective

In the years after World War II, as the economy expanded, solvents were found useful in many of the activities that would lead to an increase in our standard of living. In the first wave of solvent use, the flammable solvents were employed. Because of their flammability, however, they posed a workplace danger that was, in some cases, unacceptable. Later these solvents were regulated because they form precursors that contribute to photochemical smog. Because their vapor pressure is very high, they evaporate readily, leaving a clean, dry surface. This feature offered a particular advantage in cleaning applications for parts that had to be processed quickly. The drawback of the high vapor pressure, however, was that use of the solvents and their emissions were very high.

The chlorinated and chlorofluorocarbon (CFC) solvents replaced the flammable solvents in a large fraction of the cleaning operations. These solvents contain halogens -- chlorine and/or fluorine -- which means that, unlike the flammable solvents, they do not have a flash point. These solvents offered the answer to the thorny problem of fire or explosion and they could be heated safely and used in a process called vapor degreasing that was fashioned for them. Now it has become apparent that the chlorinated and CFC solvents pose problems of their own. As the regulations on these solvents become increasingly stringent, users are adopting alternatives.

Even within the chlorinated solvent class, there has been substitution over the years. In the 1960s, TCE was the most widely used solvent in cold cleaning and vapor degreasing applications. In the late 1960s, the chemical was found to be very photochemically reactive and it was tagged as a VOC. In the early 1970s, animal studies suggested that TCE was a carcinogen. Local and Federal agencies began passing regulations to discourage its use. Indeed its use declined substantially over the next 15 years and it was largely replaced in cleaning applications by TCA. The latter chemical, of course, will be banned for its contribution to stratospheric ozone depletion.

The script has been written. Historically, there has been a movement from one class of chemical that poses a particular problem to another class that poses a different problem. Regulations focus on one class at a time and the regulations force users out of one class but provide little guidance on what desirable alternatives exist. There is no systems approach to the substitutions before they occur and the consequences of the substitutions are not understood until much later. With the bans on the ozone depleting solvents and the heavy regulation of the chlorinated solvents, a movement to less scrutinized chemicals is occurring again. Users are moving to other classes of chemicals without understanding their characteristics, their possible health effects or their environmental impacts.

The framework presented here is a way of analyzing the problem that may help to stop this cycle. At this juncture, there is a great opportunity to influence the choice of alternatives. All alternative chemicals and processes pose problems. It is a matter of recognizing what these problems are from the outset. The alternatives that pose too many or unacceptable problems can be rejected altogether; those that pose acceptable problems can be used in a manner that minimizes their negative effects.

The era for the chlorinated solvents in cleaning applications is at an end. Although the solvents will likely be used for these purposes for some years yet, there will be an increasing transition away from them. The imminent bans on TCA and CFC-113 will spur the adoption of substitutes. Alternatives identified as suitable for TCA and CFC-113 will, in many cases, also be suitable for the other chlorinated solvents. Over the next several years, firms will identify alternatives, test them and implement them.

SECTION 3:
REGULATIONS AFFECTING THE CHLORINATED SOLVENTS AND THEIR ALTERNATIVES

Section 2 provided background on the five major chlorinated solvents that have been historically used in solvent cleaning applications. As was discussed, however, these solvents pose serious human health and environmental problems and, as a result, stringent regulations have been and will continue to be imposed on them. The production of two of the solvents, TCA and CFC-113, will be banned in the U.S. on January 1, 1996. The other three solvents, PERC, METH, and TCE, are all suspect carcinogens and their continued use in cleaning applications will be limited by current and future regulations on toxic and hazardous air pollutants.

Alternatives to the chlorinated solvents in cleaning applications are being investigated vigorously. Chemical and process alternatives to chlorinated solvents are available in cleaning applications. This section outlines and describes the regulations that apply to the chlorinated solvents; the same regulations, in many cases, also affect the choice and use of the alternatives. The information presented here sets the stage for the more detailed discussion of the alternatives in Sections 4, 5 and 6.

3.1 Overview of Air Regulations

The Federal Clean Air Act (CAA) was originally enacted in 1970; it was amended in a substantive way in 1990. The 1990 Amendments to the Clean Air Act include six titles. Title I contains provisions for attainment and maintenance of national ambient air quality standards. The discussion on air quality regulations below involves the provisions of Title I. Title II contains provisions relating to mobile sources. Title III contains provisions and standards for hazardous air pollutants. The section on air toxic regulations below involves this title. Title IV contains provisions for acid deposition control. Title V requires states to establish a program whereby "major sources" would be required to obtain federal operating permits. Title VI contains provisions and details of the production phaseout and ban on ozone-depleting substances. The discussion below on ozone depleting substances focuses on this title.

3.1.1 Air Quality Regulations Under the Clean Air Act implementing legislation, the U.S. Environmental Protection Agency (EPA) regulates air quality. The EPA sets the minimum standards that all states must meet. The EPA also adopts Control Techniques Guidelines (CTGs) to provide guidance to states for implementing their environmental control programs. States are required to be at least as stringent as any federally adopted CTG.

To help protect human health and the environment, the CAA requires states to meet ambient air quality standards (AAQS). With the 1990 amendments, the CAA now contains many provisions that strengthen emission standards and compliance of state programs.

3.1.1.1 California Requirements In California, the state air regulatory agency is the California Air Resources Board (CARB). Until recently, California was the only state in the country that had separate local air pollution agencies. By law, local air pollution districts (districts), generally known as either Air Quality Management Districts (AQMDs) or Air Pollution Control Districts (APCDs), have the primary responsibility for regulating stationary sources of air pollution, such as solvent cleaning operations. CARB, by law, has the primary responsibility for regulating mobile sources of air pollution and consumer products. In addition, CARB has oversight responsibility for the APCDs and AQMDs. CARB exercises this oversight responsibility by providing guidance to the local districts in their adoption of stationary source regulations. Such guidance can come in the form of actual guidelines, suggested control measures, reasonable and best available control technology determinations, and state regulations. Local districts are expected to adopt rules and regulations that are at least as stringent as any state regulation or guideline.

One provision contained in Title I of the CAA that is spurring the development of state programs to control VOC emissions concerns what are known as "nonattainment areas". VOCs and nitrogen oxides react in the presence of sunlight to form lower atmospheric ozone (photochemical smog). The CAA requires that all states meet an AAQS for ozone of 0.12 parts per million (ppm). If a state has met this standard then that state is said to be in "attainment" for ozone. If a state has not met that standard then it is said to be "nonattainment" for ozone. Nonattainment areas are further classified as to their nonattainment status. Many industrialized areas of California are nonattainment areas for ozone.

Table 3-1 lists select areas of California and their attainment status. As shown in the table, many industrialized California counties are designated as serious, severe, and extreme nonattainment. The CAA requires that serious, severe, and extreme nonattainment areas achieve attainment by the years 1999, 2005, and 2010, respectively. In addition to periodic State Implementation Plan (SIP) submittals, many requirements must be met to demonstrate progress towards attainment.

Four of the counties shown in Table 3-1 -- Los Angeles, Orange, Riverside and San Bernardino -- are extreme nonattainment. They must achieve attainment by the year 2010. Severe nonattainment areas include two other southern California counties, San Diego and Ventura; they must reach compliance by 2005. Sacramento and San Joaquin Valley in Northern California, are serious nonattainmment areas that must achieve compliance by 1999. The San Francisco Bay Area is classified as a moderate nonattainment area.

In California, the separate APCDs and AQMDs are treated as states by the CAA and must separately demonstrate attainment to the EPA through their SIP submittals. The South Coast Air Quality Management District (SCAQMD), with

Table 3-1 Ozone Attainment Status of Select Areas in California

Designated Area	Designation	Classification
Los Angeles County (South Coast Basin Area)	Nonattainment	Extreme
Orange County	Nonattainment	Extreme
Riverside County (South Coast Basin Area)	Nonattainment	Extreme
San Bernadino County (South Coast Basin Area)	Nonattainment	Extreme
Sacramento Metro Area	Nonattainment	Serious
San Diego Area	Nonattainment	Severe
San Francisco Bay Area	Nonattainment	Moderate
San Joaquin Valley Area	Nonattainment	Serious
Ventura County Area	Nonattainment	Severe

jurisdiction over Los Angeles, Orange, San Bernardino, and Riverside counties, regulates over half of California's emissions sources. The Bay Area Air Quality Management (BAAQMD) regulates about 20 percent of California's emissions sources. Although there are more than 30 local air pollution districts in California, the SCAQMD, the BAAQMD, the San Diego County APCD, the Sacramento Metropolitan AQMD, the San Joaquin Valley Unified APCD, and the Ventura County APCD, together account for over 90 percent of California's emissions sources.

The SCAQMD includes the four counties in Table 3-1 classified as extreme nonattainment. It is the only area in the nation that has been so designated. Because of the severe conditions there, the SCAQMD's rules and regulations are, overall, the most stringent in the country. As required by the CAA, the SCAQMD and most of the other five California nonattainment districts are seeking to impose additional requirements on sources of VOC emissions in order to achieve ozone attainment by the required dates.

3.1.1.2 Definition of VOC VOCs or Volatile Organic Compounds are defined by the EPA. All substances that are more reactive than ethane are considered by EPA to be VOCs. This is not explicitly stated but it is accepted as the implicit standard. Unless a chemical is specifically exempted by EPA, then it is defined as a VOC. The EPA definition of VOC is "any volatile compound of carbon, excluding methane, ethane, carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, ammonium carbonate, and exempt compounds." Currently exempt compounds include TCA, METH, the CFCs that are used industrially and certain other chemicals with long atmospheric lifetimes.

The EPA uses a particular test method to determine the VOC content of a material. EPA Test method number 24 was designed for coating and adhesive formulations, but it is currently also used to measure the VOC content of various cleaning formulations.

3.1.1.3 New Source Review Requirements As required by the CAA, districts must limit new sources of emissions through New Source Review (NSR) programs. In principle, new sources of emissions must be more than "offset" by decreases of emissions elsewhere. Emissions offsets are said to be "internal" if they come in the form of an emissions decrease within the same facility seeking to increase emissions. Emissions offsets are said to "external" if the facility seeking to increase emissions purchases or trades the offsets from another facility or broker. Market prices of offsets fluctuate and depend on the trading zone. For example, the current price for VOC emissions in Los Angeles is between $2,000 and $4,000 per pound per day. In Ventura County, VOC emissions recently traded for $19,000 per ton. In the SCAQMD, an emissions trading market known as RECLAIM (Regional Clean Air Incentives Market) was recently started for sources of nitrogen oxides (NOx) and sulfur oxides (SOx). A RECLAIM program for sources of VOCs is currently in the development stage.

The term "offset ratio" refers to the additional amount of emissions decreases required by new sources under the CAA. For example, if a new source will be emitting 100 pounds of VOC per day and the offset ratio required by the local district is 1.2, then 120 pounds of VOC per day reduction must be provided as an offset before the source would be allowed to operate. Depending on the attainment status of the district or state, the CAA requires different offset ratios. Serious nonattainment areas must require an offset ratio of 1.15, severe nonattainment areas must require an offset ratio of 1.2, and extreme nonattainment areas must require an offset ratio of 1.5, unless best available control technology is required for all major stationary sources; in that case, the offset ratio must be at least 1.2.

In addition to offset requirements, many NSR programs require new sources to install Best Available Control Technology (BACT). BACT means different things for different sources. The SCAQMD has a very complex scheme for determining BACT. In general, BACT means the most stringent emissions limitation or control technology that is applicable to a source of emissions.

3.1.1.4 Solvent Degreasing Regulations In July, 1991, CARB adopted a determination of reasonably available control technology (RACT) and best available retrofit control technology (BARCT) for controlling VOC emissions from solvent cleaning and degreasing operations. The RACT/BARCT determination is intended as guidance to local districts in developing plans to attain state ambient air quality standards. Local districts that are not in attainment of state standards are expected to update their rules to the latest RACT and BARCT rules if an existing rule is modified and if the district needs further emission reductions to achieve the state ambient air quality standards. The serious, severe and extreme nonattainment districts are hard-pressed to achieve attainment with the federal AAQS for ozone of 0.12 ppm; the California Clean Air Act mandates that districts achieve the lower state ambient air quality standard for ozone of 0.09 ppm.

Users converting to alternative solvents in degreasing applications will have to comply with local air district rules and regulations. Most of the large and medium sized air districts in the state have solvent degreasing rules. Table 3-2 presents a summary of the major requirements contained in solvent degreasing rules for eight major districts in California. Also included in the table is a summary of the RACT/BARCT determination for solvent degreasing. The eight districts listed in the table are all nonattainment for ozone and will most likely update their solvent degreasing rule to the RACT/BARCT determination.

The San Diego County Air Pollution Control District does not meet the RACT/BARCT requirement for conveyorized and vapor degreasers. The Ventura County Air Pollution Control District does not meet the RACT/BARCT requirement for allowable exemptions. The RACT/BARCT determination allows exemptions only for cleaning operations which use formulations containing less than 2 percent by weight VOC and for cold cleaners with surface areas less than 1 meter square. In some cases, the exemptions in the rules may be equivalent to the exemptions allowed under RACT/BARCT. If equivalence is demonstrated, then the exemptions might be allowed to stand.

Table 3-2 Summary of Select Solvent Degreasing Regulations in California

istrict	Rule Name and Number	Exemptions	Conveyorized	Vapor Degreasing	Cold Cleaning	Cover Requirements	Other Requirements
AAQMD	Regulation 8, Rule 16, Solvent Cleaning Operations	Semiconductor solvent sinks less than 10 gallons, aerospace stripping operations; emulsion or solution cleaners with less than 1% VOC, small unheated solvent cleaning equipment (less than 1 gal or less than 1 ft²), vapor phase solder reflow operations	0.75 freeboard ratio, a refrigerated freeboard chiller, or an approved emission control device	0.75 freeboard ratio, a refrigerated freeboard chiller, or an approved emission control device	0.75 freeboard ratio, water cover, a refrigerated freeboard chiller, or an approved emission control device	An apparatus, cover, or enclosed reservoir which reduces solvent evaporation when not processing work. Vapor degreaser covers are to be designed to easily open and close without disturbing the vapor zone.	A person shall not use more than 3.2 gallons of trichloroethylene (TCE) per operating day in any solvent cleaning operation
CAQMD	Rule 1122, egreasing perations	cleaners less than 1 ft² and 1 gallon per day; cleaning solvent less than 2% VOC; exempt solvent blends less than 10% VOC	freeboard or carbon adsorption for sizes between 1m² and 2 m²; or below refrigerated freeboard chiller or carbon adsorption for sizes over 2 m².	greater than 10 ft.; 1.0 freeboard ratio for all other units; plus refrigerated freeboard chiller, carbon adsorption, or enclosed batch design for units greater than 1 m².	ratio, high volatility solvents must have either a water cover or a 0.75 freeboard ratio.	either roll-top, canvas curtain, biparting, or any over cover that will not disturb the vapor layer or the solvent surface.	must be automated, powered, or mechanically-assisted and slide off the degreaser in a horizontal motion.
an Joaquin	ule 4662, rganic Solvent egreasing perations	Single unheated equipment with surface area less than 1ft² unless the aggregate surface area of all degreasers is greater than 10 ft².	0.75 freeboard ratio plus one or a combination of the following: condenser equipment; 85% efficient carbon adsorption system ; other 85% efficient equipment. If greater than 2 m², equipment must have carbon adsorption or equivalent.	0.75 freeboard ratio plus one of the following: 1) condenser equipment; 2) enclosed design; 3) a carbon adsorption system; any other 85% efficient emission control device	0.75 freeboard ratio; if a high volatility solvent is used equipment must have either a water cover or 85% efficient emissions control device; if a low volatility solvent is used freeboard height must be at least 6 inches.	An apparatus or cover which prevents the solvent from evaporating when not processing work in the degreaser. For cold cleaners, the cover must be operable with one hand; for vapor degreasers the cover must be operable without disturbing the vapor zone.	The 85% efficiency requirement is an overall capture and control efficiency.

Table 3-2 Summary of Select Solvent Degreasing Regulations in California

District	Rule Name and Number	Exemptions	Conveyorized	Vapor Degreasing	Cold Cleaning	Cover Requirements	Other Requirements
Kern	Rule 410.3, Organic Solvent Degreasing Operations	Single unheated equipment with surface area less than 1 ft² unless the aggregate surface area of all degreasers is greater than 10 ft².	0.75 freeboard ratio plus one or a combination of the following: condenser equipment; 85% efficient carbon adsorption system ; other 85% efficient equipment. If greater than 2 m² equipment must have carbon adsorption or equivalent.	0.75 freeboard ratio plus one of the following: 1) condenser equipment; 2) enclosed design; 3) a carbon adsorption system; any other 85% efficient emission control device	0.75 freeboard ratio; if a high volatility solvent is used equipment must have either a water cover or 85% efficient emissions control device; if a low volatility solvent is used freeboard height must be at least 6 inches.	An apparatus or cover which prevents the solvent from evaporating when not processing work in the degreaser. For cold cleaners, the cover must be operable with one hand; for vapor degreasers the cover must be operable without disturbing the vapor zone.	The 85% efficiency requirement is an overall capture and control efficiency.
Sacramento	Rule 454, Degreasing Operations	Partial exemption for non-vapor degreasers with surface area less than 1m²; remote reservoirs using a non-volatile spray which is drained concurrently; atomization 4 inches below vapor zone.	Requirements are the same as non-vapor (or cold) for non-vapor type equipment or vapor for vapor type equipment.	0.75 freeboard ratio, a refrigerated freeboard chiller, or a carbon adsorption system.	Non-vapor degreasers must have 0.75 freeboard ratio or a water cover if using solvents which are agitated, heated above 122 °F, or volatile. Low volatility solvents must have a 6 inch freeboard or a water cover.	An apparatus or cover which prevents the solvent from evaporating when not processing work in the degreaser. For cold cleaners the cover must be operable with one hand; for vapor degreasers the cover must be operable without disturbing the vapor zone.	Alternative control with an overall 85% efficiency is allowed
Santa Barbara	Rule 321, Control of Degreasing Operations	Single unheated equipment with surface area less than 1 ft² unless the aggregate surface area of all degreasers is greater than 10 ft².	0.75 freeboard ratio plus one or a combination of the following: refrigerated freeboard chiller; carbon adsorption system with 95% control; other 85% efficient equipment. If greater than 2 m² equipment must have carbon adsorption or equivalent.	0.75 freeboard ratio plus one or a combination of the following: refrigerated freeboard chiller; carbon adsorption system with 95% control; other 85% efficient equipment.	0.75 freeboard ratio. If vap. press. is greater than 32 mm Hg or if the solvent is heated above 122 °F, either a water cover or an equivalent system with an overall control efficiency of 85%, plus internal drainage method.	An apparatus or cover which prevents the solvent from evaporating when not processing work in the degreaser. For cold cleaners the cover must be operable with one hand; for vapor degreasers the cover must be operable without disturbing the vapor zone.	The 85% efficiency requirement is in terms of overall efficiency (95% control efficiency and 90% collection efficiency). The 95% carbon adsorption efficiency is control efficiency only.

Table 3-2 Summary of Select Solvent Degreasing Regulations in California

District	Rule Name and Number	Exemptions	Conveyorized	Vapor Degreasing	Cold Cleaning	Cover Requirements	Other Requirements
San Diego	Rule 67.6, Solvent rations	TCA, CFC-113, or methylene chloride units before 9/1/80 or less than 5 ft². before 10/16/90. Cold cleaners less than 1 ft² or capacity less than 1 gallon.	For units greater than 2 m² one of the following: 1) an automated cover - elevator system; 2) a 0.75 freeboard ratio; 3) a refrigerated freeboard chiller; 4) a carbon adsorption system with 90% control efficiency; 5) other approved control system.	For units greater than 1 sq. meter one of the following: 1) an automated cover - elevator system; 2) a 0.75 freeboard ratio; 3) a refrigerated freeboard chiller; 4) a carbon adsorption system with 90% control efficiency; 5) other approved control system.	For solvents with vap. press. above 33 mm Hg an internal drainage device and either a 0.75 freeboard ratio or a water cover. For all other solvent s a 0.50 freeboard ratio is required.	For cold cleaners, an apparatus or cover which completely covers the solvent container when not processing work. For vapor and conveyorized degreasers, a cover which can be easily operated without disturbing the vapor layer.	
Ventura	Rule 74.6, Surface Cleaning and Degreasing; Rule 74.6.1, Cold Cleaning Operations; Rule 74.6.2, Batch Loaded Vapor Degreasing; Rule 74.6.3, Conveyorized Degreasing	Rocket engine flushing operations with 85% recovery; non-conveyorized degreasers less than 1 ft². using unheated solvents. Partial exemption for vapor degreasers less than 10% ROC or less than 1 m².	Either a 0.75 freeboard ratio, a refrigerated freeboard chiller (or refrigerated condenser equipment), or an emission control system with 95% control efficiency (this is a mandatory requirement for units greater than 2 m²).	For units greater than 1 m², either a refrigerated freeboard chiller (condenser equipment) which maintains a 1.0 freeboard ratio, a carbon adsorption system with 95% control efficiency; or other 85% efficient emission control system.	Low volatility solvents must have a 6 inch freeboard, high volatility solvents must have either a water cover, a 0.75 freeboard ratio, or an 85% efficient emission control system.	An apparatus or cover which prevents the solvent from evaporating when not processing work in the degreaser. For cold cleaners the cover must be operable with one hand; for vapor degreasers the cover must be operable without disturbing the vapor zone.	The 85% efficiency requirement is an overall capture and control efficiency. If vapor degreasers are larger than 1 m², the cover must be mechanically assisted by a spring loaded, counterweighted sliding, rolling or powered system.
RACT/BARCT		Cleaning operations using emulsions or solutions with less than 2% VOC; cold cleaners with surface areas less than 1ft².	For vapor units, a primary condenser plus either a 0.75 freeboard ratio, a refrigerated freeboard chiller (RFC) or an alternative emission control system with an 85% overall efficiency requirement. For cold units, either a 0.75 freeboard ratio, or RFC.	A primary condenser and a 0.75 freeboard ratio, for units greater than 1m² a RFC is required. Alternatively, an emission control system with an 85% overall efficiency can be used in lieu of freeboard and chiller requirements.	Low volatility solvents must have a 6 inch freeboard, high volatility solvents must have either a water cover or a 0.75 freeboard ratio.	A cover, where appropriate	

The various districts' degreasing regulations are geared specifically to vapor degreasing and cold solvent cleaning applications. Since chlorinated solvents have been widely used in these applications, the rules generally focus on controls for these solvents. For instance, in order to be used in vapor degreasing, a solvent must not have a flash point; this way, the solvent can be heated to its boiling point and solvent vapors will define the vapor zone. As discussed in Section 4, most chemical alternatives cannot be used in vapor degreasers. Unfortunately, the vapor degreasing regulations still apply to the alternatives because rules specific for the alternatives have not yet been written.

3.1.1.5 Permit Regulations Table 3-3 presents a summary of the exemptions for solvent cleaning applications contained in district "permit" regulations. Operating permits are documents issued by districts to facilities. The so-called operating conditions allow a limited amount of emissions under prescribed conditions. Users installing operations listed in Table 3-3 do not have to obtain permits to operate. Exempting a source from requiring a permit does not exempt that source from complying with the appropriate district rule. In many cases, however, degreasing regulations are not enforced for a source that is exempt from permitting requirements.

Four of the eight districts listed in Table 3-3 -- SCAQMD, Sacramento, San Diego, and Ventura -- exempt water cleaning equipment from permitting requirements. Four districts, SCAQMD, San Joaquin, Kern, and Ventura, exempt equipment employing the use of high-boiling solvents. Two of the four districts, San Joaquin and Kern, place a size limitation on equipment employing the use of high-boiling point solvents. Some of the districts exempt a source from both the rule and permitting requirements. In SCAQMD, for example, equipment employing the use of formulations containing less than 2 percent VOC by weight is exempt from both Rule 1122 (Solvent Degreasing Applications) and Rule 219 (Equipment Not Requiring a Written Permit Pursuant to Regulation II) under (l) (4). Thus firms that use these formulations do not have to observe the rule requirements and they do not have to obtain a permit for the equipment.

Users of equipment employing the use of formulations containing more than 2 percent by weight VOC must apply for a permit to operate in the SCAQMD and in those districts where water cleaning equipment is not specifically exempt (BAAQMD, San Joaquin, Kern, and Santa Barbara). It is worth noting that, although the Ventura rule does exempt water cleaning equipment from permitting requirements, that District does not believe the exemption was intended for water cleaning equipment. Thus, firms in Ventura's jurisdiction may have to go through the permitting procedure.

3.1.1.6 Wipe Cleaning Regulations The SCAQMD is the only district in California that has a rule that controls emissions from miscellaneous solvent cleaning applications. SCAQMD Rule 1171 -- Solvent Cleaning Operations -- applies to anyone performing a solvent cleaning operation that is not subject to Rule 1122 (Solvent Degreasers), Rule 1164 (Semiconductor Manufacturing), Rule 1141.1 (Coatings and Ink Manufacturing), and Rules 1102 and 1102.1 (Petroleum

Table 3-3 *Summary of Select Permit Regulations in California*

District	Rule Name and Number	Equipment and Processes not Requiring a Permit to Operate
BAAQMD	Regulation 2 - Permits, Rule 1	Equipment or operations which use unheated solvent containing less than 1 gallon or surface area less than 1ft². Does not apply to wipe cleaning using more than 5 gallons per year of solvent or semiconductor and aerospace stripping operations.
SCAQMD	Rule 219, Equipment Not Requiring a Written Permit Pursuant to Regulation II	Unheated, non-conveyorized units with a surface area of 1 m² or less and an int. vol. of 92.5 gallons or less; or using organic solvents with an initial boiling point of 302 °F or greater; or using solutions with 2% VOC or less.
San Joaquin	Rule 2020, Exemptions	Unheated, non-coveyorized units with a surface area of 10 ft² or less, and an int. vol. of 92.5 gallons or less, and using only organic solvents with an initial boiling point of 248 °F or greater; and losing less than 25 gallons of solvent per year.
Kern	Rule 202, Exemptions	Unheated, non-coveyorized units with a surface area of 1 m² or less, and an int vol. of 92.5 gallons or less, and using only organic solvents with an initial boiling point of 248 °F or greater; and losing less than 25 gallons of solvent per year.
Sacramento	Rule 201, General Permit Requirements	Water solution for surface preparation, cleaning, stripping or etching. Unheated non-conveyorized solvent rinsing containers or coating dip tanks of 100 gallon capacity or less.

Table 3-3 Summary of Select Permit Regulations in California

District	Rule Name and Number	Equipment and Processes not Requiring a Permit to Operate
Santa Barbara	Rule 202, Exemptions to Rule 201	Unheated, non-conveyorized solvent rinsing containers or coating dip tanks of Rule 321). are greater
San Diego	Rule 11, Exemptions from Permit Requirements	Equipment using aqueous solutions with less than 10% VOC. Cold solvent cleaning and paint stripping tanks with a liquid surface area of 1 ft or less.
Ventura	Rule 23, Exemptions from Permit	Unheated, non-coveyorized units 1 ft² or less or 1 m² or less if inti is greater than 302°F. Degreasing equipment and wipe cleaning operations losing less than 25 gallons of solvent per year. Dilute aqueous solutions.

Solvent and Perchloroethylene Dry Cleaning). Also exempt from Rule 1171 are solvent cleaning operations subject to Rule 1124 (Aerospace Assembly and Component Manufacturing Operations), except for coating application equipment cleaning, and storage and disposal of VOC-containing materials used in solvent cleaning operations.

Table 3-4 lists the major solvent requirements of Rule 1171. The column entry "Substrate Cleaning During Manufacturing Processes, and Surface Preparation for Coating, Adhesive, or Ink Applications" applies to uses generically described as wipe cleaning applications. This would include the final wipe of a product before packaging, the surface preparation of a substrate prior to coating or adhesive application, or the use of solvent as a lubricant during the assembly of a product.

Most solvents that are classified as VOCs have a VOC content per liter of material in the 700 to 1,000 grams per liter range. Solvent blends with water would have lower VOC content since water is not classified as a VOC. Other solvents that are not VOCs include TCA, CFC-113 and METH. The 70 grams of VOC per liter of material requirement in Table 3-4 for substrate cleaning and surface preparation is quite stringent and can only be met with exempt solvents or water-based formulations.

The repair and maintenance cleaning category in Table 3-4 would include cleaning work stations at the end of the day or interim cleaning of tools and machinery. The requirements for repair and maintenance cleaning are 900 grams of VOC per liter of material and 20 mm Hg VOC composite vapor pressure. This requirement can be met with various petroleum distillates and mineral spirits. Ink application equipment cleaning is regulated under four broad categories: screen printing; lithographic and letterpress; ultraviolet ink removal; and other ink application equipment cleaning.

The vapor pressure of a solvent is an indication of its evaporation rate. Volatile solvents, like the chlorinated solvents, have high vapor pressures and they evaporate readily. Solvents with lower vapor pressures evaporate less readily. The vapor pressure levels in Table 3-4 restrict wipe cleaning solvents to the lower vapor pressure solvents. Air regulators believe that overall emissions will be lower if lower vapor pressure solvents are used.

Table 3-5 lists the other provisions and exemptions of Rule 1171. The first column entry "Cleaning Devices and Methods Requirements" lists the types of cleaning techniques that are allowed under Rule 1171. The important point here is that the user must meet both the solvent requirements listed in Table 3-4 and the cleaning devices and methods requirements listed in Table 3-5. The acceptable methods and devices include wipe cleaning, 16 fluid ounce or less spray bottles, and cleaning equipment that is closed while cleaning. Atomization into open air is specifically prohibited and solvent flushing is allowed only if the cleaning solvent is discharged into a closed container.

Table 3-4 Major Solvent Requirements of Rule 1171

Category	VOC Per Liter of Material Limit	VOC Composite Vapor Pressure Requirement
Substrate Cleaning During Manufacturing Processes, anc Surface Preparation for Coating, Adhesive, or Ink Applications	70 grams per liter	—
Repair and Maintenance Cleaning	900 grams per liter	20 mm Hg
Cleaning of Coatings and Adhesives Application Equipment	950 grams per liter	35 mm Hg
Cleaning of Polyester Resin Application Equipment	200 g/L; or 1100 g/L + 1.0 mm Hg; or solvent reclamation system	—
Cleaning of Screen Printing Equipment	1070 grams per liter	5 mm Hg
Cleaning of Lithographic and Letterpress Printing Equipment	900 grams per liter	25 mm Hg
Cleaning of Other Ink Application Equipment	100 grams per liter	3 mm Hg
Cleaning of Ink Application Equipment Involving the Remova of Ultraviolet Inks	800 grams per liter	33 mm Hg

Table 3-5 Other Provisions and Exemptions of Rule 1171

Cleaning Devices and Methods Requirements	Other Requirements	Exemptions
Wipe Cleaning	All VOC-containing materials used in solvent cleaning operations are to be stored in non-absorbent, non-leaking containers which must be kept closed at all times except when filling or emptying.	Cleaning carried out pursuant to Rules 1122, 1102, 1102.1, 1164, 1124, 1141.1
Spray bottles or container with a maximum capcity of 16 fluid onces from which solvents are applied with a propellant-induced force	Approved control equipment is allowed in lieu of complying with solvent or equipment requirements	Janitorial cleaning
Cleaning equipment that can be and is closed when used, except when depositing or removing objects	Atomization into open air is prohibited	Stripping of cured coatings, cured adhesives, an cured inks.
Cleaning device which is listed in the Office of Operations' manual "Alternative Devices for Rule 1171 Compliance" dated July 1, 1991. (Currently the only equipment that is listed in one gun cleaning device)	With the exception of methylene chloride, use of Group II exempt compounds are not allowed after January 1, 1997.	Wipe cleaning is not subject to the solvent requirements when carried out for cleaning of sol cells, laser hardware, and high-precision optics.
Remote reservoir cold cleaner used pursuant to requirements that are specified in paragraph (c)(3) of Rule 1171		Wipe cleaning is not subject to the solvent requirements when carried out for cleaning for: conducting performance laboratory tests on coatings, adhesives, or inks; research and development programs; and laboratory tests in quality assurance laboratories
Non-atomized solvent flow method where the cleaning solvent is collected in a closed container or collection system		Wipe cleaning is not subject to the solvent requirements when carried out for cleaning of polycarbonate plastics
Solvent flushing method where the cleaning solvent is discharged into a closed container		Wipe cleaning is not subject to the solvent requirements when carried out for cleaning of motor vehicles on application lines subject to Rul 1115 - Motor Vehicle Assembly Line Coating Operations
		Internal cleaning of tips of automated spray equipment systems, except for robotic systems, and cleaning with compliant spray bottles or containers are allowed to atomize the solvent
		The use of aerosol products at a usage level belo 160 fluid ounces or less per day is not subject to solvent requirements or the atomization prohibitio
		Cleaning of cotton swabs to remove cottonseed o before cleaning of high-precision optics are not subject to solvent requirements
		Facilities that are exempt from keeping records of any other Regulation XI rule are exempt from the recordkeeping requirements of this rule
		Cleaning operatiions performed with a solvent tha has a water content of 98 percent or more, by weight, or a VOC composite partial pressure of 0. mm Hg or less, or contains VOC consisting or more than 12 carbon atoms do not have to keep records.

The exemptions listed in Table 3-5 include janitorial cleaning, stripping of cured material and several unique applications such as high precision optics and cleaning of polycarbonate plastics.

Table 3-6 provides a summary of select wipe cleaning provisions in California in the SCAQMD, the Ventura APCD and the San Diego APCD. SCAQMD Rule 1124 (Aerospace Assembly and Component Manufacturing Operations) contains a provision that specifies that solvents used in wipe cleaning operations on aerospace components (i.e., components that fly) meet a VOC requirement of 200 grams per liter of material or less or a VOC composite vapor pressure limit of 45 millimeters of mercury (mm Hg) at a temperature of 20° C. The 45 mm Hg limit is much more permissive than the solvent limitations required in Rule 1171.

The San Diego APCD recently relaxed the wipe cleaning provision contained in Rule 67.12 (Polyester Resin Operations). The current version of Rule 67.12 allows solvents with initial boiling points of 190° C or greater to be used as an alternative to solvents with maximum VOC contents of 200 grams per liter of material. According to a San Diego APCD official, the district will add the alternate provision to all of its source-specific rules.

It is worth noting that while SCAQMD has a rule that controls emissions from miscellaneous solvent cleaning operations, SCAQMD Rule 219 does not require permits to operate for such sources. In many cases, rule provisions for emissions sources that are exempt from district permitting requirements are not enforced. The South Coast, however, does enforce the Rule 1171 provisions.

The Ventura APCD and the BAAQMD, are the only districts in California that require permitting of wipe cleaning stations. As indicated in Table 3-6, the BAAQMD requires wipe cleaning stations using more than 5 gallons per year to be permitted and the Ventura APCD requires wipe cleaning stations using more than 25 gallons per year to be permitted. While the BAAQMD and Ventura APCD require wipe cleaning stations to be permitted, they do not have a broad-based rule like SCAQMD's Rule 1171 that controls emissions from miscellaneous solvent cleaning operations. The BAAQMD, Ventura APCD and other districts regulate wipe cleaning provisions through source-specific rules. Such rules only apply to wipe cleaning applications performed in conjunction with a regulated activity, such as the manufacture of metal parts and products.

3.1.2 Ozone Depletion Regulations Because ozone depletion is a world environmental problem, the regulations have been developed at the international and national level. Early on, state and local governmental agencies proposed regulations and ordinances; at this stage, the national regulations are more encompassing and they generally supercede any local regulations that were implemented.

3.1.2.1 World Regulations In 1987, the major world nations met and signed the Montreal Protocol. At the time, the Protocol called for a reduction in production of the CFCs of 50 percent by 1998. Subsequent amendments to the Protocol

Table 3-6 Summary of Select Wipe Cleaning Provisions in California

District	Rule Name and Number	VOC Requirements	Alternative Material Requirements	Alternative Equipment Requirements	Exemptions
SCAQMD	Rule 1124 - Aerospace Assemby and Component Manufacturing Operations	200 grams per liter of material or less	45 mm Hg composite vapor pressure or less		Space vehicle manufacture; less than 3 gallons of coatings and solvents per day.
SCAQMD	Rule 1164 - Semiconductor Manufacturing	200 grams per liter of material or less	33 mm Hg composite vapor pressure or less	Components are totally enclosed during processing; or the cleanup solvents are flushed or drained in a manner that does not allow evaporation into the atmosphere.	none
San Diego APCD	Rule 67.12 - Polyester Resin Operations	200 grams per liter of material or less	190 °C initial boiling point or greater	VOC Reclaimation System	less than 0.5 gallons per operating day
San Diego APCD	Rule 67.3 - Coating of Metal Parts and Products	200 grams per liter of material or less	none	Add-on control device	none
Ventura APCD	Rule 74.3 - Paper, Fabric and Film Coating Operations	200 grams per liter of material or less	Emissions from clean-up operations are less than 120 grams per liter of clean-up solvent used.	Emissions from the clean-up operation are reduced by a combined capture and destruction efficiency of no less than 90 percent.	none

called for a complete phaseout, added other substances including TCA and, most important, accelerated the production phaseout date to Jan 1, 1996. Alternatives that, themselves cause ozone depletion, are also scheduled for phaseout and their phaseout dates may be accelerated in subsequent meetings of the parties.

3.1.2.2 Federal Regulations Title VI of the CAA amendments required EPA to develop and promulgate regulations to implement a variety of actions. These include a ban on venting of refrigerant at servicing and disposal of automobile air conditioners, chillers, retail food units and home refrigerators. Title VI also required EPA to implement a production phaseout of the CFCs by 2000. At the news that ozone depletion was more serious than had been previously thought, President Bush announced in February, 1992 that the ban would be accelerated to January 1, 1996. EPA has promulgated a regulation to that effect; it will phase out the production of the cleaning solvents, TCA and CFC-113, by that date.

Title VI also required EPA to implement a labeling program for items that are introduced into interstate commerce that contain or are made with ozone depleting substances. In March of 1993, EPA proposed the labeling regulation and in November, 1993, it was finalized. It requires items that are cleaned with TCA or CFC-113 to carry a label warning that the item was made with an ozone depleting substance. To lessen the impact, however, the labeling law also contains a pass-through provision. This allows a firm to avoid labeling if the firm did not, itself, use TCA or CFC-113 in cleaning. In other words, firm A, which uses TCA to clean a piece of metal in the fabrication of a fastener, must label it. When it is sent to firm B, which will assemble the fastener into an aircraft device without the use of an ozone depleting solvent, the part does not have to carry a label when it is sold.

Title VI also required EPA to implement what has come to be referred to as the Significant New Alternatives Policy (SNAP) program. EPA published the final SNAP regulation on March 18, 1994. For major uses of ozone depleting substances, the regulation requires those firms who wish to market alternatives to submit information on the alternative to EPA. EPA then makes a judgement as to whether the substance is acceptable, unacceptable, or pending for a particular application. EPA intends to publish quarterly Federal Register notices updating the evaluation of submitted alternatives.

The March 18 regulation covers many alternatives for cleaning. As discussed in the next section, EPA forbids or restricts the use of only a few substances and all of these substances contribute to stratospheric ozone depletion and/or global warming. Although EPA was given the authority to forbid or restrict the use of alternatives for other reasons, they have not done so. In effect, if a substance does not deplete the ozone layer or cause global warming, it is not likely that it will ever be deemed unacceptable under the SNAP program.

3.1.3 Global Warming Regulations The Rio Convention on Climate Change, a worldwide effort to reduce emissions of global warming gases, has been ratified by the required 50 nations. It entered into force on March 21, 1994. In October, 1993, the Climate Change Action Plan, the U.S. plan to reduce emissions of greenhouse gases, was released. The components of the plan are intended to comply with the international convention. It calls for a voluntary commitment from industry to reduce greenhouse gas emissions. Two classes of chlorinated solvent alternatives, the hydrofluorocarbons and the perfluorocarbons, are covered by the convention and the U.S. plan and this will be discussed later.

3.1.4 Air Toxic Regulations Under Title III of the CAA amendments, EPA is required to develop and implement regulations for the industries using one or more of a list of 189 hazardous air pollutants (HAPs). These so-called National Emission Standards for Hazardous Air Pollutants (NESHAPs) will set Maximum Achievable Control Technology (MACT) standards. In 1992, EPA published a list of 174 industries that would be subject to Title III.

Title III directs EPA to base the MACT "floor" (the lowest or starting MACT standard applicable) on the average emission limitation achieved by

- the best performing 12 percent of the existing sources for categories with 30 or more sources, or

- the average emission limitation achieved by the best 5 sources in the category or subcategory for categories with fewer than 30 sources.

EPA will promulgate regulations for the 174 industries covered by Title III in 1994, 1997 and 2000.

3.1.4.1 Solvent Cleaning NESHAP On November 29, 1993, EPA published the proposed NESHAP for new and existing chlorinated solvent cleaning operations. The proposed NESHAP covers vapor degreasing and cold cleaning with TCA, TCE, METH, PERC, carbon tetrachloride, and chloroform. It is anticipated that the NESHAP will be finalized in November, 1994. Under the proposed regulation, companies will have two years to comply with the requirements. A flexible mix of equipment and requirements is allowed by the proposed NESHAP. The NESHAP requirements are summarized in Table 3-7.

As mentioned earlier, the production of TCA and carbon tetrachloride will be banned because of their contribution to stratospheric ozone depletion. Thus the NESHAP, in practice, will affect only TCE, PERC, METH and chloroform. Since chloroform is used only to a small extent in cleaning, the regulation will put further restrictions primarily on users who continue to use TCE, METH, or PERC. It is already very difficult for new sources of TCE and METH to be permitted in California and firms currently using the chemicals face increasingly stringent regulations. This will be described later.

There are two provisions in the proposed NESHAP that are more stringent than existing California regulations. One of these provisions affects conveyorized degreasers that employ PERC, TCE, or METH. Most of the California degreasing rules discussed earlier specify a freeboard ratio of 0.75 for conveyorized degreasers (see Table 3-2). As indicated in Table 3.7, the proposed NESHAP would require a freeboard ratio of 1.0 for existing operations. Thus, firms with conveyorized degreasers which do not have a freeboard ratio of 1.0 will have three

Table 3-7 Control Equipment Combinations And Idling Limits

Type of Cleaning	Control Equipment Combination Options	Alternative Idling Limit (kg/hr)
Batch Vapor (<1.21 m^2)	1. Freeboard ratio of 1.0, freeboard refrigeration device, reduced room draft 2. Biparting cover, freeboard refrigeration device, reduced room draft 3. Biparting cover, freeboard ratio of 1.0, reduced room draft 4. Freeboard refrigeration device, manual cover, reduced room draft	0.15
Batch Vapor(>1.2m^2)	1. Biparting cover, freeboard refrigeration device, reduced room draft 2. Dwell, freeboard refrigeration device, reduced room draft 3. Biparting cover, freeboard refrigertion device, superheated vapor 4. Freeboard ratio of 1.0, reduced room draft, superheated vapor 5. Dwell, reduced room draft, superheated vapor 6. Biparting cover, reduced room draft, superheated vapor 7. Biparting cover, dwell, reduced room draft	0.15
Batch Cold Cleaning	1. Cover, water layer	N/A
Existing In-Line Cleaning	1. Freeboard ratio of 1.0, freeboard refrigeration device	0.10
New In-Line Cleaning	1. Superheated vapor system, freeboard refrigeration device	0.10

Note: Users have the freedom to adopt one of the control equipment options or the alternative idling limit. For example, a user of a batch vapor degreaser with a surface area of 1M^2 could choose to adopt option 1, 2, 3, or 4 for control equipment combinations or could meet the idling limit of 0.15 kg/hr.

options. The first option is to modify the degreaser to increase the freeboard height. The second option is to purchase a new conveyorized degreaser with a higher freeboard. The third option is to meet an alternative idling limit of 0.10 kilograms (0.22 pounds) of solvent emissions per hour. Because most conveyorized degreasers that are used today do not have a 1.0 freeboard ratio, firms with such degreasers which continue to use PERC, TCE or METH could be faced with a substantial capital outlay to comply with the NESHAP requirements.

The other provision of the proposed NESHAP that may pose problems for chlorinated solvent users concerns automated parts handling systems. In addition to complying with either the equipment or idling requirement of the proposed NESHAP, all users must install an automated parts handling system. The proposed NESHAP states that an "automated parts handling system means a mechanical device that carries all parts and parts baskets from the initial loading of soiled parts through the removal of the cleaned parts at a controlled speed. Automated parts handling systems include, but are not limited to, hoists and conveyors."

Conveyorized degreasers are considered to have inherent automated parts handling systems. At least 90 percent of the degreasers are not conveyorized. Many of the batch degreasers are small and they do not have automated parts handling systems. Since there is no size limit cutoff in the proposed NESHAP, even small cold cleaning or vapor degreasing batch units that use PERC, TCE, or METH would be required to install automated parts handling systems. Because installing such systems on small units would be infeasible and/or cost prohibitive in most cases, the result of the final NESHAP could be an effective ban on small batch degreasers using PERC, TCE, or METH.

3.1.4.2 Aerospace Industry NESHAP EPA published the proposed aerospace NESHAP in June, 1994; the final regulation is expected in November, 1994. The regulation covers several applications of the 189 HAPs in the aerospace industry including paint stripping, coating and handwipe. In the cleaning arena, because the solvent degreasing NESHAP described above covers aerospace degreasing operations, the aerospace NESHAP includes only provisions for wipe cleaning operations.

The proposed regulation for wipe cleaning is based on the SCAQMD Rule 1124 provisions. In surface preparation wipe cleaning, the proposal allows a choice. A firm can use any solvent for wipe cleaning as long as it has a vapor pressure of 45 mm Hg or less at 20° C. As an alternative, a firm can opt to use a solvent with a vapor pressure of 7 mm Hg or less at 20° F; choosing this option will allow the firm to avoid certain record keeping procedures and to forgo a solvent approval process.

These provisions will have a profound effect on the aerospace industry. About 80 percent of the solvents used currently in the aerospace industry for wipe cleaning are CFC-113 and TCA. Because of the impending ban, alternatives must be identified, tested and implemented by January 1, 1996. Virtually all of the potential alternatives are classified as VOCs and the industry will be limited to alternatives with lower vapor pressure.

3.1.4.3 California Air Toxic Regulations In California, CARB has the authority to declare certain substances to be Toxic Air Contaminants (TACs). Over the last several years, CARB has declared three of the chlorinated solvents -- TCE, PERC and METH -- to be TACs. In certain cases, CARB may identify major uses of the TACs and develop Air Toxic Control Measures (ATCMs) for the major use. CARB has recently developed an ATCM for PERC dry cleaning operations, for example. CARB has begun to investigate the possibility of developing an ATCM on degreasing; this regulation would affect firms using TCE, PERC and METH in degreasing operations.

In 1987, the California legislature passed AB 2588 which is known as the Air Toxics "Hot Spots" Information and Assessment Act Bill. AB 2588 provides a list of substances that are classified as toxics and this list includes TCE, PERC, METH, TCA and CFCs in general.

The primary purpose of AB 2588 is to provide comprehensive inventories of air toxics "hot spots" where emissions from specific sources may expose individuals and population groups to increased risk. The bill applies to sources that emitted (or have the potential to emit) more than 10 tons per year of total organic gases, particulates or oxides of nitrogen or sulfur. Depending on the emissions level, facilities were covered by AB 2588 in July 1989 or July 1990.

The affected facilities were required to submit air toxic inventory reports (ATIRs). Local districts reviewed the ATIRs and required facilities classified as high priority to prepare health risk assessments (HRAs). HRAs typically use atmospheric dispersion models to predict the ambient concentration of a particular chemical at certain "receptor" points. Unit risk factors (URFs), which represent the hazard posed by a chemical, are then used to predict what the health risk would be at individual receptor sites. TCE, PERC and METH have fairly high URFs and most facilities using them would pose an unacceptable risk.

Senate Bill (SB) 1731 "Risk Reduction Plans and Audits" implements the risk reduction provision of AB 2588. Districts must establish significant risk levels and require affected facilities to reduce their risk over a prescribed period of time. Districts will be implementing SB 1731 over the next year.

3.1.4.4 South Coast Air Quality Management District Toxic Regulations The SCAQMD is one of two air districts in California that currently have a rule controlling new sources of TACs (the other one is Monterey). Rule 1401 (New Source Review of Carcinogenic Air Contaminants) currently regulates only certain carcinogenic TACs but may be amended to include additional carcinogenic TACs as well as non-carcinogenic TACs. The current regulation includes METH and TCE; the proposed amendment would add PERC and TCA.

Rule 1401 directs the Executive Officer of SCAQMD to deny permits to operate to new sources that pose a maximum individual cancer risk (MICR) greater than one in one million (1×10^{-6}) if the permit unit is constructed without T-BACT. The unit may pose a higher MICR of ten in one million (1×10^{-5}) if the permit unit is constructed with T-BACT. The MICR is obtained by multiplying the ambient concentration of the TAC, normally obtained by modeling, by a URF assigned to each chemical. The higher the URF of a chemical, the higher the resulting MICR will be. METH has been assigned a URF of 1.0×10^{-6} and TCE has been assigned a URF of 2.0×10^{-6}.

When Rule 1401 is amended to include PERC, because PERC has a URF of 5.9×10^{-6}, new sources of PERC will be even more difficult to permit than new sources of METH or TCE. TCA, a non-carcinogenic toxic air contaminant, will be regulated on the basis of a so-called hazard index since it is not a suspect carcinogen like TCE, PERC and METH. TCA has a fairly low hazard index and its use in solvent cleaning applications will most likely be allowed. Because of the production ban, however, virtually no plants will be using the chemical so firms will no longer seek permits to use it.

SCAQMD Rule 1401 only applies to "permit units." As explained earlier, wipe cleaning operations in the South Coast Air Basin are exempt from permitting requirements. Therefore, it is technically possible to use METH -- a listed 1401 chemical -- in wipe cleaning applications. This is because METH is not classified by SCAQMD as a VOC.

SCAQMD recently adopted a new rule that controls existing sources of TACs. Rule 1402 (Control of Toxic Air Contaminants from Existing Sources), which implements SB 1731, requires risk reduction for facilities that pose health risks exceeding a risk level of one hundred in one million (1.0×10^{-4}) or a total acute or chronic hazard index of five. Rule 1402 will primarily affect facilities that were required to submit health risk assessments under AB 2588. Some large solvent cleaning operations might exceed the risk cutoff level but most operations would not be affected by Rule 1402. The District has the freedom to require risk reduction in plants that did not submit risk assessments under AB 2588 but it is not likely this power will be exercised.

3.1.4.5 Toxic Regulations in Other California Air Districts Several air districts in California are currently in the process of developing air toxic rules similar to SCAQMD Rules 1401 and 1402. Through guidance by CARB, other air districts are currently regulating new sources of TACs through individual policies. For new sources, these policies are similar in intent to SCAQMD Rule 1401. Some of the air districts have policies with no written prescription. CARB distributed what is known as a "brightline risk guideline" which is intended as a guidance document for local air districts. For certain chemicals that pose a risk that is above the brightline risk cutoff level, districts are free to deny permits to operate. The CARB guideline document, however, does not tell districts how or to what extent the policies should be implemented. Thus districts without rules are free to make arbitrary judgements on the permitting of new sources of toxics.

3.2 Overview of Hazardous Waste Regulations

Federal and state hazardous waste regulations have had an effect on chlorinated solvent handling in cleaning applications and they will have a substantial effect on the use of some of the possible alternatives. In general, the Resource Conservation and Recovery Act (RCRA) governs the disposition of hazardous waste at the Federal level. In California, Title 22 of the Health and Safety Code regulates hazardous waste in California. States must be at least as stringent as the Federal government but they have the freedom to be more stringent. In many instances, the California regulations are more stringent than the RCRA requirements.

3.2.1 Federal RCRA Regulations RCRA was passed in 1976 and substantially amended through the Hazardous and Solid Waste Amendments (HSWA) in 1984. Prior to the HSWA amendments, land disposal was an acceptable method of disposal for virtually all hazardous waste. The HSWA called for a phaseout of land disposal beginning in 1986 and ending by 1992. Solvents, including the chlorinated solvents, were among the first substances to be banned from land disposal; the ban became effective in 1986.

RCRA Subtitle C regulates hazardous waste. It divides the types of hazardous wastes that are covered into two categories: listed wastes and characteristic wastes. The chlorinated solvents are listed wastes and they fall into the F001 and F002 classifications. F001 includes "spent halogenated solvents used in degreasing" and "still bottoms from the recovery of these spent solvents and spent solvent mixtures." It applies to TCE, PERC, METH, TCA, CFC-113 and mixtures or blends of these solvents containing 10 percent or more by volume of one of these or of other listed solvents. F002 is more general and it includes "spent halogenated solvents." It lists the same chlorinated solvents (and various other solvents) and their still bottoms and mixtures.

Other chemicals are regulated as hazardous wastes by reason of a so-called characteristic. Characteristics include:

- Ignitability. This category includes liquids containing less than 24 percent alcohol with closed cup flash points less than 60° C or 140° F. This provision also covers certain nonliquids, ignitable compressed gases and oxidizers.

- Corrosivity. This applies to aqueous wastes that have a pH less than or equal to 2 (an acid) or a pH greater than 12.5 (an alkaline material or a base). It also applies to liquids that corrode steel at a certain rate.

- Reactive. This applies to substances that are unstable, reactive or explosive.

- Toxicity. This criterion applies to wastes which, when tested according to a specified procedure, contain certain listed substances. These listed substances include PERC and TCE.

The chlorinated solvents and all wastes derived from them are hazardous wastes under RCRA. Some of the potential alternatives are listed hazardous wastes and some are characteristic hazardous wastes. It is worth noting, however, that many of the potential alternatives were not used at the time RCRA was developed and, as a result, even if they are known to be dangerous, they are not listed. Often, in these cases, they are not characteristic wastes either.

After land disposal of the chlorinated solvents was banned, it became cost effective to recycle the spent solvents that were used in bath cleaning operations. A network of recycling firms gradually evolved nationwide. They would provide a credit for the spent solvent and charge a fee for disposal of the still bottom residue. Generally, recyclers would pay a net credit for the spent chlorinated solvents. The recycling firm would clean up the solvents using distillation or thin film evaporation. The solvents would be sold back into the market at a reduced rate compared with the price of virgin solvent. The still bottom from the recycling operation would be blended with flammable solvents and the resulting mixture (which had high heat value) would be sent to cement kilns for use as supplementary fuel or to destructive incinerators.

For other solvent applications, like wipe cleaning, the solvent contaminated rags have commonly been shipped off-site as hazardous waste and sent to cement kilns or destructive incinerators. Generally it is not cost effective to remove the solvent from rags or other media for recycling.

3.2.2 California Hazardous Waste Regulations The California Department of Toxic Substances Control (DTSC) is the agency in California charged with implementing Title 22 of the California Code of Regulations which contains the state hazardous waste regulations. Chapter 11 focuses on the identification and listing of hazardous wastes and Chapter 12 describes the standards applicable to hazardous waste generators. The California regulations include RCRA wastes as hazardous wastes as they are required to do but they also include other materials as non-RCRA hazardous wastes. California uses the same "characteristic" hazardous waste categories but includes additional wastes under a so-called "toxicity" category. Various criteria are included in the evaluation of toxicity. Some of the potential alternatives to the chlorinated solvents would be classified as hazardous waste in California but would not be hazardous waste under RCRA. In other cases, the wastes would not be classified as hazardous in either case.

The DTSC has recently established a tiered permitting system as required under Assembly Bill 1772. It applies to hazardous waste that is treated on-site by generators; wastes that are recycled are exempt from the new system. The program establishes five tiers of authorization for the treatment of hazardous waste. Three of the five tiers apply to on-site treatment processes and the other two apply to facilities that provide off-site treatment.

The tiers for on-site treatment include:

- Permit by Rule (PBR)

- Conditional Authorization
- Conditional Exemption

The DTSC provides flowcharts to generators so they can determine whether they fall into one of the tiers and, if so, which tier applies.

On-site recycling processes are not subject to tiered permitting. For example, many firms use batch or continuous distillation units to separate the contaminants from spent solvent on-site. The recycled solvent can be reused in the cleaning process. Some of the potential alternative chemicals and processes to the chlorinated solvents may fall under tiered permitting whereas recycling of the chlorinated solvents does not. This may deter firms from converting to the alternatives.

3.3 Overview of Water Regulations

Water effluent regulations affect firms that use chlorinated solvents in cleaning operations only indirectly. Firms that are attempting to implement certain of the alternative processes, however, will be heavily affected by the effluent regulations. Users converting away from solvent degreasing operations into water cleaning operations will be faced with the question of whether or not to discharge all or part of their wastewater into the sanitary sewer. Regardless of the amount or the type of wastewater, approval must be obtained from the local or regional agency that regulates discharges to the sanitary sewer system. In some cases, the sanitation district will allow operation without a permit; in other cases, a permit will be required.

3.3.1 Federal Effluent Requirements Though the federal effluent requirements are quite complex, they generally seek to control wastewater discharges in certain categories. Firms currently performing solvent cleaning operations with chlorinated solvents that are evaluating alternatives would be most concerned with the National Categorical Pretreatment Standards for the Electroplating and Metal Finishing Point Source Categories, as codified in 40 CFR Parts 413 and 433, respectively. The Electroplating Categorical Pretreatment Standards cover wastewater discharges from six electroplating categories:

- Electroplating
- Electroless Plating
- Anodizing
- Conversion Coatings
- Chemical Etching and Milling
- Printed Circuit Board Manufacturing

In addition to the six categories covered under 40 CFR Part 413, the Metal Finishing Point Source Categories cover another 40 categories, for a total of 46. These operations are the first six operations listed in Table 3-8. A firm must perform at least one of the six operations covered under 40 CFR Part 413 in order to be subject to requirements for the additional 40 categories. If a plant falls into one of the categories, the additional requirements would also apply to other operations within the same plant.

Table 3-8 Metal Finishing Categories

Unit	Operation	Unit	Operation
1	Electroplating	24	Electric Discharge Machining
2	Electroless Plating	25	Electrochemical Machining
3	Anodizing	26	Electron Beam Machining
4	Conversion Coating	27	Laser Beam Machining
5	Chemical Etching and Milling	28	Plasma Arc Machining
6	Printed Circuit Board Manufacturing	29	Ultrasonic Machining
7	Cleaning	30	Sintering
8	Machining	31	Laminating
9	Grinding	32	Hot Dip Coating
10	Polishing	33	Sputtering
11	Barrel Finishing (Tumbling)	34	Vapor Plating
12	Burnishing	35	Thermal Infusion
13	Impact Deformation	36	Salt Bath Descaling
14	Pressure Deformation	37	Solvent Degreasing
15	Shearing	38	Paint Stripping
16	Heat Treating	39	Painting
17	Thermal Cutting	40	Electrostatic Painting
18	Welding	41	Electropainting
19	Brazing	42	Vacuum Metalizing
20	Soldering	43	Assembly
21	Flame Spraying	44	Calibration
22	Sand Blasting	45	Testing
23	Other Abrasive Jet Machining	46	Mechanical Plating

Many of the plants that fall into the Electroplating category have cleaning operations that use chlorinated solvents. In fact, solvent degreasing is one of the operations listed in Table 3-8. If these plants convert their solvent cleaning processes to water-based processes, they would continue to be covered under the Electroplating category. Plants not currently covered by the Electroplating category, if they choose to release the effluent from their water-based cleaning process to the sewer, proboably would have to obtain a sanitation district permit.

A case in point is the manufacture of printed circuit boards. If a manufacturer of printed circuit boards acts as a "job shop" that owns less than 50 percent of the materials undergoing metal finishing, then the Electroplating and Metal Finishing Pretreatment Standards would not apply. The category "Printed Circuit Board Manufacturing" is defined in 40 CFR Part 413 as "including all manufacturing operations required or used to convert an insulating substrate to a finished printed circuit board". The term operation is defined as "any step in the printed circuit board manufacturing process in which the board is immersed in an aqueous process bath which is followed by a rinse".

As discussed earlier, printed circuit board defluxing is one of the applications where chlorinated solvents are heavily used. Some firms manufacture the boards and then assemble them. Assembly involves adding flux to the boards, soldering components to them and defluxing them with a chlorinated solvent. Other firms do not manufacture the boards but simply perform the assembly and cleaning operations. Firms only performing assembly operations would not be covered by the categorical classification given above. Since printed circuit board assemblers which use chlorinated solvents for cleaning are typically zero-discharge processes (i.e. they do not discharge to the sewer), they would not be considered a categorical process. If these firms converted to a water-based cleaning process and released the effluent to the sewer, they would have to apply for a sanitation district permit.

Table 3-9 summarizes the pretreatment standards for existing sources and Table 3-10 summarizes the pretreatment standards for new sources as well as the additional performance standards applicable to new sources. In general, both standards specify effluent concentration limits for heavy metals, cyanide and a category called Total Toxic Organics. The limits for new plants are, as expected, more stringent than those for existing plants. New plants must also meet limits for oil and grease and total suspended solids and for pH. For cleaning operations using water-based cleaning formulations, the meaningful effluent limits are those for oil and grease and pH. Cleaning operations generally do not involve heavy metals or total toxic organics.

3.3.2 Local Effluent Requirements There are many agencies in California that regulate sewer discharges. In the southern California area, there are three major regulating agencies:

- The Bureau of Sanitation within the Department of Public Works for the City of Los Angeles (Los Angeles City Bureau of Sanitation);
- The Los Angeles County Sanitation District; and

Table 3-9 Pretreatment Standards for Existing Sources

Pollutant	Daily Maximum (mg/L)	Maximum Monthly Average (mg/L)
Cadmium (T)	0.69	0.26
Chromium (T)	2.77	1.71
Copper (T)	3.38	2.07
Lead (T)	0.69	0.43
Nickel (T)	3.98	2.38
Silver (T)	0.43	0.24
Zinc (T)	2.61	1.48
Cyanide (T)	1.20	0.65
Total Toxic Organics (TTOs)	2.13	---
Alternative to total cyanide: Cyanide, amenable to chlorination	0.86	0.32

Table 3-10 Pretreatment Standards for New Sources and NewSource Performance Standards

Pollutant	Daily Maximum (mg/L)	Maximum Monthly Average (mg/L)
Cadmium (T)	0.11	0.07
Chromium (T)	2.77	1.71
Copper (T)	3.38	2.07
Lead (T)	0.69	0.43
Nickel (T)	3.98	2.38
Silver (T)	0.43	0.24
Zinc (T)	2.61	1.48
Cyanide (T)	1.20	0.65
Total Toxic Organics (TTOs)	2.13	---
Alternative to total cyanide: Cyanide, amenable to chlorination	0.86	0.32
Oil and Grease(1)	52	26
Total Suspended Solids(1)	60	31
pH(1)	Within 6.0-9.0	Within 6.0-9.0

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(1) Additional performance standards for new sources

- The Orange County Sanitation District

All three of these agencies jointly or individually own wastewater treatment plants where wastewater is treated before discharge to the ocean.

Because the wastewater agencies are themselves regulated by regional, State, and federal agencies, they must carefully restrict the amount and type of industrial wastewater that is received at their treatment plants. For this reason, individual dischargers must obtain approval and/or permits before any wastewater is discharged to the sewer. Before permits are granted, the dischargers must demonstrate that the agency's effluent requirements can be met. In some cases, on-site wastewater treatment systems, such as clarifiers or oil-grease interceptors, may be required. As discussed later, it is unlikely that firms using water-based cleaning equipment will need treatment systems if water-based formulations with low levels of additives are used.

The effluent requirements vary from agency to agency. Table 3-11 provides a sample of the effluent requirements from 14 wastewater agencies in California. The standards listed in the table are the ones most likely to be of concern if wastewater from a water cleaning operation is discharged to the sewer. Federal categorical standards may apply if a facility's operations fall into one of the six categorical industries listed earlier.

Since standards are set at the local level, depending on the presence or complexity of the agencies' treatment plants, higher or lower limits may apply. Some wastewater agencies do not own treatment plants and they discharge industrial wastewater to surface waters or directly to the ocean. In these cases, the effluent requirements are generally stricter because the agencies do not own the means to clean up the wastewater themselves.

The values of Table 3-11 show the variation in the requirements from agency to agency. In the City of Merced, for example, the upper pH cutoff limit is 8.5; in the Central Marin Sanitation Agency, the limit is much higher, at 12.5. Total organics or grease and oil have limits ranging from 15 mg/L in the City of Merced to 600 mg/L in Los Angeles.

Also listed in Table 3-11 is a sampling of the effluent standards required by the California Ocean Plan. Some agencies may defer to the California Ocean Plan and some may defer to the federal requirements for categorical pretreatment standards. The important point here is that most wastewater agencies will evaluate each application for discharge on a case-by-case basis and they will apply less or more stringent standards as appropriate.

3.4 Overview of Worker Safety Regulations

The Occupational Safety and Health Administration (OSHA) is the federal agency responsible for protecting the safety and health of industrial workers. Facility owners and operators must institute appropriate safety measures which range from

Table 3-11 Sampling of Effluent Requirements From Select Agencies

Wastewater Agency	pH	Total Toxic Organics (mg/L)	Temperature	Total Organics or Grease and Oil
Los Angeles County Sanitation District	6.0 - 10.0	Essentially None	140° F	Excessive
Orange County Sanitation District	6.0 - 12.0	0.58	140° F	100 mg/L
Los Angeles City Bureau of Sanitation	5.5 - 11.0	Federal	140° F	600 mg/L
Ontario (City)	6.0 - 9.0	2.13	140° F	100 mg/L
San Jose/Santa Clara Water Pollution Control Plant	5.0 - 10.5	2.13	150° F	150 ppm
San Diego Metropolitan	5.0 - 11.0	Federal	140° F	500 mg/L
Central Marin Sanitation Agency	6.0 - 12.5		140° F	
Central Contra Costa Sanitary District	5.5 - 12.4	2.10	150° F	100 mg/L
Cucamonga County Water District	5.0 - 10.5		140° F	375 mg/L
City of Merced	6.5 - 8.5	0.23	80° F	15 mg/L
Fresno	6.0 - 9.0	none	none	none
San Luis Obispo	6.0	0.02	150° F	100 mg/L
City of Daly City	5.5 - 9.0	1.0	140° F	100 mg/L
California Ocean Plan	6.0 - 9.0	(1)		75 mg/L

(1) Measured in terms of acute and chronic toxicity units; 2.5 daily maximum for acute toxicity and 1.0 daily maximum for chronic toxicity

instructing workers in proper lifting procedures to ensuring that the concentrations of work-related chemicals remain below Permissible Exposure Limits (PELs). The California Occupational Safety and Health Administration (CAL OSHA) is the California agency charged with the same mission as the federal OSHA. Both OSHA and CAL OSHA have established PELs for many industrial chemicals. Example PELs are listed in several tables in this document, including Tables 2-3, 4-2 and A-1; they are based on an eight-hour time-weighted average concentration. Table A-1 in the Appendix shows both OSHA and CAL OSHA PELs. The CAL OSHA PELs are typically more stringent than the federal OSHA PELs. California facilities are required to meet the more stringent CAL OSHA PELs.

PELs are generally based on available toxicity data. In general, the lower the PEL of a substance, the more dangerous that substance is perceived to be. New chemicals that enter the market often do not have established PELs. In such cases, the chemical manufacturers or distributors will recommend an exposure level that they believe to be adequate for protecting the health of industrial workers.

There are two primary methods that facilities can use to meet the established PELs. One method is to provide sufficient ventilation in the workplace to dilute the chemical to the required concentration. Another method is to require that workers use personal protective equipment such as respirators or gloves. Chemicals with very low PELs -- for example, 5 ppm -- would generally not be used in a cleaning operation. Such a low PEL could not be met without a respirator and, since there are many chlorinated solvent alternatives that would not require a respirator, they would be less expensive to use. Even a PEL of 25 ppm is difficult to meet without protective equipment.

SECTION 4:
CHEMICAL SUBSTITUTES

The heavy and increasingly stringent regulations on the chlorinated solvents has forced plants using the solvents in cleaning to evaluate alternative chemicals, processes and technologies. There has been particular urgency to finding alternatives to TCA and CFC-113 because of the imminent bans. Alternatives for these two solvents in cleaning applications can often serve as alternatives to the other chlorinated solvents as well. Many vendors are offering alternatives that they claim are "ozone safe." Users are bombarded by literature and visits from these vendors and equipment manufacturers seeking to profit from the ban. There are literally hundreds of different chemicals and formulations that can be used as alternatives to the chlorinated solvents in cleaning applications. Users often are unable to understand the differences in the myriad of products that are being offered and some users, before they select an alternative, evaluate hundreds of different cleaning formulations.

This product-by-product assessment is not productive and it is unnecessary since all of the chemical alternatives can be classified generically. The class in which a chemical fits determines its properties and its environmental effects. With a knowledge of a particular product's class, users can often decide whether the product would be effective in their operation, what kind of equipment would be necessary for use with the alternative and what regulations are in place now or might be in place in the future that would affect its use. Such a generic classification system can save evaluation time and resources and it can help users easily reject hundreds of formulations that distributors are marketing without unnecessary testing.

The first part of this section provides the framework that can be used to approach chemical substitution generically in cleaning applications. It lays out a systems analysis method that greatly simplifies the case-by-case testing and evaluation that is conducted today. It analyzes individual solvents available for cleaning and demonstrates the utility of the classification system. It then focuses on the cleaning systems that are used with the chemical alternatives.

The second part of this section discusses the methods by which the chemical alternatives can be implemented. It identifies and describes the equipment needs and the regulatory requirements for the alternative cleaning agents. The third part of this section identifies and describes a few other solvent options that do not fit well into the generic classes.

4.1 Generic Classification of Chemicals

Before embarking on the generic classification scheme, it is useful to discuss certain criteria before alternatives can be evaluated. These criteria are termed "rules of the game" and they provide generic guidelines for placing alternatives in a particular class so that their limitations can be understood and accommodated from the outset.

4.1.1 Rules of the Game As discussed in Section 2, some organic chemicals have short atmospheric lifetimes and others have long lifetimes. Those chemicals that have short atmospheric lifetimes break down readily in the lower atmosphere or troposphere. In doing so, they form so-called smog precursors. Thus chemicals that break down readily in the lower atmosphere cause smog and are regulated as volatile organic compounds (VOCs). As is apparent later, even some chemicals that are not especially volatile are classified as VOCs.

Other chemicals with long atmospheric lifetimes do not break down readily in the lower atmosphere. They are very stable and they survive for many years in the atmosphere. During that time, they make their way to the stratosphere or upper atmosphere. Once there, ultraviolet light decomposes them. If they contain chlorine or bromine, the chlorine or bromine will react with the ozone, depleting the protective ozone layer. Thus chemicals with long atmospheric lifetimes cause ozone depletion if they contain chlorine or bromine.

Halogens are a group of chemicals that include fluorine, chlorine and bromine. Chemicals that contain fluorine are very stable, which means they are likely to have reasonably long atmospheric lifetimes. Chemicals that contain fluorine -- which makes them very stable -- and chlorine or bromine will cause ozone depletion. If these chemicals contain hydrogen, they will be less stable and they will break down more readily in the lower atmosphere. They will contribute to ozone depletion but less so than chemicals containing no hydrogen.

Chemicals that contain fluorine but no chlorine or bromine do not deplete the ozone layer. Chemicals that contain any one of the halogens -- fluorine, chlorine or bromine -- contribute to global warming. The longer the atmospheric lifetime, the more the chemical causes global warming. Chemicals with one of the halogens and a hydrogen do cause global warming but less so than chemicals that contain no hydrogen. Again, the presence of the hydrogen renders the chemical less stable.

Chemicals containing one of the halogens, fluorine, chlorine or bromine, generally have no flash points. All organic chemicals that do not contain one of the halogens have flash points. Those with lower flash points are flammable and those with higher flash points are combustible.

Virtually all organic solvents with no halogens are VOCs. Some chemicals with chlorine or bromine are VOCs.

Chlorine imparts a chemical good cleaning capability whereas fluorine alone does not.

Adding hydrogen to a chemical containing chlorine or fluorine increases the chance that the chemical will be toxic.

4.1.2 Classes of Chemicals Once the rules of the game have been clearly defined, the generic chemical classes can be described. Most useful industrial or naturally occurring chemicals that might be used as solvents can be placed into one of these categories. The analysis begins with the chemical classes that have been used historically; these include flammable solvents, chlorinated solvents and CFC solvents. It then considers the classes that are emerging; these include the combustible solvents, HCFCs, HFCs, FCs, HBCs and FICs.

4.1.2.1 Flammable Solvents These solvents have flash points below about 100° F. Examples of flammable solvents include isopropyl alcohol (IPA), acetone, toluene, methyl ethyl ketone (MEK) and mineral spirits which are familiar and have been used for decades. These chemicals are low molecular weight organics with no halogens. Because they have low molecular weight, they have low flash points which means they present a worker danger. Again, because of their low molecular weight, they have high vapor pressure which indicates they are volatile and evaporate readily. As the rules of the game indicate, they break down readily in the atmosphere and so are classified as VOCs.

4.1.2.2 Chlorinated Solvents Examples of chlorinated solvents include carbon tetrachloride (CT), TCE, PERC, METH and TCA. These chemicals replaced the flammable solvents because they were perceived to be safer. Since they contain chlorine, according to the rules of the game, they do not have flash points. Like the flammable solvents, they have high vapor pressures and are volatile; they evaporate readily, leaving a clean, dry surface.

Some of the chlorinated solvents, like CT and TCA, have long atmospheric lifetimes and, because they contain chlorine, they cause ozone depletion. Others, like TCE, have short atmospheric lifetimes, and they are regulated as VOCs. PERC and METH have intermediate atmospheric lifetimes and they are not VOCs nor do they deplete the ozone layer. As mentioned in Section 2, PERC is currently regulated as a VOC but EPA has proposed exempting it.

4.1.2.3 CFCs Examples of CFCs that are liquids at room temperature and have been used as solvents include CFC-11 and CFC-113. These substances have long atmospheric lifetimes because they contain no hydrogen and they contribute to stratospheric ozone depletion because they contain chlorine. Their production will be banned on January 1, 1996 for that reason.

The CFCs are very low toxicity chemicals. Like the chlorinated solvents, they have high vapor pressures and evaporate readily. They have no flash points because they contain fluorine and chlorine.

4.1.2.4 Combustible Solvents These are high molecular weight organic solvents with flash points above about 100° F, in the combustible range; they are therefore less dangerous to workers than the flammable solvents. The flash points are higher but the vapor pressure is also lower than the flammable solvents. This is an advantage because combustible solvents are less volatile and emissions are lower; it is a disadvantage, however, because they do not evaporate readily. They require a water rinse or vacuum drying for complete removal; otherwise they leave a residue that requires an extremely long time to dry. Members of this class include certain terpenes, dibasic esters (DBE), N-methyl pyrrolidone (NMP), glycol ethers and alkyl acetates.

The combustible solvents do not contain chlorine so they do not cause ozone depletion. They do not contain chlorine or fluorine so they do not cause global warming. They have short atmospheric lifetimes and they are regulated as VOCs. These chemicals, because they are new, are relatively unscrutinized for their human health and environmental effects.

4.1.2.5 HCFCs The hydrochlorofluorocarbons or HCFCs contain chlorine and fluorine and they have fairly long atmospheric lifetimes so they cause ozone depletion and global warming. They are slated to be banned because of their ozone depletion potential. They are similar to CFCs except they contain hydrogen. The presence of the hydrogen causes them to break down more readily in the lower atmosphere and they have shorter atmospheric lifetimes than the CFCs. They therefore contribute less than the CFCs to global warming and ozone depletion. Nevertheless, because they do contribute to ozone depletion, they are slated to be banned sometime in the next century.

Three HCFCs -- HCFC-141b, HCFC-123 and HCFC-225 -- are liquids at room temperature and have been examined for solvent applications. Two of these HCFCs -- HCFC-123 and HCFC-225 -- have toxicity problems and one of them -- HCFC-141b -- has a higher ozone depletion potential than TCA. In the SNAP rule, described in Section 3, EPA has banned the use of HCFC-141b in solvent cleaning applications because of its high ozone depletion potential.

4.1.2.6 HFCs The hydrofluorocarbons or HFCs contain no chlorine so they do not cause ozone depletion. They do contain fluorine and they have fairly long atmospheric lifetimes so they contribute to global warming. Because they contain hydrogen, however, their contribution to global warming is less than that of the CFCs.

There are few HFCs being examined for use in solvent applications; most are gases at room temperature. The HFCs, because they contain no chlorine, are poor cleaners. They do form blends with other chemicals but the other chemicals they may be combined with would have limitations depending on the generic chemical class they fall into.

4.1.2.7 FCs or PFCs The fluorocarbons (FCs), also known as perfluorocarbons (PFCs), do not contain chlorine or bromine so they do not deplete the ozone layer. They contain fluorine but no hydrogen so they have extremely long atmospheric lifetimes. They are very strong global warming gases and are likely to be regulated in the future for this reason. EPA has limited their use in solvent cleaning applications under the SNAP rule because of their global warming capability.

The PFCs are very poor cleaners. One process being offered is a mixture of a PFC with a combustible solvent. The addition of the PFC suppresses the flammability of the combustible solvent. EPA is discouraging the use of this process because PFCs are such a strong Greenhouse gas.

4.1.2.8 BHCs Only one bromohydrocarbon (BHC) is being offered for use in solvent applications. Methylene bromide is extremely unstable and is combined with a terpene which acts as a stabilizer (see combustible solvents above). EPA indicates that methylene bromide's atmospheric lifetime is long enough for it to contribute to ozone depletion. Although the chronic toxicity of the chemical has not been examined, it appears to have high acute toxicity.

4.1.2.9 FICs The FICs or fluoroiodocarbons are an emerging class of chemical that is just beginning to be examined. These chemicals have no flash points because they contain halogens. One FIC, in particular, trifluoroiodomethane, is being examined as a potential cleaning agent. It is not clear whether the chemical is a VOC and toxicity testing has not been performed. One CFC manufacturer indicates that similar chemicals used as intermediates have proven to be extremely toxic.

4.1.3 Characteristics of Generic Chemical Classes Table 4-1 shows the generic chemical classes and certain of their characteristics. These characteristics are predicted based on the rules of the game. The flammable and combustible solvents which do not contain halogens all have flash points. The flammable solvents have high vapor pressures and evaporate readily; the table indicates they are volatile. The combustible solvents, because they have low vapor pressures, are not volatile. Flammable and combustible solvents are VOCs. They do not cause ozone depletion or global warming and they are generally good cleaners.

All other chemical classes listed in the table contain halogens so they have no flashpoints. They have high vapor pressures and are classified as volatile. Some of the chlorinated solvents are classified as VOCs. Members of the other classes have relatively long atmospheric lifetimes so they are not VOCs but they do contribute to ozone depletion. The long atmospheric lifetimes and the fact that they contain halogens also cause them to be greenhouse gases. The HFCs are poor cleaners and the PFCs, if used alone, have virtually no cleaning ability.

4.1.4 Characteristics of Alternative Cleaning Classes Table 4-2 lists some of the chlorinated solvents used in cleaning and some of the specific chemical alternatives that are being marketed as replacements. It provides a comparison of some of their physical, health and environmental characteristics. Appendix A also contains a table that specifies and compares certain characteristics of the chlorinated solvents and a number of specific alternatives.

The first column in Table 4-2 gives the PEL, the worker exposure level set by OSHA. As mentioned earlier, in general, the lower the PEL, the more acutely toxic is the chemical. An NE in Table 4-2 indicates that the chemical is relatively new to the market and OSHA has not yet established a PEL When a value is shown in parentheses, it indicates that OSHA has not yet set a PEL and the values given are those recommended by the manufacturer. The lowest PELs are for 2-butoxy

Table 4-1 Characteristics of Generic Chemical Classes

Classes	Examples[a]	Flash Point	Volatile	VOC	Ozone Depletion	Global Warming	Cleaning
Flammable Solvents	IPA, Acetone	Yes	Yes	Yes	No	No	Good
Combustible Solvents	Terpenes, DBE, NMP	Yes	No	Yes	No	No	Good
Chlorinated Solvents	CT,TCE, PERC,TCA	No	Yes	Some	Some	Some	Good
CFCs	CFC-11,CFC-113	No	Yes	No	Yes	Yes	Modest
HCFCs	HCFC-123, HCFC-141b,HCFC-225	No	Yes	No	Yes	Yes	Good
HFCs	HFC-43-10	No	Yes	No	No	Yes	Poor
FCs or PFCs	--	No	Yes	No	No	Yes	None
BHCs	Methylene bromide	No	Yes	No	Yes	Yes	Good
FICs	Fluoroiodomethane	No	Yes	NA	NA	NA	NA

NA is not available

[a] See text for full names of abbreviated names

Table 4-2 Technical and Environmental Characteristics of Potential Alternatives in Cleaning

Solvent	PEL (ppm)	VOC	HAP	Flash Point(°F)	Evap Rate[a]	Solvent Strength[b]	ODP	GWP	TOX[c]
TCE	50	Yes	Yes	No	6.39	VG	--	--	S
PERC	25(100)	Yes[d]	Yes	No	2.59	VG	--	--	S
METH	500	No	Yes	No	14.50	VG	--	--	S
TCA	350	No	Yes	No	6.00	VG	0.1	0.026	--
CFC-113	1000	No	No	No	21.00	M	0.8	1.4 --	
d-limonene	NE	Yes	No	117	(0.05)	VG	--	--	S
DBE	NE	Yes	No	212	0.009	VG	--	--	NT
NMP	NE	Yes	No	187	0.03	VG	--	--	R
2-butoxyethanol	25	Yes	Yes	140	0.072	VG	--	--	CN
Acetone	750	Yes	No	0	6.06	VG	--	--	IT
IPA	400	Yes	No	72	1.70	G	--	--	IT
HCFC-123	(10)	No	No	No	(25)	G	0.02	0.017	BT
HCFC-141b	(400)	No	No	No	(25)	G	0.15	0.087	--
HCFC-225	NA	No	No	No	(15)	M	0.01-0.04	0.04-0.06	IT
HFC-43-10	(400)	No	No	No	(18)	P	--	0.25	U
Methylene Bromide	NE	No	No	No	NA	G	0.17	NA	T

NE indicates that OSHA has not yet set a PEL for the chemical.
NA indicates the information is not available
[a] Relative to butyl acetate which has been assigned a value of 1. Author has estimated values where values appear in parentheses.

Source: Wolf, 1993/1994

[b] VG is very good; G is good; M is moderate; and P is poor.
[c] S is suspect carcinogen; NT is not tested; R is reproductive toxin; CN is central nervous system problems; IT is in testing; BT is benign tumors; U is unknown; and T is toxic.
[d] EPA has proposed exempting PERC from VOC regulations.

ethanol, PERC and HCFC-123. As discussed earlier, the PERC PEL may be lowered to 25 ppm in the future. The National Institute for Occupational Safety and Health (NIOSH), the research arm of OSHA, has recommended that the PEL of 2-butoxy ethanol be lowered further, to 5 ppm. The value for HCFC-123 was set at 30 because the chemical caused benign testicular and pancreatic tumors in rat toxicity studies.

The second column indicates whether the chemical is a VOC. METH, and the ozone depleting chemicals and the global warming chemicals (i.e. those with longer atmospheric lifetimes) are the only chemicals in the table that are not VOCs.

The third column indicates whether the chemical is listed as one of the 189 Hazardous Air Pollutants in the Clean Air Act Amendments of 1990. Only the chlorinated solvents and 2-butoxy ethanol are on the list. The other chemicals in the table are not listed, not because they are actually safer, but because they are relatively new chemicals that have not experienced widespread use. As they are more widely used, it is likely that some of these chemicals may be on a similar list in the future.

The fourth column provides the flash point for the chemical. Only the flammable and combustible solvents have flash points. The solvents that contain halogens do not, as dictated by the rules of the game.

The evaporation rate relative to butyl acetate, which has been assigned an evaporation rate of 1, is given in the fifth column. In some cases, the rate has been estimated and the values are shown in parentheses. The higher the evaporation rate, the higher the emissions will be during use. The chlorinated solvents -- TCE, PERC, METH and TCA -- all have high evaporation rates. CFC-113, the HCFCs and HFC-43-10 have even higher evaporation rates. The flammable solvents -- acetone and IPA -- also have high rates. In contrast, the combustible solvents -- d-limonene, DBE, NMP and 2-butoxy ethanol -- have lower evaporation rates, below 1. Losses of these solvents in bath cleaning operations will therefore be lower.

The sixth column provides a qualitative measure of the solvent strength. VG indicates a very good solvent; G indicates a good solvent; M indicates a moderate solvent; and P indicates a poor solvent. The chlorinated and combustible solvents listed in the table all are strong solvents. HFC-43-10 is a poor solvent.

The seventh column shows the ozone depletion potential (ODP) of the solvent. Again, as mentioned earlier, this is a measure of the ozone depletion capability of a chemical relative to the ozone depletion potential of CFC-11 which has a defined ODP of 1.0. TCA, the CFCs, the HCFCs and methylene bromide all have ODPs because they have relatively long atmospheric lifetimes and contain chlorine or bromine. As the rules of the game dictate, HFC-43-10 does not have an ODP because it does not contain chlorine or bromine.

HCFC-141b has an ODP that is higher than the ODP of TCA. Many users are substituting the HCFC for TCA. This is not good policy and, in fact, EPA is forbidding the use of the chemical in cleaning applications under the SNAP Program.

The eighth column lists the Global Warming Potential (GWP) of the chemicals. This is a measure of a substance's GWP relative to the GWP of CFC-11 which is defined as 1.0. Those chemicals with relatively long atmospheric lifetimes which contain any one of the halogens, fluorine, chlorine or bromine, are greenhouse gases as indicated by the rules of the game.

The ninth column provides a qualitative measure of the toxicity of the chemical. Three of the chlorinated solvents -- TCE, PERC and METH -- are suspect carcinogens, indicated by an S. D-limonene also has given a positive carcinogenicity test in male rats. In addition, EPA is concerned about the chemical's aquatic toxicity. DBE has caused eye problems at high concentrations and EPA has expressed an interest in having it tested for neurotoxicity but, to date, no chronic testing has been conducted; NT signifies not tested. NMP has been tested and is a reproductive toxin, signified by R. 2-Butoxy ethanol causes central nervous system effects and liver and kidney problems. EPA has required testing of both acetone and IPA and both chemicals are currently in testing (indicated by IT). HCFC-123 causes benign testicular and pancreatic tumors in rats (signified by BT). HCFC-225 is undergoing testing but it is known that one of the two isomers that makes up HCFC-225 is toxic. HFC-43-10 has unknown toxicity, indicated by U; initial toxicity results indicate that the chemical has reasonably low toxicity. Methylene bromide is expected to be more toxic than methylene chloride; this is indicated with a T. Trifluoroiodomethane has unknown toxicity.

4.1.5 Other Factors in Evaluating Alternative Chemical Classes Many of the alternatives listed in Table 4-2 are being marketed in place of TCA and CFC-113 because of the imminent bans. They are being marketed alone and in formulations with other chemicals under a variety of tradenames. Table 4-3 lists all of the solvents and provides their CAS number and the other chemical or common names by which some of them are known.

As discussed earlier, many users seeking alternatives are confused by the literature and claims made by vendors. Using the information provided here, Material Safety Data Sheets (MSDSs), and product literature can often be used to determine the identity and characteristics of the major ingredient in a formulation. For instance, the chemicals that are identified as HAPs in Table 3-3 often will be listed under the "hazardous ingredients" section of the Material Safety Data Sheet (MSDS) for solvent formulations containing the chemical. Those that are not listed are either thought to be less toxic (IPA and acetone), are relatively unscrutinized (the combustible solvents, HCFC-225, HCFC-43-10 and methylene bromide) or are too new to the market (HCFC-123 and HCFC-141b). In years to come, as more is known about them, they, too, may eventually be listed.

MSDSs containing "non-hazardous" chemicals will not list the chemicals under "hazardous ingredients." In some cases, the MSDS or the product literature will identify the chemical even if it is not required. The HCFCs, in some cases, are listed on the MSDS even though they are not required to be listed. In certain

Table 4-3 Identification Methods for Potential Alternatives In Cleaning

Solvent	CAS #	Other Names
TCE	79016-	1,1,2-trichloroethylene trichloroethene
PERC	127184	tetrachloroethylene tetrachloroethene
METH	75092	dichloromethane
TCA	71556	methyl chloroform
CFC-113	76131	1,1,2-trichloro-1,2,2-trifluoroethane freon 113, FC-113
d-limonene	5989275	--
DBE[a]	1119400 627930 106650	Dimethyl Gluterate Dimethyl Adipate Dimethyl Succinate
NMP	872504	N-methyl-2-pyrrolidinone M-pyrol
2-butoxyethanol	111762	ethylene glycol butyl ether ethylene glycol monobutyl ether EGME butyl cellosolve
Acetone	67641	--
IPA	67630	propyl alcohol
HCFC-123	306832	1,1-dichloro-2,2,2-trifluoroethane dichlorotrifluoroethane
HCFC-141b	1717006	1,1-dichloro-1-fluorethane dichlorofluoroethane
HCFC-225[b]	NA	1,1-dichloro-2,2,3,3,3-pentafluoropropane (ca) 1,3-dichloro-1,1,2,2,3-pentafluoropropane (cb)
HFC-43-10	NA	1,1,1,2,3,4,4,5,5,5-decafluoropentane
Methylene bromide	NA	dibromomethane

[a] Combination of three dibasic esters
[b] Combination of HCFC-225 ca and HCFC-225cb
NA is not available

instances, other types of information can be used to identify the chemical. For example, if the literature indicates the formulation has a citrus odor, then d-limonene is probably present. If it indicates a pine odor, then it is likely to be a pine- rather than citrus-based terpene. These pine-derived terpenes are also classified as combustible solvents.

Products are being marketed that are mixtures of substances shown in Table 4-3. In some products, for instance, methylene bromide is combined with a terpene that apparently acts as a stabilizer. One MSDS for this product does not list the ingredients and, in fact, does not accurately list the decomposition products; it indicates that the products of decomposition are carbon dioxide and water when bromine gas or hydrogen bromide, which are very toxic, would be generated as well. In another case, a combination of a PFC and a combustible solvent is being marketed; since it is not required, these materials are not listed under "hazardous ingredients."

Many distributors of products containing flammable or combustible solvents claim their products are "ozone safe." This is self-evident, of course, since these materials contain no chlorine or bromine and have short atmospheric lifetimes. Indeed, their short atmospheric lifetime is the characteristic that makes them a VOC. Distributors of CFC-113, TCA and the HCFCs might very well make the claim that their chemicals are not VOCs. This claim is also self-evident.

Because of processing requirements, users may want to identify an alternative that will dry quickly without leaving a residue before it goes on to the next step in the production process. This would eliminate from consideration the combustible solvents because they have low evaporation rates. As discussed later, there are methods of removing or drying the combustible solvents more rapidly.

Users who need to remove a large amount of grease or oil would want an alternative that is a fairly strong solvent. Such users would not want to consider HFC or PFC alternatives as viable candidates since they are very poor solvents. In contrast, certain users might have a precision cleaning operation where sensitive parts require particulate removal. In such cases, the HFCs might make suitable cleaning agents.

4.2 Methods of Employing Chemical Alternatives

The equipment and methods of optimally employing the alternatives to chlorinated solvents have been the subject of intense work over the last several years. Because chlorinated solvents have been used so widely, the equipment for cleaning had been designed with their characteristics in mind. Now, with the impending bans of TCA and CFC-113, vendors had an incentive to examine alternatives and to devise equipment with which they could be used and methods by which their features could be optimized. For each alternative class, these are discussed below.

As described in Section 3, in California, the regulations are especially stringent. In some cases, firms will not be able to adopt some of the alternatives easily and others may not be able to adopt them at all. The regulatory requirements that accompany each of the alternatives are described here to provide guidance to users concerned with implementation. In many cases, the regulatory constraints may be prohibitive and the user should consider other alternatives that can be more readily implemented.

4.2.1 Flammable Solvents There are two definitions of "flammable." One of these, a chemical that has a flash point of 100° F or below, is used by local fire departments. Another, a chemical that has a flash point of 140° F or below, is used in RCRA to define ignitable hazardous waste. The former definition of the term will be used here.

Flammable solvents cannot be used alone in vapor degreasers. Ignition or combustion occurs if fuel (in this case, the flammable solvent) is heated in the presence of oxygen. The boiling point of the solvents -- which must be achieved in a vapor degreaser -- is higher than the flash point. They would spontaneously ignite before the boiling point was reached. For this reason, it is dangerous to heat the solvents at all. In this light, flammable solvents are almost always used at room temperature, either in small baths, remote reservoir cleaners or in handwipe applications.

Commonly used flammable solvents include IPA, methanol, acetone, MEK and mineral spirits. Fire departments have strict regulations on the storage and use of these solvents and they generally forbid the use of large baths of the solvents without certain safety features. In some cases, equipment manufacturers introduce nitrogen, an inert gas, into the closed cleaning system. The nitrogen displaces oxygen and ignition, because no oxygen is present, is no longer possible. Such equipment is then referred to as "inerted."

IPA, methanol and acetone are often used in small containers for dipping parts. Acetone, because it contains a ketone group, is a stronger cleaner than either of the alcohols. It is more effective in removing resin-like contaminants. IPA, because it has a lower vapor pressure than acetone, takes longer to evaporate but it still evaporates quite readily. Chlorinated solvents are used today in cold cleaning bath applications. In some applications, the flammable solvents may be technically suitable alternatives. For instance, acetone has solvency similar to that of METH and it might be a viable technical alternative. As discussed in Section 2, however, air district regulations may not allow the substitution depending on the application.

TCA and CFC-113 are the chlorinated solvents most often used in so-called handwipe applications today. The other chlorinated solvents, because of their low PELs, are more dangerous for workers. Of the flammable solvents, IPA, acetone and MEK are commonly used in handwipe applications. Small containers of the solvents are used with rags or cotton swabs to do touch-up work on parts. In some cases, the solvents are used to wipe down large or small parts prior to coating or adhesive application. In other cases, they are used to clean coating or adhesive application equipment. IPA is also often used to rework printed circuit boards. Again, the flammable solvents, with some compromises, are likely to be suitable technical alternatives in handwipe applications. As discussed in Section 2, however, the stringent regulations on the flammable solvents because they are high vapor pressure VOCs make them difficult to use.

Mineral spirits are most often used in remote reservoir cleaning units for heavily oiled parts. The units are constructed with a sink, a drain and an application wand. The solvent is applied to the part and the excess solvent and oil fall into the sink and enter the drain, which is connected to a drum of waste solvent. Natural gravity separation allows the contaminants to separate from the solvent and travel to the top of the bath. The cleaner solvent is continuously pumped from the bottom of the tank until the entire solution is "spent" or too contaminated for further use. The waste solvent is picked up and recycled on a periodic (monthly or quarterly) basis. In certain cases where chlorinated solvents are currently used to remove heavy oil from parts, mineral spirits may be a viable technical alternative.

In electronics, TCA and CFC-113 are commonly used, in combination with a small amount of alcohol, to remove flux from printed circuit (PC) boards. One alternative option being offered by vendors is to use pure IPA for this use. In general, the boards require spraying to ensure that the flux is adequately removed from under the components so a later failure will not occur. Again, as mentioned earlier, using a flammable solvent like alcohol in a spray system is very dangerous and the equipment must be inerted and should be placed in a remote location. Another option is to use terpenes in conjunction with a water rinse. The equipment for use with terpenes is also inerted for safety reasons. Terpene cleaning is discussed in more detail under the section on combustible solvents below.

The flammable solvents are all classified as VOCs. In one case, a petition has been submitted to EPA to exempt acetone from VOC regulations. In testing and atmospheric modeling, results suggest that acetone is no more reactive than ethane which is the cutoff EPA uses for classifying chemicals as VOCs. EPA plans to publish a proposal to exempt acetone in June, 1994 in the Federal Register. If the chemical is exempted by EPA, it must also be exempted by each individual air district in California.

Several issues arise in the regulatory arena when a firm attempts to convert from a chlorinated solvent to a flammable solvent. As described in Section 3, in a California air district, a firm will have to go through New Source Review (NSR) to effect the conversion. In most cases, NSR requires that VOCs be used in conjunction with Best Available Control Technology (BACT) and that emissions offsets be provided. Most air districts specify controls for cold cleaning equipment that must be met to satisfy BACT requirements. In handwipe applications, some air districts do not permit the operations (e.g. SCAQMD) and some grant permits for whole facilities that include handwipe operations (e.g. Ventura APCD).

In many cases where a facility is converting from an exempt chemical like TCA, CFC-113 or METH to a VOC, there will be emissions offset requirements. That is, the increase in VOC use may have to be offset by an equal or a larger decrease in VOC use. This offset may come from another process within the facility or it may be purchased from a second party interested in selling excess emissions. As discussed in Section 3, most local air districts have rules that specify equipment standards and the VOC content of the solvents that are allowed in operations. Depending on the location of the facility, a particular alternative may not meet the rule requirements.

Conversion to flammable solvents will also have to be approved by local fire department officials. Storage and usage requirements will have to be met. In some cases, nitrogen inerting or isolation may be necessary to protect workers adequately.

The flammable solvents, because they have flash points below 100° F, must be disposed of as hazardous waste. In handwipe applications, since these solvents are generally listed materials under RCRA (F001 or F002), the rags and cotton swabs must also be handled as hazardous waste.

4.2.2 Combustible Solvents The combustible solvents, as defined here, have flash points above 100° F. These solvents are generally fairly new to the market and have not been used widely. Historically, there was no need for them because users generally employed either the chlorinated or the flammable solvents which have more desirable technical characteristics. The combustible solvents have lower vapor pressure than the chlorinated or flammable solvents. This is an advantage in that emissions of the solvents are lower than emissions of chlorinated or flammable solvents. The lower evaporation rate can be a technical disadvantage, however, when a part needs to be completely dry to move on to the next operation immediately.

Combustible solvents that are currently being offered include dibasic esters, N-methyl pyrrolidone, certain terpenes, alkyl acetates, various mineral spirits and combinations of these materials. All of these solvents are classified as VOCs. They are often touted by the vendors as being "largely non-VOCs." This is a meaningless categorization. What is really meant is that the solvents have lower vapor pressures and they evaporate less readily. In certain applications, their emissions would be lower than the flammable or chlorinated solvents. Nevertheless, they are 100 percent VOCs.

These solvents are technically suitable alternatives to chlorinated solvents in cold cleaning bath applications. In some cases they are used alone and the part is dipped in the tank and the contaminants are removed by the combustible solvent. If the part is required to be dry immediately, the combustible solvents may not be a technically suitable alternative since they take much longer to evaporate. Methods of removing the solvents more rapidly are available. They include rinsing the part with water to displace the combustible solvent or using an air or vacuum dryer to dry the solvent from the part.

Combustible solvents are also technically suitable as alternatives to chlorinated solvents currently used for vapor degreasing. Currently, When chlorinated solvents are used, the parts emerge from the degreaser clean and dry. Combustible solvents cannot be boiled because the flash point is lower than the boiling point; like flammable solvents, these solvents would self-ignite before the boiling point was reached. The combustible solvents generally leave a residue on the part because of their low evaporation rate.

A new cleaning system -- called semi-aqueous cleaning -- has been devised to minimize the disadvantages of the combustible solvents. It involves heating a bath of the combustible solvent somewhat, but well below the flash point. The part is immersed in the bath or sprayed with the pure solvent to remove the contaminants. The part is then passed through an air knife to remove some of the solvent. It goes on to the next bath which is an emulsion of the solvent and water. The part is then rinsed in one or more baths of water to remove the combustible solvent from the part. Finally, water is dried from the part in a forced air or infrared dryer.

PC board defluxing, which is currently performed with TCA and CFC-113, can utilize the semi-aqueous process. The first bath, in this case, generally includes a high pressure spray of the solvents. Because they are combustible, the solvents are subject to spontaneous explosion if an ignition source is present. To avoid this problem, the equipment has been designed to include nitrogen inerting systems.

Another method of using the combustible solvents in place of the chlorinated solvents in vapor degreasing is to use them alone without the water. The part is dipped in a heated bath or sprayed and then vacuum dried to remove the residue of the solvent.

In handwipe operations, the combustible solvents pose some technical problems. Because of the low evaporation rate of the solvents, they will leave a residue in remote reservoir or wipe cleaning. For some parts this may not matter; for example, some cuts of mineral spirits are combustible solvents and they are used in repair and maintenance cleaning to remove gross oil. It is not necessary to have a residue-free part. In other cases, where the substrate is being prepared for coating or adhesive application, the part must be residue-free. In these cases, a second wipe operation, either with a dry cloth or a water-wet cloth, will be necessary. This can double the time to perform the operation which may not be acceptable to all firms.

An important regulatory issue arises with the use of the combustible solvents. When RCRA was first written, many of these solvents were not used widely. As a consequence, they are not listed under RCRA as hazardous wastes. The flash points of many combustible solvents are above 140° F, the cutoff level for characteristic ignitable hazardous waste. Unless the contaminants removed in the cleaning process are hazardous waste themselves, the combustible solvents do not have to be disposed of as hazardous waste.

This poses a policy issue. Many of these solvents, as discussed earlier are either known to be toxic or are unscrutinized and may be found to cause problems at a future date. Baths of the solvent and rags containing the solvent can be disposed of as sanitary waste or they may simply be poured into the sewer. These practices are not responsible, but they may be legal.

A related problem is that the combustible solvents are generally not included on other lists of toxic or hazardous chemicals. Most do not appear, for instance, on the CAA HAP list or on the SARA Title III list. Neither do they appear on California's Proposition 65 list or the Toxic Hot Spots list. For example, EPA has released a report designating NMP, a combustible solvent being marketed heavily, as a reproductive and developmental toxin. Even so, it does not appear on RCRA or any Federal or California list of hazardous or toxic chemicals. Yet the chemical can be poured into the sewer or disposed of in sanitary landfills.

As discussed in Section 3, certain air regulations do affect the combustible solvents since they are all VOCs. If a firm converts from an exempt solvent, like TCA or CFC-113 to a combustible solvent, local air district regulations may require offsets. Depending on the rules of the local air districts, the solvents may not be allowed to be used in certain applications. For example, SCAQMD Rule 1171 would forbid the use of any of the combustible solvents in substrate surface preparation processes that are part of a manufacturing process because the VOC content of all of them exceeds the allowable level of 70 g/L.

Other air district regulations for bath cleaning operations have certain requirements that must be met. These rules generally have not been revised to accommodate the transition away from ozone depleting and chlorinated solvents. For example, the rules may require equipment containing the combustible solvents to have a particular freeboard height or a refrigerated freeboard chiller. Much of the equipment appropriate for use with these solvents has not been designed with these requirements in mind.

4.2.3 HCFCs As discussed earlier, three HCFCs that are liquids at room temperature are suitable for solvent applications. These include HCFC-141b, HCFC-123 and HCFC-225. Early on, these solvents were thought to pose great promise as alternatives to the chlorinated solvents. Because they do not have flash points, they can be used in vapor degreasing processes as well as cold cleaning, printed circuit board defluxing and wipe cleaning operations. They have high vapor pressures, like the chlorinated solvents, which means they evaporate readily. HCFC-141b and HCFC-123 have good solvent cleaning capability whereas HCFC-225 has a more gentle solvency, like CFC-113.

The cleaning equipment proposed early on for these solvents was designed to be lower emitting than the equipment used with the chlorinated solvents. The boiling points of HCFC-141b and HCFC-123 are very low and the solvents would be more expensive than the other chlorinated solvents. Thus, there was effort devoted to designing equipment to minimize emissions. The equipment included very high freeboards, triple refrigeration coils and various other additions that would reduce evaporative losses.

The promise for the HCFCs has now dimmed and it is unlikely that any of the three solvents will be used in solvent cleaning applications in the U.S. HCFC-141b has an ozone depletion potential that is higher than that of TCA and production of the latter chemical is slated to be banned on January 1, 1996. It did not seem reasonable to allow users to replace one chemical with another that had a higher ozone depletion potential. EPA's SNAP regulation forbids the use of HCFC-141b in virtually all cleaning applications. Furthermore, because of its high ozone depletion capability, production of the chemical will be banned altogether in the year 2003; after that date, it cannot be produced for use in refrigeration or foam applications either.

The HCFCs, because they would eventually have widespread use, were tested voluntarily by the producers for toxicity. HCFC-123, in the chronic toxicity tests, caused benign testicular tumors in male rats and benign pancreatic tumors in male and female rats. At that stage, DuPont, the likely major producer of the chemical, lowered the allowable exposure level of the chemical to 10 ppm. This effectively prevented its sale for solvent applications. More recently, as the toxicity data have been examined, the exposure level has been increased to 30 ppm. Nevertheless, the producers do not plan to offer the chemical for use in solvent applications.

HCFC-225 is essentially a drop-in alternative to CFC-113 in terms of its physical properties. The chemical is produced as a mixture of two isomers, one of which appears to be quite toxic. One Japanese producer plans to go forward with manufacture of the chemical, pending the results of toxicity tests. U.S. producers have declined to produce the chemical. It is not clear, at this stage, whether a production process that selectively produces the non-toxic isomer is cost effective. Commercial production cannot go forward until the toxicity testing is completed and the HCFCs are slated to be banned in the next century. Because users must adopt alternatives soon due to the pending ban, HCFC-225 is not a good alternative. Its gentle cleaning capability makes it a candidate for CFC-113 replacement but it does not have strong enough solvency to replace the other chlorinated solvents in most applications.

4.2.4 HFCs The HFCs, unlike the HCFCs, do not deplete the ozone layer since they contain no chlorine or bromine. Because they contain fluorine, however, they do contribute to global warming. As discussed below, the presence of the hydrogen atom in the chemical shortens the lifetime of these chemicals substantially and they are much lower than the lifetimes of the FCs, which contain no hydrogen.

The HFCs, also because they contain no chlorine, are poor cleaning agents. Nevertheless, they do have some cleaning capability and they are likely to be used in certain niche applications. For instance, in cases where displacement drying is needed, the HFCs would be suitable. In the cleaning of movie film, which employs TCA today, an HFC will probably be used. Other precision cleaning uses, like particulate removal, may employ the solvent.

Dupont is pursuing one particular HFC, HFC-43-10, for these applications. Toxicity testing is underway and the results should be available in June, 1994. At that time, if the toxicity profile appears to be good, the chemical will become commercially available on a larger scale. DuPont has tested the chemical for film cleaning (Wolf and Jones, 1993) and it appears to be a viable alternative to TCA. Other testing has been conducted and the HFC seems to have applicability in certain specialty applications. Other manufacturers are also pursuing other HFCs but they have not been identified publicly. The hydrogen in the HFCs increases the likelihood of toxicity and the challenge is to identify an HFC that is a liquid at room temperature and has low toxicity.

HFC-4310 forms azeotropes with several other chemicals which, in the combination, could improve the cleaning capability. However, most of the chemicals it would be combined with are flammable, combustible or chlorinated solvents, and the resulting combination would have the limitations of these latter chemical classes. If the HFC were combined with alcohol, for example, the presence of the HFC might suppress flammability, depending on the amount of alcohol present, but the alcohol is still a VOC.

The HFCs are obviously not listed wastes under RCRA. Neither do they fall into the category of a characteristic waste. Thus, unless the contaminants that are removed are hazardous wastes, the spent chemical can be disposed of as sanitary waste. Again, this is probably not good public policy and the State should move to rectify this issue. Because the HFCs are expensive, recyclers will probably be willing to pay users a large fee for disposing of the chemical. They may be recycled and sold back into the market and this may be the mechanism for ensuring that proper disposal occurs.

As described in Section 3, the government has adopted the Climate Change Action Plan that will limit the growth in global warming emissions. It is so far a voluntary plan but the environmental community is committed to making it mandatory. It is likely that emissions of global warming gases will be restricted and/or taxed in the future. A tax on global warming gases would likely be set according to the global warming capability of the particular gas. For HFCs which have relatively low global warming potential compared with the FCs, the tax will be lower. Nevertheless, because the price will rise to discourage use of the chemicals, they should be used only where other options are unsuitable and they should be controlled well.

4.2.5 FCs The FCs or PFCs are fully fluorinated chemicals. Since they contain no hydrogen, their atmospheric lifetimes are very long. Whereas the CFCs have atmospheric lifetimes of about 100 years, the FCs have atmospheric lifetimes of 3,000 to 5,000 years. The major disadvantage to the use of these chemicals is that they will probably be regulated. Again, as discussed above, the form of the regulation is likely to be a tax. This tax will probably be very high for the FCs since it will be set according to the global warming potential of the chemical.

Another strong disadvantage of the FCs is that they are very poor cleaners, much poorer even than the HFCs. They may have potential use in drying or certain specialty applications but they are unlikely to be good replacements for the chlorinated solvents in most applications.

The PFCs, like the HFCs, are not listed or characteristic hazardous wastes under RCRA. They can be disposed of in sanitary landfills if they contain no hazardous contaminants. Again, because of the expense of the solvents, proper handling practices may become routine. Recyclers are likely to find the chemicals desirable.

4.2.6 BHCs Only one bromohydrocarbon, methylene bromide, is being marketed as a potential solvent. The chemical is being combined with a terpene and it is referred to as a "brominated terpene." The terpene apparently serves as a stabilizer for the methylene bromide. The mixture is volatile and does not have a flashpoint; in principle, it could be employed in existing vapor degreasers.

According to EPA, methylene bromide has an ozone depletion potential of 0.17, which is higher than that of TCA (SNAP, 1994). The chemical is also quite toxic and, in fact, is more toxic than methylene chloride, which is a suspect carcinogen. Under the SNAP Program, EPA plans to forbid its use as an alternative to CFC-113 and TCA because of its high ozone depletion potential and its toxicity. It is not likely that the chemical will be used in the future for this reason.

4.2.7 FICs Fluoroiodocarbons as a chemical class are being investigated for their potential as solvents. All of those being evaluated are straight chain compounds that are fully fluorinated except for one iodine atom. Those that are liquids at room temperature and might therefore be considered as solvents include the two-carbon chain and higher members of the class. The FICs have no flashpoints and the group investigating them is testing their cleaning capability alone and in combination with other flammable and combustible solvents.

The group that is marketing the chemicals claims that the FICs have short atmospheric lifetimes of about two days and that, because of the short atmospheric lifetimes, they do not contribute to ozone depletion or global warming. They also claim that the FICs are not VOCs because iodine has been shown to decrease lower atmospheric ozone (Nimitz, 1993). Even if this were the case, it would not mean that the radical formed after removal of the iodine atom was not photochemically reactive. The group apparently has not submitted a petition to EPA for exemption from smog regulations.

The toxicity of the FICs has not yet been examined. One source (DuPont, 1994) indicates that molecules with this structure were evaluated in the 1980s and that they showed substantial toxicity. This issue will have to be investigated before the chemicals are brought to market.

Not enough is known about the toxicity, cleaning capability or properties of these solvents to speculate on the regulations that might affect them or the end uses where they might be employed. Presumably these issues will be resolved over the next several years.

4.3 Other Solvent Classes and Class Combinations

A variety of other chemicals and combinations of chemicals are potential alternatives to the chlorinated solvents. These include monochlorotoluenes/benzotrifluorides, volatile methyl siloxanes (VMSs) and PFC/combustible solvent combinations. Each of these chemicals and the processes for using them are discussed below.

4.3.1 Monochlorotoluenes/Benzotrifluorides Monochlorotoluene (MCT) actually consists of three isomers, including parachlorotoluene, orthochlorotoluene and small amounts of metachlorotoluene. These and two other chemicals, parachlorobenzotrifluoride (PCBTF) and 3,4-dichlorobenzotri-fluoride (DCBTF), are being marketed as replacements for chlorinated solvents (Ostrowski, 1993). The atmospheric lifetimes of the solvents are being investigated to evaluate whether the chemicals should be classified as VOCs.

Some of the chemicals are flammable and the producer has added small amounts of PERC to certain of the formulations to reduce flammability. The chemicals have not been tested for chronic toxicity and they are currently undergoing short-term toxicity testing. Their structure, however, indicates that toxicity could prevent them from being marketed. EPA's SNAP rule lists these chemicals as pending substitutes; the Agency will rule on the acceptability after the toxicity testing results are available.

4.3.2 Volatile Methyl Siloxanes VMS fluids are being offered as cleaning agents for precision cleaning applications. They are apparently technically suitable for removing cutting fluids, greases and silicone fluids. The VMSs have either a linear or cyclic structure containing silicon. The VMSs are flammable or combustible and they are less aggressive solvents than CFC-113 (Burrow, 1993); as a result, they have poor cleaning capability and they would not be suitable as replacements for TCA and the other chlorinated solvents in demanding cleaning applications. Their primary facility would be in precision cleaning and drying tasks.

Studies conducted at U.C. Riverside indicate that the atmospheric lifetime of the VMS fluids ranges from 10 to 30 days. Dow, the producer of the VMSs, has petitioned the EPA to exempt the chemicals from VOC regulations. Generally chemicals must have atmospheric lifetimes of at least 2 months to qualify for exemption. Unless or until they are specifically exempted, the VMSs must be considered to be VOCs.

4.3.3 PFC/Combustible Solvent Combinations This mixture is used in a cleaning process described as Advanced Vapor Degreasing (AVD). The process has been designed to minimize the disadvantages of the two components. The PFC used in the process is a six carbon straight chain fully fluorinated chemical that has no flash point. Its cleaning capability is very poor. It is combined with a combustible solvent in a proportion that renders the combination nonflammable. The combustible solvent performs the required cleaning and the PFC displaces the combustible solvent (which does not evaporate readily), leaving a clean and dry surface.

This combination solvent is being marketed for use in existing and modified vapor degreasers; it is a potential alternative to the chlorinated solvents in vapor degreasing applications. It apparently can be heated to its boiling point since it is not flammable. It is not clear whether the mixture is a true azeotrope; that is, a solution where the composition of the liquid and vapor is identical. If it is not a true azeotrope, there could be selective evaporation of the more volatile component --

in this case, the PFC -- leaving a combustible solvent at a temperature that exceeds its flash point. This would be a dangerous situation.

The disadvantage of this blend is that the PFC is a strong global warming gas with an atmospheric lifetime of some 3,000 years; it is likely to be regulated eventually for this reason. The EPA SNAP rule restricts PFC uses to certain applications. The combustible solvent, like other combustible solvents, has a flash point and is a VOC; it also has unknown toxicity. Because one of the components is a VOC, an air district permit may be difficult to obtain in most areas in California. The combination is probably not classified as hazardous waste unless the contaminants that have been removed are so classified. The blend is very expensive and, unless it is used in very tight equipment, would be a very high cost option.

SECTION 5:
PROCESS ALTERNATIVES TO CHLORINATED SOLVENTS

There are a variety of alternative processes that can be substituted for chlorinated solvents in cleaning applications. Some of these processes are applicable to only a very small portion of the market. They are discussed here and their advantages, disadvantages and applicability are presented.

5.1 No Clean Technologies

This category includes a range of different methods and technologies that make cleaning unnecessary. Generally, these techniques are process specific and careful matching of characteristics or process control is required. It is likely that there are many more operations that could utilize these technologies but the option is not readily seen and implementing it might require substantial effort. Several instances where cleaning is unnecessary are described below.

5.1.1 Use of Fluids Not Requiring Removal An alternative to cleaning is to use products that have been specifically designed to be compatible with subsequent processing steps and not interfere with the operations so the cleaning step can be eliminated. Oil based products are available that can be designed to be welded over, vaporized in processing or to have paint compatibility. So-called vanishing oils are generally based on mineral spirits containing metal working additives. The light residue from the lubricant provides short-term rust protection and often, the parts can be welded, brazed and painted without cleaning. Some water-based lubricants can be painted over without cleaning or they can be put through welding and brazing systems without cleaning. There are many waterborne paint systems that are compatible with water-based lubricants (Landers, 1993).

This option is technically applicable in cases where oil is added to parts to perform certain operations. Whether or not it is technically suitable is obviously case specific. Users must be willing to pursue this alternative rather than to assume that cleaning is necessary. This method is obviously not suitable for "job shop" types of operations where the parts come to the shop containing the contaminants.

5.1.2 Use of No-Clean Flux This option is applicable in PC board defluxing operations. Today, rosin-based fluxes are often used to prepare the boards for soldering. The components are soldered to the boards and the flux is commonly removed with either a CFC-113 or TCA formulation containing alcohol. The alcohol is necessary since flux is ionic and the solvents, by themselves, would be unable to remove it.

Historically, no-clean flux contained aggressive halide activators that could lead to later board failures; users understandably were cautious about adopting them. Today, there are many less aggressive fluxes and they are being adopted increasingly. The so-called no-clean fluxes are actually low-solids fluxes which contain between about 3 and 5 percent solids. This is in contrast to traditional rosin fluxes which contain 25 or 30 percent solids. The thesis is that the low solids in the no-clean flux can be left on the board and need not be removed, making cleaning unnecessary.

Many users in the commercial sector are investigating and adopting no-clean fluxes. They have been difficult to use since stringent process control is required. However, many of the bugs have been and continue to be worked out. Many industry experts believe that the future of PC board manufacturing lies in the use of no-clean flux. The major resistance to adopting the flux comes from the military sector which is often still wedded to the use of rosin based flux with solvent cleaning. As this sector shrinks, the trend to no-clean is likely to become more pronounced.

5.1.3 Fluxless Soldering A new technology called ROSA (reduced oxide soldering activation) is being investigated; its use would eliminate the cleaning requirement for PC boards (Hwang, 1994). One of the major reasons flux is added to boards is to prevent oxidation of the tin, tin/lead or copper surfaces. With the ROSA technique, the oxides are removed by processing them in an aqueous solution containing highly reducing vanadous ions that can be continuously regenerated by an electrochemical process in a closed-loop system. No flux residue needs to be removed and cleaning is unnecessary. This technology is still in the development stage.

Another emerging technology, PADS (plasma assisted dry soldering), uses fluorine radicals to remove surface oxides of the boards (Hwang, 1994). The source of the fluorine is either carbon tetrafluoride or sulfur hexafluoride. The fluorine free radicals react with the oxides, forming a passivation film. As the solder melts, the film breaks apart, exposing the clean metal substrate that is now ready for wetting. This process, like the ROSA process described above, makes flux application and cleaning unnecessary.

5.1.4 Not Adding Contaminants Some processes can be accomplished without the addition of the contaminants that later require removal. Each process must be examined on a case-by-case basis to determine whether it can be changed sufficiently to make cleaning unnecessary.

In one case, for instance, a firm was joining a backing to a PC board metal heat sink. The backing was used to hold the sink steady during the stamping process and to prevent damage to the table underneath. A vapor degreasing process was the next step and it separated the backing from the stamped sink. When the assemblies were put on the coffee maker in the facility, the backing readily separated from the sink. It was concluded that the heat from the vapor in the degreaser was separating the backing from the sink and that a small oven could replace the large degreaser.

5.1.5 Vacuum Deoiling In this process, oil is removed from parts by placing them in a vacuum chamber with hot walls (Littlefield, 1991). The chamber is evacuated to remove oxygen and to degas the oils. It is then backfilled to a low vacuum -- in the 50 to 100 mm Hg range -- with nitrogen or another inert gas. An internal gas circulator is used to heat the parts by forced convection heating from the preheated chamber shell. After the parts reach the required temperature, the chamber is evacuated to 10 to 30 mm Hg. It is then backfilled with nitrogen or another inert gas. The parts are unloaded and put back into production.

The oil vaporizes from the part surfaces as the chamber pressure is reduced. It is drawn out the vacuum line to an oil condenser which is later heated, driving off the oils. The oils can then be reused or sold back to the supplier.

The vacuum deoiling method is suitable for parts contaminated with grease and oil. It may not be suitable for parts that have additional or other contaminants. Although this process eliminates the need for cleaning, the capital investment in the required equipment can be quite high. Both horizontal and vertical design chamber configurations are available.

5.2 Cleaning With Other Media

In some instances, solid media or inert gases can be substituted for traditional solvents for cleaning.

5.2.1 Absorbent Cleaning This technique involves using absorbent media rather than solvents for removing oils from parts. Boeing has been investigating various media, including wheat starch, walnut hulls, corn cobs, rice hulls and sponge jet foam, for removing machining and forming lubricants and hydraulic fluid from aluminum parts. The method uses, in some cases, a blast cabinet to apply the media. The work is on-going and the initial effectiveness was less than anticipated (Golden, 1993).

5.2.2 Supercritical Carbon Dioxide This method utilizes carbon dioxide at its supercritical point (very high pressure) to remove contaminants from parts. At the supercritical point (31° C and 74 bars pressure), carbon dioxide -- normally a gas at room temperature and pressure -- exhibits liquid-like densities and liquid-like properties. At this stage, it is a good solvent for nonpolar or slightly polar compounds. It also has gas-like characteristics which leads to improved mass transport and no surface tension. As a consequence, it can penetrate blind holes and crevices to effectively remove oils and other nonpolar contaminants. The method has been used for many years in extraction processes including caffeine and hops extraction and has, for the last few years, been investigated as an alternative to solvents in cleaning.

The method is not suitable for cleaning parts with hermetically sealed items since the high pressures required to achieve the supercritical point crushes them (Hale, 1992). Polar contaminants, like solder flux, are difficult to remove with the method. In principle, a cosolvent that is polar, like water or alcohol, might be combined with the carbon dioxide for polar contaminant removal. The two-component process would be very complex, however, and it has not been investigated fully. Supercritical carbon dioxide is not suitable for removing particles but liquid carbon dioxide may be technically suitable for this purpose (Hale, 1992).

Carbon dioxide is compatible with many metals including stainless steel, copper and gold, porous metals and silica and alumina ceramics. Compatibility with polymeric and composite materials must be determined on a case-by-case basis (CF, undated).

The advantage of the system is that the contaminants are the only remaining process residue that require disposal. The carbon dioxide can be separated from the oils by pressure control since carbon dioxide is a gas at ambient pressure and the contaminants are liquids or solids. The carbon dioxide, free now of the contaminants, can then be recycled and reused in the next operation.

This method is most applicable to cleaning high value, small parts contaminated with nonpolar contaminants. It is only suitable for batch operations since pressurized vessels are required. Small systems exceed $100,000 in cost so the process must be high value. One application where the process is being implemented is for removing organic contaminants from plutonium parts (Hale, 1992). This method allows the removal of the oil without generating another mixed hazardous/radioactive waste requiring disposal.

5.2.3 Carbon Dioxide Snow Two methods of using carbon dioxide snow are possible. The first method uses pressurized liquid carbon dioxide to remove sub-micron particles and other contaminants from precision parts and assemblies like disk drive components and subassemblies, optics, semiconductors and medical devices. In these applications, the carbon dioxide is passed through a specially designed nozzle to create a mixture of dry ice snow crystals and carbon dioxide gas. The jet is directed to the surface of the part requiring cleaning. The snow crystals sublime (convert to a gas) and the carbon dioxide gas carries away the contaminants, leaving no residue. Some of the systems are small, hand held manual systems and others are fully automated computer-driven and integrated into the process.

Particles and thin films of hydrocarbon and silicone oils have been successfully removed using this technology. The cost of these systems ranges from $1,000 to several thousand dollars depending on the complexity of the system required.

The second method of using carbon dioxide is designed for large, heavily contaminated industrial equipment. These systems can perform manufacturing-related cleaning without disrupting production. In-place production equipment and tooling can be cleaned without the need for disassembly. The high pressure units designed for this purpose have been used to clean manufacturing equipment like robots, rollers, mixers and conveyors; in-place molds; continuous web production equipment; and electrical panels and controls (Alpheus, undated).

There are two possible disadvantages of carbon dioxide snow systems. The first is that the technique is line-of-sight so it is not suitable for parts with contaminants that must be removed from crevices, blind holes or other inaccessible locations. The second is that carbon dioxide, a greenhouse gas, is emitted to the atmosphere. The carbon dioxide used in these processes is taken from other processes that emit carbon dioxide so use of the method does not increase carbon dioxide emissions. Nevertheless, it is possible that a local air regulatory agency might eventually place controls on the level of carbon dioxide emissions under their jurisdiction.

A distinct advantage of the method is that the only hazardous waste resulting from the process is the contaminants that have been removed. When liquid solvents, water or media are used for cleaning, the cleaning agent can become hazardous waste and it will require disposal. In this case, since the carbon dioxide sublimes, the only material requiring disposal is the removed contaminants.

5.2.4 Nitrogen In some cases, hot and/or pressurized nitrogen can be used for cleaning in place of solvents. It is especially applicable when particles or low levels of organics require removal from confined spaces like pipes, tubes or other assemblies. Chlorinated solvents have commonly been used for flushing in these operations.

One example is the engine testing performed by a large aerospace firm. This firm used TCE for flushing shuttle engines after testing. Many alternatives were tested, including water formulations which offered promise. In the end, however, the firm was able to demonstrate that heated and pressurized nitrogen was capable of removing the organic contaminants that coated the inside of the engine chambers as unburned or burned fuel residue (O'Rourke, 1993). Use of nitrogen was a better option than water. The nitrogen, since it is a gas, can be easily separated from the organic contaminants and these contaminants are the only waste.

Other examples where this technique might be applicable include tube cleaning where particles and organics require purging. An aerospace subcontractor historically flushed tubes containing small amounts of oil from the fabrication process with CFC-113. After the CFC-113 was used to remove the organics, the tubes were dried with nitrogen. Nitrogen alone was found to be a suitable alternative for both the cleaning and drying, which allowed the firm to avoid the use of water.

In PC board defluxing, inert gas soldering with nitrogen is increasingly being adopted by firms. Flux is generally added to the PC boards prior to soldering to prevent oxidation of the board. Inert gas soldering involves using a nitrogen atmosphere and only a very small amount of flux to prevent the oxidation. The oxygen is evacuated from the system and is replaced with nitrogen; this prevents the board from being oxidized during the soldering process. Virtually no flux is applied to the board and cleaning of the flux after the process is not necessary.

5.2.5 Spectroscopic Cleaning Methods of cleaning that utilize the interaction of light with surfaces are being investigated. Some of these are currently being used in paint stripping applications; they are less appropriate for cleaning. Lasers and flashlamps are being evaluated. The principle is that the surface contaminants will absorb the light of a particular frequency and the substrate material will not. The contaminants absorb the light and decompose and the surface is clean. The advantage of this method is that the amount of waste generated, as was the case for carbon dioxide snow, is minimized and limited to the decomposed contaminants.

There are several disadvantages to using this method in cleaning. First, the contaminants could decompose to yield harmful materials and worker exposure to the dangerous substances would have to be prevented. Second, in certain instances, the technology itself would pose a danger. Lasers, for example, might have to be used with automated equipment. Third, substrate damage could occur if the frequency of the light is not chosen judiciously. Fourth, the technique is a line-of-sight method and is not suitable for parts with complex geometries.

SECTION 6:
WATER-BASED CLEANING

In Section 4.0, a generic classification scheme for evaluating and selecting a suitable chemical alternative was described. When users are presented with a new chemical being marketed by a vendor, that chemical can be placed into a generic chemical class. Given a knowledge of the chemical class into which an alternative falls, the user will also know many of the properties of the chemical and the environmental problems posed by the chemical. The user can then eliminate chemicals from further consideration easily or, with a knowledge of the limitations, can conduct testing on a limited number of chemical alternatives.

In most vapor degreasing and cold cleaning applications where chlorinated solvents are used today, water-based cleaners are suitable alternatives and solvents need not be evaluated at all. In fact, IRTA's field experience suggests that perhaps as many as 95 percent of the bath cleaning operations using chlorinated solvents today could be converted to water. In a substantial fraction of the handwipe applications, water is likely to be appropriate as well. Because water-based cleaners allow users to avoid the use of traditional solvents, they are "better" than chemical alternatives because their use minimizes environmental and human health problems. Only in cases where the process is water-intolerant from a technical standpoint should chemical alternatives be considered.

Firms are often reluctant to consider water alternatives. They have used solvents for years and they simply do not believe that water -- even with the proper additives -- can effectively clean parts. These users are strongly biased in favor of solvents. If there were a safe solvent with virtually no environmental problems that had the physical properties of the chlorinated solvents, then this bias would be justified. There is not now and there will not be a "drop-in" solvent alternative. This means that a compromise must be made and that compromise might as well be made with water.

There are hundreds and perhaps even thousands of water-based cleaning formulations being offered by vendors. Firms often spend large amounts of time and significant resources testing tens or hundreds of water cleaners. This section describes a systems approach to choosing a water based cleaning formulation that will reduce the number of cleaning formulations that require testing. It allows the user to select only those cleaners that appear to be the most environmentally sound and to conduct testing on only a few cleaners. This minimizes the time and resources required to effect the conversion.

6.1 The Cleaning Process

In general, users want to remove contaminants of various types from their parts so they can perform subsequent operations. These operations include fabricating metals, plastics or other substrates, plating, anodizing, chem filming, and applying adhesive or coating. In other cases, cleaning is the last step in the fabrication process before the product is sent for display or to customers. Contaminants requiring removal are numerous; they include oils, dirt, grease, flux, particulates, fingerprints and metal fines.

In some instances, as discussed in earlier sections, when users reevaluate their processes, they may find that cleaning is not necessary at all. Some parts that are cleaned using solvents today may simply not be dirty; others may require only a simple surface wipe with a rag. In other instances, users may be able to adopt various other technologies. One example is the use of no-clean flux for printed circuit boards. In still other instances, water alone may be capable of cleaning the parts sufficiently. The pressure, for example, of a wet rag in a handwipe operation may be adequate to remove particulates from a part.

In cases where more aggressive cleaning is required, water-based formulations or solvents will be required. A general rule is that "like" removes "like." That is, ionic contaminants like fingerprints or flux are best removed with alcohol or water which are ionic solvents. Oils, which are organic in nature, are often best removed by organic solvents. Water can be used to remove oils, however, if surfactants that make the oil and water miscible are added. Wetting agents in water-based cleaners will allow the cleaner to penetrate and loosen the bond between the contaminant and the substrate by lowering the surface tension. Once wetting occurs, the oil droplets are coated with a thin film of surfactant which prevents them from redepositing on the substrate. Thus water-based cleaning agents can be formulated to contain additives that will remove both ionic contaminants and organic contaminants.

6.2 Water Bath Cleaning Processes

In general, water cleaning bath operations require at least two stages and, in many cases, three or more. The first stage is the cleaning step. More than one cleaning stage may be required depending on the extent and type of the contamination. The second stage is the rinse stage. Because the water cleaning formulations contain additives, these additives must be rinsed from the parts. More than one rinse step may be required depending on the cleanliness requirements. The third step is drying. In some cases, the parts may not require drying if the next processing step is aqueous-based, like plating or anodizing.

Mechanical methods can be combined with water cleaning formulations for better effectiveness. It is the mechanical action in the cleaning process that will help to remove particulates and metal fines through displacement. Mechanical action of the appropriate kind will also increase the removal rate of organic and ionic contaminants. As discussed later, the proper kind of equipment and fixturing for a specific operation is essential.

Five variables are important in the cleaning process. The first variable is the amount of the concentrate or the additives in the cleaner. The second variable is the temperature used in the cleaning bath. The third variable is the cleaning time. The fourth variable is the mechanical action used in the cleaning process. The fifth variable is fixturing. Each cleaning application requires the optimization of these variables for the specific process.

A typical cleaning process with water would be operated as follows. One part concentrate is diluted with ten parts tap water in the cleaning chamber. The formulation is heated to between about 110 and 170° F, depending on the soil and substrate. The parts to be cleaned are placed in a basket and cleaned. Depending on the type of equipment, the parts might be spray-in-atmosphere cleaned, submerged and agitated vertically or horizontally or sprayed under immersion. The cleaning cycle might take 1 to 10 minutes. The parts are removed and placed in the rinse chamber where again, they may be spray rinsed or immersion rinsed. This activity may require 3 minutes. The parts may then go on to be further processed or they may be dried. A variety of drying mechanisms including hot air drying, infrared (IR) drying or vacuum drying are available.

The rinse bath can generally be plumbed directly to the sewer. The rinse bath contains only small amounts of contaminants which have been largely removed in the cleaning bath. It also contains only small amounts of the additives from the cleaning concentrate. A sanitation permit will most likely be required to release this water to the sewer. As discussed earlier in Section 2, the requirements of each local sanitation district differ depending on the other streams the POTW is receiving. Another option is to use the first rinse as makeup water for the wash bath; water evaporates slowly and must be replaced periodically. The second rinse can then be used as makeup for the wash bath and so on. Only the final rinse, in this case, would be plumbed to the sewer. Yet another option is to close loop the rinse bath; this would require filtration.

The wash bath is used continuously to clean parts. The water cleaning formulations used for cleaning parts are generally alkaline; that is, they have a pH above 7. When the concentrate in the wash bath becomes depleted, more must be added to ensure good continuing cleaning capability. Distributors often supply users with a test kit that measures the alkalinity of the wash bath. If the concentrate is depleted, the user adds more concentrate to increase the concentration to the required pH or alkalinity level.

As parts move through the equipment, the cleaning formulation eventually becomes contaminated. Common contaminants that are removed include oils of all kinds and particles. A filter can be used to remove the particles from the wash bath. For many operations not requiring precision cleanliness, an oil skimmer can be used to remove the oil from the cleaning bath. Two types are available: a disc skimmer and a belt skimmer. If more stringent cleanliness standards for the oil must be met, then coalescers, filtration devices or ultrafiltration methods should be considered. These methods can be used continuously and the cleaner should be tested with the filtration method to ensure that filtration will not remove the active ingredients (surfactants, for instance) in the water formulation as the water passes through the filter.

An oil skimmer operates when the cleaning process is not operating. With certain water cleaners that are properly formulated, the oil rises to the top of the wash bath and the oil skimmer skims the oil from the surface. The oil is placed in a separate container, perhaps a drum, and it can be recycled or disposed of as hazardous waste. Even with the continuous oil removal, the wash bath eventually becomes too contaminated for further use. The timeframe varies and can range from 3 months to a year, depending on the contaminant loading in the particular process. At this stage, if the bath is hazardous waste, it should be disposed of properly. Generally, the wash bath will be hazardous waste if the pH is very high, if the cleaner contains solvent additives that are listed wastes or if the removed contaminants are listed wastes. Such cleaning baths rarely contain heavy metals which would also render them hazardous waste.

The cleaning process will vary depending on the type of equipment and the type of processing that the specific operation requires. For example, if a user has a conveyorized cleaning unit, then the parts move through the wash, rinse and dry chambers continuously. The equipment may contain multiple wash and rinse stages and ultrasonics or manifolds for fixturing.

6.3 Handwipe Cleaning Processes

So-called handwipe operations include traditional wipe cleaning that is performed with a cloth, rag or cotton swabs to remove contaminants from a part during the manufacturing process or prior to coating or application of an adhesive. It also includes repair and maintenance cleaning that is often performed with remote reservoir units today. The part is flushed to remove oil or other contaminants in a sink and the contaminated solvent is drained to a waste drum. Water formulations can be used for wipe cleaning in many instances. Equipment manufacturers are offering plastic or stainless steel remote reservoir units for use with water cleaning formulations.

6.4 Choosing a Water-Based Cleaner Water cleaning formulations are commonly offered in concentrate form. The concentrate contains the wetting agents, the surfactants, the builders that give it alkalinity, and other additives required for cleaning. The concentrate is diluted with water in accordance with the cleaning requirement. Most vendors recommend diluting to a concentration of 3 to 30 percent, depending on the demand of the cleaning task. For light cleaning applications, a solution containing 5 percent of the concentrate may be sufficient; for heavy oil contamination or heavy uncured resin residue, a 30 percent solution of the concentrate may be necessary. It is in the users' interest to dilute the concentrate as much as possible so the cost will be lower.

Many water-based cleaning formulations contain large amounts of solvent additives. Common additives include ethylene glycol ethers, propylene glycol ethers and terpenes. As indicated earlier, these solvents fall into the "combustible solvents" category and are classified as VOCs. Some of the glycol ethers are listed hazardous wastes. Terpenes are not listed hazardous wastes because they were not employed for cleaning when RCRA was written.

Certain of the glycol ethers have been found to cause birth defects. Another glycol ether -- 2-butoxy ethanol (also called butyl cellosolve) -- that is used widely in water based cleaners poses health problems and is likely to be regulated more stringently in the future. It is on the Hazardous Air Pollutant (HAP) list in Title III of the CAA Amendments, it is on the SARA Title III list and it is on the Toxic Hot Spots list in California. The propylene glycol ethers are a new class of glycol ethers and the distributors refer to them as the "good" glycol ethers. The reason they appear to be "good" relative to the other glycol ethers is that they have not been tested for chronic toxicity and there is no requirement for the manufacturers to do so. EPA is considering adding the propylene glycol ethers to the HAP list.

D-limonene, one of the major ingredients of terpene formulations, is sometimes employed in water-based cleaners as a solvent and sometimes for aroma. This chemical, and indeed all other terpenes, is extremely photochemically reactive. Moreover, EPA is concerned about the aquatic toxicity of the terpene family. The chemicals are very biologically active and environmental and human health problems associated with their use may emerge in the future.

Other "combustible" and "flammable" solvents are often added to water-based cleaners to improve their solvent action. Possible additives include NMP, DBE and alcohols of various types. Generally, for most cleaning applications, water formulations without solvents can be used successfully if the proper concentration, temperature, mechanical agitation and fixturing is employed. Thus, there is no reason to adopt a water-based cleaning formulation that contains solvents. In fact, one of the reasons for choosing a water-based cleaner is to avoid the use of solvents. The solvents increase worker exposure, cause smog, may require reporting if they are listed chemicals and may cause the spent formulation to be classified as hazardous waste.

Many distributors are offering water-based cleaners with very high pH, above about 12. Some of these cleaners have traditionally been used for etching and brightening applications by platers. They are not appropriate as substitutes for chlorinated solvents in the vast majority of cleaning applications. Formulations with much lower pH, in the 7 to 11 range, can usually be used effectively. A lower pH will reduce worker danger, may qualify the depleted wash bath for sewer release, and will keep the bath from being classified as hazardous waste from a pH standpoint alone. In California, if a user wants to neutralize an aqueous-based hazardous waste (before sewer release or off-site shipment), a hazardous waste treatment permit will be required. To avoid these problems and because many good, low pH cleaners are available, users should certainly screen out high pH formulations and not evaluate them further.

6.4.1 Cleaner Selection Procedure When firms are evaluating alternative cleaners, they should ask the distributor for a Material Safety Data Sheet (MSDS). In the case of water-based cleaners, the MSDSs are not particularly revealing. They can be used to quickly screen out cleaners that are not appropriate, however. To demonstrate how the screening evaluation might work, five MSDSs for aqueous based cleaners are included here. The names of the actual products are deleted and the names of the cleaners will be designated as Water Cleaning Formulation (WCF)-1 through -5.

WCF-1 is a multi-metal safe alkaline cleaner. Under the category of "Physical Data", the pH of a 1 % solution is listed at 11.9 and the pH of the concentrate is listed as greater than 13. This is an extremely high pH and, if the chemical were

WCF-1

MATERIAL SAFETY DATA SHEET

I - PRODUCT IDENTIFICATION

COMPANY NAME:

ADDRESS:

Tel No:
Nights:
CHEMTREC:

PRODUCT NAME:

Product No.:

Synonyms: Multi-Metal Safe Alkaline Cleaner

II - HAZARDOUS INGREDIENTS OF MIXTURES

MATERIAL: (CAS#)	% By Wt.	TLV	PEL
Potassium hydroxide (1310-58-3)	<10	2mg/m3 (ceiling)	2mg/m3 (ceiling)
Sodium metasilicate (6834-92-0)	<10	ne	ne

III- PHYSICAL DATA

Vapor Pressure, mm Hg: Like water
Evaporation Rate(ether=1): N/A
Solubility in H2O: Complete
Freezing Point F: 32
Boiling Point F: > 212
Specific Gravity H2O=1 @25C: 1.11

Vapor Density (Air=1)60-90F: Like water
% Volatile by wt @ 105C/2 hrs 70%
pH @ 1% Solution 11.9
pH as Distributed: >13
Appearance: Clear, straw liquid
Odor: Slight detergent odor

IV - FIRE AND EXPLOSION

Flash Point F: >200 F

Flammable Limits: N/A

Extinguishing Media: Product is not flammable or combustible. Use media appropriate for the primary source of fire.

Special Fire Fighting Procedures: Use caution when fighting any fire involving chemicals. A self-contained breathing apparatus is essential.

Unusual Fire and Explosion Hazards: None known.

V - REACTIVITY DATA

Stability - Conditions to avoid: None known.

Incompatibility: Acids, oxidizers.

Hazardous Decomposition Products: CO, CO2, oxides of nitrogen.

Conditions Contributing to Hazardous Polymerization: Product will not polymerize.

VI - HEALTH HAZARD DATA

EFFECTS OF OVEREXPOSURE (Medical Conditions Aggravated/Target Organ Effects.

A. ACUTE (Primary Route of Exposure) EYES: Causes burns. Mists of use dilution cause irritation. (Primary Route of Exposure) SKIN: May cause severe irritation or burns. INHALATION: Mists extremely irritating to mucous membranes, upper respiratory tract. INGESTION: Corrosive to mouth, throat and stomach.

B. SUBCHRONIC, CHRONIC, OTHER: None known.

VII - EMERGENCY AND FIRST AID PROCEDURES

EYES: Flush with plenty of water for at least 15 minutes. Get immediate medical attention. SKIN: Wash with soap and plenty of water for at least 15 minutes while removing contaminated clothing. If irritation persists, get medical attention. Wash clothing before reuse. INHALATION: Remove to fresh air. If irritation persists, get medical attention. INGESTION: Do not induce vomiting. Give 1 or 2 glasses of milk or water to dilute. Get immediate medical attention.

VIII - SPILL OR LEAK PROCEDURES

Spill Management: Contain spill. Neutralize with dilute acid and take up on inert material for disposal. Flush residue to sewer with plenty of water.

Waste Disposal Methods: Unused material is hazardous waste (D002, characteristic of corrosivity) due to high pH.

IX - PROTECTION INFORMATION/CONTROL MEASURES

Respiratory: Not normally required	Eye: Chemical splash goggles and face shield	Glove: Rubber

Other Clothing and Equipment: Rubber apron and rubber boots

Ventilation: Local exhaust ventilation recommended to maintain air concentrations below established limits.

X - SPECIAL PRECAUTIONS

Precautions to be taken in Handling and Storing: Do not get in eyes, on skin or on clothing. Do not breathe mist. Wear goggles, gloves and protective clothing when handling. Wash thoroughly after handling.

Additional Information: Use only in well-ventilated areas that will maintain air levels below established limits.

Prepared by:

Revision Date: 01/29/93

Seller makes no warranty, expressed or implied, concerning the use of this product other than indicated on the label. Buyer assumes all risk of use and/or handling of this material when such use and/or handling is contrary to label instructions.

While Seller believes that the information contained herein is accurate, such information is offered solely for its customers' consideration and verification under their specific use conditions. This information is not to be deemed a warranty or representation of any kind for which Seller assumes legal responsibility.

used at about 10 percent concentrate, which is appropriate for many cleaners, the pH would likely exceed 12. A pH above 12.5 would cause the cleaner to be classified as hazardous waste. Furthermore, the high alkalinity poses a safety problem and other cleaners with lower pH are available.

WCF-2 is an alkaline cleaning liquid. Under the category "Physical Data," the MSDS indicates that a 1 % solution is alkaline. It is irresponsible of the distributor to not list the actual pH at that dilution or to specify the pH of the concentrate. A clue to the fact that the pH of this cleaner is likely to be very high can be found under the category "Disposal, Spill or Leak Procedures." Under "Waste Disposal Method," the MSDS indicates that dilute working solutions must be neutralized before they are released to the sewer. It also indicates that the unused concentrate must be disposed of at an "approved dumpsite" which probably means that it is classified as hazardous waste. The pH of the concentrate is likely to be high and the cleaner should be rejected for this reason.

There is another reason to reject this cleaner. Under the category of "Hazardous Ingredients," an unspecified glycol ether is listed. In this section of an MSDS, distributors are required to list chemicals that are specified on any one of three lists of chemicals that pose health problems. The glycol ether in the cleaner could be butyl carbitol, which is in the same family as 2-butoxy ethanol; as discussed earlier, many water cleaning formulations contain one of the two chemicals.

WCF-3 is an immersion cleaner. Under the "Physical Data" category, the pH of the concentrate is listed as 12.4 which is fairly high. Of more concern, however, and the major reason to reject this formulation, is the presence of 2-butoxy ethanol under the "Ingredients" category. The MSDS indicates that 2-butoxy ethanol is present at less than 20 % in the concentrate. It is likely present at just under 20 percent. The VOC in the concentrate, according to a calculation apparently performed by the vendor, is listed at 206 grams per liter; at an 8 to 1 dilution level, the VOC content is 23 grams per liter of material.

As discussed in Section 2, the SCAQMD provides an exemption from permitting for cleaning units using water cleaning formulations containing less than 2 % VOC (or approximately 20 grams of VOC per liter of material). The reason for this exemption is to encourage the adoption of formulations without solvent additives. At the 8 to 1 dilution rate, WCF-3 would have 23 grams of VOC per liter of material; it would not meet this cutoff level and would require a permit. At least one other air district in California is planning to adopt this permit exemption and it allows firms to avoid the permitting process and the fees associated with it. As this trend continues across the nation, there will be a real advantage to adopting cleaners that do not contain solvent additives.

WCF-4 is an immersion cleaner. The MSDS does not list the pH. Under the category "Physical/Chemical Characteristics," the MSDS indicates that the cleaner has a citrus odor. This indicates the presence of orange-based terpenes. The terpene may be present in small quantities merely for aroma or it may be present in higher concentration to act as a solvent. In either case, the cleaner should be rejected because it contains a VOC solvent that is not necessary.

WCF-2

MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION

January 30, 1989

MANUFACTURER'S NAME	REGULAR TELEPHONE NO. EMERGENCY TELEPHONE NO.
ADDRESS	
TRADE NAME	
SYNONYMS	NONE
SHIPPING NAME	DOT: COMPOUND, CLEANING, LIQUID, NOS IATA:

II HAZARDOUS INGREDIENTS

MATERIAL OR COMPONENT	CAS NO.	%	HAZARD DATA
GLYCOL ETHER	112-34-2	< 6	Irritant, TLV=50ppm
METHOXYLATED THIOETHER	9004-83-5	< 15	Irritant, TLV=3.3mg/M

III PHYSICAL DATA

BOILING POINT, 760 MM HG	Not determined	MELTING POINT	N.A.
SPECIFIC GRAVITY (H_2O = 1)	1.00	VAPOR PRESSURE	Nil
VAPOR DENSITY (AIR = 1)	< 1	SOLUBILITY IN H_2O % BY WT	Complete
VOLATILES BY VOL.	5	EVAPORATION RATE (BUTYL ACETATE = 1)	>1
APPEARANCE AND ODOR	Clear liquid	PH (1%SOLN>)	Alkaline

IV FIRE AND EXPLOSION DATA

FLASHPOINT (TEST METHOD)	N.A.	AUTOIGNITION TEMPERATURE	N.A.
FLAMMABLE LIMITS IN AIR. % BY VOL. N.A.	LOWER		UPPER
EXTINGUISHING MEDIA	Water, CO2, dry chemical		
SPECIAL FIRE FIGHTING PROCEDURES	Wear protective clothing and a self-contained breathing apparatus.		
UNUSUAL FIRE AND EXPLOSION HAZARD	NONE		

V HEALTH HAZARD INFORMATION

ROUTES OF EXPOSURE	
INHALATION	May cause irritation to the respiratory tract.
SKIN CONTACT	May cause irritation or slight burn, dryness and/or dermititis from excessive contact.
SKIN ABSORPTION	See skin contact above.
EYE CONTACT	Can cause severe eye irritation or burns if not immediately treated. See First Aid section below for treatment.
INGESTION	Can cause irritation and burning of the digestive tract. May also cause nausea, vomiting, cramps, or diarrhea.

EFFECTS OF OVEREXPOSURE	
ACUTE OVEREXPOSURE	Skin, eye, mucous membrane irritant.
CHRONIC OVEREXPOSURE	Dermititis, chemical pneumonitis, diarrhea, severe eye burns.

EMERGENCY AND FIRST AID PROCEDURES

EYES:	Flush with a lot of water for 15 minutes, holding eyelids away from eyeball. Be sure to flush under lower and upper eyelids during this flushing. Remove contact lenses. Contact a doctor.
SKIN:	Wash well with soap and water. Remove contaminated clothing and shower. Contact a doctor if irritation develops.
INHALATION:	Remove to fresh air. If breathing is difficult, give artificial respiration and take to a hospital. If not breathing, give artificial respiration and take immediately to a hospital.
INGESTION:	Do not induce vomiting. Drink 1 quart of water or milk and take to a hospital.

VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY

NONE

COMPATIBILITY

STRONG ACIDS, OXIDIZABLE MATERIALS

HAZARDOUS DECOMPOSITION PRODUCTS

NONE

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

NONE

VII DISPOSAL, SPILL OR LEAK PROCEDURES

AQUATIC TOXICITY (E.G. 96HR TLM)

NO DATA AVAILABLE.

WASTE DISPOSAL METHOD

Used concentrate product should be hauled away to an approved dumpsite. Dilute working solutions may be discharged to sewer after neutralizing pH to an acceptable range in most areas. If you are unsure of local regulations contact your local Industrial Sanitation Department or your ICP representative.

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

Dike spill to prevent from entering waterways or sewers. Absorb, neutralize, and shovel into waste drum for disposal in compliance with all legal regulations.

NEUTRALIZING CHEMICALS

MILD ACIDS

VIII SPECIAL PROTECTION INFORMATION

VENTILATION REQUIREMENTS	Sufficient to keep mist below 5 mg/M^3.
SPECIFIC PERSONAL PROTECTIVE EQUIPMENT RESPIRATORY (SPECIFIC IN DETAIL)	If ventilation is inadequate, a NIOSH-approved mist respirator is recommended.
EYE	Close-fitting chemical safety goggles.
GLOVES	Rubber or PVC
OTHER CLOTHING AND EQUIPMENT	Eyewash fountains, safety shower, rubber apron.

IX SPECIAL PRECAUTIONS

PRECAUTIONARY STA"EMENTS

1. Do not get in eyes, on skin, or on clothing.
2. Wash well after using this product.
3. When making solutions, add this product slowly to water while stirring.

OTHER HANDLING AND STORAGE REQUIREMENTS

Store in a cool, dry place away from heat sources, sparks or flames.

SEE TECHNICAL INFORMATION BULLETIN FOR MORE INFORMATION.

THIS MATERIAL MAY CONTAIN TRACE AMOUNTS OF CHEMICALS WHICH ARE LISTED UNDER CALIFORNIA PROPOSITION 65 AS CARCINOGENS AND/OR REPRODUCTIVE TOXICANTS.

PREPARED BY: ____________________

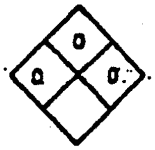
TITLE: Chemist

COMPANY: ____________________

ADDRESS: ____________________

Information presented herein has been compiled from sources considered to be dependable and is accurate and reliable to the best of our knowledge and belief but is not guaranteed to be so., Nothing herein is to be construed as recommending any practice or any product in violation of any patent or in violating of any law or regulation. It is the user's responsibility to determine for himself the suitability of any material for a specific purpose and to adopt such safety precautions as mya be necessary. We make no warranty as to the results to be obtained in using any material and, since conditions of use are not under our control, we must necessarily disclaim all liability with respect to the use of any material supplied by us.

WCF-3



MATERIAL SAFETY DATA SHEET

I. IDENTIFICATION

PRODUCT NAME:		
CHEMICAL NAME: Alkaline Degreaser		**DATE PREPARED:** October 2, 1991
DEPARTMENT OF TRANSPORTATION	**HAZARD CLASSIFICATION:** None **SHIPPING NAME:** Cleaning Compound, Class 55	

II. PHYSICAL DATA

BOILING POINT, (F°)	212°F	VAPOR PRESSURE (mm Hg at 20°C)	14.2
SPECIFIC GRAVITY ($H_2O = 1$)	1.02	WATER SOLUBILITY	Complete
VAPOR DENSITY (air = 1)	0.62	Photochemically reactive (SCAQMD Rule 102)	No
PERCENT VOLATILE BY VOLUME (%)	94.3	EVAPORATION RATE BuAC=1	>1
pH (of concentrate)	12.4	VOC (Calculated formula) SCAQMD Rules 443.1 & 1171	200 g/l (in concentrate) 23 g/l (at 8:1 dilution)
APPEARANCE AND ODOR	Light Amber liquid, mild characteristic odor		

III. INGREDIENTS

MATERIAL	%	OSHA PEL	TLV (units)	HAZARD
2-butoxyethanol	<20	25ppm	120 mg/m³	N/A
" " Cas #111-76-2	N/A	N/A	TWA-25ppm	N/A
THIS PRODUCT DOES NOT CONTAIN ANY HAZARDOUS CHEMICALS LISTED IN SARA TITLE III SEC. 313.				CONTAINS NO CFC'S

IV. FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (test method)	None/cc	FLAMMABLE LIMITS	None	LOWER None	UPPER None
EXTINGUISHING	NO FIRE HAZARD				
SPECIAL FIRE FIGHTING PROCEDURES	N/A				
UNUSUAL FIRE AND EXPLOSION HAZARDS	N/A				

V. HEALTH HAZARD DATA

TLV AND SOURCE	Not established
ACUTE EFFECTS OF OVEREXPOSURE	LD50 (for technical 2-butoxyethanol) for skin absorption on rabbits is 200 mg/kg: Oral LD for rats is 470 mg/kg. LC50 (inhalation) for rats is 700 ppm in 7 hours.
SKIN CONTACT	May cause dryness and irritation
INHALATION	None
EYE CONTACT	Flush eyes with water for 15 minutes, lifting the lower and upper lids. Obtain attention if irritation persists.
CHRONIC EFFECTS OF OVEREXPOSURE	This is relatively innocuous substance not expected to cause harm. Should treatment ever be required, it would be directed at control of symptoms.
OTHER HEALTH HAZARDS	Ingestion may cause nausea and/or diarrhea.

EMERGENCY AND FIRST AID PROCEDURES

SWALLOWING	If swallowed drink warm water to dilute stomach contents, induce vomiting.
SKIN	Flush thoroughly with soap and water.
INHALATION	None
EYE	Flush eyes with water for 15 minutes, lifting the lower and upper lids Obtain attention if irritation persists.
NOTES TO PHYSICIAN	This is relatively innocuous substance not expected to cause harm. Should treatment ever be required, it would be directed at contro of symptons.

VI. REACTIVITY DATA

STABILITY	STABLE: Yes	UNSTABLE: No	CONDITIONS TO AVOID: None
INCOMPATIBILITY:	Avoid oxidizing materials		
HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS		None	
HAZARDOUS POLYMERIZATION	MAY OCCUR No	WILL NOT OCCUR Yes	CONDITIONS TO AVOID: None

VII. SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS SPILLED	Small Spills: Flush with water. Large Spills: Absord with sawdust, sand or earth.
WASTE DISPOSAL METHOD	May be disposed of in sewer system after consulting local, county, state or Federal regulations for applicable laws pertaining to your areas.

VIII. SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (type)	None
VENTILATION	If desired. Local exhaust if sufficient.
PROTECTIVE GLOVES	Use if long exposure is expected
EYE PROTECTION	If splashing is expected use goggles
OTHER PROTECTIVE EQUIPMENT	Wear plastic apron if excessive splashing is expected. If clothing becomes soaked, remove, shower, and wash clothing.

IX. SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING	Store in cool dry area. Prevent freezing, if frozen allow to thaw, stir well and re-use.
OTHER PRECAUTIONS	NONE

WCF-4

MATERIAL SAFETY DATA SHEET

Per 29 CFR 1910.1200 DATE PREPARED : 1/1/90

SECTION I.

24 HOUR EMERGENCY NUMBER
CHEMTREC

IDENTITY (As Listed On Label) 815 QR

HMIS HAZARD RATINGS: Health: 1
Flammability: 0
Reactivity: 0

SECTION II. HAZARDOUS INGREDIENTS/IDENTITY INFORMATION

Hazardous Components (Specific Chemical Identity: Common Name(s)	CAS #	OSHA PEL	ACGIH TLV-TWA	OTHER LIMITS RECOMMENDED	PERCENT
Ethanolamine, 2-Aminoethanol, Monoethanolamine	141-43-5	3 PPM	3 PPM	STEL 6 PPM	5-10

SECTION III - PHYSICAL/CHEMICAL CHARACTERISTICS

Boiling Point:	212 F	Specific Gravity (H20=1):	1.067
Vapor Pressure (mm Hg.):	Ethanolamine 0.2 @ 68 F	Melting Point:	Approx. 30 F
Vapor Density (Air=1):	Ethanolamine 2.1	Evaporation Rate (water=1):	1.0
Solubility in Water:	Complete		

Appearance and Odor: Blue green liquid, citrus odor.

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

Flash Point (Method Used): None

Flammable Limits LEL: NA UEL: NA

Extinguishing Media: Not Applicable

Special Fire Fighting Procedures: None

Unusual Fire and Explosion Hazards: None

SECTION V - REACTIVITY DATA

Stability Unstable _____ Stable _X_ Conditions to Avoid: Freezing

Incompatibility (Materials to Avoid): Strong oxidizers and acids.

Hazardous Decomposition or Byproducts: Thermal decomposition can produce carbon monoxide, carbon dioxide, nitrogen oxides.

Hazardous Polymerization May Occur _____ May Not Occur _X_ Conditions to Avoid: None

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SECTION VI - HEALTH HAZARD DATA

Route(s) of Entry: Ingestion? No Skin? Yes Inhalation? Yes

Health Hazards (Acute and Cronic):
Eye - Direct contact may cause irritation.
Ingestion - May cause gastrointestinal irritation and irritation of mouth and throat.
Skin - Prolonged or repeated contact may cause irritation.
Inhalation - Excessive exposure may cause respiratory irritation.

Carcinogenicity: NTP? No IARC Monographs? No OSHA Regulated? No

Signs and Symptoms of Exposure: Eye contact may cause irritation, seen as redness and swelling.
Prolonged skin contact may cause irritation, seen as redness.
Excessive inhalation of mists may be irritating and cause coughing and discomfort in the nose throat and chest. Ingestion may cause pain or discomfort in the mouth, throat, and stomach.

Medical Conditions Generally Aggravated by Exposure: Ethanolamine may aggravate asthma and inflammatory or fibrotic pulmonary disease. May also aggravate an existing dermatitis.

Emergency & First Aid Procedures:
Inhalation: If affected, remove to fresh air.

Eye Contact: Flush with large amounts of water for at least 15 minutes lifting upper & lower lids occasionally. Get medical attention.
Skin Contact: Wash with mild soap and water. Remove contaminated clothing and launder before reuse.

Ingestion: If conscious, dilute by giving at least two glasses of water. Call a physician immediately.

SECTION VII - PRECAUTIONS FOR SAFE HANDLING AND USE

Steps To Be Taken In Case Material Is Released Or Spilled: Small spills - Flush to sanitary sewer with plenty of water.
Large spills - Soak up on solid absorbent and shovel into containers for disposal.
Waste Disposal Method: Dispose of according to Federal, State and Local Laws and 40 CFR.

Precautions To Be Taken In Handling And Storing: Store between 40 and 120 F.

VIII - CONTROL MEASURES

Respiratory Protection (Specify Type): Not normally required. Use NIOSH-MSHA approved respirator if TLV of Ethanolamine is exceeded.
Ventilation: Local Exhaust:
Special:
Mechanical (General): Normally Sufficient
Other:
Protective Gloves: Neoprene or butyl rubber on prolonged contact.
Eye Protection: Goggles or safety glasses when handling conc.

Other Protective Clothing or Equipment: None

Work/Hygienic Practices: Avoid breathing spray mist.

WCF-5 is also an immersion alkaline cleaner. The pH is listed in the category "Physical Data" at 8.5. This is a very low pH and it makes the cleaner attractive. Under the "Ingredients" category, there are no chemicals listed. The MSDS does not indicate that the cleaner has a pine or citrus odor. This cleaner should be selected for testing.

6.4.2 Contacting the Distributor The information on the MSDS is useful for determining which cleaners can be rejected outright. More information may be required from the distributor before a decision can be made to test the cleaner. If the pH is not listed on the MSDS, for instance, the user should ask the distributor for the pH of the concentrate and perhaps that of a 10 % solution would be. Another question to ask the distributor is whether the formulation contains propylene glycol ethers. These chemicals are not required to be listed on the MSDS under "Hazardous Ingredients" even though certain other glycol ethers are required to be listed.

The information the distributors supply may be incorrect and the best strategy, if there are doubts about the information, is to contact the laboratory chemist at the company that actually formulates the cleaner. In one case, IRTA was working with a user who was evaluating a particular water-based cleaner. The pH was listed on the MSDS at 13 and IRTA indicated that the cleaner should be rejected because of a high pH. The user indicated to the distributor that the pH was too high and the distributor insisted that a 10 % solution would have a pH of only 11; she wrote a letter to that effect. Because the pH should not decline this much, IRTA was skeptical and called the chemist directly. The chemist indicated that the pH had been measured at 10 % dilution and that it was above 12.

Another strategy to determine if solvent additives are present in the cleaner is to ask the distributor to perform a test called EPA test Method Number 24. This method was developed to determine the VOC content of coatings and other formulated products. It is not especially appropriate for water-based cleaners but it will provide a good measure of the VOC content of the concentrate. The test is routinely performed by test labs in the southern California area.

IRTA requires all formulations to be tested using EPA Test Method Number 24 before recommending them to firms. The results can be used to reject or accept the cleaner or to determine whether a permit is required for the cleaning equipment. Firms should ask distributors if they have performed the test and should insist that they do so before they test the cleaner. The formulators of WCF-5 described above performed the test and the cleaner falls below the 2 % VOC cutoff level.

6.5 Testing Selected Water-Based Cleaners

After the screening procedure that weeds out the unacceptable cleaning formulations and after discussions with the distributors, a limited number of cleaners will remain. These cleaners may merit testing. The cleaners can be screened further at this stage.

WCF-5

SAFETY DATA

EMERGENCY PHONE NO.

SECTION I - IDENTIFICATION

PRODUCT (TRADE) NAME:

General Chemical Description: Aqueous alkaline cleaner

SECTION II-INGREDIENTS

Hazardous Ingredients: Not applicable

SECTION III-PHYSICAL DATA

Solubility in Water: complete

pH: 8.5 (approx.) concentrate

Appearance and Odor: straw/amber liquid; bland odor

Specific Gravity (water=1): 1.0 approx.

Vapor Pressure (mm Hg): 24 (24.4°C)

Boiling Point: 212°F approx.

SECTION IV-FIRE AND EXPLOSION HAZARD DATA

Flash Point: None to boiling

Extinguishing Media: Carbon dioxide, dry chemical, foam. Avoid water if possible, as water may cause spattering of hot material and may spread burning.

Combustion will result in the release of the usual decomposition products including oxides of carbon and nitrogen.

SECTION V-REACTIVITY DATA

Product is stable; hazardous polymerization will not occur.
Incompatible with strong oxidizers.
Do not mix with strong acids.
Do not mix with nitrites or nitrite containing compounds (49 FR 24658, 6/14/84).

SECTION VI-SPILL OR LEAK PROCEDURES

Handling Precautions: See Section VIII.

For small spills: Wipe up, or absorb with sand or other absorbent material. Collect waste in sealed containers.
For large spills: Dike area to prevent spreading. Absorb residual material with sand, or other absorbent material. Wash area with soapy water and rinse. Area will be slippery until cleaned.

The material is not a hazardous waste as defined in 40 CFR Section 261.3.

Dispose of all product wastes and water rinses in accordance with current local, state, and Federal regulations.

SECTION VII-HEALTH HAZARD DATA

Threshold Limit Values: Not applicable.

	Signs & Symptoms of Acute Exposure	Emergency First Aid Procedures
Inhalation:	Irritation may occur if material becomes airborne.	Remove to fresh air.
Eyes:	Irritation upon direct contact.	Immediately flush eyes with water for at least 15 minutes; get medical attention.
Skin:	Irritation upon direct contact.	Wash affected area with water; if irritation occurs and persists, get medical attention. Remove contaminated clothing.
Ingestion:	None known.	Dilute with water or milk; do not induce vomiting; get medical attention.

CHRONIC EFFECTS: None known.

Medical Conditions Aggravated by Overexposure: None known.

GET MEDICAL ATTENTION IF SYMPTOMS PERSIST

SECTION VIII-SPECIAL PRECAUTIONS

Handling and Storing

- Does not normally become airborne; in operations where it does, if general ventilation or local exhaust is inadequate, persons exposed to mists should wear approved breathing devices.
- Wear neoprene gloves if direct contact likely; wear eye protection.
- Store product at 40-100°F in a well-ventilated area.
- Do not mix with nitrites or nitrite containing compounds (49 FR 24658, 6/14/84).

Users will want to ask distributors for additional information before they begin a testing program. First, the user should ask if the cleaner could be damaging to the particular substrate material that requires cleaning. Not all alkaline cleaners are safe for use with all substrates. Second, the cleaner should separate from oil easily so that the life of the wash bath can be extended; this should be verified with the distributor. Third, some cleaners are foaming and they should not be used in certain types of equipment, a high pressure spray unit, for example. Fourth, certain temperatures are appropriate for specific substrates or soils.

If firms have no equipment that can be used for testing -- and this is often the case -- some distributors will offer parts testing free of charge. It is better for users to select cleaners sold by large or medium sized formulators. If there are problems in using the cleaner later, the more sophisticated, national firms will assist firms in solving the problem. Smaller formulators or distributors have no laboratories and often no chemical or technical knowledge. Firms can send contaminated parts to larger distributor's labs for testing with the selected formulations. The distributor will return the parts after they have been cleaned and the user can evaluate whether the cleaning formulation performed adequately.

For firms wishing to do on-site testing, the distributor may donate samples of the formulation free of charge. Testing of the few selected cleaners can reveal problems that were not anticipated, and, at this stage, the firm can compare the results of the cleaners and select the best one for their process. Often it will be necessary to try to optimize the process for each cleaner. Some testing that varies the concentration, the temperature and the cleaning time should be conducted.

A major issue in cleaning agent performance is choosing the proper equipment and fixturing for the cleaning problem. This is a much more important issue than it is in the case of chlorinated solvents. These solvents penetrate to blind holes and crevices easily and they leave a clean, dry part. Water has a higher surface tension and does not reach blind holes and crevices easily. When water is used for such parts, ultrasonics, which is cavitation of the cleaners, will nearly always be necessary. For cleaning small diameter tubes or long tubes, fixturing, like a manifold with an adjustable diameter, will be necessary. The fixture is attached to the tube and the formulation is pushed with pressure through the tube. The fixture must again be used to rinse the tube so that all the cleaning agent is removed.

A water cleaning formulation will fail to clean the parts adequately if equipment design and fixturing is not taken into account. Water, unlike chlorinated solvents, often does not work without effort. There are more variables with water cleaning than solvent cleaning and they must be optimized for the specific process. These variables, as mentioned earlier, include the level of the concentrate, the temperature, the cleaning time, the best mechanical action and the fixturing. The best mix of these variables must be found.

6.6 Case Studies -- Water-Based Cleaner Selection

The four case studies that follow point out some of the issues that arise in the substitution process. Firms must be committed to working out the problems so that water cleaning can be used successfully.

6.6.1 Case Study # 1 This plant is a job shop that processes parts for aerospace and commercial firms. The firm does anodizing, chem filming and coating. As part of those activities, certain portions of parts need to be anodized or coated; the remainder of the part must be masked so the anodizing or coating will not be applied to it. A heavy red wax is used to mask the parts. After the processing, the wax is removed from the part in a perchloroethylene (PERC) vapor degreaser.

Waxes and buffing compounds have very high melting points, often above 170° F. PERC, which has a boiling point of 250° F, is an excellent solvent for removing wax or buffing compounds. The vapor temperature of 250° F will melt the wax and the solvent action of the PERC will dissolve the material and remove it from the surface of the part.

Solvent distributors claim that water formulations cannot remove wax or buffing compound but this is not the case. The red wax was successfully removed from the masked parts with two formulations by raising the temperature of each water cleaner to about 175° F. This exceeds the melting point of the wax. Pure water would not result in effective removal even if it were heated above 170° F. The surfactant action of the water cleaning concentrate is necessary to prevent the wax from redepositing on the surface of the part. The wax can be removed from the bath with filters when the temperature is lowered.

6.6.2 Case Study # 2 The second case involves an aerospace subcontractor that manufactures aluminum tubes for aircraft fuel tanks. The tubes range in diameter from one-fourth inch to about six inches. A heavy lubricating oil is applied to the outside and inside of the tubes and they are processed to bend them into the final required shape. Some of the tubes have small coiled bends and some have 90 or 180 degree bends.

This subcontractor uses a 1,1,1-trichloroethane (TCA) vapor degreaser to remove the lubricating oil from the tubes after they are bent into shape. The tubes then go on to another process where they are anodized. Chlorinated solvents are very good at removing oil from the inside of small diameter tubes because of their low surface tension.

Water-based cleaning formulations were successful in removing the oil from several of the larger diameter tubes. The cleaned tubes were anodized and their ability to accept this treatment demonstrated that they were clean.

The firm is currently investigating water cleaning equipment that can be used to clean the tubes. Because of the high surface tension of water, it does not penetrate and clean the smaller diameter tubes effectively. The cleaning unit will have to be designed with a manifold with an adjustable attachment for various tube sizes. The fixture would be attached to the end of each tube and water cleaning formulation would be forced with pressure through the tube. The same procedure would be used again with rinse water and with air for drying the tubes. This is a labor intensive process but many firms that clean tubes already have one or more workers devoted full time to tube cleaning. Often, even with solvents, the smallest diameter tubes will required individual fixturing.

6.6.3 Case Study # 3 This case concerns a firm that separates, recycles, processes and resells high temperature, high value alloys. About 80,000 pounds of alloys are processed each month. The alloys are made of titanium, nickel, cobalt, stainless steel, aluminum, berylium and zirconium in various combinations. The scrap alloys are received from aircraft and commercial firms that employ them in their processes.

Some of the metals are not visibly contaminated and they are not cleaned. About 20 percent are contaminated with heavy oil and are cleaned in a PERC vapor degreaser. After cleaning, some of the metals are shot blasted and some are sent off-site for further chemical processing. The processed metals are chopped up and sold.

Water-based cleaning formulations successfully cleaned a mix of the different alloys. The firm is currently converting the vapor degreaser to use water cleaners. This involves disconnecting the cooling coils and adding piping with compressed air to obtain agitation. A second stainless steel tank has been purchased and will be used as a rinse bath.

6.6.4 Case Study # 4 This case involves a company that manufactures bladders for hydraulic accumulators. The rubber is brought in in sheets and processed to form bladders. These bladders are joined to stainless steel and carbon steel parts with different types of adhesives. The metal parts act as stems for the bladders.

The stainless steel parts are not cleaned but the carbon steel parts, which come to the facility with a film of oil that prevents rusting, are cleaned in a TCA vapor degreaser. Both types of parts are then shot blasted and adhesive is painted on them. They are then attached to the bladders.

Water cleaning formulations successfully cleaned the carbon steel parts. When water is used, parts like carbon steel that rust must be treated with a rust inhibitor after cleaning. The cleaned parts were shot blasted and coated with adhesive. They accepted the adhesive well and destructive testing demonstrated that the parts were clean. This case study is discussed in more depth in Section 7.

6.7 Issues in Water Cleaning

The case studies all involved successful water cleaning tests. In fact, the tests are not always effective initially and sometimes complex issues require resolution before water can be implemented. Firms are not always willing to commit the resources to the problem and they often do not have the expertise to find the solutions.

The first problem that may emerge is the oil or other material used in the manufacturing process. Removing this oil or material is the purpose of the cleaning operation. Some oils, particularly those used in tube bending, cannot be cleaned with water-based cleaners. Other materials also may not be removed by water cleaners. An example is a material called moly disulfide used as a dry lubricant for titanium. Alternative oils and lubricants are available that can be cleaned with water. It takes research and testing resources to accomplish the process conversion, however, and firms are often reluctant to expend the effort.

Some materials are water intolerant and they cannot be cleaned with water-based cleaners. Contact lenses, for example, will absorb water and a cleaning process without water must be devised. In these cases, the firms will have to use another solvent and this solvent can be selected using the procedure outlined in the earlier section describing the systems approach to solvent selection.

Proper post-treatment processes are necessary with water-based cleaning. Many firms use materials that rust, like hot and cold rolled steel for instance. They often believe that they cannot convert to water because water will rust their parts. This is not the case. Many water cleaners have rust inhibitors in them that protect the parts for a short time until they go on to the next processing step. In some cases, a rust inhibitor must be applied after cleaning. In other cases, where the parts go on to a coating step, a phosphate treatment system should be used.

The mechanical agitation and fixturing required for water cleaning are perhaps the most important factor. Firms will sometimes test water cleaning in the same manner as they use solvents, by dipping the part into the material and expecting it to emerge clean and dry. It will not be effective and the firm will be convinced that water-based cleaners will not work for them. Each process requires a slightly different combination of equipment, agitation and fixturing. For example, some parts have blind holes and crevices. This type of part cannot be cleaned without the use of ultrasonics. The types of water cleaning equipment that are available are discussed in the next section.

6.8 Water Cleaning Equipment

In solvent cleaning operations, the solvent is very forgiving. Particularly in vapor degreasing operations using chlorinated solvents, solvent vapors and liquid can penetrate tiny crevices and blind holes very well and can effectively clean contaminants from almost all types of parts. In a one-step process that requires minimal time, a part can be removed from a vapor degreaser clean and dry. Using water cleaning processes is more complex. Several operations, including cleaning, rinsing and drying are required. Because of the higher surface tension of water, suitable fixtures for delivering the cleaning and rinsing agent to parts with complex geometries are necessary and equipment designed specifically for each process must be used. In solvent cleaning, 90 percent of the work is accomplished by the solvent; only 10 percent is equipment and process dependent. The exact reverse is the case with water cleaning; 10 percent of the work is performed by the water cleaning agent and the remaining 90 percent is done with the proper fixtures and equipment.

Many different types of equipment are available. Several of the most common types of equipment are discussed below.

6.8.1 Conveyorized Spray Equipment High pressure spray equipment, where the spray pressure is 80 to 100 pounds per square inch, is suitable for certain operations. The parts are fed on a conveyor line which carries them through a series of processes. The first spray chamber contains the water cleaning formulation. The parts are washed and then they go through one or more rinse chambers where they are rinsed with tap or deionized water. The final chamber uses forced air to dry the parts.

Variations of the basic design are possible. Two wash baths and multiple rinse baths can be used. The rinse water can be plumbed to the sewer or it can be close looped. Other drying mechanisms, like infrared drying, for example, can be used.

Conveyorized equipment is appropriate in operations where a high level of throughput is required. This type of operation is most suitable for PC boards where the impact of high pressure spray is required to remove contaminants from low tolerance surface mounted components. Conveyorized units can be used in shops where 1,000 to 10,000 boards are cleaned per day. Another type of part that could be cleaned in this setup includes flat, thin metal panels of all sizes or disk drive assemblies.

6.8.2 Batch Equipment Numerous types of batch equipment are available. The simplest type would be an open consul with three chambers, one that serves as the wash bath, one that serves as the rinse bath and a third for drying. The parts can be introduced into the chambers manually or with an automated hoist system that automatically moves the parts from chamber to chamber. Baskets made of stainless steel mesh can be used to hold the parts in each chamber.

Another type of batch equipment can be used to clean very small metal parts like fasteners, bolts and screws. These very small parts must be exposed to the cleaning agent and the rinse water and they must be dried properly. In order to accomplish this, a rotating drum fixture can be used to rotate the small parts in all chambers. The rotation allows all sides of the parts to be exposed to the wash formulation, the rinse water and the drying air. Again the drums can be transferred manually or with an automated parts handling system.

Some parts, particularly those with blind holes or crevices that are difficult to reach, must be cleaned using ultrasonics. Ultrasonic methods rely on cavitation to move cleaning agent and rinse water into the recessed hard-to-reach areas. Again the parts can be moved manually or with an automated handling system.

Other agitation methods can be designed into batch equipment. Spray under immersion can be used to spray the immersed parts in the wash chamber. Up-and-down agitation can be used to lodge the contaminants loose from the parts.

6.8.3 Batch Dish Washers This equipment resembles the dish washers commonly used in homes. The parts are placed in the dishwasher on racks or on a rotating fixture and are sprayed under high pressure. The wash step and the rinse step are performed sequentially in the same piece of equipment by varying the feed stream. A separate dryer can be used if the parts require drying.

6.8.4 Steam Cleaning Equipment This type of equipment has been used most often outside for cleaning large assemblies that are heavily contaminated. In principle, it could also be used inside if a drain were available. It consists of a high pressure spray device that is used to spray steam or steam with additives on parts. The residue from the cleaning is generally flushed to a drain that is routed to a wastewater treatment system.

6.8.5 Remote Reservoir Cleaners Vendors are offering stainless steel or plastic units that can be used with water for repair and maintenance and production cleaning. Such units can be used with a water formulation to remove gross oil. They are not designed to provide a rinse or a dry and separate rinsing and drying operations may be required.

SECTION 7:
EVALUATION OF ALTERNATIVES

In Sections 4, 5 and 6, the chemical alternatives, the process alternatives and the water-based alternatives to chlorinated solvents were presented and discussed. In Section 2, the regulations that affect the alternatives and must figure into the evaluation of the alternatives were summarized. The analysis conducted in the previous sections implies some compelling conclusions and suggests that a hierarchical evaluation method be adopted for evaluating alternatives. One such method is described in this section.

This section also includes three case studies of substitution that are typical for solvent users. They are used to demonstrate the hierarchical evaluation method. The case studies presented here are not "real" ones; rather, they were chosen to allow discussion of several relevant issues and to emphasize the procedure of evaluating the range of alternatives. The first case study presents the options for a printed circuit board assembler. The second case study illustrates the substitution options in a standard bath cleaning application. In the third case study, an alternative in handwipe applications is required.

7.1 Hierarchical Evaluation Scheme

The vapor degreasing process is simple and efficient. The parts can be immersed in the vapor zone of a solvent, and, no matter what their configuration or substrate, they emerge clean and dry in a short period of time. None of the alternatives can be used in the same manner. For a few years, it was believed that the HCFCs would offer a close substitute to the chlorinated solvent. They could be used in vapor degreasers in the same manner as the chlorinated solvents. There are problems with these solvents, however, as described earlier, and the HCFCs will be banned because they contribute to ozone depletion.

No other "drop-in" solvent has emerged and none is likely to in the future. The simple fact of the matter is that "there is no free lunch." That is, there is bound to be some limitation to every alternative that is or will be available. The earlier sections of this document certainly make this point. This suggests that users must come to terms with the fact that whatever alternative they choose will have one or more problems. They must be willing to take these problems into account when designing and purchasing an alternative system.

Virtually all of the potential alternatives to chlorinated solvents pose technical difficulties or health and environmental problems. Nearly all chemical alternatives are VOCs or ozone depleters or global warming gases. The process alternatives generally are applicable only in certain situations. Water-based cleaning, however, is applicable on a widespread scale. In fact, this conclusion is represented by the firms marketing the alternatives.

Originally when the bans on the ozone depleting chemicals were put in place, there was much jockeying for position and many firms were offering chemical alternatives in bath cleaning applications. Several equipment manufacturers who had sold vapor degreasers for many years began building equipment for use in semi-aqueous processes. At this stage, the market has "shaken out" and there is strong activity in only the water sector. This reflects the fact that the semi-aqueous process is complex and expensive.

In some cases, firms can avoid cleaning altogether or can adopt no-clean processes. The instances where this is possible, however, are limited. If cleaning cannot be avoided, then the next best option is to use water-based cleaning processes or other processes that do not use a chemical. If this is not possible, then a chemical must be employed. The technical requirements of the process will determine the type of chemical that must be employed.

A simplistic decision tree that makes this evaluation procedure explicit is shown in Figure 7-1. The first question to ask is whether cleaning is necessary at all. If it is not, no-clean alternatives should be adopted. These might include use of no-clean flux in PC board defluxing or using a vanishing oil on parts.

If cleaning is necessary, then two parallel solutions should be investigated. The first is other processes. In some cases, these will prove to be feasible and less costly than water-based cleaning. The second parallel process is water-based cleaning and in most cases, this will be the option chosen. For instance, there may be firms that can employ nitrogen for cleaning; in this case, the nitrogen process may be easier, more effective and less costly than a water-based cleaning process. There may be other firms that can use either supercritical carbon dioxide cleaning or water. Since the supercritical carbon dioxide process is likely to be more expensive, the firm would choose a water-based process.

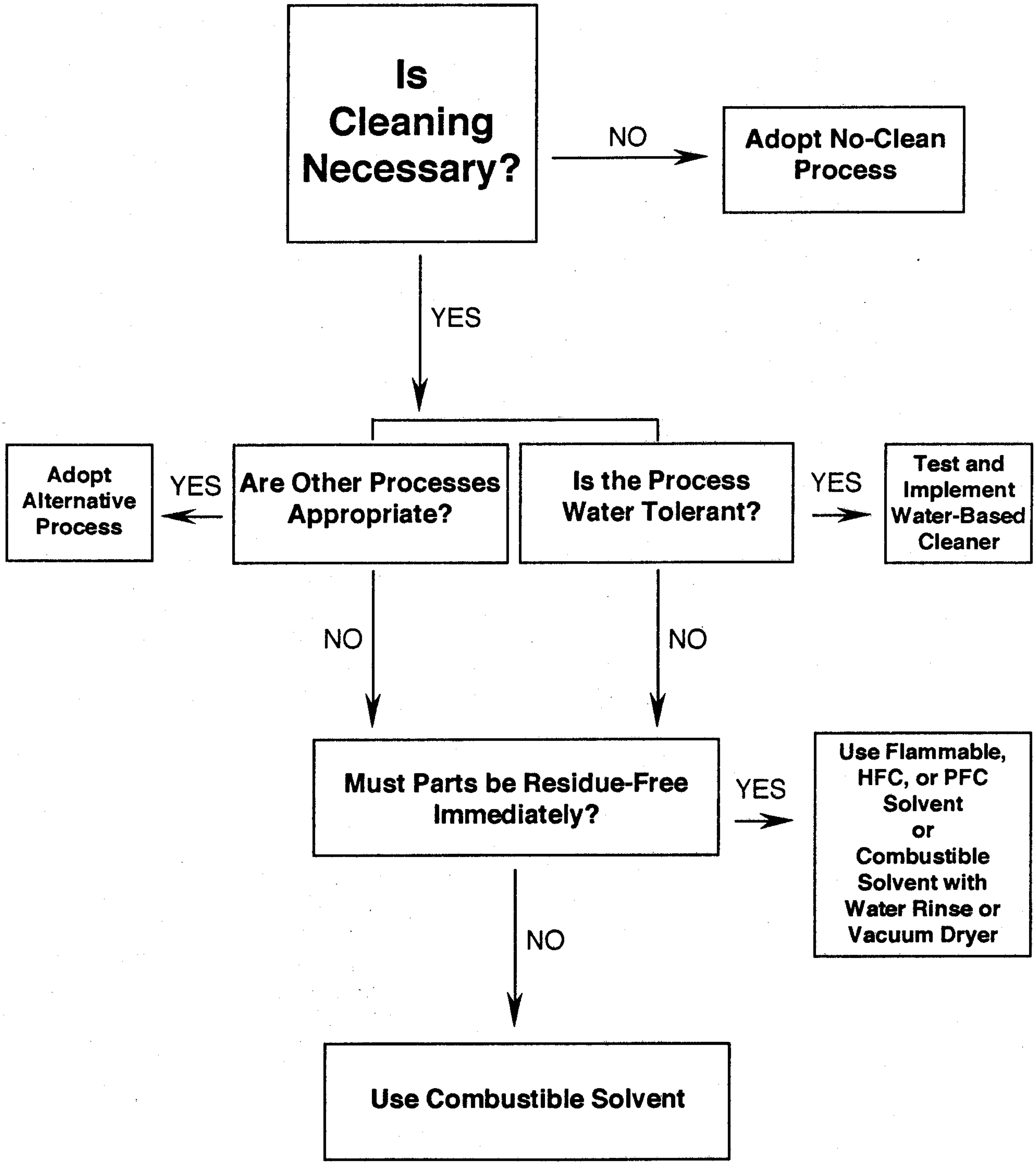
If the part is not water tolerant and other processes are not appropriate, then the firm must decide whether a residue-free part is necessary in a short period of time. In some cases, it may be essential to have a process that leaves a residue-free part immediately; in such instances, flammable, HFC and PFC solvents could be used. Another option would be to use a combustible solvent in the semi-aqueous process or with a vacuum dryer.

If a residue-free part is not required, then a combustible solvent can be used in the process.

At each stage of the evaluation, the firm should consider the regulations that influence the choice of alternatives. For instance, if a firm decides to select a PFC, the SNAP regulation restrictions for use of PFCs should be taken into account. In other cases, the air district and sanitation district regulations should be investigated so the firm will be able to make an informed decision about cost and permitting.

This hierarchy presented here is very simplistic and in any real case of substitution, the choices are more complex than described here. The complexity of any real problem is apparent in the case studies described below.

Figure 7-1 Cleaning Alternative Decision Tree



7.2 Case Study #1 -- Printed Circuit Board Defluxing

Ace Contracting is a firm in Orange County, California that assembles printed circuit (PC) boards. The boards are fabricated by another firm and they are sent to Ace for assembly. Ace assembles the boards and sells them to both military and commercial customers. Assembly, or placing and soldering components to the boards, is sometimes called "stuffing" the boards. Ace currently uses a CFC-113/methyl alcohol blend to clean the boards. The cleaning is performed in a conveyorized vapor degreaser that sprays the solvent on the boards.

In the process, the boards are first shipped to the facility. A standard rosin-based flux is applied to the boards to effect heat transfer during the soldering step, to facilitate solder flow, and most important, to prevent oxidation from occurring on the board. After the flux is applied, the components are soldered to the board. The boards are of mixed type. That is, they contain both through hole and surface mount components. The through hole components are soldered through holes that were drilled in the boards in the fabrication process. The surface mount components are soldered to the surface of the board. The clearance between the surface mounted components and the board is 4 mils or more.

After soldering, the flux and other contaminants are removed from the boards in the conveyorized defluxing machine. The CFC-113 is good at removing the organic contaminants like oils; the alcohol is good for removing the ionic contaminants like fingerprints and flux. The boards emerge from the defluxing machine clean and they are inserted into devices that are then sent to military and commercial customers. Ace assembles between 5,000 and 10,000 boards per day. The cleaning was performed in a 150 gallon in-line vapor degreaser. Solvent use amounted to 100,000 kilograms or 220,000 pounds per year.

Under the Montreal Protocol, production of CFC-113 is scheduled to be banned on January 1, 1996. Congress levied a tax on the CFCs and, by January 1, 1994, the tax was $4.35 per pound. CFC-113 has an ozone depletion potential of 0.8 compared with CFC-11 and CFC-12 which are the standard, at 1.0. Because of the alcohol in the CFC-113/methanol blend used by ACE, the ozone depletion potential of the blend is about 0.75. Thus, the tax alone on a 650 pound drum of the solvent is more than $2,000. The price of CFC-113 itself is close to $3 per pound. Thus the cost for a drum of the solvent is currently more than $3,500. The Congressional tax is expected to increase further by $1 per pound on January 1, 1995.

John, the environmental engineer at Ace, was attempting to convince the firm's management to allow him to research and implement an alternative. He needs to devote time to analyzing and testing the alternatives. He will also need a budget to purchase a new piece of equipment for use with the alternative that appears most attractive. The management has been reluctant to allow him to begin the evaluation process because business has not been good.

The issue that finally got management's attention is the labeling law that requires products made with CFC-113 to be labeled. Some of Ace's customers, the commercial ones, asked the firm to certify that they did not use ozone depleting substances. Ace lost some of the accounts and the management gave the go-ahead to John to investigate the options further in November, 1993 when EPA began enforcing the labeling law.

Since only production of the CFC-113 will be banned, many people believe that recycled CFC-113 can still be used and will be available. Management asked John to report back to them on the whether the firm could continue to use recycled solvent and whether the firm should begin stockpiling CFC-113 in preparation for the ban. After checking with several recyclers and studying the firm's use figures, John understood the CFC loss process better. About 55 percent of the total losses of CFC-113 were atmospheric emissions; the remaining 45 percent was sent off-site for waste recycling. Make-up solvent averaged about 7.5 gallons per day. It is not difficult to see that the firm would require much more solvent than it could recycle from the waste from Ace's own operation.

Stockpiling available CFC-113 before the production ban would be a very expensive proposition. John prepared the figures and submitted them to management. The firm was currently using 100,000 kilograms or 220,000 pounds of CFC-113 annually. To stockpile only one year's usage would require $1.6 million. About half of this is recycled solvent that could be reused; the net cost of stockpiling would amount to more than $800,000. When John reported this figure to the management, they instructed him to identify, test and implement an alternative as quickly as possible.

After talking with many solvent and equipment vendors, John felt he knew what the alternative options were. He began by considering the non-cleaning options. There were two emerging processes -- ROSA and PADs (see Section 4 for description) that did not require the use of flux. They therefore would not require cleaning. These two processes, however, were still in the development stage and were not yet commercially available.

The remaining options, after eliminating the two that are emerging included:

- No-clean flux
- Inert gas soldering
- Water with water soluble flux
- Water with rosin-based flux
- Semi-Aqueous process
- AVD process
- Alcohol process

John analyzed the AVD and the alcohol processes first. He found that the AVD process used a PFC and a solvating agent (combustible solvent). In contacting other firms, he received bad reports about the PFC option; some firms that had tested it felt that it wasn't effective for defluxing because there is no ionic component (neither the PFC nor the combustible solvent is polar). The alcohol system, John found, worked well technically but the fire department would require the cleaning unit to be remotely located and this was impractical at Ace.

John looked into the first two options listed above -- no-clean flux and inert gas soldering. He found that they are very process dependent. Some of his firms' contracts were with defense organizations and he determined that they would not look favorably on either option. Because the boards were destined for very high technology critical applications, the military contract officers indicated that they would prefer a cleaning process rather than leaving the flux on the boards. This left the two water-based options and the semi-aqueous process.

John began talking with representatives at other firms that had made a conversion. Many of those that had military contracts had converted to the semi-aqueous process and were using either terpene or hydrocarbon/dibasic ester-based solvents. The firms indicated that they had chosen semi-aqueous solvents because the spacing between their surface mounted components and the board surface was less than 4 mils. This value apparently is the rule-of-thumb that is used to determine if water would be technically suitable.

John knew that Ace's boards had spacings of 4 mils, which was just on the border of the cutoff level for using water. He began working with two vendors, one that sold terpenes and another that sold water formulations. He prepared boards and went to vendor equipment sites and tested the formulations. The semi-aqueous solvent worked well on the boards and after analysis, they were very clean. In discussions with the water cleaning equipment manufacturer, John learned that the 4 mils cutoff for water use is somewhat misleading. The vendor told him that he had successfully cleaned many boards with spacings as low as 1 mil. A high pressure, between 80 and 100 psi, was needed for the cleaning and rinsing spray but this is available on standard equipment. Analysis of the boards after removal of the water soluble flux and removal of the rosin-based flux indicated that both cleaning processes could be used successfully.

Many of the firms that had adopted semi-aqueous solvents were in other states or in Northern California. John's firm was located in the SCAQMD and John was concerned that terpenes were VOCs. Because of the lower vapor pressure of the terpenes, emissions of the solvent would be lower than the CFC-113 emissions. Nevertheless, his new cleaning unit would be subject to New Source Review and would require Best Available Control Technology. Since CFC-113 is classified as an exempt chemical and the terpene is not, Ace would have to purchase offsets in order to substitute the terpene.

John contacted one firm that had made the conversion to terpenes in Northern California to discuss the issue. He found that the air district there had required the firm to put in an incinerator to destroy the terpenes that would otherwise be emitted. The firm was not able to offset the increase in emissions any other way. The incinerator had been installed at the end of a duct to the cleaning unit and it had never performed well. John rejected the idea of using a semi-aqueous solvent on this basis. Indeed, after investigating, he found other military contractors in southern California that had converted to water cleaning formulations.

Ace's existing contracts included three that were military. All three would expire and would be up for renewal within about two years. These existing contracts were subject to Military Standard (MilStd)-2000 which requires the use of rosin-based flux. The new military specification, MilStd-2000 Rev A allows the use of any process, including water soluble flux.

John wanted to use water with water soluble flux for two reasons. First, he had determined that the water soluble flux gives better soldering. Second, plain deionized water could be used to clean the boards in the case of water soluble flux and a closed loop system could be employed easily. The organic additives in the water cleaner and the organic contaminants from the flux when rosin-based flux is used make close-looping more difficult; a filtration system that removes the organics is necessary.

More research indicated that John could purchase an in-line water cleaning unit with the closed loop feature for about $105,000. The unit would contain a wash bath with high pressure spray, two rinse baths, also with high pressure spray and a forced air dryer. Plain deionized water could be used in the wash and rinses if water soluble flux were used. A formulation with additives would be necessary in the wash bath if rosin-based flux were used; this would be followed by deionized water rinses.

Upon checking, John found that many of the water formulations for use with rosin-based flux contained glycol ethers. John knew that some of these were listed on the Clean Air Act and all glycol ethers were listed, as a group, on the Toxic Hot Spots AB 2588 list. Furthermore, many of these formulations would contain more than 2 percent VOC even after they were diluted as recommended by the manufacturer. The significance of this is that the SCAQMD permit regulation allows an exemption from permitting for water cleaning units using formulations with less than 2 percent VOC. John eventually identified two formulations that met this level so that Ace would not have to obtain an air district permit.

The solder used in the process is a tin/lead solder. The effluent generated by Ace would contain high levels of lead, higher than that allowed by the Orange County Sanitation District. Mixed bed treatment systems are effective in removing the lead and are available in packaged form. The bed must be sent off-site periodically for disposal and it is replaced with a new bed. The effluent can be passed through the beds and recirculated to the wash bath. If rosin-based flux were used, a filtration system using carbon in addition to the mixed bed would be required to treat the effluent.

John wanted to use one type of system for all of Ace's boards, both military and commercial. One option was to close loop the equipment. A closed loop feature would not only handle the lead from the solder but it would also provide deionized water. The other option was to route the rinse water to the sewer. To adopt this option, a sanitation department permit would be required.

John decided to convert to water with rosin-based flux for the two years left in the military contracts. He would purchase equipment with the closed loop feature but would not use it until the two military contracts expired. In the meantime, he would obtain a sanitation department permit and release the effluent to the sewer. When the existing military contracts had expired, the firm would begin using water with water soluble flux in a closed loop system. John presented the results to the management and they commended him for a job well done. The new system, after the capital investment was made, would actually be much less costly to operate because of the huge tax on CFC-113.

7.3 Case Study #2 -- Bath Cleaning

Best & Co. manufactures rubber bladders for hydraulic accumulators. Rubber is shipped to the firm in sheets for processing into bladders. The bladders are joined to stainless steel and carbon steel parts with different types of adhesives. These metal parts, some of which are threaded, act as stems for the bladders.

The stainless steel parts come to the plant without an oil coating. The carbon steel parts, however, because they are subject to rusting, arrive with a protective oil coating. The carbon steel parts are cleaned in a vapor degreaser that uses 1,1,1-trichloroethane (TCA). Both types of parts are then shot blasted to prepare the surface for adhesive bonding. Adhesive is painted on the parts and they are attached to the rubber bladders. The assembled bladder is heated in a compression molding operation and the heat activates the adhesive, bonding the rubber bladders to the metal.

Best uses about 1,200 gallons of TCA per year for cleaning the carbon steel parts. The parts are placed in a basket and lowered into the vapor zone of a standard vapor degreaser. They are left there for a time and the operator sprays them with a wand before they are removed from the degreaser and sent on to shot blasting.

Pete, an engineer with Best who handles the environmental requirements, has been assigned the task of identifying, testing and implementing an alternative to TCA. The management is aware that production of the chemical they use for cleaning will be banned on January 1, 1996. Best is currently labeling the bladders that are made with carbon steel parts, to comply with the labeling law which EPA began enforcing in November of 1993. Although the company management appears to be committed to the transition, Pete knows from past experience that if it involves a large capital investment, the company president may refuse to go forward.

In this light, Pete begins an investigation of available alternatives. Because of the reluctance of the president to make a capital investment, Pete starts with the options that would allow Best to continue using the vapor degreaser. He has received literature on a solvent, HCFC-141b, that the vendor claims is a "drop-in" alternative; apparently it can be used in existing vapor degreasers. Pete also has literature on another chemical, referred to as a brominated terpene; again, the vendor literature indicates that the chemical can be used in the firm's vapor degreaser.

Pete calls both vendors and they visit his plant. They both indicate that the vapor degreaser can be used with their solvents. Pete gives each vendor contaminated parts and they return them to him after cleaning with their solvent. In both cases, they appear to be clean. Pete subjects the parts to the shot blasting and the adhesive application and tests them by bonding them to the rubber. He then subjects them to stress and ageing tests to determine whether the bond will hold. The bonds are sound and Pete concludes that both solvents appear to be suitable technically.

Upon checking, Pete learns that EPA has published a list of alternatives to TCA and CFC-113 in cleaning applications of various kinds that are acceptable and unacceptable. Although the published SNAP regulation is more than 100 pages long, Pete realizes it is important to understand it so he tackles the challenge. He finds that EPA has deemed HCFC-141b an unacceptable alternative to TCA in the category "metals cleaning." It turns out that he could have used the chemical in Best's existing vapor degreaser until January 1, 1996 if he had begun the conversion before the regulation was implemented. Since this is not the case, Pete rejected HCFC-141b as an option.

The EPA SNAP regulation also indicates that his "brominated terpene" contains methylene bromide or dibromomethane. This chemical apparently has an ozone depletion potential higher than that of TCA and the chemical is likely to be very toxic. EPA lists the alternative under the category "Pending Substitutes," and states that the Agency intends to propose the chemical as an unacceptable substitute under a separate rulemaking. Pete decides that Best should not employ this alternative since it will soon be illegal to use it.

With the management constraint of having to find an alternative to use in the existing degreaser, Pete turns his attention to the other chlorinated solvents. He finds that TCE and METH are listed in the SCAQMD toxics rule (Rule 1401) as carcinogenic air contaminants. For listed chemicals, permits are difficult to obtain. The District staff performs a screening risk assessment on the operation. If the facility poses a risk to the surrounding community that is greater than 1 in a million, then Toxics Best Available Control Technology (T-BACT) is required. If T-BACT does not lower the risk to 10 in a million, the permit would be denied at the current usage level.

Best has an old degreaser and T-BACT is designated as either a refrigerated freeboard chiller and an extended freeboard or a carbon adsorption system. Pete estimates the cost of adding a refrigerated freeboard chiller to the vapor degreaser at $10,000, a substantial cost. The cost of purchasing a carbon adsorber would be much higher. Pete also performs a quick screening risk calculation based on emissions of about 1,000 gallons per year of TCE and METH. His calculations indicate that he will exceed the 10 in a million cutoff for both chemicals. He decided that TCE and METH were out.

Pete then thought about PERC. That chemical is not yet listed on SCAQMD Rule 1401 but it is proposed for listing by the SCAQMD staff. If Pete submitted a permit application before PERC was listed, there would be no use limitation and the firm could use about 1,000 gallons per year. Because PERC is classified as a VOC, however, it would be subject to the SCAQMD New Source Review (NSR) rule. The

NSR regulation requires BACT which, in this case, is a refrigerated freeboard chiller and an extended freeboard.

The NSR rule would also require the firm to provide offsets. A community bank can be accessed for offsets of less than 30 pounds per day. If Best needed 1,000 gallons per year, this would amount to an annual usage of 3,600 pounds. Since the plant operated for about 260 days each year, the offsets required would amount to 52 pounds per day. This far exceeds the 30 pound per day cutoff level. The offsets would have to be purchased on the open market and Pete determined that the going rate was $2,000 per pound. The cost of purchasing the offsets would amount to about $60,000. Pete rejected the option of converting the operation to PERC on the basis of cost.

This exhausted virtually all of the options that would allow Best to continue using the vapor degreaser. At this stage, Pete began examining water cleaning formulations. His major concern was that the carbon steel parts would rust. He contacted two formulators and sent parts to them for cleaning. They were returned to him still containing the rust inhibitor applied to the parts by the vendors. He put the parts through the shot blast operation and applied the adhesive. Again, destructive testing revealed that the parts were clean. The rust inhibitor did not appear to interfere with the shot blasting or the adhesive application steps and Pete is satisfied that water formulations can work for his application.

Pete begins looking into equipment. There are many different types of equipment and Pete chooses a simple batch cleaning unit containing a wash, rinse and forced air drying chamber. The cost of the unit is $30,000. He discusses the results of his evaluation with management and they authorize the purchase of the cleaning equipment.

The water-based formulation Pete selects has been tested by the manufacturer according to EPA Test Method Number 24 and the VOC content upon dilution in a 10:1 ratio is 0.7 percent. This falls below the 2 % VOC cutoff level under the SCAQMD permit rule. Thus, Pete does not require an air district permit for his new cleaning unit.

Pete also purchases an oil skimmer that he will use to continuously clean up the wash bath. The cost of the skimmer is $500. He decides that the rinse bath could be directly plumbed to the sewer and he contacts the L.A. County Sanitation District. After detailed conversations and correspondence, Best is granted a sanitation district permit.

The one remaining issue Pete has to deal with is whether or not the contaminated wash bath is hazardous waste. Periodically, when the bath becomes completely spent, Pete will have to ship the bath off-site. The disposal cost will obviously be higher if the bath is classified as hazardous waste. Since Pete's process does not add anything except oil to the water formulation, it would not be hazardous waste unless one of the cleaning formulation components is hazardous waste. Pete decides that he will have to have the contaminated cleaning bath tested before he ships it off-site. This one-time analysis will cost him $300. If the bath is hazardous, it will be handled as hazardous waste; if it is not, the firm may be able to release it to the sewer provided it meets all sanitation district limits.

As Pete checks into this issue further, he learns more about the DTSC regulations. It turns out that oil/water separation is covered by the DTSC tiered permitting regulations. That is, if the water cleaning formulation is considered hazardous waste, Pete might have to obtain a permit under the tiered permit system. Both the oil and water are being recycled, however, and the DTSC representative Pete contacts tells him that the recycling exemption should apply. This means he can skim the oil from the bath without obtaining a permit but, if the bath is indeed hazardous waste, Best may have to label the cleaning unit and place the cleaning unit in a secondary containment vessel. This would be impractical because the cleaning unit has to be accessible on the shop floor. If the bath is not hazardous waste, none of the provisions apply and Pete can use the skimmer without obtaining a permit and without labeling or secondary containment.

Pete calls the vendor who supplies the formulation the firm intends to use. He discusses the additives in the formulation with the chemist to try to determine whether they would be classified as hazardous waste in California. The chemist tells him the cleaner contains no hazardous components but this does not really answer the question of whether any ingredient meets the definition of hazardous waste for reasons of toxicity. Pete finally decides he will have the unused cleaner tested by a lab to determine if it is hazardous waste; since the process will add only oil, if the formulation is hazardous, it will be so classified from the outset. The test comes back negative and Pete is relieved. This means he can skim the oil without a permit, he does not have to label the unit or provide secondary containment and the bath does not have to be disposed of as hazardous waste.

7.4 Case Study #3 -- Hand Wipe

S & K Deburring is a small "job shop" that contracts with aerospace and non-aerospace customers. The firm is located in the Los Angeles area and provides processing services, including coating, anodizing and deburring. The parts processed by S & K are made of aluminum and steel. These parts are received with an oil coating which must be removed prior to processing. The oil is currently removed from the parts that are to be coated by hand with wipe cloths containing TCA. Because of the impending production ban on the chemical, Edith, the plant's environmental engineer, has been assigned the task of evaluating and selecting an alternative.

Edith begins by setting some standards for the operation. The solvent she wants should be a good cleaner, should evaporate readily and should not be dangerous to workers. She solicits samples for testing from a number of different vendors.

The first solvent she tests is a chlorinated toluene. It cleans well and evaporates readily; its allowable exposure level is only 4 ppm, however, and because this low level would be difficult to meet, she rejects the cleaner.

The second solvent she tests is a PFC. It evaporates readily and is virtually nontoxic. One drawback of the solvent is that it doesn't clean particularly well. Edith examines EPA's SNAP regulation and finds that PFCs are allowed but with limited use restrictions. Edith's use does not fall into the allowed categories so she rejects this solvent.

The third solvent Edith tests is a blend containing a terpene, d-limonene. The vendor literature claims the solvent is biodegradable and naturally occurring so therefore completely safe. Edith contacts the vendor and asks if the solvent is a VOC and the vendor indicates that its low vapor pressure means it is not really a VOC. Edith does not accept the vendor's assessment and calls the SCAQMD, the air district that has jurisdiction over her firms' operations. One of the District staff people tells her the solvent is a VOC and, indeed, that it is one of the most photochemically reactive solvents known.

Shop floor tests of the terpene solvent indicate that it does not evaporate readily and that the workers would have to use a second wipe cloth alone or with water to completely remove the solvent. The SCAQMD rules require firms to put the used rags in a closed container but Edith's investigation reveals that the terpene is not a listed hazardous waste under RCRA or under Title 22. The flash point of the blended solvent is 145° F so the blend is not a characteristic waste either. Since the material being removed in the handwipe operation is not hazardous, it appears that it would not be necessary to treat the used rags as hazardous waste. They could be disposed of in the trash. Edith thought this was a distinct advantage because it would eliminate the need for manifesting the material and it would eliminate the disposal cost.

The double wipe requirement would increase labor costs but these would easily be offset by the savings in waste disposal cost. Edith decided that this was the solvent for S & K. As a last task, she began checking the air district regulations to make sure this solvent was allowed. She found that for the firm's aerospace parts, she could use a solvent with a vapor pressure below 45 mm Hg according to SCAQMD Rule 1124. Since the blend's vapor pressure was only 2 mm Hg, the solvent was acceptable. For the firm's non-aerospace parts, however, the VOC content of a solvent for surface preparation was limited to 70 grams per liter in SCAQMD Rule 1171. The blend had a VOC content of 900 grams per liter and would not comply with this rule requirement. In fact, Edith realized that the 70 grams per liter limitation could not be met by any 100 % VOC solvent.

Edith began investigating water-based materials which were effectively the only ones that would meet the 70 grams per liter VOC cutoff. She tested two water cleaners and they were acceptable. A second wipe with deionized water was needed, however, to remove the surfactant in the water cleaner from the part. Edith realized she could use pure deionized water with only one wipe if the oil she was removing was water soluble. The parts that were coated came from 10 different sources and she began contacting them to see if they would be willing to change their oil. Two of the contractors were not willing to investigate an oil change and she gave up on this idea.

In the end, Edith decided to implement one of the water-based handwipe cleaners for both the aerospace and non-aerospace parts. She knew she would have to retrain the workers to use the double wipe procedure and that would not be easy. She had checked with the vendor and determined that the water cleaner did not contain any ingredients that were listed hazardous wastes. The used rags would not have to be disposed of as hazardous waste and this was an advantage.

SECTION 8:
SUMMARY AND CONCLUSIONS

8.1 Summary of Advantages and Disadvantages of Alternatives

Table 8-1 lists the alternatives to chlorinated solvents in cleaning applications and summarizes their advantages and drawbacks. The information in the table indicates that the generic chemical alternatives all have advantages but they all have disadvantages as well. As long as a chemical is used in the cleaning process, there is the potential to expose the worker and cause health problems or to allow the material to enter the biosphere and cause environmental problems. The alternative processes offer certain advantages where they can be used; in general, however, they are not widely applicable. Water-based cleaning, on the other hand, is widely applicable. Formulations must be selected judiciously or water cleaning will have the same problems as the chemical alternatives.

In general terms, the approach presented here will aid users in choosing alternatives that are most appropriate for their process and that minimize the human health and environmental problems. In evaluating a process, the first step is to ask whether cleaning is necessary. If a no-clean process can be used at reasonable cost, then that option should be adopted. If no-clean is not appropriate, then the user should consider water-based cleaning and other processes. Only if neither option is suitable should cleaning with chemical alternatives be considered.

The procedure recommended here is not without complexity. Indeed, selection of the "best" alternative is an art rather than a science. There is no simple formula that can be used in the analysis. Those who are best at alternatives evaluation are those who are most informed, those who can use generic schemes for analysis, those who can consider multiple dimensions simultaneously and finally, those who are comfortable with uncertainty.

8.2 Summary and Trends

Chlorinated solvents have been widely used in cleaning applications over the last 50 years. They have good cleaning capability and the fact that they have no flash points makes them the solvents of choice in many uses. They can be blended with a variety of other solvents which gives them great flexibility. They have been used in vapor degreasers effectively for removing contaminants from heavily contaminated metal and plastic parts, for precision cleaning of delicate parts and for removing the flux from printed circuit boards. They have also been used in cold cleaning applications for flushing oil and other contaminants from parts, in handwipe applications for wipe cleaning during manufacture and for repair and maintenance cleaning of various parts.

The widespread use of the chlorinated solvents and the health and environmental problems they pose brought them increased scrutiny. It is now established that two of the chlorinated solvents -- TCA and CFC-113 -- contribute to stratospheric ozone depletion. It is also accepted that the other three solvents -- TCE, PERC and METH

Table 8-1 Advantages and Disadvantages of Alternatives

Alternative	Advantages	Disadvantages
Flammable solvents	Evaporate readily; clean well	
Chlorinated solvents	Evaporate readily; clean well; can be used in vapor degreaser; no flash point	
CFC Solvents	Evaporates readily; compatible with virtually all substrates; low toxicity; no flash point	Contributes to ozone depletion and global warming, and will be banned
Combustible Solvents	Low vapor pressure means lower emissions in some applications	Regulated as VOCs; some are known to pose health and environmental problems; others are unscrutinized; have modest flash points; do not evaporate readily
HCFCs	Evaporate readily; clean well; can be used in vapor degreaser; no flash point	Cause ozone depletion and global warming and will be banned; use restricted by SNAP regulation; some pose health problems
HFCs	Evaporate readily; can be used in vapor degreaser; no flash point	Contribute to global warming; poor cleaners
FCs	Evaporate readily; can be used in vapor degreaser; low toxicity; no flash point	Contribute substantially to global warming; use restricted by SNAP regulation; very poor cleaners
BHCs	Evaporates readily; cleans well; can be used in vapor degreaser; no flash point	Contributes to ozone depletion and global warming; likely to be restricted by SNAP regulation; high toxicity

Table 8-1 Advantages and Disadvantages of Alternatives

Alternative	**Advantages**	**Disadvantages**
FIC	Not yet known	Not yet known
Chlorinated toluenes/ benzotrifluorides	Evaporate readily; clean well	Some are VOCs; likely to be toxic; have flash point
VMSs	Evaporate readily	Classified as VOCs; toxicity unknown; have flash point; poor cleaners
No clean options	Eliminates need for cleaning	Can be expensive; process dependent; process sensitive
Other media	No chemicals/water necessary	Can be expensive; process dependent
Water formulations	Low chemical use; low toxicity; effective cleaners	Process sensitive; mechanical action/fixturing important; may require sanitation district permit

-- are suspect carcinogens. All of the solvents have been identified as contaminants of soil and groundwater. Production of the ozone depleting substances will soon be banned. The other solvents are heavily regulated throughout the U.S. and particularly in California. The era of the chlorinated solvents is at an end.

Over the last several years, numerous alternatives to the chlorinated solvents have emerged. During that time, there has been a focused quest for a "drop-in" solvent that had similar properties, that could be used in all the same applications with the same procedures and that would be compatible with the same equipment. Although several solvents that had some of these characteristics were identified, upon more intensive examination, they all were found to pose at least one serious human health or environmental problem that prevented their widespread adoption. At this stage, there is no "drop-in" alternative and there is not likely to be one in the future.

This document presents a method of evaluating the alternatives to chlorinated solvents that uses a systems approach. This systems approach takes into account the characteristics of the use, the properties of the alternatives and the regulations that affect the alternatives. Indeed, all three of these dimensions must be considered together and simultaneously to determine the suitability of an alternative for a particular application. Beyond that, every operation is different and each operation has different requirements that depend on the cleanliness needs, the characteristics of the operation, the upstream and downstream processes, the financial status of the firm and the sophistication of the worker. The case studies presented here demonstrate the unique nature of every cleaning operation.

In the final analysis, each application must be evaluated on a case-by-case basis to determine the "best" alternative. The evaluator requires a great deal of information to perform the analysis for a particular process but judgement is also necessary. The information requirements include knowledge of the process, knowledge of the air, water, waste and worker exposure regulations and knowledge of the health and environmental problems posed by the alternatives. Some of this information is constantly changing and some of it is not known and may never be known. The regulations, for example, are updated at the Federal, State and local level as different priorities are accommodated. About 1,000 new chemicals enter the market each year and they are rarely required to be tested for chronic toxicity; they are unscrutinized and little is known of their potential human health and environmental effects. This means that there is great uncertainty surrounding the choice of alternatives and that judgements must be made about the wise course.

For the last few decades, chemical substitution in cleaning applications has been played like a shell game. One substance is regulated and users move to an alternative only to find later that it, too, poses problems. This is a time consuming and resource intensive exercise; it requires a new evaluation, new equipment and modified practices every few years. Although each process is individual, there is a path for choosing the "best" alternative in light of the fact that much of the information necessary for an optimal choice is unavailable and uncertain. The problem, then, is to select an alternative using all available information and the aim is to choose one that will minimize future problems. In effect, the best choice is the one that ends the shell game, the one that provides a permanent solution.

Based on the available information, this document makes judgements about what the "best" permanent solution is. Other evaluators will probably make other judgements. The important factor is that the judgements be informed ones. To this end, the purpose of this document is to provide the background for making informed decisions about alternatives and to structure a systems approach for the analysis. This simplifies the process and allows the rejection of inappropriate alternatives and fosters proper use of the alternative that is chosen. Many users test hundreds of alternatives and often they end up selecting one that is regulated today or will be regulated in the future. The system described here allows the categorization of the alternatives so that many can be eliminated from consideration from the outset and only a few need be tested.

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APPENDIX:
PROPERTIES OF CHLORINATED SOLVENTS AND POTENTIAL ALTERNATIVES

Table A-1 summarizes the properties of the five chlorinated solvents and several of their possible alternatives. The first column of the table indicates the other names for each of the chemicals and the second column provides the CAS number. The third column shows the generic chemical class into which the solvent fits. Columns four through eight give various physical properties of each of the solvents. Columns nine and ten show the California and Federal OSHA permissible exposure level. The eleventh column summarizes the regulations that apply to the solvent.

Table A-1 Typical Solvents and Their Properties

SOLVENT	ABBREVIATIONS AND SYNONYMS	CAS # (1)	GENERIC CLASSIFICATION	VOC (g/L) (2)	VP (mm Hg) (3)	FP (°F) (4)	BP (°F) (5)	EVAP. RATE (6)	CAL PEL (ppm) (7)	FED PEL (ppm) (8)	REGULATIONS
trichloroethylene	TCE, ethylene trichloride	79016	Chlorinated	1,460	59.4	none	189	6.39	25	100	A, B, C, D, E
perchloroethylene	PERC, tetrachloroethylene	127184	Chlorinated	1,619 (9)	14.2	none	250	2.59	25	100	A, B, C, D, E
methylene chloride	METH, dichloromethane	75092	Chlorinated	N/A	338	none	104	14.5	50	500 (10)	A, B, C, D, E
1,1,2-trichloro-1,2,2-trifluoroethane	trichlorotrifluoroethane, CFC-113, Freon 113, FC-113	76131	CFCs	N/A		none	75	6.39	1000	1000	
1,1,1-trichloroethane	TCA, methyl chloroform	71556	Chlorinated	N/A	100	none	165 - 169	6	350	350	A, B, C, D, E
1,1-dichloro-1-fluoroethane	HCFC-141b, dichlorofluoroethane	1717006	HCFCs	N/A		none	92		none (11)	none (11)	F
1,1-dichloro-2,2,2-trifluoroethane	HCFC-123, dichlorotrifluoroethane	306832	HCFCs	N/A		none	82	14	none (12)	none (12)	F
HCFC-225	Combination of HCFC-225 ca and HCFC-225 cb:		HCFCs						N/A	N/A	
	1,1-dichloro-2,2,3,3,3-pentafluoropropane (ca)			N/A							
	1,3-dichloro-1,1,2,2,3-pentafluoropropane (cb)			N/A							
1,1,1,2,3,4,4,5,5,5-decafluoropentane	HFC-43-10	NA	HFCs	N/A					none (13)	none (13)	
acetone		67641	Flammable	787	177.2	0	133	6.06	750	1000	
methyl iso-butyl ketone	MIBK, hexone	108101	Flammable	796		56	243 - 244	1.7	50	100	
methyl ethyl ketone	MEK, 2-butanone, ethyl methyl ketone	78933	Flammable	801		26	176	4.03	200	200	
isopropyl alcohol	IPA	67630	Flammable	780	32.4	72	180	1.7	400	400	
ethanol	ethyl alcohol	64175	Flammable	782	42.5	48	173	1.7	1000	1000	
ethyl acetate		141786	Flammable	898	70.8	26	169 - 172	4.94	400	400	
n-butyl acetate		123864	Flammable	878		72	255 - 259	1	150	150	
VM & P naphtha		Mixture	Flammable	743		58	255 - 288	1.1			
n-hexane		110543	Flammable	655	121	-10	156	6.82	50	500	
xylene (mixed isomers)	xylol, dimethylbenzene	1330207	Flammable	856	6.1	85	275 - 289	0.77	100	100	

Table A-1 Typical Solvents and Their Properties

SOLVENT	ABBREVIATIONS AND SYNONYMS	CAS # (1)	GENERIC CLASSIFICATION	VOC (g/L) (2)	VP (mm Hg) (3)	FP (°F) (4)	BP (°F) (5)	EVAP. RATE (6)	CAL PEL (ppm) (7)	FED PEL (ppm) (8)	REGULATIONS
toluene	toluol	108883	Flammable	863	21.6	40	232	2	100	200	
d-limonene		5989275	Combustible	837	1.5	119	349	0.25	none	none	
dibasic esters	DBE (combination of three dibasic esters):		Combustible	1100 (approx.)	0.2	212			none	none	
	dimethyl gluterate	1119400									
	dimethyl adipate	627930									
	dimethyl succinate	106650									
N-methyl -2-pyrrolidinone	NMP, M-pryol	872504	Combustible	1,029	0.29	187	396	0.03	none	none	
ethylene glycol monobutyl ether	butyl Cellosolve, 2-butoxy ethanol, ethylene glycol butyl ether, EGBE	111762	Combustible	899		140	336 - 343	0.072	25	200	A, B, C, D
ethylene glycol monomethyl ether	Cellosolve, methyl Cellosolve, 2-methoxy ethanol, ethylene glycol methyl ether, EGME	109864	Combustible	961	2.6	115	255 - 257	0.53	5	25	A, B, C, D
ethylene glycol monomethyl ether acetate	Cellosolve acetate, 2-methoxy ethanol acetate, ethylene glycol methyl ether acetate	110496	Combustible	1005		111	293	0.353	5	100	A, B, C, D
ehylene glycol monoethyl ether	2-ethoxy ethanol, ethylene glycol ethyl ether	110805	Combustible	926	<5	112	275	0.39	5	200	A, B, C, D
ethylene glycol monoethyl ether acetate	ethylene glycol ethyl ether acetate, 2-ethoxy ethanol acetate, 2-ethoxyethyl acetate	111159	Combustible	971		135	313	0.19	5	100	A, B, C, D
diethylene glycol monomethyl ether	methoxy carbitol, methyl carbitol	111773	Combustible	1006		183	381	0.018	none	none	
diethylene glycol monobutyl ether	butyl carbitol, butoxy ethoxy ethanol	112345	Combustible	949		232	446 - 455	0.003	none	none	
diethylene glycol monobutyl ether acetate	diethylene glycol butyl ether acetate	124174	Combustible	974	<1	240	455 - 482	0.001	none	none	
propylene glycol monomethyl ether	propylene glycol methyl ether	107982	Combustible	880		115	284 - 302	0.368	100	none	
propylene glycol t-butyl ether		57018527	Combustible	869		113	304	0.25	none	none	
dipropylene glycol monomethyl ether	dipropylene glycol methyl ether	34590948	Combustible	949		167	360 - 379	0.02	100	100	
Mineral spirits		64742887	Combustible	775		107	320 - 369	0.16			

Table A-1 Typical Solvents and Their Properties

SOLVENT	ABBREVIATIONS AND SYNONYMS	CAS # (1)	GENERIC CLASSIFICATION	VOC (g/L) (2)	VP (mm Hg) (3)	FP (°F) (4)	BP (°F) (5)	EVAP. RATE (6)	CAL PEL (ppm) (7)	FED PEL (ppm) (8)	REGULATIONS

Regulations: A = SCAQMD Proposed Amended Rule 1401; B = AB 2588; C = Title III of the Clean Air Act ; D = SARA Title III; E = Title VI of the Clean Air Act (Ozone Depletion Ban);
F = Proposed for Addition to SARA Title III

(1): Chemical Abstracts Registry Number
(2): VOC = Volatile Organic Compound content in grams per liter of material. For pure substances this is essentially the density of the material.
(3): VP = Vapor Pressure of the pure substance at 20 °C in millimeters of mercury (mm Hg).
(4): FP = Flash Point
(5): BP = Boiling Point
(6): Evap. Rate = evaporation rate relative to n-butyl acetate which has been assigned a value of 1.00.
(7): California Occupational Safety and Health Administration Permissible Exposure Limit, which is the maximum permitted 8-hour time-weighted average concentration of an airborne contaminant.
(8): Federal Occupational Safety and Health Administration Permissible Exposure Limit, which is the maximum permitted 8-hour time-weighted average concentration of an airborne contaminant.
(9): Currently, perchloroethylene (PERC) is designated as a Volatile Organic Compound (VOC). It has been known for quite some time that PERC does not contribute to atmospheric ozone. The U.S. Environmental Protection Agency (EPA) may soon exempt PERC as a VOC.
(10): There is currently a proposed rulemaking by Federal OSHA to lower to PEL for methylene chloride to 25 ppm.
(11): There are no PELs established for HCFC-141b; the manufacturer's recommended exposure limit is 400 ppm.
(12): There are no PELs established for HCFC-123; the manufacturer's recommended exposure limit is 30 ppm.
(13): HCFC-43-10 is a new chemical, thus there are no established PELs; it is expected that the manufacturer will recommed an exposure limit of 400 ppm.

N/A is not applicable