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ALTERNATIVES TO ORGANIC SOLVENT DEGREASING

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Prepared for

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ABSTRACT

Under contract with the California Air Resources Board, Eureka Laboratories, Inc. has conducted a study to evaluate degreasing alternative methods/solvent systems with the objective of reducing or eliminating the use of organic solvents for degreasing applications. This study included both hydrocarbon emissions and cost as primary criteria in the evaluation of degreasing processes.

In achieving the objectives of the study, the project was conducted in three parts. The first part was devoted to collection of data concerning degreasing methods, their costs, and hydrocarbon emissions in 1976 from degreasing users which included mainly the manufacturing and service-maintenance industries. Data were collected by questionnaire surveys and by reviewing literature on the subject. The second part identified alternative degreasing processes through literature review and analyses of survey responses. The last part studied the potential emission reduction and costs incurred in the use of photochemically less reactive or non-reactive degreasing alternatives.

Based on findings of this study, the estimated TOG emission from degreasing operations in 1976 was 119.7 TPD, and 38.6 TPD for ROG. Aircraft parts manufacturing and service-maintenance industries, which include automotive repairs and oil well maintenance operations, were the major contributors to hydrocarbon emissions resulting from degreasing operations. Emissions from automotive repairs and oil well maintenance operations represented 27 percent of TOG and 85 percent of ROG due to degreasing operations. Primary degreasing alternative processes recommended for these industries are

alkaline washing and emulsion cleaning methods, but the annual costs for using these alternatives are higher than those for solvent degreasing. These recommendations are preliminary and should be evaluated on an experimental basis.

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ABBREVIATIONS AND DEFINITIONS

Abbreviations	Definitions
APCD	Air Pollution Control District.
AQMD	Air Quality Maintenance District
BACT	Best available control technology is defined as the maximum degree of emission control which can be utilized, taking into account technologies known but not necessarily demonstrated.
CARB	California Air Resources Board
EPA	Environmental Protection Agency
K-B Value	Kauri-Butanol value is the number of milliters of solvent that can be added to a specific solution of Kauri resin in butanol before precipitation of the resin occurs.
kc/s	Kilocycle per second
Kw	Kilowatt
MAC	Maximum allowable concentration
NEDS	National Emissions Data System is developed by the EPA to provide an uniform method for assembling emissions data.
NSR	New Sources Review
OSHA	Occupational Safety and Health Act
psig	Pounds per square inch gauge
ROG	Reactive organic gases, which include all organic compounds grouped under Classes II and III of the

Abbreviations	Definitions
ROG (continued)	California Air Resources Board Reactivity Classification of Organic Compounds.
SCC	Source Classification Code assigns a code to each type of air pollution emission source.
SIC	Standard Industrial Classification assigns a code to each type of activity in business and industry.
TOG	Total organic gases, which include all organic compounds grouped under Classes I, II, and III of the California Air Resources Board Reactivity Classification of Organic Compounds.
TPD	Tons per day
TLV	Threshold limit value
TWA	Time weighted average
TPY	Tons per year

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1.0 CONCLUSIONS

The following conclusions are based on the interpretation of data presented in this study.

1. There are technically viable alternatives to conventional organic solvent degreasing. Alkaline washing and emulsion cleaning are currently widely used in several sectors of the manufacturing industry. The suitability of applying a specific cleaning system depends, however, on individual cleaning requirements and other variables.
2. If a solvent degreasing system can be replaced technically by a water-based alternative, the annualized cost for the alternative is usually higher than that for the solvent degreasing system. The actual costs incurred in specific cleaning assignments may vary widely because of the many factors involved in each degreasing process.
3. Water-based cleaning processes generally require more energy, more space, and less expenditure on solvents; they also have low cleaning efficiencies and high rejection rates; however, they have low or no solvent emissions.
4. In 1976 the estimated TOG emission from degreasing operations was 119.7 TPD, and 38.6 TPD for ROG. The ROG emissions represented about one-third of the TOG emissions. The manufacturing industry contributed the majority (71%) of TOG emission, whereas a part of the maintenance industry (automotive repair and oil well maintenance) contributed the majority (85%) of ROG emissions.
5. In 1976 Los Angeles County had the highest TOG emission, 54.9 TPD,

from solvent degreasing operations conducted by the manufacturing industry in California. The aircraft parts manufacturing industry emitted 68 percent of the TOG emissions in that county.

6. By applying solvent degreasing alternatives to the manufacturing industry degreasing operations, a potential emission reduction of 89 percent TOG, and 72 percent ROG may be achieved. The potential reduction in maintenance degreasing operations depends on the availability of a workable alternative.

2.0 RECOMMENDATIONS

1. Alkaline washing and emulsion cleaning are two viable alternatives. Any switching of the SIC categories identified in this study to these two alternatives should be carried out, however, on an individual basis.
2. Since waste solvents usually end up in the ambient air, nonreclaimable solvents should be discouraged. Solvent degreasers should be equipped with a circulating system that returns the solvent to a storage tank after it has been pumped up to the degreaser for metal cleaning.
3. From a photochemical air pollution standpoint, degreasing-solvent emission control should be focussed on those degreasing operations that use reactive solvents. For other less-reactive solvents, however, other factors such as occupational health, should be considered.
4. A demonstration project or case study should be conducted to obtain detailed information on the technical and economical feasibilities of the following metal cleaning processes:
    - Alkaline washing for aircraft industries;
    - Emulsion cleaning for automotive repair and oil well maintenance industries.

These industries are the major sources of emissions resulting from degreasing operations.

3.0 INTRODUCTION

3.1 Need for Alternatives to Organic Solvent Degreasing

Most of the recent studies done to reduce nonvehicular organic emissions have centered on the surface coating, dry cleaning, and degreasing industries.[1, 2, 3] The primary reason is that these industries are the three major organic solvent users responsible for sizeable reactive organic emissions, and they have received relatively little regulatory attention in the past. During 1974, the use of organic solvents accounted for 23 percent of all hydrocarbon emissions in California.[4] According to the 1973 emission inventory published by the California Air Resources Board,[5] the emissions of reactive organic gases in California averaged 658 tons per day. Of this total emission, 390 tons, 15 tons, and 17 tons were emitted from the surface coating, dry cleaning, and degreasing industries, respectively.

In reducing these emissions sources, attempts have been made to develop alternative solvent systems. Typically, accomplishments in the surface coating industry have centered primarily on the shift to aqueous paint coating systems.[2, 3] On the other hand, the dry cleaning industry has, by its very nature, been more involved with developing photochemically unreactive organics. Dow Chemical Company currently is marketing dry cleaning systems utilizing freon-based cleansers.[3] While there is some controversy regarding freon aerosol propellants, there are available freon cleaners that are less volatile. Other alternatives have stressed the potential of using nonreactive solvents (e.g., perchloroethylene; category 1) to mitigate the air pollution problems associated with these operations.[3]

The theoretical principle of the degreasing process is a relatively simple one. Degreasing is primarily the process of the removal of chemically hydrophobic (nonpolar) materials from metal works. Traditional methods are based, to a large extent, on the use of nonpolar organic solvents which can dissolve the nonpolar hydrophobic grease materials followed by subsequent disposal or recycling of the organic solvents. Other methods involve the use of detergents which basically are emulsifiers containing a long, nonpolar, hydrocarbon-like "tail" and a very polar, water-soluble "head," which can emulsify the grease to form micelles. This emulsification is followed by agitation and removal. The entire process of emulsification has been utilized in the surface coating industry to create the water-based paints presently on the market. Here, a highly hydrophobic substance (paint vehicle solids) is caused to emulsify in water by use of co-solvents and physical methods (e.g., by agitation or ultrasonic means).

From a chemical standpoint, any improvement of presently available methods of degreasing, which would reduce the reactive organic emissions, must be centered on the principle that the agents used must be able to dissolve the hydrophobic grease materials. There are certain physically based mechanisms for soil removal that utilize phenomena other than dissolution. For example, the works of Whittaker, Hamilton and Jennings[6] have shown that significant cleaning can be accomplished when surface tension is artificially high. This is contrary to the "classical" detergency theory based on low-surface tension. This phenomenon is termed the Dupré mechanism. Thus, in order to mitigate the air quality impacts of solvent degreasing, systems must be established that call on varied theories, rather than on a single one. This approach could be accomplished by:

(a) Dual component systems utilizing polar (hydrophilic) solutes in nonpolar carriers (hydrophobic)--e.g., glycolic sodium hydroxide or silicone systems;

(b) High surface tension detergents;

(c) Patented processes--e.g., freon systems of Dow Chemical Company;

(d) Photochemically unreactive and nonvolatile organics--e.g., perchloroethylene;

(e) Novel and nonchemical systems--e.g., ultrasonic and vacuum.

While there are theoretical and laboratory-demonstrated schemes for cleaning which utilize the various soil removal phenomena outlined above, many have been restricted to such demonstrations only under highly controlled situations. A technical alternative (as opposed to a theoretical alternative), however, would be one which has undergone some form of evaluation under the uncertainties often prevalent in many industries.

While there are certainly technical alternatives to the solvents used, there must also be an economical alternative if users are to be convinced to change operations. It seems that several of the alternatives for dry cleaning operations would be quite suitable for use in other degreasing operations as well. Further, the use of these alternatives within the cleaning industry must be strongly encouraged.

3.2 Program Objectives

In defining the feasibility of employing alternative solvent systems and processing methods to eliminate or reduce the use of organic solvents for cleaning and degreasing applications, the California Air Resources Board has initiated a program to provide the necessary technical inputs to that effort. The objectives of the program are to:

(1) Identify types of processes and products that are using organic solvent cleaning and estimate hydrocarbon emissions resulting from these sources;

(2) Identify and evaluate degreasing alternatives, and make cost comparisons;

(3) Estimate the potential reduction of hydrocarbon emissions from new substitute systems.

3.3 Scope

This report presents the results of the program, which consisted of three parts. The main objective of the first part was to conduct a degreasing solvents users' survey of California industries. This survey involved only the type and quantity of solvents used in 1976. The second part was to identify and evaluate alternative degreasing processes. The third part was to analyze potential emission reductions and costs incurred in the use of photochemically less reactive or nonreactive alternatives.

The approach taken in the first part was to send quesionnaires to about 10 percent of the California manufacturing industries which have been identified under the Standard Industrial Classification (SIC) as possible degreasing solvent users. Based on the California Chamber of Commerce 1975 statistics,[7] the number of possible degreasing solvent users is about 14,400. Approximately 1500 survey questionnaires were sent out, and the response was about 53 percent.

In addition to the manufacturing industry, service/maintenance activities, such as automotive repairs and oil well maintenance, represent the remaining major degreasing solvent users in California. Data of solvent consumption for service stations and automotive repair shops were obtained from Safety-Kleen Company and recent studies. The solvent-use data for oil well maintenance was supplied by the Kern County Air Pollution Control District.

Identification of degreasing alternatives was conducted through literature review and survey responses. In this report, solvent emission-control measures--e.g., active carbon adsorptions, refrigerated chillers, and conversion to photochemically less-reactive solvent systems--were not classified as alternatives to solvent degreasing. All alternatives can be grouped under two classifications: nonorganic solvent systems and novel nonchemical systems. Nonorganic solvent systems may include water-based alkaline washing and emulsification cleaning. Abrasive blast cleaning is an example of the novel nonchemical systems.

Based on data derived from the first two parts, emission reduction and costs resulting from the use of alternative degreasing solvent systems were calculated. Emission-reduction estimates used 1976 as the base year for comparison. Considerations in estimating the total cost attributable to a changeover to nonorganic or photochemically unreactive solvents included capital, operating, and external costs.

During the past several years, there have been several studies concerned with emissions from degreasing industries.[1, 5, 8] The California Air Resources Board (ARB) recently published the California 1973 "Emission Inventory."[5] The average emissions for reactive organic gases (ROG) and total organic gases (TOG) were 16.7 and 134 tons per day, respectively. The ARB estimation was based on data submitted by the Air Pollution Control District (APCD), which included only those sources emitting greater than 25 tons per year of pollutant.

In 1976 a more comprehensive study was conducted by the Dow Chemical Company under contract with the U.S. Environmental Protection Agency (EPA). The objective was to provide a factual background for initiating regulatory controls for reducing hydrocarbon emissions from future solvent metal-cleaning operations. Actual operations representing the best performances of existing emission control technology were studied and their effectiveness measured. Data gained were supplemented by literature reviews, laboratory testing, and information from extensive industrial experience, including that of major solvent and equipment manufacturers. The last available report relevant to this project, which was released by the EPA last December,[8] provided regional and state air pollution control agencies with information about different techniques for reducing organic emissions from solvent metal cleaning.

This present study seeks to make the following contributions and improvements over the existing information:

1. Determination of the amount of degreasing-solvent emissions from manufacturing industries of all sizes.
2. Determination of the amount of solvent emissions from maintenance-type cold degreasers (mainly from automobile and oil well service and repair activities).
3. Identification of alternatives to organic solvent degreasing.
4. Cost/benefit assessment of alternative degreasing systems.
5. Estimation of the reduction of solvent emissions by applying the alternative degreasing systems.
6. Recommendation of SIC candidates for possible switching over to the alternative degreasing systems.

3.4 References

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4.0 BACKGROUND INFORMATION

This section provides information on current degreasing practices in the manufacturing industry, emission inventory approaches, photochemistry of degreasing solvents, relevant regulations, and on prevalent types of secondary controls.

4.1 Organic Solvent Degreasing

Organic solvent degreasing processes use non-aqueous solvents to clean and remove soils from metal surfaces. Organic solvents used in degreasing operations would be expected to dissolve oils, greases, waxes, tars, and in some cases, water. Insoluble materials would be flushed away together with the dissolved substances in the solvents. These contaminants are generally referred to as "soils," and the articles to be degreased are termed as "works." Organic solvent degreasing can be classified into three basic types: cold solvent degreasing, open-top vapor degreasing, and conveyorized degreasing. Cold solvent degreasing can be further classified into maintenance degreasing and manufacturing degreasing. Maintenance cold degreasing is designed for automotive repair and general plant maintenance. Manufacturing cold degreasing is generally used as an integral stage in metal working production. Manufacturing degreasers are usually larger in size and perform a higher quality of cleaning than maintenance degreasers. Open-top vapor degreasers are more capital intensive than cold degreasers. They are usually located near the work to be degreased and usually operated manually in batch operation. Conveyorized degreasers are centralized cleaning systems, and works to be cleaned are transferred to the degreasers for cleaning. They are operated in a continuous operation by the conveyor systems. These three major types of degreasing will be discussed below together with a discussion of the major degreasing solvents currently being used.

4.1.1. Cold Solvent Degreasing

The operations in this category are performed at normal room temperature, or slightly above. They are characterized by simple equipment and activities:

- wiping
- flushing and spraying
- immersion

A. Wiping

This method of cleaning is perhaps one of the most frequently used for shop and equipment cleanings.[1] A rag or sponge is dipped into the solvent and then used to remove oily or greasy dirt that has accumulated on the item being cleaned. As can be appreciated, there is no real equipment cost for this method of cleaning, only labor and materials. This cleaning method does not lend itself to routine continuous operations. Typically, it is restricted to "as-needed" shop maintenance. Also, very little secondary control is possible except for disposing of the solvent/soil saturated rags in a closed container. This, however, reduces the vapors only within the shop itself; the rags are ultimately disposed of in a manner that allows the solvent to evaporate directly to the atmosphere.

Because of the random nature of this mode of degreasing, solvents are often chosen indiscriminately. Usually, whatever will remove the soil and is close at hand is used, little or no consideration is given to cleaning efficiency or photochemically reactive criteria. Gasoline, petroleum solvents, and paint thinners - these are some of the common solvents used in this particular mode of cleaning.[1, 2]

B. Flushing and Spraying

This mode of cleaning is very similar to wiping. Cleaning is accomplished almost solely by solvents, and with minimal physical action. However, spraying is utilized for routine manufacturing operations and particularly for small parts produced in large volume. The difference between these two very similar processes is the basis for designation of "flushing" or "spraying": flusing utilizes a continuous stream of solvent, whereas spraying employs droplets of solvent[1].

Flushing or spraying is restricted to the outer surfaces of objects; generally the solvent does not enter complex or inner structures. Both methods rely on the solubility of the soil and provide little, if any, physical action for insoluble soils removal.

Solvents used typically are petroleum solvents, such as stoddard or solvent blends. Pure halogenated solvents are seldom, if ever, used for spray or flush cleaning due to high material cost. The equipment costs for these types of cleaning operations are only slightly higher than for wiping. The labor costs are typically considerably lower on a equal work basis. The labor savings would be greatly offset if distillation equipment were used to reclaim spent solvent. Special solvents, then, are used only in unusual cases.

The equipment used for flushing or spraying is very simple. It usually consists of a solvent tank, feeder hose, and baskets for work to be cleaned.

The solvent may be fed either by pump or gravity although pump feeding is more common. The solvent is generally used continuously until it is degraded.

C. Immersion Cleaning

Immersion cleaning is seldom used alone but usually in conjunction with wiping, flushing, ultrasonic cleaning, or any combination of the three. Again, as in most cold cleaning operations, most of the cleansing action is accomplished by the solvency of the solvent. Additional cleaning is a result of added mechanical forces through any of the three methods above (ultrasonic cleaving will be discussed later).

The main use of immersion cleaning in production operations is in work that needs numerous cleanings of minimal quality.[1] One example is the removal of lubricant prior to tolerance checks in the machining of parts. This type of cleaning does not need the degree of cleanliness required in, for example, plating or painting.

The equipment for immersion cleaning is the simplest of all cold cleaning operation: all that is required is a container for the solvent and the articles being cleaned. Any other attachments are either for safety reasons or to provide the mechanical forces necessary for flushing action or ultrasonics. Because of increasing volumes of solvent being required at cleaning stations, fire-safety precautions are becoming ever more necessary. Larger volumes are required to permit complete immersion of the work. Automatic covers usually provide the safety required to prevent fires from spreading. Tank covers also help minimize solvent loss during periods of non-use if the covers are in place. However, typical operations are such that evaporation control covers are generally not in place.[1]

Solvent choice is predicated on costs and material compatibility. For general use, stoddard solvents are chosen. Fluorocarbons (e.g., freon) are generally used in operations involving the milling or machining of plastics, and in the removal of particularly stubborn soils and hard greases. These special blends usually include chlorinated hydrocarbons or olefins and are used in conjunction with ultrasonics.[1]

As previously mentioned, the quality of cleanliness is not great in a large number of operations involving immersion cleaning. The level of cleanliness is usually dependent on the amount of soil allowed to accumulate in the solvent before it is disposed. As the soil content increases, the amount of soil redeposited on the work increases.

The major sources of solvent emissions from cold solvent degreasers are:[3]

a. Direct evaporation of solvents from tanks

b. Evaporation from disposed waste solvents

c. Evaporation from drag-out on or in metal works

The amount of solvent directly evaporated from the tank depends on the air draft velocity, the room temperature, the type of solvent used, and the freeboard ratio which is defined as the height from the surface of the solvent to the top of the tank (freeboard height) divided by the length of the shorter side of the tank.

Except where pure halohydrocarbons are used, distillation of used solvents from cold degreasers is not practiced to any great extent. Disposed-of-waste solvents often contain 80-90 percent recoverable solvent. Central redistillation facilities would greatly decrease the emissions to the atmosphere from land disposal.

4.1.2 Open-Top Vapor Degreasing

The other major class of organic solvent cleaning is vapor degreasing. It differs from cold cleaning in that vapor degreasers utilize boiling organic solvents. This characteristic precludes many solvents normally used in cold cleaning due to considerable safety hazards. Solvents then are chosen for their solvency and nonflammability.

A typical open-top vapor degreaser is a tank designed to produce and contain solvent vapor. The tank is equipped with a heating system to boil the solvent. The solvent vapors generated are heavier than the air and tend to replace the air on the top of the solvent surface. Condenser coils located on the freeboards of the degreaser control the upper level of the vapor. The metal works to be cleaned, in the batch form, are lowered to this vapor zone of the degreaser. The solvent vapors condense on the works until the temperature of the work reaches the boiling point of the solvent. The soils dissolve in the solvent more thoroughly at the high temperature, and the flushing effect of solvent is enhanced by the vapor turbulence. The metal works are slowly withdrawn from the degreaser when condensation of the solvent ceases. The residue solvent left on the work evaporates rapidly as the works are removed from the vapor zone.

There are several distinct advantages of vapor degreasing over cold solvent cleaning. First, the solvent contacting the work is continuously redistilled, thereby being essentially pure. Secondly, the work being cleaned eventually reaches the boiling point temperature of the solvent and leaves the degreaser not only cleaned but also dry. Finally, because vapors are used, an intricate work can be cleaned. Liquid solvent may not reach inside intricacies but vapors do and subsequently condense.

Because of the heating requirements and the associated controls combined with automation, generally the equipment required for degreasing by vapor is of considerable more complexity than for any of the cold cleaning systems. The following are the major considerations in designing equipment for vapor degreasing operations.[4]

- Size and mass of work to be cleaned
- Specific heat of work to be cleaned
- Volume (in number) of work to be cleaned
- Soil type being removed
- Shop space allotted

Because the work must be raised to the boiling point of the solvent, the size and mass of the work to be cleaned, along with its specific heat, determine the heat requirement. Further, the heat capacity of the work determines the total amount of solvent that will condense on each part. The total amount of solvent must supply adequate solvency and flushing action to produce the level of cleanliness required.

Finally, the size of the piece determines the size of the degreaser opening. Both minimum and maximum sizes need to be taken into account. A too-small opening will result in serious vapor losses through vapor turbulence when the work is introduced, while a too-large opening will also create too-high losses because of unnecessary exposed surface. A general rule-of-thumb is for the openings to be 40-60 percent larger than the parts (or baskets) being introduced. Work must be introduced into the vapor zone slowly to minimize turbulence. The quantity of work being processed determines the ultimate total heating requirements.. This factor, along with the heat capacities of the work and the solvent, combine to determine the utilities cost for vaporizing the solvent.

The nature of the soil being removed generally determines the type of solvent required. Except for those soils that are hard or intractable, such as baked varnish or heat-set machining lubricant, chlorinated solvents can remove most of the soil types encountered in routine vapor degreasing. Chlorinated solvents may, however, be entirely too strong for some plastics or reactive metals. The fluorocarbons, having lower solubility, are used when incompatibility of strong solvents is suggested. Shop-space planning is also of importance in designing degreasers, particularly because of costs of space and heating requirements.

In addition to the considerations mentioned above, the choice of solvent for degreasing is dependent of several other criteria.[4] The solvency for the particular soil being removed is certainly the most important criterion. The higher the solubility the more efficient the cleaning both in ultimate cleanliness and in time needed to reach a specific cleanliness. Because of the necessity of heating the solvent to boiling, nonflammability is crucial. This requirement has let to general use of halogenated aliphatic and olefinic solvents for vapor degreasing. In order to save on energy requirements, a low specific heat and heat of vaporization is desired. In order to allow adequate cleaning, the heat of vaporization must be kept low to ensure sufficient condensation on the work to remove the soils. High vapor density is also required to ensure that the solvent vapors remain in the freeboard area rather than floating free into the atmosphere. Chemically the solvent should be fairly stable; it should not decompose readily, nor should it react with the material being cleaned. Low toxicity and ready availability at low cost are also important criteria. Polyhalogenated paraffins and polyhalogenated olefins are widely used in open-top vapor degreasing because they can meet most of the requirements. An inhibitor (mixture of acid acceptor), a metal stabilizer, an antioxidant, and an anticorrosion reagent are generally added to the solvent to maintain its chemical stability.

Most of the emissions from open-top vapor degreasers are vapors that diffuse out of the vapor zone of the degreaser. The amount of solvent that escapes from the tank depends on drafts, disturbances caused by moving works in and out of the vapor zone, the opening of the degreaser, the condensing capability, and the type of solvent used. Relatively small amounts of emission are from the waste solvent and drag-out. In-plant distillation is generally used to treat waste solvent. Solvent recovered can be re-used if additional inhibitors are added.

4.1.3 Conveyorized Degreasing

Conveyorized degreasers are cold or vapor degreasers that are loaded continuously by means of various conveyor systems. The automation of the cold cleaning process is restricted in application. The reason for this is that operations justifying equipment outlays of this magnitude usually choose conveyorized vapor degreasing. An exception is in the production of printed circuit boards. Film development and solder flux-removal bath require a halohydrocarbon (either 1,1,1-trichloroethane or trichlorethylene). These types of installations generally have a still to recover the more expensive halohydrocarbon solvent. There are several major types of conveyorized degreasers: monorail, cross-rod, vibra, ferri, belt, strip, and circular board cleaners.[5]

Conveyorized degreasing systems have the advantage of being enclosable to a greater extent than nonautomatic systems. This feature allows for reduced emissions of solvent to the atmosphere assuming adequate treatment of ducted air (either incineration or carbon absorption). Major emissions then result primarily from solvent drag-out and disposal of waste. Again, on-site reclamation of solvent is a general practice for this type of degreasing.

4.1.4 Degreasing Solvents

Four main types of organic solvents are used in industries with solvent-degreasing operations: alcohols, halogenated solvents, hydrocarbons, and ketones. Table 4-1 lists quantitatively the emissions of solvents nationwide from different degreasing practices.[5] The maintenance type of cold degreasing and wiping uses mainly hydrocarbons, such as mineral spirits; whereas, manufacturing cold degreasing and conveyorized cold degreasing use a wide variety of solvents. Open-top vapor degreasers and conveyorized vapor degreasers use exclusively halogenated solvents.

The important parameters of major degreasing solvents are shown in Table 4-2 and Table 4-3. Relative volatilities are based on data measured at room temperature.[1, 6-8] The wholesale prices of solvents were obtained from the Chemical Marketing Reporter.[9] The energy required to heat a ton of steel from room temperature (68°F) to the boiling point of the degreasing solvent is calculated based on the fact that 0.115 Btu of heat is required to raise one pound of steel by 1°F.

Petroleum products are generally used in the maintenance type of cold degreasing, mainly because of the low cost of solvent and the low quality cleaning requirement. Almost all the solvents listed in Table 4-2 are used in the manufacturing type of cold solvent degreasing and the conveyorized

Table 4-1. NATIONWIDE DEGREASING EMISSION SUMMARY[5]

Degreasing Process/ Solvent Type	Emission (10^3 ton/yr)	Percentage
Cold Solvent Degreasing	380	55
Alcohols	29	
Halogenated Solvents	133	
Hydrocarbons	200	
Ketones	18	
Open-Top Vapor Degreasing	200	28
Conveyorized Cold Degreasing	25	3
Conveyorized Vapor Degreasing	75	11
Wiping	20	3
TOTAL	700	100%

Table 4-2. PARAMETERS OF MAJOR HALOGENATED SOLVENTS[1, 6-9]

	Tri-chloroethylene	1,1,1-tri-chloroethane	Per-chloroethylene	Methylene Chloride	Freon-113
Boiling Point (°F)	189	165	250	104	117
Relative Volatility	0.61	1.00	0.16	3.52	4.26
Density (lbs/gal)	12.14	10.97	13.47	10.98	13.16
Wholesale Price ($/gal)	2.52	2.66	2.32	2.35	7.37
Vapor Density (air = 1)	4.53	4.55	5.76	2.93	6.5
Energy Requirement (Btu/ton steel)	30,500	24,600	46,000	9,100	12,300
Latent Heat (Btu/lb)	102	102	90	142	63
Condensate Volume (gals/ton steel)	24.6	22.0	37.9	5.8	14.8
Steam Pressure (psi)	10-15	3.6	45-60	~1	~1
Stabilizer required	Yes	Yes	Yes	Yes	No
Solvency (Kauri-Butanol)	130	124	90	136	31
Molecular Weight	131	133	166	85	187
Specific Heat (Btu/lb - °F)	0.837	0.730	0.665	0.778	0.746

Table 4-3. PARAMETERS OF MAJOR NON-HALOGENATED SOLVENTS[1, 6-9]

Solvent Type/ Solvent	Boiling Point (°C)	Relative Volatility (1,1,1-trichloroethane = 1)	Density (lbs/gal)	Wholesale Price ($/gal)
Alcohols				
Methanol	147	0.44	6.60	0.51
Ethanol	165	0.24	6.76	1.12
Isopropanol	179	0.18	6.55	1.02
Hydrocarbons				
Heptane	201	0.25	5.79	0.48
Stoddard	314	0.02	6.40	0.46
Toluene	230	0.17	7.26	0.71
Xylene	281	0.05	7.23	0.48
Ketones				
Acetones	132	1.18	6.59	1.20
Methyl Ethyl Ketone	174	0.44	6.71	1.41

cold degreasing. The exact type of solvent used depends mainly on the cleaning efficiency required and the material of the works to be cleaned.

It must be remembered that a large fraction of cold solvent cleaning is nonroutine maintenance performed in a noncentralized fashion.

The solvency of a cleaner is of course the most important criterion. A commonly accepted measurement of solvency is the Kauri-Butanol (K-B) value. The higher the K-B value, the higher the "solvency." This value is somewhat arbitrary in that it does not always indicate solvency for a particular soil. It is only a relative measurement. The K-B value is the number of milliliters of solvent that can be added to a specific solution of Kauri resin in butanol before precipitation of the resin occurs. Petroleum solvents have K-B points in the range of 30-50, while 1,1,1-trichloroethane has a K-B of over a hundred.[6] This does <u>not</u> mean 1,1,1-trichloroethane has twice the solvency of petroleum solvents. It does indicate that cleaning efficiency may be increased by usage of alternate solvents to petroleum spirits. Further, assuming halogenated solvents are substituted for petroleum solvents in cold cleaning, further advantages are achieved in higher reclaimability and reduced fire hazard.

Alcohols and ketones are selected for cold degreasing mainly because they evaporate faster than petroleum products and leave cleaner surfaces; they are preferred to halogenated solvents mainly because of their solvency and cost.

The five major halogenated solvents listed in Table 4-2 are manufactured and sold under a variety of trade names. While they are all certainly suitable to general vapor degreasing processes, each has limitations associated with it.

Trichloroethylene has been the historical favorite for vapor degreasing usage. It is felt that the development of the vapor degreasing process and associated industry was largely based on the particular properties, availabilities, and low cost of this versatile solvent. The boiling point (189°F) allows adequate vapors to condense on the work being cleaned, yet the work is not too hot to handle upon removal from the degreaser. Utility requirements also are easily met with 15 psig steam (or less) and nominal cooling.[10] The other properties of trichloroethylene has created such widespread general usage that many vapor degreasers must be retooled or otherwise modified to allow alternate solvent usage. There has been regulation on the use of trichloroethylene for vapor degreasing because of its photochemical reactivity and resultant production of atmospheric oxidants.[11]

Another halogenated solvent, 1,1,1-trichloroethane, is second only to trichloroethylene in nationwide usage for vapor degreasing.[1] General behavior is similar to trichloroethylene primarily due to a similar boiling point. However, chemical stability of 1,1,1-trichloroethane can cause significant problems associated with water contamination and use with "reactive" metals (i.e., aluminum or zinc). The primary advantages to the user of choosing 1,1,1-trichloroethane over trichloroethylene are that parts are lower in temperature on removal from the degreaser (approx. 25°F lower) and are thus easier to handle. Secondly, and probably more importantly, the conversion of existing equipment from trichloroethylene is usually minimal, particularly where construction is of stainless steel or other material nonreactive to trichloroethane. This is primarily due to the similarity between the two boiling points and specific heats.[6] A primary advantage for air quality is the substantially lower photochemical reactivity of 1,1,1-trichloroethane.[12] It should not, however, be used in any system where water is possibly present--for example, with water-based lubricants or steam leaks in the heating system. The reaction products of 1,1,1-trichloroethane and water--for example, HCl--are highly corrosive of almost all construction materials. Along with the problem of water instability is the low solvent recovery rate. Because of its reactivity with water, 1,1,1-trichloroethane cannot be steam stripped for recovery from concentrated removed soils. Additionally, thermal decomposition can result if still temperatures exceed about 200°F. Both of these factors result in waste sludge containing 20-25% solvent after reclamation.[1] There has also been problems with aluminum in stability of 1,1,1-trichloroethane. Several manufacturers have developed and are marketing trichloroethane with stabilizers added to avoid the problems of aluminum reduction of the solvent. The concentration of stabilizers in the solvent must be periodically checked to ensure that depletion does not result with subsequent damage both to the degreasing equipment.

Perchloroethylene is used in about 15 percent of the vapor degreasers nationwide.[1] Perchloroethylene has inherent stability to reactive metals and thus requires less stabilization. Because of its higher boiling point (250°F), significantly more vapor condenses on the work than with either of the other two solvents. Because of the combined effects of higher temperature and increased vapor flushing, better cleaning efficiency is generally obtained with perchloroethylene. Further, because of its significantly higher boiling point, perchloroethylene drives off transient water from the workload more quickly. As with most advantages, the higher boiling point also creates some disadvantages. A minumum of 60 psig steam is required for vapor degreasers using perchloroethylene,[8] usually requiring a larger steam coil (and probably a licensed engineer's presence.) If electric or gas heaters are used, significant additional utility costs result. Safety and comfort of employees also suffer as the vapor degreaser is operated at 250°F rather than at 189°F.

Methylene chloride may be used to remove polymer residue because of its high solvency. It is especially useful for cleaning of heat-sensitive parts because of its low boiling point. Less heat is required for degreasers using methylene chloride as solvent; however, methylene chloride diffuses more readily because of its low vapor density. Extensive modification of a vapor degreaser is required to convert from trichloroethylene to methylene chloride. The low boiling point and the low volume of condensate generated may cause the low cleaning efficiency.

Fluorocarbon-type solvents, such as Freon-113, have the same advantages as methylene chloride and are suitable to remove polymer residue and heat-sensitive parts, but since the vapor density of Freon-113 is much higher than that of methylene chloride less freon will be diffused out of the degreaser. A slightly higher boiling point and a larger volume of condensate have made freon a better solvent than methylene chloride to clean small, delicate parts. The cost of freon is, however, much higher than that of any other halogenated solvents.

4.2 Methods for Organic Solvent Emission Inventory

To determine the emissions over a given period of time from a particular class of sources, two factors must be known: the use factor and the emission factor. The product of these two factors equals the emissions of the sources included in the use factor.

The use factor is a measurement of source use, such as hours of operation, number of miles travelled, number of operational cycles, etc. The emission factor is an estimate of the rate at which pollutants are released to the atmosphere as a result of some activity. As an example, the inventory of daily emissions from a hypothetical degreasing facility is calculated below, using the simulated data specified:

- number of degreasing units in facility = 6
- average hours of operation per day = 7.5
- average hours per day of down time (equipment idling) = 16.5
- emission rate of reactive hydrocarbon vapors during operation mode = 18.4 lb/hr
- emission rate of reactive hydrocarbon vapors during idling mode = 4.3 lb/hr

MODE	(USE FACTOR) x (EMISSION FACTOR) = EMISSIONS
Operation	(6 x 7.5 hrs) x (18.4 lb/hr) = 828 lb
Idle	(6 x 16.5 hrs) x (4.3 lb/hr) = 426 lb

Therefore, the total daily inventory of reactive hydrocarbon emissions from the facility in question equals 828 lb + 426 lb = 1254 lb.

An agency or person who is developing or updating an emission inventory may obtain use factors and emission factors in a number of ways, depending upon the source type being inventoried. For stationary point sources, use factors can be obtained through the methods listed in Table 4-4.

Emission factors, like use factors, can be obtained from several sources. The most direct method is to measure the emissions from the source in

Table 4-4. USE FACTOR INFORMATION SOURCES

Information Source	Type of Information Obtained
1. Business and Telephone Directories	1. Number and location of businesses or operations operating specific source type.
2. Surveys of source operators	2. Size and type of source, emission controls employed, operation modes, and operation times.
3. Economic data, including taxes and total sales	3. Extrapolation of approximate volume of total source use in area and overtime period covered by economic data (hours of operation, number of units processed, etc.)
4. Population of area served by source(s)	4. Approximate volume of total source use in area served, based upon assumptions of per capita demand on source(s).
5. Number of employees in source-related business	5. Approximate number of sources and volume of source use, based upon assumptions of support personnel requirements of source.

Note:

This table is not intended to be an all-inclusive use factor development methodology, but rather to illustrate the diversity of approaches which can be employed to develop such factors.

question, or from a statistically representative number of sources if a population of such sources would be inventoried. This approach, however, can be very expensive and time consuming. A more practical alternative would be to obtain emission factors from published literature, such as Compilation of Air Pollutant Emission Factors (AP-42)[3] and its supplements, published by the U.S. Environmental Protection Agency. The AP-42 document is the most comprehensive and authoritative list of emission factors currently available, and includes emission factors from dozens of stationary point and area source and mobile source classifications. Another alternative for obtaining emission factors would be to consult with source manufacturers and/or operators and review their own emission testing data, if such data are available. Finally, emission factors can be estimated, based upon information known about other similar sources and upon knowledge of the design and operating characteristics of the source or sources in question.

Sources are generally divided into a number of categories or classes for inventory purposes. One widely accepted method for classifying sources is the Standard Industrial Classification (SIC) System. Under the SIC system, all source activities are assigned a four-digit code number. The first two digits designate a broad level of economic activity in which the source is included (e.g., manufacturing) and each of the following digits further elaborates on the specific classification group of the source (e.g., automotive painting). The advantage of this system is that it is widely used and accepted; therefore, it is useful for inventory purposes.

The EPA has developed the National Emissions Data System (NEDS) to provide a uniform method for assembling emissions data. The NEDS uses the Source Classification Code (SCC) which, like the SIC system, assigns a digital code to each type of source; however, the SCC system is considerably more specific and detailed in classifying sources. NEDS functions as a national emissions inventory system and includes emissions, operation, and location information for all sources which emit more than 100 tons per year of pollutants.

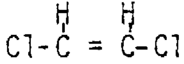
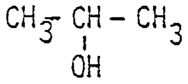
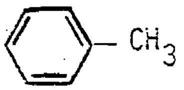
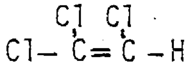
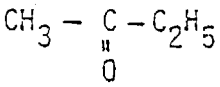
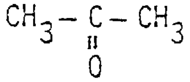
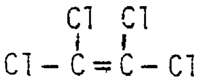
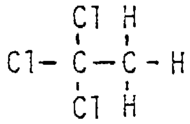
The California Air Resources Board classifies emissions according to process categories. The ARB emissions inventory has two major source categories: stationary sources and mobile sources. The stationary source category includes eleven major groups (petroleum, organic solvent users, chemical, metallurgical, mineral, food and agricultural processing, pesticides, wood processing, combustion of fuels, waste burning, and miscellaneous area sources) and a number of sub-groups under several of the major source groups. The mobile source category is divided into six major groups (motor vehicles on-road, jet aircraft, piston aircraft, railroads, ships and other off-road vehicles) with several sub-groups under "motor vehicles on-road." This inventory is provided by county, by air basin, and statewide. The individual air pollution control district emission inventories are organized in a format similar to the ARB's, although the actual emission values listed may differ somewhat from ARB's inventory of the same area due to differing methods of calculating and classifying emissions.

4.3 Photochemical Reactivities and Toxicities of Degreasing Solvents

4.3.1 Photochemical Reactivities of Degreasing Solvents

Organic solvents used in the degreasing processes are potential sources of hydrocarbon emissions that may contribute significantly to the formation of photochemical air pollution in the urban areas. Table 4-5 lists the formula structures and the photochemical reactivities of the major degreasing

Table 4-5. STRUCTURAL FORMULA AND PHOTOCHEMICAL REACTIVITY OF DEGREASING SOLVENTS

Solvent	Structural Formula	Compound Type	Reactivity
Dichloroethylene	 $Cl-\overset{H}{C}=\overset{H}{C}-Cl$	All olefinic hydrocarbons (including partially halogenated)	III
Isopropyl Alcohol	 $CH_3-\underset{OH}{CH}-CH_3$	Primary & secondary C_2^+ alcohols	III
Toluene		All other aromatic hydrocarbons	III
Trichloroethylene	 $Cl-\overset{Cl}{C}=\overset{Cl}{C}-H$	All olefinic hydrocarbons (including partially halogenated)	III
Heptane	$CH_3(CH_2)_5CH_3$	C_3^+ Paraffins	II
Methylethylketone	 $CH_3-\underset{\overset{\|}{O}}{C}-C_2H_5$	N-alkyl ketones	II
Stoddard	Petroleum Products	C_3^+ Paraffins	II
Acetone	 $CH_3-\underset{\overset{\|}{O}}{C}-CH_3$	Acetone	I
Freon	Chlorofluoroparaffins	Perhalogenated hydrocarbons	I
Methanol	CH_3OH	Methanol	I
Methylene Chloride	CH_2Cl_2	Partially halogenated paraffins	I
Perchloroethylene	 $Cl-\overset{Cl}{C}=\overset{Cl}{C}-Cl$	Perhalogenated hydrocarbons	I
1,1,1-trichloroethane	 $Cl-\overset{Cl}{\underset{Cl}{C}}-\overset{H}{\underset{H}{C}}-H$	Partially halogenated paraffins	I

solvents. The photochemical reactivities are assigned according to the ARB three-tier reactivity classification scheme (See Appendix A).[12] This scheme was designed to classify organic compounds by their chemical potentials to react with other constituents in the ambient air and thus cause the formation of oxidants. Class II and Class III organics are referred to as Reactive Organic Gas (ROG), and the sum of all three classes is referred to as Total Organic Gas (TOG).

Degreasing solvents, acting as any other hydrocarbons in the ambient air, may react with O and O_3, and thus upset the NO_2 photolytic cycle:

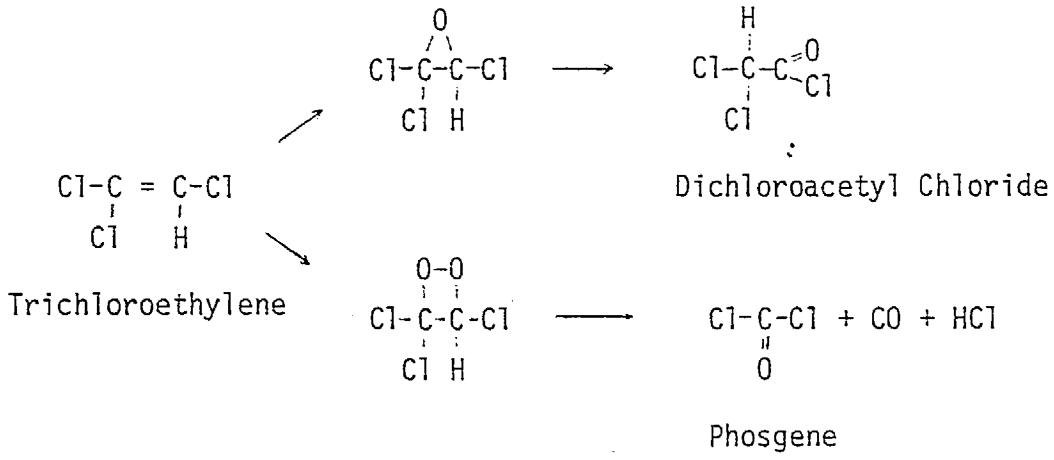
$$NO_2 + h\nu \text{ (sunlight)} \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (M = \text{third body gas molecule})$$

$$O_3 + NO \rightarrow NO_2 + O_2$$

The hydrocarbon free radicals resulting from these competing reactions are very reactive because of the unpaired electrons. By reacting with primary pollutants, other free radicals, and the normal constituents in the air, these free radicals produce a complex mixture commonly referred to as photochemical smog. High concentrations of oxidants, such as O_3, OH, and NO_2 will result in the photochemical reaction processes.

The by-products formed in the photochemical reaction processes may themselves cause severe damages that are overlooked by the photochemical reactivities of the solvents. By reacting with oxidants (for example, ozone or hydroxyl radical) in the presence of intense light and elevated temperature, trichloroethylene may form the following products:[13]



Dichloroacetyl chloride and hydrogen chloride are materials that fume in the air with an acrid, penetrating odor. They are irritating to the eyes and mucous membranes. Phosgene is a highly toxic gas with a suffocating odor. Chlorinated peroxyacetyl nitrates, formic acid, and nitric acid are also formed in the oxidation process. Perchloroethylene undergoes similar reactions with the formation of trichloroacetyl chloride, hydrogen chloride, and phosgene. Trichloroacetyl chloride is similarly an irritant to the eyes with an equally pungent and acrid penetrating odor. The reaction rate constant for the attack of 1,1,1-trichloroethane by hydroxyl radicals is 100 times slower than that of trichloroethylene.[14] While on a much lower scale, 1,1,1-trichloroethane does exhibit some photochemical reaction at room temperature with products such as hydrogen chloride and phosgene.

4.3.2 Potential to Destroy Stratospheric Ozone Layer

Simple halogenated hydrocarbons have long been reported to have the potential to reduce the ozone concentration in the stratosphere.[15] A recent report indicates that a degreasing solvent with a high photochemical reactivity has a low potential to destroy ozone in the stratosphere and vice versa.[14] The criteria for classifying solvents as potentially harmful to the stratosphere are opposite to those that are potentially harmful to the troposphere. Trichloroethylene is photochemically much more reactive than 1,1,1-trichloroethane; thus 1,1,1-trichloroethane has a much longer lifetime and more of it will be transported to the stratosphere. Once getting into the stratosphere, 1,1,1-trichloroethane will be rapidly photolyzed to form Cl and ClO, which can catalytically destroy ozone.

4.3.3. Toxicities of Degreasing Solvents

Each of the four major degreasing solvents - perchloroethylene, trichloroethylene, 1,1,1-trichloroethane, and methylene chloride - can produce an anesthetic effect upon inhalation.[8] Table 4-6 lists the Threshold Limit Values (TLV), Ceiling Limits for this anesthetic effect, the odor thresholds, and typical vapor concentrations that produce anesthetic effects of these four solvents.[8]

Trichloroethylene, perchloroethylene, and 1,1,1-trichloroethane are considered toxic. Acute exposure produces dizziness, severe headaches, irritation of the mucous membranes, and intoxication. Trichloroethylene has been reported to be genotoxic.[16] Preliminary data from the National Cancer Institute indicate that it is carcinogenic to mice.[17] It seems that trichloroethylene oxide and possibly chloral hydrate are the ulticarcinogens derived from trichloroethylene. It has been reported that exposure to 1,1,1-trichloroethane over a period of time can result in cumulative systemic retention with resulting severe depression of the central nervous system, which could have deleterious or even fatal results in human beings without being so identified.[18]

Table 4-6. HUMAN RESPONSE TO DEGREASING SOLVENT VAPORS[8]

Solvent	Odor Threshold (ppm)	Appearance of Anesthetic Effects (ppm/minutes)	TLV Limit (ppm)	Ceiling Limit (ppm)
Perchloroethylene	50	200/480 400/120	100	200
Trichloroethylene	100	400/20 1,000/6	100	200
1,1,1-trichloroethane	100	1,000/30-70 1,500/15-60	350	500
Methylene Chloride	310	900-1,200/20	500	1,000

4.3.4 Summary

Even though all chlorinated solvents on the market do contain inhibitors or antioxidants to reduce the solvents' potential to form oxidation products, these inhibitors have a minor effect in reducing the photochemical reactivities of the solvent vapors in the ambient air. Chlorinated solvents with low photochemical activites have higher potentials to destroy ozone concentration in the stratosphere, and they may have higher toxicities. Other non-chlorinated solvents do not have the non-flammable property essential for a vapor degreasing solvent. Stoddard solvents are of prime concern because they are widely used in cold degreasing processes, and they are photochemically reactive.

4.4 Degreasing Solvent Emission Regulations

The air pollution control regulations applicable to degreasing operations in California are primarily local air pollution control district (APCD) emission standards and state and federally mandated new source review (NSR) rules.

4.4.1 Local Regulations (Rule 442)

Each APCD in California has developed its own emission standards to regulate emissions from sources within its respective jurisdiction. Some of these standards are directly applicable to degreasing operations. These standards may vary significantly from one APCD to another, but a good example of such standards is seen in the case of Rule 442 of the South Coast Air Quality Management District Rules and Regulations. Since the South Coast AQMD encompasses the South Coast Air Basin, the rules of this district are generally representative of optimum emission control and are relatively stringent.

Rule 442, Usage of Solvents (Adopted May 7, 1976) places limits on the emissions of solvents from all operations. Section (f) of that rule specifically states that

> A person shall not use photochemically reactive solvent in industrial and commercial surface cleaning operations unless the emission of organic materials into the atmosphere has been reduced by at least 85 percent by weight.

A degreasing operation which utilized a non-photochemically reactive organic solvent would be subject to sections (a) and (c) of Rule 442. Section (a) would require that any emissions resulting from the use of such solvents be reduced at least 85 percent (relative to uncontrolled emission rates), or that such emissions be limited to a maximum of 180 kilograms per hour and 1350 kilograms per day. Section (c) would require that any emissions subject to Section (a) be reduced through the following technologies:

1. Incineration, provided that at least 90 percent of the organic carbon is oxidized to non-organics, or that the concentration of organics after incineration is less than 50 ppm, or
2. Adsorption, or
3. Processing in a manner approved by the air pollution control officer, and which is at least as effective as the preceding two measures.

Rule 102 of the South Coast AQMD defines photochemically reactive solvents as follows:

> ...any solvent with an aggregate or more than 20 percent of its total volume composed of the chemical compounds classified below or which exceeds any of the following individual percentage composition limitations, referred to the total volume of solvent: (a) a combination of hydrocarbons, alcohols, aldehydes, ethers, esters or ketones having an olefinic or cycloolefinic type of unsatu-

> ration, except perchloroethylene: 5 percent; (b) a combination of aromatic compounds with eight or more carbon atoms to the molecule except ethylbenzene, methy benzoate, and phenyl acetate: 8 percent; (c) a combination of ethylbenzene, ketones having branched hydrocarbon structures, trichloroethylene or toluene: 20 percent.
>
> Whenever, any organic solvent or any constituent of an organic solvent may be classified from its chemical structure into more than one of the above groups of organic compounds, it shall be considered as a member of the most reactive chemical group, that is, the group having the least allowable percent of the total volume of solvents.

Finally, Section (g) of Rule 442 regulates the disposal of photochemically reactive solvent. This section states that no more than 5 liters of such a solvent or material containing more than 5 liters of such solvent, may be disposed of in any manner which will permit the evaporation of such solvent into the atmosphere.

4.4.2 EPA New Source Review Program

The U.S. Environmental Protection Agency (EPA) has mandated that all stationary sources for which air pollution control agency permits are required be subject to "new source review" (NSR).[19] NSR is a process which involves an analysis of the proposed source (or modified existing source) and its emissions to determine whether the source would prevent the attainment or maintenance of national ambient air quality standards. The EPA "Interpretative Ruling" states that no new source (or existing source modification) which emits more than 100 tons per year of pollutants for which there are national ambient air quality standards (including precursors of photochemical oxidants, such as photochemically reactive hydrocarbons) may be granted a permit if the NSR indicates that the emissions from the source would prevent the attainment or maintenance of the air quality standards. The only exception to this would be if the prospective operators of the proposed new source or existing modified source could reduce emissions of the pollutants in question from other existing sources in the same area as the new or modified source such that a net air quality benefit would result in the area; i.e., the reduction in existing emissions would have to be at least slightly greater than the projected emission increase that would result from the new source or source modification. This requirement to reduce existing emissions is generally known as the "tradeoff" or "offset" requirement.

4.4.3 ARB Model Rules (Rule 213)

In response to this federal requirement, the California Air Resources Board (ARB) has developed a "model" NSR regulation of its own, which fulfills the federal requirements, but includes some special additional features. The ARB is attempting to pursuade all the APCDs in California to adopt a NSR rule similar to its model rule, and in the case of the Bay Area APCD and the South Coast Air Quality Management District, the ARB has adopted NSR rules for the districts themselves. The ARB "model" rule is most clearly demonstrated in the South Coast AQMD Rule 213. Essentially, this rule requires that all new sources or existing source modification which would emit more than 15 pounds per hour or 150 pounds per day (150 pounds per hour or 1500 pounds per day for carbon monoxide) of nitrogen oxides, organic gases, or any pollutant for which there is a state or national ambient air quality standard, utilize the best available control technology (BACT).* If a new source or existing source modification would

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* BACT is defined as the maximum degree of emission control which can be utilized, taking into account technologies known but not necessarily demonstrated.

result in emissions of any of the previously mentioned pollutants in excess of 25 pounds per hour or 250 pounds per day (250 pounds per hour or 2500 pounds per day for carbon monoxide), then a NSR would be required. As in the federal requirement, the state model rule would require that the necessary pollutant emissions be offset by reducing existing source emissions if the new source would prevent the attainment or maintenance of ambient air quality standards (federal or state). An exception to this NSR and tradeoff or offset requirement would be granted if the new source or source modification would utilize a

> ...unique and innovative control technology which will result in a significantly lower emission rate from the stationary source than would have occurred with the use of previously known best available control technology, and which will likely serve as a model.

4.4.4 OSHA Rules and Regulations

Degreasing processes using chlorinated solvents are required to comply with regulations of the Occupational Safety and Health Act (OSHA). Acceptable OSHA standards for vapor emissions of the four major chlorinated solvents are shown in Table 4-7.[8] The 8-hour time-weighted average (TWA) is the basic limit that may not be exceeded during any 8-hour period. The acceptable ceiling concentration can be reached only occasionally, provided there is sufficient time at lower concentration to meet the TWA limit. An absolute maximum ceiling cannot exceed the maximum duration.

4.4.5 Summary

In summary, local APCD emission standards will, in most cases, limit the emissions from degreasing operations. While such standards may not be as strict as the South Coast AQMD standards, some degree of control will likely be required. Not all new or modified degreasing operations

Table 4-7. SUMMARY OF OSHA RULES AND REGULATIONS[8]

	8-hr. TWA (ppm)	Acceptable Ceiling (ppm)	Acceptable Maximum Ceiling	
			Concentration (ppm)	Maximum Duration
Trichloroethylene	100	200	300	5 min in 2 hr
1,1,1-trichloroethane	350	---	---	---
Perchloroethylene	100	200	300	5 min in 3 hr
Methylene Chloride	500	1,000	2,000	5 min in 2 hr

would be subject to NSR rules, but some of the larger degreasing facilities will. Although some APCDs have not adopted a Rule 213-type NSR rule, the California ARB is attempting to influence state-wide adoption of such a rule at the local level. Where districts with serious air quality problems are slow to adopt such a rule, the ARB may unilaterally adopt a rule for the districts. This rule will require larger degreasing facilities to use best available control technology, regardless of the specific APCD emission standards, and may even require emission tradeoffs. In addition, degreasing operations are also required to comply with the OSHA vapor emission standards.

4.5 Degreasing Solvent Emission Control Technologies

4.5.1 General Considerations

The technologies for controlling emissions from degreasing operations vary widely in terms of cost, complexity, and effectiveness. Factors which must be considered in determining the types of emission controls to apply include applicable emission standards, new source review requirements, degreasing equipment design, and cost effectiveness.

Air pollution control regulations will often clearly dictate what control technology should be employed (see section 4.4). Emission standards may not only specify what solvent emission reductions must be achieved but may also specify that a particular control technology be employed. For larger degreasing operations in ambient air quality standard non-attainment areas, new source review rules may necessitate the use of control technology even more effective than emission standards would require; such operations could reduce costs by further reducing emissions from the new degreasing operation source rather than by having to obtain

more emission tradeoffs from other existing sources.

In order of emission rate per unit, solvent degreasers are rated in Table 4-8.[5]

Table 4-8. TYPICAL SOLVENT EMISSION FROM DEGREASERS[5]

Type	Ave. Emission Rate Per Unit (tons/yr)
Conveyorized Degreasers	27
Open-Top Vapor Degreasers	10
Cold Cleaners	0.3

Partly as a consequence of the above values, control of emissions from open-top and conveyorized degreasers is the most cost-effective degreasing operation control, followed by control of waste solvent disposal for all degreasing operations, and control of manufacturing cold cleaning and maintenance cold cleaning.

4.5.2 Solvent Emission Control Technologies

The control technology which can be applied to each of the three types of degreasers concerns not only control equipment but also the operation of the degreasing apparatus itself.

For cold cleaners, control equipment would include (in approximate order of effectiveness) a cover over the degreasing compartment(s); a facility for draining cleaned parts (preferably enclosed); the use of a solid, fluid stream rather than a fine spray if a shower is part of the cleaning process; increased freeboard above the solvent pool; a water cover over the solvent (assuming solvent is insoluble in and heavier than water); refrigerated chillers; and carbon adsorption or incineration of off-gases. Operation controls would result in the disposal of waste solvent such that little or no solvent could evaporate, the closure of degreaser cover whenever reasonably possible, in the provision of an adequate drainage interval for cleaned parts.

For open-top cleaners, control equipment includes a cover that can be operated without disturbing the vapor zone above the solvent, safety switches to prevent equipment operation which would cause excessive emissions, a flow switch and thermostat which would shut off the sump heater when the solvent is too warm or is not circulating, increased freeboard, use of refrigerated chillers, and carbon adsorption/incineration. Operational controls would ensure proper use of the cover, minimization of solvent carry-out through proper drainage of cleaned parts, non-excessive work loads, speedy repair of solvent leaks, proper disposal of waste solvent, and a minimal exhaust ventilation flow rate (< 65 ft^3/min ft^2); they would also prevent degreasing of porous or absorbent materials and ensure that solvent leaving the water separator is free of visible water.[5]

The control technology employed with conveyorized degreasers is essentially the same as that used with open-top degreasers, with some additions. These would include maintenance of relatively low vertical conveyor speeds (< 11 ft/min),[5] a drying tunnel or rotating basket to minimize solvent carry-out, the use of minimal opening dimensions for the parts being cleaned, and downtime covers for all openings.

Further elaboration on some previously mentioned control equipment is necessary. This equipment includes freeboard increase, refrigerated chilling, adsorption, and incineration.

Freeboard serves primarily to reduce drafts near the air/solvent interface in cold cleaners and open-top vapor degreasers. Freeboard height is usually expressed in terms of the freeboard ratio, which is the freeboard height divided by the width of the degreaser's air/solvent area. Typical freeboard ratios are 0.5-0.6 for open-top vapor degreasers, except when very volatile solvents are used. For an open-top degreaser that is idling (no work load), emission reductions of 20-30 percent can be achieved by raising the freeboard ratio from 0.5 to 0.75; an increase from 0.5 to 1.0 would provide reductions of approximately 50 percent.[1] Similarly, emissions can be significantly reduced by increasing the freeboard ratio in cold cleaners using relatively high volatility solvents although little effect would be realized with low-volatility solvents.

Refrigerated chillers are used in vapor degreasers to create a blanket of cold, stable air above the vapor zone to impede diffusion of vapors from that zone. Chilling coils are mounted on the freeboard of the degreaser units and operate at temperatures of -30 to 5°C. Tests performed for EPA imdicated emission reductions of up to 62 percent on open-top vapor degreasers.[5] Refrigerated chillers are not generally used on cold cleaners, since the cost of such chillers would generally be excessive for such an operation and would have about the same effectiveness as a closed cover.

Carbon adsorption systems are widely used for reducing solvent vapor emissions from degreasing operations. Vapor-laden air is passed through an activated carbon bed, which can remove 95 percent of all vapor in the air.

However, the carbon adsorption system must be designed such that the ventilation apparatus collects as much of the solvent vapor emissions from the degreaser as possible. This must be accomplished without causing turbulence at the air/solvent interface. Because of inefficiencies in the collection of solvent vapor for routing through the carbon bed, overall carbon adsorption emission reduction efficiencies are in the 40-65 percent range.[1]

Incineration of solvent vapors can be accomplished through either direct thermal oxidation or by catalytic oxidation. Like carbon adsorption, this process is very efficient in reducing vapor emissions, although it is dependent upon the ventilation system performance for overall efficiency. This system has a serious drawback when used with chlorinated hydrocarbon solvents. Incineration of such solvents produces toxic gases which would have to be removed from the exhaust stream before release to the stmosphere.

The above control technologies may be used in combinations to achieve higher control efficiencies than would be achieved with any individual technology. For example, an open-top vapor degreaser could incorporate a high freeboard ratio, refrigerated chillers, a cover, and a carbon adsorption system.

4.5.3 Summary

Table 4-9 shows the typical performances of the major control technologies applied on the three types of degreasers.[5] These control measures can achieve very low efficiencies in reducing solvent emissions, much lower than what is generally required (85%) for photochemically reactive solvents. Solvents that are photochemically less reactive may impose other hazards, such as ozone depletion or occupational safety problems; thus it is very

Table 4-9. TYPICAL PERFORMANCES OF DEGREASING CONTROL TECHNOLOGIES[5]

	Emission (tons/yr)	Percentage of Emission Reduction	Cost of Control ($/Kg of Solvent)* New Facilities	Cost of Control ($/Kg of Solvent)* Existing Facilities
Cold Degreasing (mineral spirits)				
without control	0.25			
drainage facility	0.226	9.6%	0.021	0.021
Open-Top Vapor Degreaser (1,1,1-trichloroethane)				
without control	9.5			
manual cover	7.5	21%	-0.404	-0.40
carbon adsorption	6.2	35%	0.091	0.242
refrigerated chiller	6.5	32%	-0.064	0.028
extended freeboard & power cover	6.8	28%	-0.234	0.115
Monorail Conveyorized Degreaser (perchloroethylene)				
without control	35			
carbon adsorption	21.9	37%	-0.201	-0.322
refrigerated chiller	21.9	37%	-0.125	-0.285

*Negative values are credits for control.

important to identify and evaluate the feasibility of alternatives to organic solvent degreasing.

4.6 References

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5.0 DEGREASING SOLVENT EMISSIONS DATA COLLECTION

There are two major sources of solvent emissions due to degreasing operations: the manufacturing and service/maintenance industries. In the manufacturing industry, 45 types of manufacturers are solvent degreasing users. The primary solvent degreasing users in the service/maintenance industry include service stations, automotive repair shops, oil well operations, and maintenance for railroad, civilian, and military aircrafts.

In achieving the objective of conducting a comprehensive emission inventory among solvent degreasing users, different means were used for data collection. A questionnaire survey was employed to identify manufacturers using solvent degreasing as part of their manufacturing processes and to provide solvent consumption data on an annual basis. Data for the service/maintenance industry were obtained from governmental agencies and private sectors. This section is to summarize the methodologies and results of the emission data collection effort.

5.1 Manufacturing Industry

5.1.1 Purpose

A questionnaire survey was conducted to obtain information on the types of manufacturers in California that use organic solvents for degreasing as a part of their manufacturing process. The questionnaire was also designed to gather data for estimating state-wide organic solvent emissions from manufacturers' degreasing practices and to assess the feasibility for certain types of manufacturing industries to switch from organic solvent degreasing to alternative methods. The information requested of manufacturers included methods of degreasing, amounts and types of solvent used, amount of solvent disposed, methods of disposal, prices of solvents, and suggestions for alternatives to organic solvent degreasing.

5.1.2. Questionnaire Survey

The Standard Industrial Classification (SIC) System was used to categorize the manufacturing inductry. In this survey there were sever major categories consisting of 45 subcategories of manufacturers (see Table 5-1). These categories were selected mainly because they were potential users of solvent degreasing, or some type of metal cleaning processes may be incorporated in the manufacturing process.

The survey was conducted in two parts. The questionnaires and cover letter used in both parts of the survey are included in Appendix B of this report. The California Manufacturers Register[1] was used as the master list of manufacturers for the first survey. The survey was conducted for all 45 subcategories shown in Table 5-1. The random number generator function of a Texas Instruments SR-51 Calculator was used to randomly select the manufacturers from each of the subcategories on the master list. A total of 410 survey questionnaires and cover letters were sent out with stamped, pre-addressed return envelopes enclosed in each. The results of the first survey turned out to be unsatisfactory due in part to the saml1 sample size covered and because many respondents failed to complete the questionnaire. However, most of those contacted by telephone who were asked to send the missing information complied.

The result of the first survey prompted a second survey with a revised questionnaire format and a larger sample size. The second questionnaire was shortened to two pages that were photographically reduced by 50 percent. The questionnaire was carefully reviewed, most questions were simplified, and questions that made duplicate requests for similar information were

Table 5-1. SUBCATEGORIES OF MANUFACTURERS IN THE DEGREASING SOLVENTS USERS SURVEY

SIC Code	Subcategory of Manufacturer
25	Furniture and Fixtures
251	Household Furniture
252	Office Furniture
253	Public Building & Related Furniture
254	Partitions and Fixtures
259	Miscellaneous Furniture and Fixtures
33	Primary Metal Industries
331	Blast Furnace and Basic Steel Products
332	Iron and Steel Foundries
333	Primary Nonferrous Metals
334	Secondary Nonferrous Metals
335	Nonferrous Rolling and Drawing
336	Nonferrous Foundries
339	Miscellaneous Primary Metal Products
34	Fabricated Metal Products
341	Metal Cans and Shipping Containers
342	Cutlery, Hand Tools, and Hardware
343	Plumbing and Heating, Except Electric
344	Fabricated Structural Metal Products
345	Screw Machine Products, Bolts, etc.
346	Metal Forgings and Stampings
347	Metal Services,
348	Ordnance and Accessories
349	Misc. Fabricated Metal Products
35	Machinery, except Electrical
351	Engines and Turbines
352	Farm and Garden Machinery
353	Construction and Related Machinery
354	Metalworking Machinery
355	Special Industry Machinery
356	General Industrial Machinery
357	Office and Computing Machines
358	Refrigeration and Service Machinery
359	Misc. Machinery, except Electrical
36	Electric and Electronic Equipment
361	Electric Distributing Equipment
362	Electrical Industrial Apparatus
363	Household Appliances
364	Electric Lighting and Wiring Equipment
365	Radio and TV Receiving Equipment
366	Communication Equipment
367	Electronic Components and Accessories
369	Misc. Electrical Equipment & Supplies
37	Transportation Equipment
371	Motor Vehicles and Equipment
372	Aircraft and Parts
373	Ship and Boat Building and Repairing
376	Guided Missiles, Space Vehicles, parts
379	Miscellaneous Transportation Equipment
38	Instruments and Related Products
381	Engineering and Scientific Instruments
382	Measuring and Controlling Devices

eliminated. The results of the first survey allowed for the exclusion of SIC 251 due to a completely negative response.

A mailing list of 7,426 California manufacturers was obtained from the National Advertising and Marketing Enterprises.[2] This list contained 52 percent of the total 14,404 manufacturers in California for the SIC subcategories surveyed.[3] The SIC and the number of employees of each manufacturer were also provided. The manufacturers on this list were first grouped by their SIC numbers and were then divided into three sets by their number of employees (20 or less, 21 to 100, and more than 100). The division into three groups was to provide a more accurate extrapolation of the estimated emission of degreasing solvents for each SIC subcategory. Table 5-2 shows the number of manufacturers on the mailing list in each SIC subcategory by the sizes and the percentage of California manufacturers on the mailing list. For SIC subcategories 331, 339, and 361, the numbers of manufacturers on the mailing list exceed those provided by the Chamber of Commerce; therefore, 100 percent was assigned.

A state-wide manufacturer response of 5 percent was desired, so approximately 10 percent of the manufacturers were surveyed because a 55 percent total response was attained in the first survey. Therefore, approximately 1,100 additional questionnaires were needed to supplement the 405 questionnaires of the first survey ({405 + 1,100}/14,404 = 10.4%). Consequently, 15 percent (1,100/7,336 = 15%) of the manufacturers on the mailing list were randomly selected from each size division of each SIC subcategory on the mailing list, and each one was mailed a revised questionnaire, cover letter, and stamped, pre-addressed return envelope. Cross-checking was done to assure that no manufacturer was surveyed twice.

Table 5-2. STATISTICS OF MANUFACTURERS ON THE MAILING LIST PROVIDED BY NATIONAL ADVERTISING AND MARKETING ENTERPRISES

SIC NO.	No. of Manufacturers on Mailing List				Total No. of Mfgs. in CA in 1975+	% of Mfgs. on Mailing List
	1-20*	21-100*	over 100*	Total		
252	7	17	7	31	72	43
253	5	9	4	18	36	50
254	43	36	8	87	271	32
259	24	16	7	47	90	52
331	47	54	26	127	110	100
332	10	24	20	54	108	50
333	0	0	0	0	15	0
334	7	14	2	23	37	62
335	23	25	19	67	98	68
336	82	90	20	192	240	80
339	47	44	7	98	78	100
341	4	6	8	18	70	26
342	96	71	27	194	309	63
343	26	44	13	83	101	82
344	315	277	66	658	1270	52
345	94	136	19	208	242	86
346	94	77	14	185	295	63
347	204	143	25	272	777	48
348	7	14	3	24	36	67
349	144	132	45	321	461	70
351	6	7	7	20	35	57
352	41	38	10	89	149	60
353	77	85	42	204	248	82
354	158	159	28	475	864	55
355	111	90	26	227	305	74
356	169	217	49	345	411	84
357	24	25	44	93	258	36
358	56	49	20	125	183	68
359	586	191	27	804	2797	29
360	0	2	3	5	---	---
361	63	89	46	199	113	100
362	56	58	26	140	156	90
363	13	15	9	37	51	72
364	47	69	33	149	316	47
365	19	24	19	62	317	20
366	88	120	76	284	350	81
367	115	182	105	402	932	43
369	44	29	11	84	126	67
371	77	103	37	217	470	46
372	72	102	53	227	565	40
373	32	32	10	74	340	22
375	11	7	4	22	---	---
376	2	0	3	5	52	10
379	17	25	22	64	222	29
381	44	49	14	107	123	87
382	76	66	27	169	305	55
				7426	14404	52%

*Employees

+From California Chamber of Commerce

Manufacturers on the mailing list for each size of each of the SIC subcategories, as shown in Table 5-2, were grouped by county. This measure was essential to accurately estimate the emission of degreasing solvent for each county and subsequently for each air basin. This information is included in Supplement A.

5.1.3 Results and Conclusions

The returned statistics for both of the surveys and their combination are tabulated in Table 5-3. Positive responses are from manufacturers who indicated that organic solvents were used for degreasing in 1976; negative responses claimed that no organic solvent degreasing was performed. For 14,404 manufacturers of the 45 SIC subcategories, with a 5.8 percent response from the 10.3 percent surveyed, one third of the manufacturers used organic solvent for degreasing. The condensed summary of information provided by the manufacturers that degrease is in Supplement B.

The solvent emission inventory is discussed in the emission inventory section (8.0). The solvent prices provided by the survey respondents will be used in the cost analysis section (7.0). Some respondents stated that the reason they used a particular halogenated solvent was due to specifications of a government contract. Other reasons for using a particular solvent usually included one or more of the following: cleaning effectiveness, safety, price, availability, degreaser manufacturer recommendation, OSHA recommendation, APCD requirement, and convenience.

Some manufacturers stated that changing to an aqueous system would cause metal contamination (corrosive oxidation), while others cited the expense of new equipment and lack of floor space to accommodate an alternative system; however, some stated that the only problem with switching to

Table 5-3. DEGREASING QUESTIONNAIRE SURVEY RETURN RESULTS

	1st Survey	2nd Survey	Combined Survey
a. No. Questionnaire Sent	410	1,100	1,510
b. No. Returned Undeliverable	5	16	21
c. No. Actual Surveyed (a-b)	405	1,084	1,489
d. No. Total Response	221	620	841
e. No. Positive Response	85	180	265
f. No. Negative Response	136	440	576
g. % Response in Survey (d/c)	55%	57%	56%
h. % Surveyed (c/14,404)	2.8%	7.5%	10.3%
i. % Responded (d/14,404)	1.5%	4.3%	5.8%
j. % Positive in Survey (e/d)	38%	29%	32%
k. % Negative in Survey (f/d)	62%	71%	68%

an alternative system would be that of a possible loss in cleaning performance. Few recommendations for switching from an organic solvent to an alternative system were received except when a manufacturer currently using both alkaline washing and organic solvent methods would suggest switching to that type of alkaline washing system. In some industries, notably the electronics and aircraft industries, a few respondents stated that cleaning had to be done with certain organic solvents due to the composition of some electronic components and some aircraft alloys. The most common responses to the type of emission control used were: "none", "exhaust fans", "covered degreasing tank", and "freeboard cooling system" on vapor degreasers.

Manufacturers using non-organic solvent degreasing processes will be discussed in section 6.0 and will be used as prime examples for other manufacturers in their respective SIC categories in switching to alternative degreasing processes.

5.2 Automotive Repair

5.2.1 Purpose

Degreasing solvent emissions from automotive repair businesses are relatively small when considered on an individual basis; however, the combined emissions from the 33,201 automotive repair businesses registered in California in 1976 is quite substantial.[4] It is the major maintenance industry that emits large amounts of hydrocarbons from cold degreasers. Petroleum products - for example, mineral spirits and stoddard - are widely used as degreasing solvents in the automotive repair industry, and these solvents are classified as sufficiently photochemically reactive to cause smog problems. Therefore, it is essential to determine the total solvent emissions in the state, by county and by air basin, from organic solvent degreasing performed by the automotive repair industry.

5.2.2 Data Collection Methodology

The automotive repair industry includes service stations, car and truck dealers, specialized auto maintenance, small engine repair, and general auto maintenance. Solvents used by these shops are almost exclusively of the stoddard or mineral spirits type and are used at or slightly higher than room temperature. These solvents are used for cleaning parts to facilitate inspection and repair.

For the purpose of this study, cold solvent degreasing used in the automotive repair industry can be divided into two systems. One system is that in which the part washers are owned and periodically serviced by the Safety-Kleen Company. This type of degreasing is done in parts washers in which solvent is stored in a drum, pumped up to a wash tank for degreasing, and then returned to the drum for re-use. The contaminated solvents are removed for recycling, and fresh solvent is provided by the equipment supplier. With this system, the emissions from solvents are minimized to the difference between the amounts of solvent delivered and the recyclable solvent picked up. The other parts washer system is that in which a repair business maintains its own parts washer by periodically decanting all the solvent in the washer and refilling it with fresh solvent. The contaminated solvent is usually dumped into the waste oil tank; and for the purpose of this study, all of it eventually evaporates into the ambient air. Emissions of solvents from parts washers should be calculated differently for the two different systems.

The first step to estimate the amount of solvent emissions from the whole automotive repair industry was to obtain information on the average emission rate of a standard Safety-Kleen parts washer and that of a typical non-Safety-Kleen parts washer. Information in this respect was obtained from several recent studies, and directly from the data supplied by the Safety-Kleen Corporation.[5-7] The next step was to find the total number of automobile repair shops that used each of the two types of parts washers in California in 1976. Data provided by the California Bureau of Automotive Repair indicate that there were 33,201 automotive repair shops totally. The distribution of these shops by county is shown in Table 5-4. Data provided by Safety-Kleen Corporation indicate that it supplied 20,400 parts washers to 15,400 customers and 81 percent of them to the automotive repair industry. Therefore, 37.6 percent (15,400 x 0.81/33,201 = 0.376) of the automotive repair shops in California used Safety-Kleen washers. It was assumed that this ratio would be applied for each county; that is, 37.6 percent of the automotive repair shops in each county were customers of Safety-Kleen. Another assumption used was that there were an average 1.3 (20,400/15,400 = 1.3) washers in each repair shop. Based on these assumptions and the average emission rates of the two types of washers, an average solvent emission rate for each repair shop was derived. This average emission rate, together with the number of shops in each county (see Table 5-4), were used to estimate the emission of solvents from the automotive repair industry in each county. Solvent emissions resulting from automotive repairs are presented in the emission inventory section of 8.0.

5.3 Oil Well Maintenance

5.3.1 Purpose

Table 5-4. DISTRIBUTION OF AUTOMOTIVE REPAIR DEALERS IN CALIFORNIA

Co. #	County	No. of Automotive Repair Dealers	Co. #	County	No. of Automotive Repair Dealers
01	Alameda	1,538	30	Orange	2,315
02	Alpine	2	31	Placer	213
03	Amador	43	32	Plumas	57
04	Butte	288	33	Riverside	937
05	Calaveras	35	34	Sacramento	1,105
06	Colusa	35	35	San Benito	37
07	Contra Costa	788	36	San Bernardino	1,276
08	Del Norte	35	37	San Diego	2,259
09	El Dorado	174	38	San Francisco	727
10	Fresno	922	39	San Joaquin	500
11	Glenn	55	40	San Luis Obispo	315
12	Humboldt	249	41	San Mateo	866
13	Imperial	133	42	Santa Barbara	527
14	Inyo	61	43	Santa Clara	1,654
15	Kern	688	44	Santa Cruz	259
16	Kings	152	45	Shasta	246
17	Lake	89	46	Sierra	5
18	Lasses	50	47	Siskiyou	115
19	Los Angeles	10,028	48	Solano	334
20	Madera	97	49	Sonoma	502
21	Marin	362	50	Stanislaus	384
22	Mariposa	15	51	Sutter	95
23	Mendocino	159	52	Tehama	87
24	Merced	221	53	Trinity	25
25	Modoc	25	54	Tulare	447
26	Mono	22	55	Tuolumne	81
27	Monterey	424	56	Ventura	613
28	Napa	155	57	Yolo	184
29	Nevada	97	58	Yuba	89
				TOTAL	33,201

Oil wells require periodic maintenance, which includes organic solvent degreasing; and petroleum products are widely used for degreasing in this industry for obvious reasons. In the base year 1976, there were 42,292 oil wells in operation in California.[8] Because of the large number of oil wells involved and the high photochemical reactivities of the solvents used, it became important to determine the solvent emissions from degreasing operation in maintaining oil well equipment.

5.3.2 Data Collection Methodology

A recent study was made by the Kern County APCD to determine the emissions from solvent degreasing performed at oil wells in Kern County, California.[9] In 1976, 58.1 percent of the active oil wells in California were located in Kern County. Data for the study were obtained from five major oil companies that represented 51.9 percent of the active wells in Kern County. Data were used to calculate a weighted average emission rate for a typical active well in California (see section 8.2.3). The distribution of active oil wells in California by county is shown in Table 5-5.[8] The average emission rate and the number of active oil wells in each county were used to calculate the solvent emission from oil well maintenance degreasing in each county. It should be noted that specific uncertainties exist with respect to using Kern County emission factors for degreasing at oil wells as a state-wide average (see 8.2.3).

5.4 Railroad Maintenance

5.4.1 Purpose

The railroad industry, like the other transportation industries, must maintain their vehicles on a scheduled basis to assure the performance required by an industry that operates by precise time tables. Equipment

Table 5-5. DISTRIBUTION OF ACTIVE OIL WELLS IN CALIFORNIA[8]

County	Average No. of Active Wells*
Alameda	10
Contra Costa	45
Fresno	2,553
Kern	24,568
Kings	138
Los Angeles	5,988
Monterey	958
Orange	3,158
Riverside	15
San Benito	35
San Bernardino	42
San Luis Obispo	253
San Mateo	13
Santa Barbara	1,849
Sonoma	1
Tulare	31
Ventura	2,613
California Total	42,292

* Base Year 1976

failure due to maintenance oversight is usually very costly and intolerable to any company. One important aspect of scheduled maintenance is cleaning and degreasing of locomotives to facilitate inspection and maintenance.

In California there are 21 minor railroads that operate less than 10 locomotives each; the Northwestern Pacific Railroad (R.R.) Co. with 34 locomotives; the Western Pacific R.R. Co. with 144 locomotives; the Union Pacific R.R. Co. with 665 locomotives; the Southern Pacific Transportation Co. with 1816 locomotives; and the Atchinson Topeka and Santa Fe R.R. with 1817 locomotives.[10] Therefore, due to the large number of railroads operating in California, it was considered necessary to assess the maintenance degreasing performed by the railroads operating in California.

5.4.2 Data Collection Methodology

The railroad companies perform their scheduled maintenance at their specific maintenance depots in California. Maintenance depots are primarily of two types: heavy maintenance depots and running maintenance depots. All emissions from degreasing operations performed by the individual railroads are assumed to originate from these depots. Telephone calls to the large railroads were made to obtain information concerning the location of their depots and their degreasing operations.

Inquiry was made at the Southern Pacific running maintenance depot in Roseville, California where approximately 700 locomotives are maintained. Their degreasing operations are detailed in Table 5-6. It was determined that the same degreasing operations can be applied to the running maintenance depot in Los Angeles, California where approximately another 700 locomotives are maintained. Degreasing emission information for Southern Pacific's heavy maintenance depot in Sacramento was obtained from recent CARB emission

Table 5-6. MAINTENANCE DEGREASING PERFORMED BY THE MAJOR RAILROADS OPERATING IN CALIFORNIA

Items Cleaned	Method of Degreasing	Type of Solvent Used	Amount of Solvent Used
Southern Pacific Transportation Co. Roseville, CA (To Maintain 700 Locomotives)			
Aluminum	Hot Tank	Strong Alkaline Cleaners	One Drum of Powder/mo.
Locomotive Exterior	Steam Clean	Strong Sodium Hydroxide	110 gal/mo.
Locomotive Exterior	Spray Clean	Strong Sodium Hydroxide	1000 gal/mo.
Painted Surfaces	General Cleaning	Mild Alkaline Cleaner	30 Drums of Powder/mo.
Locomotive & Engine Room	Brush or Spray Pump	Liquid Alkaline Cleaner	3000 gal/mo.
Diesel Engines		Rinsing Oil (Like Kerosene)	667 gal/mo.
Electrical Parts		Mixture of Chlorinated Solvents[1]	55 gal/mo.
Sacramento, CA Heavy Maintenance			
Parts		1,1,1-trichloroethane	1213 gal/mo.
Atchison Topeka and Santa Fe R.R. San Bernardino, CA Heavy Maintenance			
Locomotives	Wash Rack	Assorted Alkaline Cleaners	
Generators	Vapor Degrease	Perchloroethylene	Minimal
Barstow, CA Running Maintenance			
Locomotives	Wash Rack	Assorted Alkaline Cleaners	
Ramps		Cleaning Solvent	Minimal
Union Pacific R.R. Los Angeles, CA Running Maintenance			
Locomotives	Wash Rack	Assorted Alkaline Cleaners	
Generators		Mixture of Chlorinated Solvents	10 gal/mo.
Crane Parts		Petroleum Distillate[2]	12 gal/mo.
Western Pacific R.R. Stockton & Sacramento, CA			
Locomotives	Wash Rack	Assorted Alkaline Cleaners	
Electrical Parts		Mixture of Chlorinated Solvents	330-440 gal/mo.

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[1] Mixture of 1,1,1-trichloroethane and Perchloroethylene

[2] Petroleum Distillate Assumed to be Stoddard Solvent

inventory data.

The Atchison Topeka (A.T.) and Santa Fe (S.F.) Railroad has major depots at San Bernardino, California, where heavy maintenance is performed, and at Barstow, California where running maintenance is done, and at Los Angeles, San Francisco, and Stockton, California where virtually no maintenance degreasing is done (see Table 5-6). Locomotives are cleaned with alkaline cleaners at a wash rack, and a perchloroethylene vapor degreaser with condenser coils is used to clean electrical generators. Tests made by A.T. and S.F. showed minimal emissions from the vapor degreaser. The chemist for A.T. and S.F. that screens all chemicals used by the railroad indicated that they are trying to get completely away from organic solvents primarily due to occupational health and safety.[11]

The Union Pacific Railroad Company performs only running maintenance at its depot in Los Angeles, California. Major maintenance sites are at Omaha, Nebraska and Salt Lake City, Utah. The majority of the maintenance cleaning is done at a wash rack with alkaline cleaners. Similar to the other railroads, only a small amount of chlorinated solvents are used for cleaning electrical generators[12] (see Table 5-6).

The Western Pacific Railroad performs the majority of their maintenance at their depot in Stockton, California. Some very minor degreasing is done at their depot in Sacramento, California. Locomotives are washed with alkaline cleaners and electrical parts are cleaned with a moderate amount of chlorinated solvent[13](see Table 5-6).

Inquiry at Northwestern Pacific Railroad revealed that their locomotives are leased from Southern Pacific and maintained by Southern Pacific at their depot in Roseville, California.

Some of the small railroads that operate in California were contacted by telephone, and it was found that the cleaning performed by these railroads was primarily alkaline washing.

5.5 Civilian Aircraft Maintenance

5.5.1 Purpose

The civilian aircraft maintenance industry includes both privately- and commercially-owned aircraft. All aircraft require periodic scheduled maintenance to assure continuous safe performance. An important aspect of scheduled maintenance is degreasing to facilitate inspection and maintenance. Therefore, it was considered necessary to assess the maintenance degreasing performed by the civilian aircraft maintenance industry.

5.5.2 Data Collection Methodology

The major airlines perform degreasing operations at specific airports where their maintenance facilities are located. Inquiry was made at the United Airlines maintenance facility at San Francisco International Airport to try to determine the types and quantities of degreasing that is performed by a major airline. United Airlines asked for a formal letter of request and at the time of this writing there has been no reply. However, from a telephone conversation with the chemist for the airline, it was found that emulsion cleaners are used for washing the exterior of the planes, and there are several vapor degreasers located throughout the facility.[14]

Inquiry was made at the Executive Airport in Sacramento and at Phoenix Field outside Sacramento to attempt to determine the types of degreasing performed. These small airports are serviced by a number of small companies that perform aircraft washing and maintenance as requested by private individuals and companies that own aircraft. The aircraft service company located at Executive estimates a monthly consumption of 3 gallons of Shell solvent. The aircraft service company located at the smaller Phoenix Field reported using approximately 20 to 25 gallons per month of Chevron solvent.

Another source of degreasing emissions from the civilian aircraft maintenance industry is the private plane owner who brings his own solvent and degreases the engine himself.

5.6 Military Aircraft Maintenance

5.6.1 Purpose

As a part of periodic military aircraft maintenance, aircraft are washed, and engines and various aircraft subassemblies are degreased to facilitate inspection and maintenance performed at specific intervals. Therefore, it was considered necessary to assess the maintenance degreasing performed by the military aircraft maintenance industry.

5.6.2 Data Collection Methodology

The most recent available literature listed 28 military installations in California that had control tower operations in 1974.[15] These military bases are each different in that the host organization and the number and type of tenant organizations varies from base to base; the size, type, and number of aircraft assigned to each organization varies greatly; and the number of flight hours which ultimately determines the frequency of periodic maintenance varies significantly between organizations.

Inquiry was made at Mather Air Force Base near Sacramento, California to determine the types and amount of maintenance degreasing performed at that base. The host organization at Mather is the Air Training Command (ATC) which maintains 19 converted Boeing 737 aircraft and 38 T-37 aircraft used for navigator training. Tenant organizations at Mather include: the

Strategic Air Command (SAC) which maintains B-52 bombers and KC-135 tanker aircraft, the U.S. Army which maintains helicopters, and the 940th U.S. Air Force Reserve which also maintains KC-135 tanker aircraft. Table 5-7 details the maintenance degreasing performed at Mather AFB.

Degreasing emissions inventory data for two other military installations in Sacramento County were obtained from recent CARB emissions inventory data.

Table 5-7. MAINTENANCE DEGREASING PERFORMED AT MATHER AFB, CALIFORNIA

Organization	Type Acft. Cleaned	Location of Degreasing	Method of Degreasing	Type of Solvent Used	Approximate Amount (gal) of Solvent Used Per Month
Air Training Command (ATC) (Host Organization)	Boeing 737 T-37	ATC Wash Rack	Soap & Water Wash	Alkaline, Biodegradable Soap	Unknown
			Spray/Rinse	Solvent, Dry Cleaning PD 680 Type II (Stoddard w/15% Aromatics)	50
	Parts	ATC Cleaning Shop	Vapor Degreaser	1,1,1-trichloroethane	50
			Cold Solvent Dip (6 Tanks Graded Clean to Dirty)	PD 680 Type II	50
	AGE	ATC Aerospace Ground Equip. (AGE) Shop	Cold Solvent Dip	PD 680 Type II	3-4
Strategic Air Command (SAC) (Tennant Organization)	B-52 KC-135	SAC Wash Rack	Soap & Water Wash	Alkaline, Biodegradable Soap	Unkown
			Spray/Rinse	PD 680 Type II	50
U.S. Army (Tennant Organization)	Helicopters	Army Wash Rack	Unknown	Unknown	Unknown
940th U.S.A. F.R. (Tennant Organization)	KC-135	ATC or SAC Wash Rack	Same as ATC and SAC	Same as ATC and SAC	Included in ATC and SAC Estimates

5.7 References

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5. Letter from Safety-Kleen to Mr. Martin L. Kay, South Coast Air Quality, Management District, El Monte, California, concerning Safety-Kleen Metal Parts Cleaning Service.

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7. U.S. Environmental Protection Agency (1977). Control of Volatile Organic Emissions from Solvent Metal Cleaning, EPA-450/2-77-022, Research Triangle Park, North Carolina.

8. California Division of Oil and Gas (1976). 62nd Annual Report of the State Oil and Gas Supervisor 1976. Report No. PR 06.

9. Personal Communication with Larry Landis of Kern County Air Pollution Control District (1978). "Organic Solvent Use, Kern County Oil Fields."

10. The Pocket List of Railroad Officials, Third Quarter (1975). Vol. 81, No. 3, National Railway Publications Co., New York, New York.

11. Personal Communication with Dennis Swick, Chemist for A.T. & S.F. R.R. at San Bernardino, CA.

12. Personal Communication with the Engine Maintenance District Supervisor for Union Pacific R.R. at Los Angeles, CA.

13. Personal Communication with Mr. Jennings in the Purchasing Department of Western Pacific R.R. at San Francisco, CA.

14. Personal Communication with Mr. Owens, Chemist for United Airlines at San Francisco International Airport.

15. Military Air Traffic Activity, Calendar Year 1974. U.S. Department of Transportation, Federal Aviation Administration.

6.0 ALTERNATIVES TO ORGANIC SOLVENT DEGREASING

6.1 Introduction

Before describing various alternatives to organic solvent degreasing, it is of benefit to examine the general field of cleaning. The basic types of cleaning will be discussed along with various criteria to be used when evaluating cleaning methods.

Cleaning is defined as the removal of unwanted matter ("soil") from a surface to which it adheres. For the purpose of this report, the surface is assumed to be a hard surface as opposed to a soft surface (e.g., textiles). In order to remove this unwanted matter, cleaning methods rely on one or more of four processes:[1]

1. Solvency: Dissolve soil in solvents such as water, petroleum products, halogenated hydrocarbons, or other organic solvents.
2. Detergency: Lift soil from the surface by replacing it with surface-active agents which have a greater affinity for the surface than for the soil.
3. Mechanical Removal: Remove soil and sometimes even portions of the surface by wiping, brushing, abrasing machining, or agitating.
4. Chemical Reaction: React with soil to form soluble or non-interfering products.

It is usually atypical to find any single one of the above used for any cleaning need. They are most often used in combination of two or more. Predominantly, mechanical action in the form of agitation is used together with either detergency or solvency.

Defining the "best" method to meet a specific cleaning need is not an easy task. It must begin with a definition of the type and amount of soil that must be removed, as well as what amount of residue can be tolerated. It is evident that the type and amount of soil are usually predetermined by the manufacturing or maintenance operation under consideration. The amount of tolerable soil then becomes of primary concern in arriving at a "best" method for cleaning. Perfectly clean surfaces are usually not attainable, desirable, or maintainable. Thus, to properly clean a surface one must know as well the extent of cleaning to be achieved as the most efficient method to arrive at that point. Generally, the selection of a cleaning process is influenced by the following major factors:

1. type and amount of soil
2. nature of material; geometry and shape of work
3. required degree of cleanliness
4. cost (discussed in Section 7.0)

The soil to be removed has two characteristics that determine how stubborn it may adhere to the surface which is being cleaned. The first is the actual chemical nature of the soil in relation to the substrate. The attractive force between the soil and substrate are significantly determined by the relative electronegativity of the two materials. Secondly, the physical state of the soil further affects the tenacity of the holding power. Finally, divided solids and liquids hold much more firmly than do, for example, large particles.

Soils may be broadly classified into six major types:[2, 3]

1. pigmented drawing compounds
2. unpigmented oil and grease

3. chips and cutting fluids
4. polishing and buffing compounds
5. rust and scale
6. miscellaneous surface contaminants

Solvent degreasing processes are applied primarily to remove unpigmented oil and grease. They are of limited value for removing pigmented drawing compounds, chips and cutting fluids, or for polishing and buffing compounds. They are not used for removal of the other two types of soils at all. Based on the purpose of this study, only those alternatives that can be used to remove the first four types of soils will be considered, and particularly those alternatives that can remove unpigmented oil and grease.

Pigmented drawing compounds are normally oil-based material to which an inorganic pigment is added to increase the formability of the material. They are difficult to remove from a metal surface because of their chemical inertness and strong adherence to the metal. Unpigmented oils and greases include mineral oil, vegetable or animal oil, fats, and common shop grease. They are relatively easier to remove than are pigmented drawing compounds. Chips mixed with cutting fluids are generally very easy to remove. Cutting fluids, composed of mineral or fatty oils, sulfur, soaps, salts and chlorinated mineral oils, come in several different types for different proportions of constituents. Polishing and buffing compounds are generally very difficult to remove. They are composed of greases, metallic soaps, waxes, and fine metal particles. With buffing compounds, further problems arise because the compound becomes "heat set" as a result of the heat of abrasion. They invariably contain inorganic particulates (the abrasive and the removed substrate). This again necessitates some agitation to mobilize the particulates. Further, the oily portion is less soluable since it is partially carburized. Agitation becomes a necessity for baked-on buffing compounds. Alternatively, electrolytic cleaning can be used.

The method used to clean an object should not render that object unsuitable for its intended purpose. As an obvious example, it would be inadvisable to destroy a finely polished surface by abrasive blasting to remove an oil used as a lubricant during the polishing process. Moreover, the cleaning solution should not chemically attack the surface to any great degree.

Once compatibility of materials is established within a cleaning system, another important consideration is the geometry and shape of the part being cleaned, particularly if detergency is the basis involved. Since the cleaning medium must come into contact with the soil to be removed, it is crucial that the attraction of the medium to the substrate be of greater magnitude than the medium to itself. If it is not greater, the surface tension of the medium will preclude its wetting the substrate. Further, it will result in the medium's inability to enter small volumes such as capillaries and other intricacies. However, removal of the cleaning medium is of equal importance; therefore, the attraction for the substrate should not be significantly greater than the minimum necessary to allow contact. If greater surface attraction is evident, drying (a further treatment) is hampered.

Finally, what is to be done with the cleaned part may exclude certain types of cleaning. For future coating with a oil-base paint, the surface should be free from water. If a water-free condition is required, a drying-cycle process is necessitated. If a large volume-to-surface ratio is encountered (e.g., in a capillary), drying may be very difficult. Actually, this is one reason many manufacturers rely on vapor degreasing; the organic solvent evaporates considerably faster than any aqueous cleanser rinse.

The solvent degreasing alternatives were identified through literature surveys and surveys among degreasing users. The basic cleaning mechanisms, the cleaning agents used, the application methods, the advantages and drawbacks, and the technical applicability for each major alternative are discussed. Alternatives that can be applied to metal cleaning, but which are of less importance in removing oil and grease types of soils, are also included in this section.

6.2 Alkaline Washing

6.2.1 Cleaning Mechanisms

The most common aqueous cleaning method is alkaline washing. It is a general term for probably the oldest form of cleaning known to man. In contrast to solvent degreasing, the removal of soil from component metal parts by alkaline washing is accomplished by a detergency action characterized by a displacement activity rather than by a direct solution in the degreasing solvent.

The mechanisms that are involved in alkaline washing processes may be considered as physical processes. Soils are removed by one or more of these processes:[3]

Saponification: In this process, the separate production of the soap is often bypassed. Animal and vegetable oil or other grease may be partially removed by this reaction. A warm alkaline solution is used to saponify the soil being removed. The soil is thus made into a primitive soap and is easily removed. However, not all grease-type soils are saponifiable, and thus are not susceptible to this form of cleaning. Saponification is a slow and usually incomplete process.

Wetting Action: This is a mechanism whereby the entire metal surface is wetted and the soils are penetrated by the alkaline washing solution. This penetration power is important in alkaline washing mainly because the solution may reach the deep part of the soils. The degree of alkalinity and the presence of suitable colloidal material determine the wettability.

Emulsification: Because of the low interfacial tension of the washing solution, the high operation temperature and the agitation, soils are removed from the metal surface, broken up, and suspended in the solution in the form of very fine liquid particles.

Dispersion: Soil particles suspended in the solution are dispersed and distributed evenly throughout the solution in this process. By lowering the concentration of soil particles at the metal surface, this mechanism prevents the redeposition of soil particles on the metal surface.

Aggregation: In this aggregation process, suspended soil particles are re-united away from the works. The resultant aggregated are precipitated out or skimmed off.

6.2.2 Alkaline Cleaners

The most important component in an alkaline washing solution is water. Hot water, in combination with agitation, has adequate cleaning properties. Water transmits heat and agitation evenly to the work, reduces soil viscosity, carries the cleaner to the work, and flushes soil away from the work. An alkaline cleaner is added to improve these activities of water. In order to be effective, an alkaline cleaner should possess the following properties:[3, 4, 5]

- Reduce surface and interfacial tension to enhance the penetration power and emulsibility of the solution.
- Provide active and available alkalinity to facilitate saponification.
- Provide a buffering action to preserve the original pH.
- Soften hard water to prevent the building up of hard-to-remove films of calcium, magnesium, and iron soaps.
- Disperse suspended soil particles to prevent redeposition.
- Possess rinseability so that no clear particles will remain on the metal surface.
- Exhibit a compatibility such that its ingredients will not adversely react with one another and release heat and cause inefficient cleaning.
- Have no corrosive properties toward parts being cleaned.
- Have good storage stability and physical form so that no cracking or dusting occurs.
- Have a tolerable or desirable foam level.
- Be free-flowing, dustless, and non-hygroscopic.

Although these properties are usually desirable for cleaners, there is no universal or all-purpose cleaner available. In order to meet the requirements for various cleaning jobs, the cleaners are made in formulations to fit specific applications. Generally, the cleaners are composed of builders (alkaline salts) and surfactants. The bulk of the materials of a cleaner are the builders. Several builders are used in a given cleaner in different proportions to provide suitable alkalinity and other desirable properties for different applications. Heavy duty cleaners, with a pH of about 12.4 to 13.8 are used to clean steel.[5] Cleaners with a pH between 11.2 and 12.4 are used to clean aluminum, zinc, and other less-resistant metals. Metals that are very susceptible to corrosion must use a cleaner with a pH between 10.5 and 11.2. The major builders are all sodium salts: carbonates, phosphates, silicates, and hydroxide.[6, 7]

Carbonates

This type of builder includes sodium carbonate, sodium bicarbonate, soda ash, and sodium sesquicarbonate. They all serve as buffers, sources of alkalinity, softeners, drying agents, and as free-flowing enhancers. They are all low in cost. Soda ash and carbonate can offer a high alkalinity, whereas bicarbonate and sesquicarbonate are used as builders in cleaning solutions in which a low alkalinity is desired.

Phosphates

This type of builder includes trisodium phosphate, tetrasodium pyrophosphate, and sodium tripolyphosphate. Their common characteristics include their rinseability, alkalinity, buffering action, and their ability to soften water. These builders are good emulsifiers and sequestering agents (chemicals that combine with calcium, magnesium, and other heavy-metal ions to form a complex in which the ions are held so securely that they can no longer react), and they have the capacity to disperse and to reprecipitate the soil particles. Trisodium phosphate is low in cost but has a lower softening efficiency. Tetrasodium pyrophosphate and sodium tripolyphosphate are good builders except that they tend to revert to the inactive orthophosphate under high temperatures.

Silicates

This type of builder includes sodium orthosilicate, sodium metasilicate, and sodium sesquisilicate. They are important ingredients in a cleaner's formulation (particularly in a heavy duty cleaner's) mainly because they are excellent emulsifiers, sources of alkalinity, and good buffers. Silicates are added to most cleaners for aluminum and zinc because they inhibit the attack of alkaline salts on these metals. However, rinsing of silicates is generally incomplete.

Hydroxide

Caustic soda is a cheap source of alkalinity. It also increases the electrical conductivity and improves saponification. The major disadvantages of it as a builder are its poor rinseability and the fact that it is hygroscopic.

The exact alkaline content of a builder is important in alkaline washing so that detrimental effects of a too-strong alkali on less-resistant metal surfaces can be avoided, while the alkali will still be strong enough for heavy duty cleaner. The alkaline contents of the major builders are shown in Table 6-1.

Surfactants are added in the cleaner formulation to increase the wettability, to lift the soil from the surface, and to assist in forming emulsion. These three functions can be fulfilled by soaps derived either from a fatty acid or from a resin acid, and synthetic detergents (syndets).

Soap

Soap consists of a long chain of carbon atoms which is oil-soluble and a terminal ionic group which is water-soluble. Each end, therefore, can dissolve in either the water or the hydrocarbon grease. The surface tension of water is lowered, which permits more penetration. Due to its low cost, sodium resinate (mostly sodium abietate) is more extensively used than are the common soaps, such as sodium laurate, stearate, or palmitate. These soaps can be made insoluble, however, by calcium, magnesium

Table 6-1. ALKALINE CONTENTS OF MAJOR BUILDERS[5]

Builders	pH (for Weight Percent Indicated)			Amount of Alkalinity*	
	0.1%	0.5%	1.0%	Phenolphthalein	Methyl Orange
Sodium hydroxide (caustic soda)	12.0	12.7	13.3	122	122
Sodium orthosilicate	11.8	12.6	13.0	100	100
Sodium sesquisilicate	11.6	12.3	12.6	58	60
Sodium metasilicate	11.3	12.0	12.5	45	48
Trisodium orthophosphate	11.5	11.8	11.8	18	35
Sodium carbonate (soda ash)	10.7	11.3	11.3	56	95
Soap	10.2	----	----	---	---
Tetrasodium pyrophosphate	10.0	10.1	10.4	12	38
Sodium sesquicarbonate	9.6	9.7	10.0	28	68
Sodium tripolyphosphate	9.1	9.0	9.5	---	---
Borax	8.5	8.7	9.2	20	28
Sodium bicarbonate	8.0	8.2	8.4	3	61
Sodium metaphosphate	6.5	6.2	6.9	---	---

*Expressed as the number of milliequivalents of acid required to bring 1 liter of 0.5% solution to the phenolphthalein and methyl orange end points.

or other heavy-metal ions and thus cause the formation of hard-to-remove scum in hard water. They should be used with a strong water-softening agent. Soaps cost less than syndets, but some soaps have limited solubility in water; and soaps have limited effectiveness against certain soils.

Syndets

Synthetic detergents are excellent water softeners.[7] They also have high rinseability and soil dispersion properties. There are four main types of syndets: anionic, cationic, non-ionic, and amphoteric (cationic--anionic). Cationic and amphoteric syndets are seldom used because they are expensive. Anionic syndets are made from: (1) alcohol derived from sodium lauryl sulfate, (2) petroleum derived fraction combined with benzene and sulfonated with sulfuric acid (alkylaryl sodium sulfonate). This type of syndet has a low cost and exhibits good detergency but foams readily and profusely. The non-ionic syndets most commonly used are sulfonated esters and ethers, and polyoxyethylenes. They produce less foam but may come out and float on top of the solution under high temperature.

Table 6-2 lists the typical formulations of alkaline washing cleaners for the major washing methods applied to clean various metals.[4] These formulations apply to average soils encountered in general cleaning processes.

6.2.3 Alkaline Washing Methods

Alkaline cleaning methods (here referring to general aqueous solutions) can be broken down into immersion cleaning (similar to cold solvent cleaning) and steam cleaning (similar to vapor degreasing) types. Immersion cleaning is normally processed at supra-ambient temperatures.

The major methods employed in alkaline washing are soak cleaning and ultrasonic cleaning.[4, 5] Other methods are variations incorporating the

Table 6-2. TYPICAL ALKALINE WASHING CLEANERS[4]

	Aluminum		Copper			Cu Plate	Iron and Steel			Magnesium		Zinc		
	So*	Sp*	So	Sp	El*	El	So	Sp	El	So	Sp	So	Sp	El
Builders														
Sodium hydroxide, ground	---	---	20	15	15	55	20	20	55	20	20	---	15	15
Sodium carbonate, dense	---	---	18	---	---	8	18	19	8.5	18	29	---	---	---
Sodium bicarbonate	21	24	---	34	34	---	---	---	---	---	---	---	35	34
Sodium tripolyphosphate	30	30	---	---	10	---	20	20	10	20	20	90	10	10
Tetrasodium phosphate	---	---	20	10	---	10	---	---	---	---	---	---	---	---
Sodium metasilicate, anhydrous	45	45	30	40	40	25	30	30	25	30	30	---	40	40
Surface Active Agents														
Sodium resinate	---	---	5	---	---	---	5	---	---	5	---	5	---	---
Sodium alkylaryl sulfonate	3	---	5	---	---	---	5	---	1	5	---	5	---	---
Alkylaryl polyether alcohol	---	---	2	---	---	1	2	---	---	2	---	---	---	---
Nonionics high in ethylene oxide	1	1	---	1	1	1	---	1	0.5	---	1	---	---	1
Operating temperature of solution, °F.	160	160	180	170	160	180	200	170	180	200	170	180	170	180
Concentration of cleaner, oz./gal. of water	4	1	8	1	8	8	8	1	8	8	1	4	1	6

* So: Soaking

Sp: Spraying

El: Electrolytic Cleaning

essential features of these two. These two main methods are differentiated primarily by their comparative levels of agitation. The agitation level largely determines the degree of efficiency in soil removal.

Soak Cleaning: This type of cleaning has a low level of agitation. The cleaner itself removes most of the soil; thus the selection of cleaner is especially important here. Works are immersed in the cleaner bath for a relatively long period of time, withdrawn, rinsed and dried. The cost is low, but it is a slower and less efficient method and is employed only for small volumes of work.

Pressure-spray Cleaning: This is generally a conveyorized process that can be used to clean large volumes of work. Soils are removed from the work as the result of the combination of detersive properties of the cleaning solution and the impinging of sprays. A relatively high level of agitation is provided by the spray. The degree of agitation is dependent on the design of the spray head and the impinging pressure. This is a very high cost process. It may not, however, be suitable for cleaning small basketed parts and parts with an intricate shape, since the solution would not be able to reach the hidden areas and the impact of spray would be quenched at the first contact with the exposed areas. Because of the foaming problem associated with a high level of agitation, spray cleaning has a lower detergency than soak cleaning. Antifoaming agents may be added to ease the problem.

Electrolytic Cleaning: Strong agitation in this process results from the evolution of large volumes of gas and oxidation-reduction reactions during electrolysis. This high level of agitation produces a mechanical action at the metal surface. Therefore, the cleaner chosen should have fairly good non-foaming characteristics. Sodium hydroxide is generally an important ingredient because it provides high conductivity in the solution. The resulting surfaces are suitable for electroplating. Since the same electrical charges are imparted to both the dirt particles and the work, the dirt is repelled from the work surface.

Ultrasonic Cleaning: This process can provide high quality cleaning, but the capital cost is relatively high. A more detailed discussion on ultrasonic cleaning is presented in the later part of Section 6.4. A high level of agitation is provided by ultrasonic vibration; however, the cleaner must be carefully chosen to remove the soil and inhibit the formation of foaming.

6.2.4 Advantages and Limitations

Compared to solvent degreasing, alkaline washing has several distinctive advantages and several serious drawbacks.[4, 8] The major advantages of alkaline washing are:

- Since no photochemical reactive organic solvents are used in alkaline washing, there would be a total elimination of solvent emissions in switching from solvent degreasing to alkaline washing. Any other problem associated with solvent usages, such as occupational safety for degreaser operators, would be mostly resolved.
- Alkaline washing is normally the first choice in situations where the next step in the manufacturing process is plating, phosphatizing, or other wet operations. A large energy demand is avoided because it is unnecessary to have the works dried, and the hydrophilic surface created by the alkaline washing would enhance the following wet operations.

- There is a lesser need for confinement in alkaline washing than in solvent degreasing. The works can be processed on one horizontal plane instead of moving the works up and down, and in and out, of the solvent degreaser. Higher spray pressure may be applied in the washer; therefore, the removal or flushing away of metal chips, dry lubricant residue, and other insoluble or less-soluble contaminants would be greatly enhanced.
- The removal of pigmented-drawing types of soils, cutting fluids, buffing compounds, and other inorganic contaminants may be more easily accomplished with alkaline washing by dissolution or chemical reaction.
- The alkaline cleaners are much cheaper than most other solvents used in degreasing. There is no waste residue generated; thus the expense of solid or liquid waste disposal is eliminated.

Here are the major disadvantages of alkaline washing compared to solvent degreasing:

- In general, in removing grease and oil, solvent degreasing can achieve a higher quality of cleaning than can alkaline washing. Vapor degreasing is usually used to clean small delicate parts. The spray and flushing effects of alkaline washing may not reach parts of the surface that are not exposed for washing.
- Any residual water left on ferrous parts can lead to the formation of rust. For non-ferrous metals, corrosion or staining may result if the alkaline cleaner is not properly selected and used.
- The quantities of washing solution in the washers are generally very large, and the latent heat of water is much higher than those of

degreasing solvents; therefore, longer start-up time is needed for the washers and they generally have higher heating energy demands.

- Alkaline washing is seldom used to clean electrical insulating parts mainly because washing solutions have high electrical conductivity. Parts that require low moisture content can not be cleaned by alkaline washing.
- Large volumes of wastewater are generated in alkaline washing processes. This emulsive-type of wastewater has high concentrations of grease, oil, and cleaning agents that are generally required to be treated before discharging to the sewer. Manufacturers may have economic difficulties in constructing and maintaining separate treatment plants. Phosphates in the alkaline cleaners are currently the subject of considerable controversy because they may contribute to the occurence of eutrophication.

6.2.5 Current Users of Alkaline Washing in California

Table 6-3 summarizes factors to be considered for selecting suitable metal cleaning processes.[8] The table might be used as a guide for preliminary screening of processes. It is quite possible for certain types of industry to switch to other processes; however, even for manufacturers in the same SIC category, the requirements of works to be cleaned is so specific that the suitability to switch from one process to another has to be dealt with on an individual basis. The reduction of solvent emission as the result of switching from solvent degreasing to alkaline washing should be incorporated in the cost-effectiveness analysis.

Table 6-4 summarizes the current users of alkaline washers in California by SIC categories. These users were identified in the survey. The per-

Table 6-3. FACTORS TO BE CONSIDERED FOR SELECTING SUITABLE METAL CLEANING PROCESSES[8]

Solvent Degreasing	Water-based Cleaning
•Non-ferrous Metals	•Ferrous Metals
•Small Parts	•Large Work Pieces
•High Precision Parts	•Low Tolerance Parts
•High Cleaning Requirements	•Lower Cleaning Requirements
•Electric and Electronic Parts and Assemblies	•Pre-plating, Phosphatizing or other Wet Processes

Table 6-4. SUMMARY OF CURRENT USERS OF ALKALINE WASHING IN CALIFORNIA

SIC	Category	% of Respondents Using Degreasing	% of Alkaline Washing Users*
253	Public Building Furniture	20%	100%
332	Iron & Steel Foundries	37%	66%
341	Metal Cans & Containers	33%	100%
342	Cutlery, Handtools	25%	25%
344	Fabricated Structure Metal Products	5%	20%
346	Forgings & Stampings	4%	11%
347	Metal Services	55%	16%
349	Misc. Fabricated Metals	18%	16%
351	Engines and Turbines	100%	100%
356	General Machinery	45%	14%
359	Misc. Machinery	33%	14%
366	Communicating Equipment	48%	41%
367	Electronic Components	40%	11%
369	Misc. Electrical	33%	50%
371	Motor Vehicles & Equipment	45%	25%
372	Aircrafts & Parts	60%	13%
376	Guided Missles, Space Vessels	75%	33%

* Based on positive respondents

centage of manufacturers in each category that use some sort of metal cleaning process (solvent degreasing or water-based cleaning) is also shown. It further indicates the percentage of metal cleaners in each category that are users of alkaline washers. Because similar types of cleaning requirements are experienced within a particular SIC category, it is reasonable to conclude that the majority of individual manufacturers within those SIC categories could technically switch to alkaline washing.

6.3 Emulsion Cleaning

6.3.1 Cleaning Mechanisms

The most popular and probably most appropriate definition of an emulsion was stated by Paul Becher as "a heterogeneous system, consisting of at least one immiscible liquid intimately dispersed in the form of droplets, whose diameters, in general, exceed 0.1 μ. Such systems possess a minimal stability, which may be accentuated by such additives as surface-active agents, finely-divided solids, etc."[9]

According to current estimates,[8, 10] approximately 15 percent of the metal cleaning processes used in this country are emulsion cleaning. generally, emulsion cleaning is a process for removing soils from metal surfaces by the use of common organic solvents dispersed in an aqueous medium with the air of an emulsifying agent.[11] Depending on the solvent used, cleaning is done at temperatures from room temperature to 140-180°F.

A vast increase in interfacial surface results from emulsification. For example, the emulsification of only 10 cubic centimeters of oil to form droplets of radius 0.1 μ in water creates a total interfacial area of 300 square meters,[9] an increase of a millionfold. The interface is defined as where two immicible liquids are placed in contact. Because of the large solvent surface provided in the emulsion, less solvent is required to achieve the same efficiency. Surface-active materials added to the solution are attracted to the surface of the droplet, and they provide a mechanical barrier between the solvent droplets to keep them dispersed in water rather than to permit them to coalesce. On the other hand, emulsions permit a more intimate contact with aqueous cleaning, especially with the presence of emulsifiers and alkali; thus the mechanisms in emulsion cleaning are a combination of detergency and solvency.

The size of the droplets has a pronounced effect on emulsion stability; smaller drops result in greater stability. On the other hand, larger drops generally impart greater solubility and cleaning efficiency. For most cleaning operations using emulsion cleaners, it is generally felt that stability is a more important criterion than the relatively slight increase in cleaning efficiency.

Emulsifiable solvent mixtures can also be applied without prior dispersion in water. In this way, the advantage of solvent cleaning (greater soil removal) is coupled with the ability to rinse with water. This results in less solvent usage than with straight solvent usage.

6.3.2 Emulsion Cleaners

Emulsion cleaners are generally used on the same types of materials and soils that would be subject ot classical solvent cleaning. Oily and greasy soils and lubricants are removed, generally at lower cost, with equivalent cleaning efficiency. The lower cost arises because the volume requirement is largely met by the water. Most emulsion cleaners may be used as emulsifiable solvents, which are then rinsed from the work with water. Because of their neutrality and only slight alkalinity, these cleaners are suitable for use on almost any metal. Most emulsion cleaners consist of three basic ingredients:[11, 12, 13]

1. Organic Solvent: It is the major portion of a formulation. The solvent is generally of petroleum origin and may be paraffinic, napthenic, or aromatic with boiling points of 140 to 500°F. The low boiling solvents are usually more effective in removing soils but have higher evaporation rates.

2. Emulsifying Agent: The presence of an emulsifying agent increases cleaning effectiveness by stabilizing the emulsion system. This ingredient causes the formation of interfacial film, which may affect the emulsion viscosity in such a way as to decrease the interfacial tension between the liquid phases and/or to increase the electrical charge of individual particles. There are three major classes of emulsifying agents:[9, 10, 13]

- surface-active materials
- naturally-occuring materials
- finely-divided solids

Surface-active materials are most often used. They include anionic emulsifiers like polyethers, sodium or amine soaps, amine salt of alkylaryl sulfonates, polyglycerides, glycerols, or polyalcohols. Cationic, non-ionic and amphoteric emulsifiers are of limited usage.

3. Blending Agent: The presence of this material enhances the formation of a homogeneous and stable mixture of solvent and emulsifying agent. Usually a higher alcohol or a wetting agent is used for this purpose. These organic coupling agents have verying degrees of solubility in solvent as well as water; thus they provide a fine adjustment for controlling the ease of dispersibility in water as well as the size of the

droplets of solvent dispersed in the water.

Similar materials are used in the formulation of all types of emulsion cleaners. Depending on the proportions of the various ingredients and the manner in which they are diluted, the emulsion cleaners may be broadly classified into three major categories:[11, 12]

1. Stable Emulsion Cleaner: In this type of cleaner the solvent particles are dispersed throughout the aqueous medium, and no agitation is required to maintain a uniform dispersion.

2. Unstable Emulsion Cleaner: Moderate to high levels of agitation are required to maintain the uniform dispersion of solvent particles for this type of cleaner. The two liquid phases tend to separate from each other without agitation.

3. Diphase Emulsion Cleaner: In this type two layers are formed in the cleaning tank, and the cleaner is used in this separated condition. Work is immersed through the upper solvent layer into the lower aqueous layer so that the surfaces to be cleaned may come in contact with both phases.

The typical compositions of emulsion cleaners are summarized in Table 6-5.[11]

Stable emulsion cleaners are low in cost and are used where in-plant rust protection is required. These cleaners may be further divided into single-phase emulsion cleaners and emulsifiable solvent cleaners. Basically, both are of the same formulation, but a single-phase emulsion cleaner is one that is diluted with water, whereas an emulsifiable solvent cleaner may be used either in the undiluted state or as a diluent with a petroleum solvent. Single-phase emulsion cleaners may be diluted with water at

Table 6-5. TYPICAL COMPOSITIONS OF EMULSION CLEANERS[11]*

Constituent	Stable	Unstable	Diphase
Petroleum Solvent	250-300	350-400	250-300
Soaps	10-15	15-25	0
Petroleum Sulfonates	10-15	0	1-5
Nonionic Surface-active agents	5-10	0	1-5
Glycols, glycol ethers	1-5	1-5	1-5
Aromatics	5-10	25-50	5-10
Water	5-10	0	0

* Relative "parts-by-volume"

almost any ratio, but the more common ratio is 1:50.[12] They are very effective in removing the bulk of greasy and oily soils, which may include some solid particles. Emulsifiable solvent cleaners with or without solvent dilution are very effective in removing the tightly adherent and heavy soils.

Unstable emulsion cleaners are higher in cost but can achieve higher cleaning efficiency than stable emulsion in removing heavy shop soils. The hydrocarbon fraction makes more intimate contact with the metal surface, permitting greater action on the soil. They are not adversely affected by hard water.

Diphase emulsion cleaners are used to remove the most difficult hydrocarbon soils. They are usually used in dip tanks. Because the organic layers are usually on the top, large amounts of organic solvent tend to evaporate. They cost more than the stable and unstable cleaners, and they are adversely affected by hard water.

6.3.3 Cleaning Methods

The size and configuration of the part and the nature of the soil are the main considerations that influence the selection from immersion and spray methods candidates.

Immersion Cleaning: This method is preferred for small parts that must be placed in baskets. Combination cycles of immersion, spray washing, and pressure-spray rinsing are often used to clean intricate parts. Agitation is usually provided to help in removing soil. About 4 to 6 percent of cleaner concentrate is used for stable cleaners, and a 2-inch layer of solvent over a sufficient depth of water is needed for diphase cleaning.

Spray Cleaning: Spray cleaning is often used to clean large parts with surfaces exposed for impinging. Hard-to-remove soils are generally removed with this method. The use of emulsifiable solvent cleaners is usually more practical in this type of application: the cleaner in a concentrated form is sprayed on the work surface and then rinsed with a pressure spray. About 2 to 5 percent of cleaner concentrate is used in this method.

Major factors have to be considered in each method:[11]

- level of agitation
- operating temperature
- duration of exposure
- concentration of cleaner
- degree of rinsing

6.3.4. Advantages and Limitations

Compared to solvent degreasing, emulsion cleaning has the following advantages:[11, 12]

- Emulsion cleaning is an effective means of removing a wide variety of soils from metal surfaces, especially when rapid superficial cleaning is required. This is mainly because a mixture of solvent and water is used.
- It is usually less costly than solvent cleaning because a large amount of water is added to a relatively small amount of solvent.
- Since it can be operated at room or slightly elevated temperatures, hazards from fire and toxic fumes are not great. Much less hydrocarbon is emitted to the ambient air.
- Emulsion cleaning leaves a thin film of oil on the work; this thin film provides some protection against rusting.

The disadvantages of emulsion cleaning, compared to solvent degreasing, are:[11, 12]

- Emulsion cleaning is not recommended for parts that are difficult to rinse thoroughly.
- Emulsion cleaning cannot be used to clean parts that are to be plated because a thin film of oil would be left on the parts. Since this emulsified oil would usually contaminate the plating bath sufficiently to cause excessive rejections, additional cleaning would be required to remove the film before plating.
- Emulsion cleaning is not recommended for use in cleaning aluminum or zinc if the alkali contamination has brought the pH above 10.
- A large amount of spent emulsion is generated in the emulsion cleaning process. It has to be treated before entering the sewers. Emulsion generally has to be broken and separated.
- At high operating temperatures, evaporation rates will increase and polymerization of emulsion cleaner ingredients may occur, causing the formation of a hard-to-remove varnish-like film on the metal surface.
- If hard water is used for stable emulsions, insoluble precipitates may form and remain on the metal surface or plug drains.

6.3.5 Technical Applicability

Most industries use emulsion cleaning to carry out the following functions:[10]

- maintenance in steel mill operation
- steel sheet coating for rust protection
- engine blocks cleaning and protection
- cleaning and coating of welded auto wheels prior to their shipment

- cleaning and rust-protection coating of bearings in process and before final assembly.

A detailed summary of the typical applications of emulsion cleaning is shown in Table 6-6.[11]

From the air pollution standpoint, emulsion cleaning is preferable to straight solvent cleaning. While it is recognized that the solvent portions of emulsion cleaners are the same or similar solvents that are used in solvent degreasing, there is a distinct advantage to using emulsion cleaning. The amount of solvent emitted is a function of the exposed surface area occupied by the solvent and a function of the viscosity of the emulsion. Therefore, the solvent emission rate really depends on the type of cleaner used, the solvent/water ratio, and the method of application. For diphase emulsion cleaner, the emission rate from the tank should be close to that from the cold solvent degreaser if the solvent is floating on the top. On the other hand, if the aqueous phase is on top of the solvent, there would be no emission of organic solvent. For stable and unstable emulsion cleaners, the solvent emission rates should be smaller than the estimated rate based on solvent degreasing. For example, if the solvent/water ratio is 1:1, the solvent emission rate for emulsion cleaning should be smaller than 50 percent of the pure solvent degreasing. The main reason is that there are attractive forces between the two phases, especially if a blending agent is added. Spray cleaning, in general, would result in larger amounts of solvent emission than dip (or immersion) type cleaning.

By summarizing information provided by the survey respondents, Table 6-7 lists the categories of manufacturing industries that are potential emulsion cleaning users[10, 11] together with the percentage of manufacturers

OF EMULSION CLEANING

Type of Part	Soils Removed	Cleaning Cycles	Cleaning Time, min	Subsequent Operations
	Stable Emulsion, Dip Cleaning			
Cast iron parts and machined parts	Machining oil, chips	Alkaline clean, emulsion clean	1	Storage
	Stable Emulsion, Spray Cleaning			
Aluminum and brass carburetor parts	Machining oil, shop dirt	Clean, blow off	1	Assembly, storage
Aluminum and brass	Dirt, machining oil	Clean, blow off	2	Assembly, storage
Aluminum cabinets	Machining oil, chips	Clean	1	Assembly, storage
Aluminum housing (automatic transmission)	Alkali	Alkaline clean, emulsion clean	1	Assembly, storage
Automobile wheel assembly, 160 sq in.	Drawing compound, chips	Clean, no rinse	1	Assembly, storage
Brass valves	Machining oil	Clean, blow off	2	Assembly, storage
Cast iron motor blocks	Machining oil, chips	Clean, no rinse	2	Assembly, storage
Cast iron motor heads	Machining oil, chips	Clean, no rinse	1	Assembly, storage
Retainer plate, 16 sq in.	Shop dirt, drawing compound	Clean	1	Assembly, storage
Steel rings, 4-in. diam	Machining oil	Clean, no rinse	1	Assembly, storage
Steel sinks	Drawing compound, oil	Clean	4	Alkaline soak, then enamel
Tractor parts	Machining oil, dirt	Clean, blow off	1	Wash, then paint
Valves (steel and brass)	Machining oil	Clean, blow off	1	Assembly, storage
Washing-machine tubs	Drawing compounds	Clean, no rinse	3	Alkaline soak, then paint
	Unstable Emulsion, Spray Cleaning			
Brake assembly, 20 sq in.	Shop dirt, chips	Clean, no rinse	1	Assembly; storage
Brake plates, 8-in. diam	Machining oil, chips	Clean, no rinse	1	Assembly, storage
Brass cases, 4 by 4 in.	Drawing compound	Clean, blow off	2	Assembly, storage
	Diphase Emulsion, Dip Cleaning			
Zinc die castings	Buffing dirt	Soak, spray	4	Wash, then plate

hat use metal cleaning processes in their manufacturing cycle. There are o data from the respondents on the percentage of metal cleaners used in nulsion cleaning. It is felt that specific identification of emulsions as not experienced because many potentially current users would have identified them as "aqueous cleaners." The questionnaire was not conducive identification of emulsion cleaners separate from aqueous.

Table 6-7. POTENTIAL EMULSION CLEANING USERS[10, 11]

SIC	Classification	% of Metal Cleaner*
331	Basic Steel Products	19
332	Iron & Steel Foundries	38
336	Non-ferrous Foundries	15
342	Cutlery, Handtools & Hardware	24
343	Plumbing, Heating (except Electric)	37
345	Screw Machine Products	55
351	Engines & Turbines	100
371	Motor vehicles & Equipment	43

* From all responses

Emulsion cleaning is a possible alternative to cold solvent degreasing tomotive repair and oil well maintenance industries. The immersion of diphase emulsion cleaner may be used together with some sort of tion to achieve the same cleaning efficiency as solvent degreasing. onstration project is needed to determine the exact technical and ical feasibility.

6.4 Ultrasonic Cleaning

6.4.1 Cleaning Mechanisms

Ultrasonic cleaning methods have been employed in many industrial processing applications. Primarily, most of these applications are based upon two characteristics of ultrasonics. One is the cavitation which is produced in liquids by an ultrasonic wave, and the second involves friction reduction resulting from the effect of high acceleration of ultrasonic waves on the frictional bonds between solid materials in contact.[14] Since ultrasonic cleaning is brought about by cavitation, the discussion here will be limited to cavitation.

The word "cavitation" means "the formation of a cavity." The cavities in which cleaning is done are bubbles in liquids. An example of cavitation occurs in boiling water. The first cavitation takes place when the dissolved gas bubbles are evolved. As soon as the boiling temperature is reached, the water passes into the vapor phase and forms more bubbles. These newly formed bubbles either collapse immediately or rise to the surface.

In bubble formation, a nucleus is required. The nucleus may take the form of a small bubble, a pocket of gas, or a dust particle. The nucleus remains in a quiescent state until some thermal or mechanical changes occur which upsets its state of equilibrium and causes the release of the bubble.

The phenomenon of cavitation is essentially a mechanical disturbance consisting of positive and negative pressure fluctuations. A reduction in pressure encourages the growth of small bubbles while a pressure above that in the liquid will cause bubbles to collapse or discourage any bubble growth. It is the sudden collapse of bubbles, together with appropriate cleaning liquids and other operating conditions, that produces the characteristic cleaning effects associated with cavitation.

Besides cavitation, the other basic mechanism in ultrasonic cleaning is agitation. The cleaning process is mainly due to agitation at higher frequencies, while at lower frequencies cavitation is the principal agent. Agitation is essentially a stirring action which produces concentration gradients needed to promote diffusion or a more rapid dissolving of the surface contaminant.

In producing a cleaning action, either by cavitation or by agitation, ultrasonic energy may act in any one or a combination of the following three ways:

1. Cause erosion.
2. Disperse a solid or liquid film.
3. Increase the rate at which a surface film is dissolved.

In regard to the efficiency of these cleaning actions, one has to consider other factors, such as cleaning solutions, temperature, and operating conditions in addition to the cleaning mechanisms. These factors which affect the cleaning efficiency will be subjects of consideration in the sections that follow.

6.4.2 Cleaning Procedures and Efficiency

Most ultrasonic cleaning applications are carried out under a frequency range below 100 kilocycle/second (kc/s). The work is usually immersed in a tank containing a liquid selected for its cleaning characteristics.[14, 15] However, susccessful ultrasonic cleaning requires not only an appropriate cleaning liquid but also an optimization of various factors in the system. Factors of primary consideration which affect the cleaning efficiency include the following:

- tank holding the cleaning solution
- sound field
- frequency
- temperature of solution

Cleaning Tanks: There are two important parameters in a tank affecting cleaning efficiency: the tank size and the material of which the tank is made. The tank size for ultrasonic cleaning ranges from a pint to as large as that required to accomodate the item to be cleaned. The primary consideration here is not the absolute tank size, but rather the tank size relative to the locations of the transducers which dictate the effective range of waves generated. Unless a focusing transducer is used, the limit in linear dimensions of a tank is such that the surface of the part to be cleaned must not be more than 2 to 3 feet from the nearest transducer. The transducers are usually mounted along the walls or on the bottom of the tanks.

The main concern with the tank material is its eroding property. Tanks should be made of a material that will not erode away very rapidly as a result of cavitation action. Studies indicate that a 50% reduction in relative cleaning efficiency may result from cavitation erosion of the walls of the tank after 10,000 hours of operation.[14] Erosion of the tank walls and transducer surface will be less if the material for those areas has the following properties:

- tough, homogeneous, fine crystal structure
- high corrosion-fatigue limit
- high tensile strength

- high hardness
- tendency to work-harden as a result of mechanical action

Sound Field: Cleaning efficiency varies at different locations of a sound field within a tank. It has been shown that a higher cleaning efficiency is achieved at the antinodes than at the nodes in a sound field.[14] This is due to the maximum cavitation effect produced at the antinodes. In order to optimize the use of a sound field, one has to take advantage of the cavitation effect at the antinodes as well as to produce greater amplitudes of standing sound waves. The latter can be accomplished by proper choice of tank width and liquid depth.

Standing waves, however, have the undesirable effect of producing nonuniform cleaning. This problem can be minimized by employing one or more of the following techniques:

- Use two different frequencies simultaneously, such as 20 and 40 kc/s.
- Raise and lower the liquid level in the tank at a slow rate.
- Continuously move the work around in the tank.
- Avoid standing waves entirely by not having any two surfaces in the tank parallel with each other.
- Modulate the ultrasonic frequency which drives the transducers at a slow rate above and below their resonant frequency.

Frequency: The most effective frequencies in ultrasonic cleaning are between 16-45 kc/s. Since at these lower frequencies the bubbles have more time to grow before they collapse, they collapse with a greater force and release more energy. Another advantage of low frequencies is that there is better coverage of surfaces that are not directly exposed to the initial sound beam; acoustical blocking and overshadowing are avoided.

For example, the wavelength of a 20 kc/s sound wave in water is about 3 inches. This means that an object or obstacle has to be at least this size before it casts much of an acoustical shadow.

Temperature of Solution: The temperature of the cleaning solution is an important factor in cleaning efficiency. The cavitation process is temperature-dependent since several important characteristics of a liquid that affect cavitation intensity are themselves temperature-dependent. These characteristics include, among others, viscosity, surface tension, and vapor pressure. Increasing the temperature above certain limits increases the chemical activity of the cleaning liquid; the viscosity and surface tension are decreased with a simultaneous increase in vapor pressure. These changes cause a reduction in the corosive activity of the cleaning solution and in the efficiency of cavitation-destruction ability.[15] It is important to note that for each cleaning liquid there is a critical effective temperature interval. It is at this interval that the solution will provide the maximum cavitation activities.

6.4.3 Cleaning Solution Selection

This section presents a summary on cleaning solution selection according to the type of soil. Since the selection of a medium for ultrasonic cleaning is dictated by the soil type, classifications of soil will be considered first.

All soil types can be grouped under any one or a combination of the following six classifications:[15]

1. cavitation-resistant
2. noncavitation-resistant
3. strongly bound with the surface to be cleaned

4. weakly bound with the surface to be cleaned
5. chemically interacting with detergent
6. chemically non-interacting with detergent

This classification is based on three criteria:

1. the ability to withstand the action of micro-impact loading
2. the bond strength with the surface to be cleaned
3. the nature of the chemical interaction with the detergent

Any type of soil can be characterized by a combination from the six classifications. For example, if water is used to clean a metal surface with thin grease films, the soil type is classified as cavitation-resistant, weakly bound with the cleaned surface, and chemically noninteracting with the detergent. Inefficient cleaning in water is readily apparent from the classification criteria. Water has to be replaced with a chemically active medium in order to achieve high-quality cleaning.

In Table 6-8[15, 16] the most often-encountered soil types are listed and classified according to the classification criteria discussed above.

Basically, there are three types of solutions for ultrasonic cleaning: alkaline, acidic, and solvent. Derived from these three types, there are a number of variations of cleaning solutions available on the market.

Alkaline Materials: Alkaline solutions consist of alkalies such as caustics, phosphates, silicates, carbonates, and surface-active agents. Surface-active agents serve the following functions:

- Speed the wetting, penetrating, and emulsifying actions of the solution.
- Accelerate the effects of lime-sequestering materials.
- Control salts in hard water.

Table 6-8. IDENTIFICATION AND CLASSIFICATION OF DIFFERENT SOIL TYPES[15, 16]

Soil Type	Classification
Dust or slurry after etching	Noncavitation-resistant, weakly bound with cleaned surface, chemically non-interacting with detergent
Grease films	Cavitation-resistant, weakly bound with cleaned surface, chemically interacting with detergent
Lacquer films, dyes	Cavitation-resistant, strongly bound with cleaned surface, chemically interacting with detergent
Buffing, polishing compounds	Noncavitation-resistant, strongly bound with cleaned surface, chemically interacting with detergent
Scale, oxide films	Cavitation-resistant, strongly bound with cleaned surface, chemically interacting with aggressive liquids
Corrosion products	Noncavitation-resistant, strongly bound with cleaned surface, chemically interacting with aggressive liquids
Pickup, resin deposits, rubber	Cavitation-resistant, strongly bound with cleaned surface, chemically non-interacting with detergent

- Help buffering agents to maintain the pH of solution.
- Assist colloidal agents in their task of keeping soil suspended and preventing redeposition on surfaces being cleaned.

The pH of alkaline detergents recommended for ultrasonic cleaning is between 7.5 and 13. The operating temperatures range from room temperature to 200°F. The milder alkalies with lower pH are recommended for metal, glass, and plastic to remove buffing and polishing compounds. Detergents with a slightly higher pH range are recommended for removal of tougher soils, such as rough buffing compound, palm and vegetable oils, and fats from aluminum, brass, and zinc. These alkalies contain additives, which inhibit their attact on metals. Stronger alkalies are recommended for the removal of buffing and lapping compounds and more difficult soils from precious metals, iron, and steel. Some of the strongly alkaline detergents that contain chelating agents can sometimes remove even rust, scale, and oxides from ferrous surfaces.

Acids: Concentrations of acid used for ultrasonic cleaning usually range from 5 to 50 percent, while 20-50 percent ranges are for stronger solutions. For effective ultrsonic cleaning purposes, the acid solutions must meet the following conditions:

1. Density of solution must be about that of water or a little higher.
2. The vapor pressure should be low and at the working temperature of the bath.
3. The solution must remain thin-bodied and nonviscous at operating temperatures.

Acids are recommended for the removal of oxides, tarnish, scale, rust, and stains in ultrasonic cleanings. The concentration of acid used will depend on the nature of the metal to be treated.

Solvents: In selecting a solvent for ultrasonic cleaning, several factors should be considered: flammability, toxicity, reclamation, and degreasing.

Both flammability and toxicity of solvents used involve the question of safety. It is obvious that highly flammable solvents should not be used. Safety principles should also be applied to solvent toxicity. In safegarding workers and the public, governmental agencies have set maximum allowable concentration ratings (MAC) for different solvents. MAC figures give comparative information as to the safety of different solvents. Materials that have an MAC rating of lower than 150 are considered to be too toxic for use.

The third factor to be considered is solvent reclamation. Due to economic reasons, solvent reclamation is a common practice among industries. The areas of concern here are the purity and stability of the solvent. Reclained solvents are usually contaminated with soils. The only method of ensuring high purity of reclaimed solvents is that of distillation. The solvents must be quite stable to permit distillation without breakdown.

In ultrasonic cleaning, aqueous solutions are usually first degassed. Some solutions can be sufficiently degassed in a very short time, while others may take many hours. In selecting an appropriate solution, the factor of degassing should be taken into consideration.

Many solvents have been employed in ultrasonic cleaning. The common ones include freon, perchloroethylene, and 1,1,1-trichloroehtane.

Table 6-9 summarizes the types of solutions that may be used in some soil types, including grease, in ultrasonic cleaning.[15, 16]

Table 6-9. LISTING OF CLEANING AGENTS FOR DIFFERENT SOIL TYPES[15, 16]

Material	TYPE OF SOIL			
	Buffing and Polishing Compounds	Grease and Heavy Oil	Lapping & Grinding Compounds	Scale and Oxide films
<u>Metals</u>				
Aluminum	A-15,3	B-5,3	A-6,3	B-7
Brass	A-15,3	B-14,5	A-10,3	B-7,11
Bronze	A-15,3	B-5,14	A-10,3	B-7,11
Copper	A-15,3	B-5,14	A-10,3	B-7,11
Gold	A-15,3	B-5,14	---	A-6
Iron	A-15,3	B-5,14	A-11,5	B-7,11
Magnesium	A-15	B-5,14	A-14,5	B-11
Nickel	A-15,3	B-5,14	A-14,5	B-6
Silver	A-15,11	B-14,5	A-14,5	B-6
Steel, mild	A-15,4	B-5,14	A-14,5	B-7
Steel, stainless	A-15,4	B-5,14	A-14,5	B-6,11
Titanium	A-15,4	B-5,14	A-14,5	B-6
Zinc	A-15,9	B-5	---	---
<u>Nonmetals</u>				
Ceramics	---	---	A-10,2	---
Ferrites	---	---	---	---
Glass	A-15,2	---	A-10,3	---
Precious stones	A-15 & 9	---	A-11,8	---
Quartz crystals	A-15 & 9	---	A-9,2	---
<u>Plastics</u>				
Acrylics	A-13	---	---	---
Nylon	A-15,10	B-4,3	---	---

Continued on next page

Table 6-9. Continued

Material	TYPE OF SOIL			
	Buffing and Polishing Compounds	Grease and Heavy Oil	Lapping & Grinding Compounds	Scale and Oxide films
<u>Plastics</u>				
Phenolics	A-15,13	B-13,4	B-12,4	---
Polyethylene	A-15,13	B-3,13	B-12,3	---
Polypropylene	A-15,14	B-14,3	B-14,3	---
Polystyrene	A-15,13	B-14	B-14	---

KEY:

A = ultrasonics required
B = ultrasonics recommended (more thorough cleaning, more consistent results, faster)

Cleaning Agents:

Solvents:

1 = Trichlorotrifluoroethane
2 = Trichlorotrifluoroethane water emulsion
3 = Methylene Chloride
4 = 1,1,1-trichloroethane
5 = Perchloroethylene

Acids:

6 = Acidic solution
7 = Acidic, inhibited
8 = Acidic, plus solvent

Alkaline: Chelated Detergents-

9 = Neutral (pH 5-8)
10 = Mild alkaline (pH 8-10)
11 = Strong alkaline (pH 11-14)

Non-chelated Detergents-

12 = Neutral (pH 5-8)
13 = Mild alkaline (pH 8-10)
14 = Strong alkaline (pH 11-14)
15 = Soap-free alkaline cleaners

6.4.4 Advantages and Limitations[17, 18]

Principle advantages of ultrasonic cleaning over conventional techniques including the following:

- It provides very thorough cleaning of most parts or assemblies. Because ultrasonic energy penetrates into crevices and cavities, both exposed and hidden areas are effectively cleaned. In many instances, ultrasonics may be the only technique which can meet the cleaning requirements. A case in point is the removal of blood from surgical instruments after use.
- The cleaning action is fast. Cavitation produces a scrubbing effect that accelerates the solution's cleaning action.
- It ensures efficient cleaning without causing scratching or damage to the surface. Higher frequencies, usually above 100 kc/s, are used to clean delicate objects which might be damaged by cavitation.

There are certain disadvantages in employing ultrasonic cleaning:

- After cleaning, soil remains in the bath and requires removal intermittently. When emulsive cleaners are used, the soiled solutions may require special attention to avoid water pollution.
- Ultrasonic cleaning is not effective for viscous-insoluble film.

6.4.5 Current Users of Ultrasonic Cleaning in California

Current users of ultrasonic cleaning in California are listed in Table 6-10. Data were compiled from responses to the questionnaire survey. The percentage of respondents that use degreasing as well as the percentage of ultrasonic cleaning users are presented. The types of cleaning agents used by the ultrasonic cleaning respondents are also included in the table. It is of interest to note that freon is the most common cleaning agent

Table 6-10. SUMMARY OF CURRENT USERS OF ULTRASONIC CLEANING IN CALIFORNIA

SIC		% of Ultrasonic Degreasing Users*	% of Respondents Using Degreasing	Reported Cleaning Agents
332	Iron & Steel Foundries	33%	37%	1,1,1**
335	Nonferrous Rolling & Drawing	50	12	Freon
347	Metal Services	6	55	"
354	Metalworking Machinery	8	28	"
359	Misc. Machinery, except electrical	4	33	1,1,1
360	Electric & Electronic Component	100	100	Freon
361	Electric Distributing Equipment	20	28	1,1,1
362	Electrical Industrial Apparatus	10	56	Freon
366	Communication Equipment	17	48	Vythene, G.T.
367	Electronic Components & Accessories	5	40	Acetone
372	Aircraft and Parts	4	60	"
376	Guided Missiles, Space Vehicles, Parts	33	75	Freon
381	Engineering & Scientific Instruments	17	33	Freon, 1,1,1

*Based on positive respondents

**1,1,1 = 1,1,1-trichloroethane

reported next to 1,1,1-trichloroethane.

For the purpose of this study, ultrasonic cleaning using alkalies as media will not be considered as an alternative to solvent degreasing. This omission is not to discredit ultrasonic cleaning as a viable alternative to solvent degreasing; it is becasue major manufacturers, such as aircraft and space vehicle industries, which may serve as good candidates to switch to ultrasonic-alkaline cleaning, have already been identified in Section 6.2 and 6.3 as prospects for alkaline and emulsion washings.

6.5 Other Solvent Degreasing Alternatives

In addition to the major alternatives discussed above, there are several alternatives that either are used in a very limited way or have less potential as an effective alternative. It would not be prudent to encourage widespread use of these alternatives until further evaluation is undertaken. These additional alternatives are briefly explained along with particular considerations pertaining to industrial degreasing in the following discussion.

6.5.1 Pickling

Pickling is essentially the acidic analogy to alkaline cleaning. Two modes of physical action (separately or together) account for soil removal by pickling. In one mode the base material is chemically attacked. As the base material dissolves, the soil is released with it. In the other mode the soil being removed is an oxide of the metal substrate itself. The oxide may be soluble in a particular acid while the reduced (base) metal is unreactive. Further, various inhibitors may be added to reduce substrate attack. Generally, however, some attack is desirable to remove all soil and provide a surface texture for latter treatment.

Typical applications for pickling are performed prior to electroplating or for mill scale removal. A guide to uses for pickling acids is illustrated in Table 6-11.[19] It should be noted that the strength of the acid must be determined for the specific end use, amount and type of soil to be removed, and surface texture desired. This value may range from a 5% solution to concentrated acid. Beacuse of the types of soil (inorganic oxides, mill scale, etc.) removed in most pickling operations, pickling is not considered an alternative to organic solvent degreasing. Generally, attempts to remove these types of soil by solvent degreasing are not made.

6.5.2 Glow Discharge Surface Clenaing

Glow discharge surface cleaning is a specialized technique that produces "ultra-clean" surfaces. Such surfaces are generally found in research activities or in other work in which special cleanliness requirements are dictated. there are variations of glow-discharge surface cleaning. They will be only briefly described here, since they are not currently considered viable alternatives to organic solvent degreasing.

Sputtering techniques involve bombardment of a substrate surface with high energy atomic particles; thus surface contaminations are knocked off or vaporized, leaving behind a clean surface. Because of the energy of the particles, significant surface deteriorations also result.

Vacumn glow-discharge cleaning methods also employ ion bombardment but utilize lower-energy particles (1-10 ev).[20] The lower energy of the particles necessitates the vacumn but also significantly decreases the amount of surface deterioration. Early attempts at use of ion bombardment have resulted in only limited cleaning, which is generally attributed to contamination of the ambient atmosphere with soil. Thus the ions do not

Table 6-11. ACIDS USED FOR PICKLING OF METALS[19]

Acid	Copper	Steel	Stainless Steel	Aluminum	Magnesium	Zinc	Nickel
Sulfuric acid	x	x					
Hydrochloric acid		x					
Nitric acid	x						
Hydrofluoric acid			x		x		
Nitric and sulfuric acid mix	x	x			x		x
Nitric and hydrofluoric acid mix			x	x			x
Nitric and chromic acid mix					x		
Sulfuric and chromic acid mix				x	x	x	

effectively reach the substrate to effect cleaning; further, soil redeposition results unless the ion chamber is continually purged.

Most ion bombardment cleaning processes are applicable only to cleaning situations in which a minimal layer of contamination must be removed (i.e., 1-2 monomolecular layers).[20]

6.5.3 Abrasive Blasting

There are many materials used as abrasives in blast cleaning operations. Usually these materials are simple sands, slags, or steel shots. An abrasive material is entrained in a stream of air or water by aspiration and, as part of the stream, bombards the surface to be cleaned.

Abrasive costs account for at least 30 percent, and sometimes as much as 75 percent, of the total blast cleaning expenditures. Selection of the best abrasive can mean the difference between profit and loss on the project[21] There are four factors of primary consideration in selecting an abrasive.[21] In order to achieve the best cost-effective results, these factors have to be weighed and balanced:

- finish required
- abrasive consumption
- production rate
- equipment replacement costs

Since the finish required is the reason for performing the task, its attainment must be the first factor of consideration. Cleaning efficiency is achieved through selection of an abrasive with proper cleaning characteristics and by maintaining a proper balance between impact and coverage in the operating mix. Large pieces of abrasive give maximum impact, and small pieces give maximum coverage. The appropriate balance of impact and coverage will develop naturally as the abrasive breaks down if proper attention is given to exhaust and replenishment factors.

Abrasive consumption is directly related to the life of abrasives used. It is axiomatic that the longer the abrasive life the higher the initial price, and the lower the cleaning efficiency. It is important that evaluation of shot or grit should not be made on the factor of life alone.

In order to increase the production rate in blast cleaning, selection of an abrasive with rapid cleaning characteristics is essential. In many instances, employment of fast cleaning abrasives enables one to reduce surface-preparation time by one half, resulting in savings on labor, power, and overhead; in addition, a superior finish is often produced. On the other hand, it should be realized that the faster cleaning abrasives have shorter lives and tend to cause greater wear on the equipment. Under normal operations, an economical balance between these variables can be maintained only when standards for the varying types of work have been established.

The last factor to be considered is equipment wear. Normal equipment wear is unavoidable but unusual wear should be identified and controlled. One of the main reasons for unusual wear is an improper separator and exhaust practice. Presence of sand or small metallic particles in the operating mix will cause increases in repair costs.

In using abrasive blasting as a cleaning technique, it should be realized that because of the hardness of the abrasives a certain amount of abrasion takes place on the part being cleaned as well as on the material being removed. Thus, this type of blasting is not recommended for parts with close tolerance or with a significant necessity for balance. With heavy (i.e., dense) abrasives, deformation of thin structures is likely to occur.

In order to reduce the problems associated with deformation, a significant reduction of the hardness of the abrasive must be realized. The hardness must be reduced to avoid these problems, but not so much as to reduce the abrasive efficiency for the soil (grease) being removed. Some suggestions for alternate abrasives include waste agricultural products, such as almond or walnut hulls. This method of blasting has been used in a very limited manner. One example is that of removing protective coatings from turbines used in steam electric power plants. The coatings removed are utilized to protect the turbine during construction of the remainder of the plant. For routine manufacturing processes, viability should be demonstrated in a test operation.

6.5.4 Acid Cleaning

This type of metal cleaning, similar to pickling, is generally used to remove inorganic and pigmented compounds and can also be used to remove unpigmented soils. Since acid cleaners will etch aluminum and other nonferrous metals, the current main use of this type is to remove soils from large ferrous components.

Acid cleaning is a process in which a solution of acid or acid salt, in combination with detergent and wetting solution, is used to remove oxide, oil, grease, and other contaminants from metal surfaces with or without the application of heat.[22] The acids can be either mineral acid or organic acid. Mineral acids include sulfuric, phosphoric, nitric, hydrochloric, fluoboric, and hydrofluoric acids. Organic acids include citric, tartaric, acetic, oxalic, and gluconic acids. Acid salts used are ammonium persulfate, sodium acid sulfate, and bifluorides. Solvents such as ethylene glycol monobutyl ether, alkylaryl polyether alcohol, wetting agents, and detergents are included in the acid cleaner. Methods of application include wiping, spray cleaning, immersion, barrel acid cleaning, and electrolytic cleaning.

6.5.5 Pyrolysis

Pyrolysis of soils from heat-resistant surfaces has been limited to laboratory applications. There are numerous problems associated with pyrolytic soil removal. These problems complicate the use of pyrolysis to such a degree that consideration of pyrolysis for cleaning is virtually eliminated.

Temperatures that must be obtained (and maintained) are in the range of 700°F. This in itself creates substantial energy requirements. particularly when routine introduction of cold parts is considered. Most parts that require degreasing are not contaminated with only organic soil. There is residual particulate or oil ash that would still need to be removed. Finally and most importantly, the parts being pyrolytically cleaned would be very susceptible to differential expansion or heat deformation. High temperatures would also create a significant safety hazard.

6.6 Modified Solvent Degreasing

While there is a number of alternatives to organic solvent degreasing, there may be special situations in which some form of solvent usage is still required. In these situations, it is still necessary to consider photochemical smog problems in choosing solvents. There are two approaches that may ease the problem:

1. Use water soluble solvents.

2. Use photochemically less reactive solvents.

These are the least preferable methods of reducing the air quality impact from degreasing operations.

6.6.1 Water Soluble Solvents

Currently on the market are several organic compounds used as cold degreasing agents when dissolved in water. Not classifiable as detergents, these organic compounds act very similar to conventional detergents; that is, they have bifurcated characteristics -- they are able to dissolve both in water and "grease" substances, thereby acting as a coupling agent. An example of this type of cleaning agent is ethylene glycol mono-ethyl ether acetate. A 20%-by-volume mixture in water removes most light oils. When it is used in conjunction with ultrasonics, heavier greases or those with particulate inclusions should also be removable. Other solvents with these characteristics are alcohols, ketones, some aldehydes, and simple organic acids. However, many if not all, would exhibit photochemical reactivity and are thus not inherently suitable for large-scale substitution for organic solvent degreasing. In certain cases, they may reduce the total organic solvent load.

While this type of cleaning was not specifically identified in the survey, discussions with manufacturers indicated limited current utilization in manufacturing processes. Potential applications would be in areas and processes in which emulsion cleaners are suitable. Thus, specific candidates for this form of cleaning will not be identified separately. It should be noted that specific solvent condidates must be separately evaluated both for cleansing ability and photochemical reactivity.

6.6.2 Photochemically Less Reactive Solvents

Generally, solvents with less reactivities indicate that their potentials to cause oxidant formation are low; thus the local concentration of photochemical exidants could be reduced if less reactive solvents were used in place of trichloroethylene or petroleum solvents. Table 6-12 identifies solvents by their photochemical reactivities and suitability for degreasing purposes.

Reasons for eliminating solvents with negligible or low reactivity for degreasing purposes are:

Negligible Reactivity

METHANE: Methane is a gas at room temperature and thus is not suitable for degreasing operations.

ETHANE: Ethane, also a gas at room temperature, is not suitable for degreasing operations.

Low Reactivity

PROPANE: Propane, like methane and ethane above, is a gas at room temperature and thus is not suitable for degreasing operations.

ACETONE: Because of its high flammability and low specific heat, acetone is suitable only for limited cold cleaning. It is, however, an effective solvent but evaporates too fast.

METHANOL: Becasue of its flammability, Methanol is not considered suitable for vapor degreasing.

METHYL BENZOATE, TERTIARY ALKYL ALCOHOLS, PHENYL ACETATE: These three compounds do not exhibit the necessary solvency to be effective degreasers.

METHYL ETHYL KETONE: Because of its flammability and low specific

Table 6-12. SUITABILITY OF SOLVENTS FOR DEGREASING

Solvents	Degreasing Suitability	Reactivity Negligible	 Low
Methane	No	x	
Ethane	No	x	
1,1,1-trichloroethane	Yes	x	
Freon 113	Yes	x	
Methylene Chloride	Yes	x	
Propane	No		
Acetone	Cold Cleaning Only		x
Methanol	Cold Cleaning Only		x
Perchloroethylene	Yes		x
Methyl Benzoate	No		x
Tertiary Alkyl Alcohol	No		x
Phenyl Acetate	No		x
Methyl Ethyl Ketone	Cold Cleaning Only		x

heat, methyl ethyl ketone is not considered suitable for vapor degreasing.

6.7 Conclusions and Recommendations

Based on the technical evaluations made in this section, the following conclusions may be made:

- There are viable alternatives to conventional organic solvent degreasing. Two of them, alkaline washing and emulsion cleaning, are currently used in several sectors of the manufacturing industry.
- Since the suitability of applying a specific cleaning system depends on numerous variables, the selection has to be made on an individual basis.
- In the absence of suitable operational alternatives, solvents are available that are efficient cleaners and at the same time less photochemically reactive.

Here are preliminary recommendations:

- Alkaline washing and emulsion cleaning are two viable alternatives. SIC categories identified in Table 6-4 and Table 6-7 are those that currently utilize alkaline washing or emulsion celaning; they are first candidates for total switching to these alternative methods. Additional SIC designations are based upon the following major criteira:

Alkaline:

a. nonreactive substrate

b. particulate and nonorganic soils for removal

Emulsion:

a. nonchemically clean surface needed

b. in-plant protection

c. necessity for organic soils removal

d. reactive base metal (reactive to alkaline)

Table 6-13 identifies candidate industries for secondary switching to alternatives. It includes only those categories presently using exclusively solvent degreasing.

Table 6-13. POSSIBLE CANDIDATE INDUSTRIES FOR ALKALINE WASHING AND EMULSION CLEANING

SIC	Category	Alkaline Washing	Emulsion Cleaning
335	Non-ferrous rolling & drawing	x	x
339	Misc. Primary metal products		x
349	Misc. fabricated metal products	x	x
364	Electric lighting & wiring		x

While it is felt that these categories would be suitable condidates for either of the two alternatives (emulsion or alkaline), it should be stressed that additional verification is necessary. Pilot scale evaluation would be needed before a recommendation of switching could be justified.

- A demonstration project or case study should be conducted to obtain detailed information on the technical and economical feasibilities of the following metal cleaning processes:

  a. alkaline washing for aircraft and electronic industries

  b. emulsion cleaning for automotive repair and oil well maintenance industries

These industries potentially are the major sources of solvent emissions. The use of non-reclaimable solvents should be discouraged, because waste solvents most frequently end up in the ambient air.

6.8 References

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7.0 COST ANALYSIS OF SOLVENT DEGREASING ALTERNATIVES

7.1 Introduction

7.1.1 Purpose

The purpose of this cost study is to present a comparison of estimated costs for applying organic solvent degreasing processes with estimated costs for applying alkaline washing and emulsion cleaning, the two most promising alternatives for replacing organic solvent degreasing practice. In most cases, the cleaning requirement itself determines which is the most practical --solvent degreasing or one of the alternatives. It may be argued that both solvent degreasing and water-based cleaning satisfy unique cleaning needs and are not interchangeable metal cleaning processes; however, there are many categories of industry in which both techniques can be applied. This cost analysis was based on the assumption that applicable alternatives could handle the same workload and achieve the same cleaning efficiency as the solvent degreasing.

7.1.2 Scope

As indicated in Table 4-1, cold-degreaser emissions represent 55 percent of the degreasing solvent emissions; open-top vapor degreasers account for 28 percent; and conveyorized degreasers, 14 percent; thus it is reasonable to choose these three major types of degreasers as bases for cost analyses. The annual costs for each type of solvent degreaser operation will be compared with those for alkaline washing and emulsion cleaning. In this comparison it is assumed that the same cleaning load is subjected to each type of cleaner.

7.1.3 Model Parameters

In order to estimate the costs for solvent degreasing or its alternatives, detailed information of the cleaning processes should be examined first. The variables involved in a cleaning process are listed in Table 7-1. Because there are so many variables, cleaning parameters for each degreaser model type are presented in subsequent pages of this section. Because of the unique characteristics that each degreaser may have, the data presented herein may not be suitable for a generalized application.

7.1.4 Elements Involved in Cost Analysis

The two elements involved in cost estimates are capital costs and operating costs. Capital cost estimates include costs for purchasing and installing major and auxiliary equipment for building construction, for space to accomodate the equipment, for maintenance, and for insurance on equipment and building space. However, the costs involved in re-arrangement or removal of any existing equipment, or in site preparation and taxes, were not included in capital cost estimates, mainly because these costs were site-specific. They should be considered on a more comprehensive basis. Research and development costs, production losses, and other highly variable costs were also not considered in this analysis. Operating cost estimates included costs for labor, maintenance, utilities material, waste disposal, and administrative overhead. These principal items of expense are discussed in more detail below.

Equipment Costs

For vapor degreasing, equipment costs include estimates for heating coils, condensing coils, redistillation units, and ventilation equipment. The costs of steam and other power-generating equipment were not considered here, since these costs will be incorporated into those for steam and electricity. For cold solvent degreasing, cost estimates are provided for the

Table 7-1. MAJOR VARIABLES INVOLVED IN DEGREASING PROCESSES

Item	Description
Equipment	•Models of solvent degreasers, alkaline washers, and emulsifiers •Energy requirement and source (gas, steam or electricty) •Availability of equipment •Installation cost •Depreciable lifetime •Types of cleaning processes
Works	•Materials of works (tolerance) •Shapes and sizes of works •Quantities of works to be cleaned
Solvents	•Types of solvents •Costs of solvents •Solvent reclamation •Amounts of solvents used and disposed •Room temperature •Draft velocity •Freeboard ratio
Soils	•Types of soils •Cleaning efficiency required •Thickness and viscosity of soils
Operating Condition	•Frequency of cleaning •Working hours •Operating requirements •Solvent loading and heating practices
Cost Factor	•Interest rate •Local utility rates •Insurance and maintenance rate •Administrative overhead •Rejection rate and cost of recleaning

tanks (including storage tanks) and pumps. For alkaline washing and emulsion cleaning, estimates include costs for tanks, steam coils, ventilation equipment, pumps, piping, nozzles, risers, headers, and bus bars.

Building Space Costs

Building space is needed to accomodate major and auxiliary equipment. An additional space requirement is necessary to provide enough room for workers to operate the equipment.

Labor Costs

Labor cost estimates include costs for salaried workers to operate and maintain equipment and for expenses incurred in removing residue or waste solvent. Labor is needed to empty and refill the tanks; to change parts; to clean the stills, chambers, cooling coils, and water jackets of degreasers; to remove scale and sludge from tanks and drains; and to lubricate valves and pumps.

Utilities Costs

Utility costs include estimates for steam, electricity, and gas. These utilities are used to maintain the solvent at its boiling temperature for vapor degreasing, to agitate the solvent for cold degreasing, to heat the alkaline solution, and to power the pumps employed with spray equipments for alkaline washing and emulsion cleaning. Water, another utility, is needed for cooling in vapor degreasing, for flushing, and for preparing the washing solution in alkaline washing and emulsion cleaning.

Material Costs

Material costs include those for degreasing solvents which have evaporated, experienced drag-out, and been disposed of; the alkaline chemicals; detergent consumed in alkaline washing; and emulsifying agents or surfactants

used in emulsification cleaning. Costs of parts regularly required for equipment maintenance are also included.

Waste Disposal

In vapor degreasing soil residue remaining after distillation has to be removed and disposed of in landfills as class I waste, or be incinerated. In cold solvent degreasing soil residue is usually discarded along with the solvents. Soils removed from the works end up in the sewer together with the cleaners. Cost estimates here, therefore, include those for solid waste disposal (although it is generally in a liquid form for solvent degreasing) and wastewater treatment (in the case of aqueous cleanings). Large manufacturers are generally required to treat effluents in their own treatment facilities before discharging them to the municipal sewage system; thus such additional costs are included in their total operating expenses. Small plants tend to sewer their wastewater without pre-treatment.

Other Costs

Since most other costs are either site-specific or equipment-oriented, it is impractical to estimate them for general usage. These costs include those for equipment installation, insurance, indirect building space, maintenance, and administrative overhead. Unless otherwise specified in the original studies, flat cost rates were assigned for the analysis performed in this project.

7.1.5 Annualized Costs and General Cost Factors

Annualized cost estimated for applying solvent degreasing processes and alternatives are used as a basis for comparison in this study. Annual capital charges were calculated by using the capital-recovery factor formula based on a constant interest rate and a constant depreciable life of the cleaning equipment and building space. All the items of operating costs were also calculated on an annual basis. The annualized cost estimates were for a one-year period commencing with the first quarter of 1978.

General cost factors used in this study to estimate the annual costs for applying solvent degreasing processes and their alternatives are listed in Table 7-2. Computation for some of these factors are shown in Appendix C. These factors are used only if there were no published data available. The utility rates for industrial users varied widely with different cities. Constant rates were assigned in this study. In some aqueous cleaning processes, however, energy costs may be the major expense. In such cases, the utility rate is a critical factor, and local rates must be consulted and be included in cost estimation. Since the cost of steam varies with steam pressure and temperature, a flat rate was assigned for this analysis; this cost includes the capital cost of a steam-generating system.

The prices of solvents and chemicals depend on the quantities involved in the transaction. Small quantities of solvent are sold at higher prices. Information obtained from the degreasing survey responses was used to estimate the prices of solvents for certain amounts of solvents bought by the manufacturers. The average prices for each of the four quantity groups were then normalized by comparing them with current wholesale prices listed in the Chemical Marketing Reporter[1], since the survey cost data were obtained in 1976. Current prices for major chemicals used in aqueous cleaning were obtained from the manufacturers.[2] Prices of major solvents and chemicals used in metal cleaning are listed in Table 7-3. It should be noted, however, that price ranges for different alkaline cleaners or emulsion cleaners varied widely depending on their end uses. The choice of particular alkaline or

Table 7-2. GENERAL COST FACTORS

Utilities	
Electricity	\$0.04/kwh
Water	\$0.04/1,000 gal
Gas	\$2.00/10^6 Btu
Steam	\$0.031/gal
Waste Disposal	
Liquid Residue Disposal	\$0.22/gal
Wastewater Treatment	
With on-site treatment	\$0.49/1,000 gal
Without on-site treatment	\$0.22/1,000 gal
Labor	\$10.00/man-hr
Factors	
Equipment Lifetime	20 years
Building Lifetime	25 years
Interest Rate	10 percent
Indirect Space Requirement	50 percent of equipment
Annual Inflation Rate	8 percent
1-Shift Working Hours	2,000 hr/yr
Installation Cost	15 percent of equipment cost
Annual Insurance Rate	2 percent of the total equipment and building capital, without the installation cost
Annual Maintenance Rate	4 percent of the equipment cost
Administrative Overhead	25 percent of all labor cost
Building Space	\$32.80/ft^2

Table 7-3. PRICES OF SOLVENTS AND CHEMICALS ($/gallon)

Solvent	Over 40 Drums*	10-39 Drums	3-9 Drums	1-2 Drums
Mineral Spirits	0.56	0.61	0.68	0.75
Perchloroethylene	2.39	3.03	3.13	---
Trichloroethylene	2.52	2.70	3.04	3.42
1,1,1-trichloroethane	2.66	3.04	3.33	3.60
Methylene Chloride	2.35	2.44	2.65	2.85
Acetone	1.20	1.86	1.98	2.95
Toluene	0.80	0.84	0.90	1.00
Detrex Detergent	3.35	3.65	4.00	4.38
Detrex Emulsion	2.60	2.83	3.10	3.40

*1 Drum = 55 gallons

emulsion cleaners for this cost analysis was mainly based on their end uses and data availability.

7.1.6 Relative Cost Estimation

General cost factors shown in Tables 7-2 and 7-3 are used to update the "approximate relative costs in metal cleaning" estimated by the Committee on Cost of Metal Cleaning of the American Society for Metals[3] (see Tables 7-4 and 7-5). All the cost relations shown in these two tables are generally for large-scale metal cleaning processes performed at a relatively high efficiency level. Ranges are assigned to cover most of the regular cleaning processes, even though they are "approximate" estimates.

7.2 Cost Comparison: Cold Solvent Degreasing Versus an Alternative

The automotive repair industry is the largest user of the cold-solvent degreasing process in California, and large quantities of photochemically reactive solvents are emitted from this source; accordingly, cold-solvent degreasing systems and one possible alternative cleaning system applicable to the automotive repair industry were evaluated to determine their economic feasibility.

Specifically, estimates for three degreasers are included in this cost analysis. Two of the degreasers are used in cold-solvent degreasing, the third in alkaline emulsion cleaning.

Safety-Kleen Washers

Safety-Kleen Corporation is the major supplier of cold-solvent degreasers for the automotive repair industry. It provides equipment and maintenance, including solvent replenishment, and charges users at a standard rate. It will be recalled that this type of degreasing is done in parts washers in which the solvent is stored in a drum, pumped up to a wash tank for degreasing,

Table 7-4. APPROXIMATE RELATIVE OPERATING COSTS IN METAL DEGREASING

Method	Direct Labor	Disposal Labor	Material	Water Supply Sewage Treatment	Energy	Maintenance	Overhead	Total Operating Cost
Vapor Degreasing	35	10	27	0.1	10	6	12	100
Cold Degreasing	35	10	27	0	3	4	12	91
Alkaline Washing								
Tank, hot	39-46	9-11	8-15	0.9-1.1	4-10	3-5	12-14	76-102
Spray, cold	32-39	9-11	6-15	0.9-1.1	1-3	3-5	11-13	63-87
Spray, hot	32-39	9-11	4-10	0.9-1.1	15-50	5-7	12-14	78-162
Electrolytic	39-46	9-11	8-40	0.9-1.1	10-40	3-4	11-13	81-155
Emulsion Cleaning								
Tank, hot	32-40	9-11	7-15	0.9-1.1	10-50	3-5	11-13	73-135
Spray, hot	32-40	9-11	5-12	0.9-1.1	15-60	5-7	12-14	79-145

Table 7-5. APPROXIMATE RELATIVE CAPITAL COSTS IN METAL CLEANING[3]

Method	Equipment Cost	Building Space Requirement
Vapor Degreasing	100 (Basis)	100 (Basis)
Cold Degreasing	20	100
Alkaline Washing		
Tank, hot	30	600
Spray, cold	80	300
Spray, hot	80	300
Electrolytic	140	600
Emulsion Cleaning		
Tank, hot	30	600
Spray, hot	80	300

and then returned to the drum for re-use; then the contaminated solvents are removed for recycling, thereby preventing emissions from the waste solvent. The average solvent emission from a Safety-Kleen washer is estimated at 0.168 tons/year (see Appendix D). Safety-Kleen has two major sizes of washer: 16-gallon and 30-gallon capacities. The current standard rates for renting the Safety-Kleen washers are listed in Table 7-6.[4]

Table 7-6. SAFETY-KLEEN WASHERS RENTAL RATES[4]

Service Frequency (weeks)	16 Gallon Parts Washer ($)	30 Gallon Parts Washer ($)
4	20.00	27.50
5	22.25	30.25
6	23.75	32.50
7	25.00	35.00
8	26.50	37.00

The smaller washers are widely used in automotive repair shops. The typical frequency for solvent replenishment is once every 6 weeks. Besides equipment rental, the users have to pay for the building space, insurance on the building space, and electricity. The overall machine size is 20"x30"x30", and the power requirement is around 1 hp.

Non-Safety-Kleen Washer

A Kleer-Flo parts washer, model J 50, was selected for evaluation. The current equipment cost, including installation, is $368.75.[5] It is pump agitated with a 1 hp power requirement. The overall machine size is 22"x24.5"x35". The soaking space inside the machine is 22"x14"x6". The solvent used is Kleer-Flo Hi-T Degreasol; its price is $177.90 per 55 gallon-drum. The residue is generally removed every 2 months. The clean solvent is removed from the top for re-use, and the residues at the bottom, usually 1 inch thick, are removed from the tank and disposed as solid waste. Every 6 months, all the solvent in the tank is decanted and recycled. The average emission rate for this type of cleaning system is estimated to be 0.326 tons/year (Appendix D).

Water-Based Washer

It should be noted that data presented here are for water-faced washers normally used for parts cleaning on a larger scale than that performed in an average-size automotive repair shop. Under the current practice, cold solvent degreasing is the preferred process and most used by repair shops, whereas alkaline washers are used for larger-scale operations. It is difficult to convert the data to that for an average shop. The cost shown here for alkaline washers, therefore, may be regarded as the maximum for average shops. The cost of emulsion cleaning should be similar to that of alkaline washing because of the same equipment requirements.

The Kleer-Flo Model PW-50E Powermaster parts washer was selected for this cost evaluation.[6] This model is generally used in automotive repair shops that have large volumes of parts to be cleaned; shops that also have car dealers are one type of example. The floor space is 33"x26". The designed capacity is 50 pounds. There are two compartments in the washer for washing and rinsing. The soaking space for each compartment is 15"x18"x14", and the liquid capacity is 16.5 gallons each. The power requirement is 2.4 kw. The equipment cost (including installation) is $1,322.50. The chemical recommended for this machine is Hi-T Greasoff (No. 1 for iron and steel only, No. 3 for non-ferrous metals), a powdered compound with excellent detergency and free-rinsing properties. The cleaning solution is a mixture of 0.5 pounds of chemical per gallon of water. The price of the chemical is around $265 per 400-pound drum. The cleaning solution is usually changed every month, and the rinsing water every day. The waste solutions are disposed in the sewer. The labor required to change the solvent each time is estimated as 0.5 man-hour.

Cost comparisons of the three cleaning systems are shown in Table 7-7. Comparisons were made with the following assumptions:

- Labor involved in operating each of the three systems is the same, and therefore excluded from the table.
- Labor involved in removing residues from non-Safety-Kleen degreasers is 0.5 man-hour each time.
- Operating time for all three systems is 1.5 hour/day, 300 days/year.

Comparisons were made from a user's point of view. The high cost of alkaline washing is attributed to the use of equipment with design capacities larger than actually needed. A demonstration project using an alkaline washer of the appropriate size for a cold-solvent degreaser is thus recommanded. Such a washer may not, however, be currently available.

7.3 Cost Comparison: Vapor Degreasing Versus Alternatives

The data source for this analysis is the cost data published by the American Society for Metals.[3] Because the data were out of date, the cost factors shown in Table 7-2 and 7-3 were used for updating. All the data were converted to an annual basis, and only one shift per day of operation was applied to each degreasing process. The comparative costs analyses presented in the following pages cover vapor degreasing versus alkaline

Table 7-7. COST COMPARISONS OF CLEANING SYSTEMS USED IN AUTOMOTIVE REPAIR INDUSTRY

	Safety-Kleen Solvent Degreaser	Non-Safety-Kleen Solvent Degreaser	Water-Based Degreaser
Capital Costs			
Equipment & Installation	---	368.8	1,322.5
Initial Solvent	---	25.9	5.5
Building Space	136.7	122.8	195.4
50% Indirect	68.3	61.4	97.7
Annual Capital Charge			
Equipment & Installation	---	46.4	156.0
Building Space	22.6	20.3	32.3
Insurance	4.1	11.1	32.3
Maintenance	---	14.8	52.9
	26.7	92.6	273.5
Annual Operating Costs			
Material/Rent	205.8	69.1	66.0
Water	---	---	0.2
Wastewater Treatment	---	---	1.1
Electricity	13.4	13.4	43.2
Residue Disposal	---	1.2	---
Labor to Remove Residue	---	30.0	60.0
	219.2	113.7	170.5
Total Annual Cost	245.9	206.3	444.0

washing, vapor degreasing versus emulsion cleaning, and alkaline washing versus emulsion cleaning.

Vapor Degreasing Versus Alkaline Washing

Both processes were used to clean cabinets made from 18-gauge steel. The cabinets weigh 100 lbs each, and 100 cabinets were cleaned per hour. Trichloroethylene was used as the degreasing solvent, and 0.55 lbs of it were lost for each cabinet cleaned. Detergent was used in alkaline washing, and the consumption rate was 12 lbs per operating hour. Six hundred gallons of cooling water were needed per hour for the vapor degreaser. Five hundred and sixty lbs per hour of steam were needed for vaporizing the solvent, heating the work, spraying, re-distilling, and compensating for the radiation loss from the degreaser. The power requirements for degreasing and washing were 2 kw and 14 kw, respectively. Natural gas with 6 million Btu heat content per hour was required for the washer. The maintenance labor requirements were 7 man-hours and 10 man-hours a week for degreasing and washing, respectively. Direct labor required was 35 man-hours a week for each process. Two percent of the cabinets cleaned by alkaline washing were rejected and an expenditure of four times the normal cleaning cost was required to re-clean them. The degreaser occupied 150 ft^2 of space, whereas that for the washer was 1000 ft^2. The annual expenses on parts changing were $1,410 for the degreaser and $2,000 for the washer. The cost comparison of these two processes for this specific application is shown in Table 7-8.

Vapor Degreasing Versus Emulsion Cleaning

Both processes were used to clean aluminum alloy reflectors weighing 4 lbs each. Trichloroethylene was consumed at the rate of 2.25 gallons per operating hour. The chemical used in emulsion cleaning was Emulsion

Table 7-8. COMPARISON OF COSTS FOR VAPOR DEGREASING AND ALKALINE WASHING ($)

Item	Vapor Degreasing			Alkaline Washing		
Capital Costs						
Equipment	52,800			70,400		
Installation	7,900			10,600		
	60,700	7,130		81,000	9,520	
Building Space	4,920			32,800		
50% Indirect	2,460			16,400		
	7,380	810		49,200	5,420	
Insurance		1,200	9,140		2,390	17,330
Operating Costs						
Direct Labor		17,500			17,500	
Material		22,740			7,580	
Utilities						
Water		50			---	
Steam		4,170			---	
Electricity		160			1,120	
Gas		---			24,000	
Maintenance						
Labor		3,500			5,000	
Parts		1,410			2,000	
Reject Handling		---			9,390	
Overhead		5,250			5,630	
			54,780			72,220
Total Annualized Cost			63,920			89,550

Cleaner, and 0.75 gallons of it were lost per hour. Four hundred gallons of water and 200 lbs of steam were consumed per hour in the vapor degreasing process. The power requirements for vapor degreasing and emulsion cleaning were 2 kw and 8.3 kw, respectively. Gas with 2.2 million Btu heat content per hour was needed for the emulsion cleaning. Direct labor required was 35 man-hours a week for each process, and maintenance labor was 4 man-hours a week for each. Two percent of the reflectors cleaned in the emulsion cleaning process were rejected, and an expenditure four times their original cost was required to re-clean them. The annual cost for parts was $1,160 for the degreaser and $2,320 for the emulsifier. The cost comparison of these two processes on this specific application is shown in Table 7-9.

Alkaline Washing and Emulsion Cleaning

Both processes were used to clean gears at a rate of 100 gears per hour. Sodium orthosilicate was used in the alkaline washing process at the rate of 0.36 lbs per hour. In the emulsion cleaning process soluble oil was used at the rate of 0.70 gallons per hour. Seven gallons of water were needed per hour for each process. The steam requirement for alkaline washing was 33.2 lbs per hour, and for emulsion cleaning 39.8 lbs per hour. For each process the power requirement was 6 kw. Direct labor required for each process was 33.6 man-hours per week, and the annual maintenance cost, including both labor and parts, was $1,560 per year. Disposal labor needed was 1.5 hours a week for each process. Cost comparisons of these two water-based cleaning processes are shown in Table 7-10.

The cost comparisons shown in Tables 7-8, 7-9, and 7-10 indicate that there is only a 2 percent difference in the total annualized cost between alkaline washing and emulsion cleaning, whereas 40 percent and 21 percent

Table 7-9. COMPARISON OF COSTS FOR VAPOR DEGREASING AND EMULSION CLEANING ($)

Item	Vapor Degreasing			Emulsion Cleaning		
Capital Costs						
Equipment	32,300			49,900		
Installation	4,840			7,480		
	37,140	4,360		57,380	6,740	
Building Space	3,280			13,670		
50% Indirect	1,640			6,830		
	4,920	540		20,500	2,100	
Insurance		740			1,410	
			5,640			10,250
Operating Costs						
Direct Labor		17,500			17,500	
Material		11,340			4,250	
Utilities						
Water		30			---	
Steam		1,490			---	
Electricity		160			670	
Gas		---			8,800	
Maintenance						
Labor		2,000			2,000	
Parts		1,160			2,320	
Reject Handling		---			3,010	
Overhead		4,880			4,880	
			38,560			43,430
Total Annualized Cost			44,200			53,680

Table 7-10. COST COMPARISONS OF EMULSION CLEANING AND ALKALINE WASHING ($)

Item	Emulsion Cleaning			Alkaline Washing		
Capital Costs						
Equipment	29,900			29,900		
Installation	3,000			3,000		
	32,900	3,870		32,900	3,870	
Building Space	6,560			6,560		
50% Indirect	3,280			3,280		
	9,840	1,080		9,840	1,080	
Insurance		800			800	
			5,750			5,750
Operating Costs						
Direct Labor		16,800			16,800	
Disposal Labor		210			210	
Material		1,260			108	
Utilities						
Water		---			---	
Steam		250			300	
Electricity		510			510	
Maintenance		1,560			1,560	
Overhead		4,640			4,640	
			24,720			24,130
Total Annualized Cost			30,470			29,880

additional costs would result from switching from vapor degreasing to alkaline washing and to emulsion cleaning, respectively. These comparisons, however, are case-specific; the individual case should be taken into account before drawing generalized conclusions. The summaries of cost distributions for vapor degreasing and its alternatives are listed in Tables 7-11 and 7-12. In each process the largest expense in metal cleaning was the cost of labor. For the two processes in each comparison, the total expenses for labor were almost identical; thus the labor cost could be used as a comparative reference item in Tables 7-11 and 7-12. Capital costs of the water-based cleaning process were higher than those of the vapor degreasing process. Costs of degreasing solvents were higher than those of the chemicals used in aqueous cleaning, whereas energy costs were higher for aqueous cleaning than for solvent degreasing. Additional costs were incurred in alkaline washing and emulsion cleaning to re-clean the rejected works.

7.4 Cost Comparison: Conveyorized Degreasing Versus Alternatives

Data for this cost analysis were based on those published by Kearney *et al*.[7] and Surprenant.[8] To update these data to 1978 cost levels, cost factors presented in Tables 7-2 and 7-3 were used. In updating, only one shift per day of operation was assumed for each degreasing process. All data were converted to an annual basis. The cost comparisons presented below include conveyorized degreasing versus emulsion cleaning and conveyorized degreasing versus alkaline washing.

Conveyorized Degreasing Versus Emulsion Cleaning[7]

Both methods were used to clean automatic transmission parts at the rate of 40,000 lbs per hour. The conveyor speed was 18 ft per minute. The degreaser occupied 45'x9'. The cost comparison of these two processes is

Table 7-11. SUMMARY OF COST DISTRIBUTIONS FOR VAPOR DEGREASING AND ALKALINE WASHING

Item	Vapor Degreasing	Alkaline Washing
Capital Cost	14.3%	19.4%
Labor, Maintenance, Overhead	41.1	31.4
Material, Parts	37.8	10.7
Utilities	6.8	28.0
Rejects	---	10.5
	100.0	100.0

Table 7-12. SUMMARY OF COST DISTRIBUTIONS FOR VAPOR DEGREASING AND EMULSION CLEANING

Item	Vapor Degreasing	Emulsion Cleaning
Capital Cost	12.7%	19.2%
Labor, Maintenance, Overhead	55.2	45.4
Material, Parts	28.3	12.2
Utilities	3.8	17.6
Rejects	---	5.6
	100.0	100.0

shown in Table 7-13. The most important differences in expenses between the two processes were:

- The energy requirement of emulsion cleaning was much larger than that of degreasing.
- The expense for degreasing solvent was higher than that for the emulsion chemical.

The annualized cost for operating the emulsion cleaner was about 52 percent more than that for operating the conveyorized degreasing. Most of the chemicals used in emulsion cleaning ended up in the sewer, whereas in vapor degreasing more of the solvent ended up in the ambient air. The costs for wastewater treatment in emulsion cleaning and for residue disposal were not included in the estimates.

Conveyorized Degreasing Versus Alkaline Washing[8]

Relevant information for this analysis, obtained from Surprenant's work,[8] is summarized in Table 7-14. Basic operating parameters were derived from these summarized data (see Table 7-15).

Solvent loss can be the result of any combination of these three activities:

- diffusion
- drag-out
- disposed-with residue

Diffusion is a continuous process as long as the degreaser is in operating condition. Based on the rate of solvent consumption in an idling open-top degreaser[9], the amount that diffused was calculated. The drag-out and the waste disposal should be a linear function of the amount of works cleaned. The total solvent consumption less that of diffusion was divided

Table 7-13. COMPARISON OF COSTS FOR CONVEYORIZED VAPOR DEGREASING AND EMULSION CLEANING ($)

Item	Conveyorized Degreasing		Emulsion Cleaning	
Capital Costs				
Equipment	53,070		74,130	
Installation	15,000		17,500	
Plant Space	13,290		14,700	
50% Indirect	6,650		7,350	
Annual Capital Charges				
Equipment & Installation	8,000		10,770	
Plant Space	2,200		2,430	
Insurance	1,460		1,920	
		11,660		15,120
Annual Operating Costs				
Maintenance	2,120		2,970	
Material	12,350		5,720	
Steam	9,180		27,280	
Electricity	150		2,980	
Water	100		10	
		23,900		38,960
		35,560		54,080

Table 7-14. OPERATING DATA FOR CONVEYORIZED DEGREASER AND ALKALINE WASHER[8]

	Conveyorized Degreasing	Alkaline Washing
Equipment	Vibra Degreaser	Spiral Washer
Manufacturer/Type	Detrex Model No. RV 918-8-75	Ransohoff Serial No. 10443
Size	64"x64"x110" (high) Storage Tank:65"x78"x33"(high)	21'x6'x7'10' (high)
Solvent/Chemical	Trichloroethylene	Detrex 75LN Degergent Solution
Test Period	3 weeks/23 shifts	2 weeks/19 shifts
Metal Cleaned	304 metric tons	169 metric tons
Chemical/Solvent Used	192 gallons	104 gallons
Steam Used	13639 gallons	12774 gallons
Electric Power	7.10 kw	11.84 Kwh
Water	1,355,540 gallons	10,748 gallons
Wastewater	0	3972 gallons
Make-up Air Heat Requirement	0	82,416 Btu/hr
Solvent Left in the Residue	31%	0
Residue Generated	338 gallons	0

Table 7-15. OPERATING PARAMETERS FOR CONVEYORIZED

	Conveyorized Degreasing	Alkaline Washing
Solvent/Chemical	0.47 gal/hr	0.615 gal/ton
	0.35 gal/ton	
Steam	69 gal/hr	76 gal/ton
	3.2 gal/ton	
Water	7370 gal/hr	63.6 gal/ton
Electricity	7.10 kw	11.84 kw
Make-up Air Heat	---	82,400 Btu/hr
Wastewater Generated	---	23.5 gal/ton
Residue Generated	1.11 gal/ton	---
Solvent Emitted	0.44 gal/ton	---

by the total tonage cleaned to give the solvent requirement per ton of work cleaned. In alkaline washing chemicals were consumed only during the cleaning process.

Based on the fact that 0.115 Btu of heat is required to raise 1 lb of steel 1°F, the energy required to bring a certain amount of works from room temperature (68°F) to the boiling point of the solvent trichloroethylene (189°F) can be calculated. The total energy required to keep the degreasing process operational is the total heat content of the steam less that used for heating up the steel; whereas for aqueous washing, the total energy in the steam consumed should be linearly related to the amount of works cleaned. Water was utilized continuously for cooling purposes in solvent degreasing, whereas in washing water was used mainly for flushing. The amount of water consumed, therefore, depends on the amount of works cleaned. The residue left in the stills had to be removed continuously. The residue was a mixture of soil, other contaminants, and solvent. Thirty-one percent of the total solvent consumed ended up in the residue, and the rest of the solvent was presumed to have been dissipated into the ambient air.

The annualized cost comparison of using these two processes to clean 5,000 tons is shown in Table 7-16. The cost for alkaline washing is about 13 percent higher than that for conveyorized degreasing. The annual emission reduction by switching from conveyorized degreasing to alkaline washing was about 11.2 tons. For each ton of works cleaned, there were 0.34 gallon emitted from the degreaser to the ambient air. The cost to achieve 1 ton/year reduction of solvent emission was approximately $340. The cost distributions of conveyorized degreasing and its alternatives are

Table 7-16. COMPARISON OF COSTS FOR CONVEYORIZED DEGREASING AND ALKALINE WASHING ($)

	Conveyorized Degreasing		Alkaline Washing	
Capital Costs				
Equipment	62,380		42,920	
Installation	9,360		6,440	
Building Space	2,090		4,130	
50% Indirect	1,040		2,070	
Annual Capital Charges				
Equipment & Installation	8,430		5,800	
Building Space	340		680	
Insurance	1,310		980	
		10,080		7,460
Annual Operating Costs				
Maintenance (labor, parts)	5,980		4,000*	
Material	6,780		9,230	
Steam	4,770		11,780	
Water	590		13	
Wastewater Treatment	0		58	
Electricity	570		950	
Make-up Air Heat	0		330	
Residue Disposal	1,220		0	
		19,910		26,360
Total Annual Cost		29,990		33,820
Cost/Metric Ton of Metal Cleaned		6.00		6.76

*Assume $2380/year as the cost for parts

Table 7-17. SUMMARY OF COST DISTRIBUTION FOR CONVEYORIZED DEGREASING AND EMULSION CLEANING

Item	Conveyorized Degreasing	Emulsion Cleaning
Capital Charge	32.8%	28.0%
Maintenance	6.0	5.5
Material	34.7	10.6
Utilities	26.5	55.9
	100.0	100.0

Table 7-18. SUMMARY OF COST DISTRIBUTIONS FOR CONVEYORIZED DEGREASING AND ALKALINE WASHING

Item	Conveyorized Degreasing	Alkaline Washing
Capital Charge	33.6%	22.1%
Maintenance	19.9	11.8
Material	22.6	27.3
Utilities	19.8	38.8
Waste Disposal	4.1	---
	100.0	100.0

listed in Tables 7-17 and 7-18. These data were derived from presentations in Table 7-13 and Table 7-16, respectively. As shown in these tables, the energy requirements for water-based cleaning are much higher than those for conveyorized degreasing.

7.5 Summary and Discussion

A summary of comparative annual costs for solvent degreasing processes and their alternatives is presented in Table 7-19. In all cases, annual costs for applying water-based cleaning processes are about 10 to 50 percent higher than those of their solvent counterparts. Major differences in costs exist in three areas: equipment, building space, and chemicals. Water-based degreasing equipment is usually higher and requires 2 to 6 times more building space. Chemical costs, however, are usually higher for solvent degreasing processes. In addition, water-based cleaning demands higher energy consumption.

There are two other considerations that deserve some discussion. The first involves the type of energy source in degreasing operations. Most of the vapor degreasers used in California are heated by electrical energy; those considered in this study, however, used steam heating. Since the prices for both forms of energy are about the same, this difference in energy forms should neither have any significant effect on the cost analysis made in this section nor on the applicability of this analysis to California.

The second consideration is the pollution potential of water-based cleaning. The soils removed by alkaline washing or emulsion cleaning become greatly diluted into the form of a water emulsion, which can add pollutants to our waters. This characteristic is generally regarded as a serious disadvantage of water-based cleaning. Based on data presented

Table 7-19. SUMMARY OF COST COMPARISONS FOR SOLVENT DEGREASING PROCESSES AND THEIR ALTERNATIVES

Item of Comparison	Annual Cost ($) Solvent Degreaser	Annual Cost ($) Alternative
Cold Solvent Degreasing vs. Water-Based Degreasing	245.9 (Safety-Kleen) (Solvent Degreaser)	444.0
	206.3 (Non-Safety Kleen) (Solvent Degreaser)	444.0
Vapor Degreasing vs. Alkaline Washing	63,920	89,550
Vapor Degreasing vs. Emulsion Cleaning	44,200	53,680
Conveyorized Degreasing vs. Emulsion Cleaning	35,560	54,080
Conveyorized Degreasing vs. Alkaline Washing	29,990	33,820

in Table 7-16, however, the cost for wastewater treatment accounts for less than 0.2 percent of the total annual cost, while 4.1 percent of the total annual cost is for disposal of waste residue generated by conveyorized vapor degreasing.

There are several limitations in this cost analysis:

- Relatively few cost analysis comparisons were made between solvent degreasing processes and their alternatives.
- Few cost comparisons were based on detailed operating data obtained from applying sets of equivalent with the same installed capacities.
- No study has been made to date to compare costs of small cold-solvent degreasing operations with those of water-based cleaning operations of comparable size.
- Fixed cost factors were used in this study wherever there was insufficient information. Costs for the removal of existing equipment, site preparation, and taxes were not included.

A word of caution should be made to those who may use data presented in this section. It should be understood that for a comparative cost analysis such as this one, it is assumed that the two processes of solvent degreasing and water-based cleaning are interchangeable. This assumption may be far from the truth. Actually, these processes are often used to satisfy unique cleaning needs, and the substitution of one for the other may not always be predicated only on economic grounds.

Finally, from the data in this section one may conclude that the annual cost for water-based cleaning is higher than that for solvent degreasing. In selecting an appropriate degreasing process, however, cost should not be the sole factor for a decision. Environmental benefits as well as specific cleaning needs should also be considered. Due to the limitations of the data base used for this analysis, any conclusions made here should be tentative. The analysis may be used as a basis, however, for future demonstration or case studies.

7.6 References

1. Chemical Market Reporting, January 23, 1978.
2. Data provided by Detrex Chemical Company.
3. ASM Committee on Cost of Metal Cleaning. "Metal Cleaning Cost," Metal Progress, August 15, 1955. p. 169.
4. Data provided by Safety-Kleen Corporation.
5. Data provided by Kleer-Flo Company.
6. Data provided by Magnus Chemical Company.
7. Kearney, T. J., and C. E. Kircher. How to Get the Most from Solvent-Vapor Degreasing: Part II, Metal Progress, May 1960, p. 93.
8. Surprenant, K. S. Study to Support New Source Performance Standards for Solvent Metal Cleaning Operations. Appendix C - 1. Report prepared by EPA, April 30, 1976.
9. Archer, W. L. Selecting Alternative Chlorinated Solvents, Metal Progress, October 1974, p. 133.

8.0 DEGREASING SOLVENTS EMISSION INVENTORY[1]

8.1 Introduction

An objective of this project was to identify the potential reduction in organic solvent emissions in California that would result from the conversion of organic solvent degreasing operations, where practicable, to water base or other solvent systems that use photochemically unreactive materials. A determination of the potential reduction in organic emissions required a more detailed state-wide emissions inventory for current degreasing operations than that presently reported by the Air Resources Board.[1] Therefore, an emission inventory based on an industry survey was developed to define reactive organic (ROG) and total organic (TOG) solvent emissions for each manufacturing SIC category in which degreasing operations were found to occur during 1976, and where feasible, to identify the particular organic solvent emitted. Solvents were reported as either reactive or nonreactive according to the reactivity classification of organic compounds presented in reference 1.

In addition, petroleum solvent emissions from degreasing operations associated with automobile repair dealers (including service stations) and oil well production activities were estimated. These emissions (reported as all ROG) were added to the emissions calculated for the manufacturing industries to arrive at an estimated total amount of organic solvent emissions from degreasing operations for each air basin in the state. The estimated total emissions were compared to the degreasing emissions reported by the ARB for 1973.[1]

The potential reduction in solvent emissions which would result from the use of alternative alkaline and emulsion solvents in place of organic solvents, where recommended under this project, was determined. The potential reduction in emissions was compared to the total estimated degreasing emissions for each air basin.

8.2 Methodology and Assumptions

8.2.1 Manufacturing Industry

The basis for development of the emissions inventory for degreasing operations carried on by manufacturing industries in California was the survey conducted as part of this project. A description of the survey is presented in Section 5.0.

The determination of total organic gases (TOG) and reactive organic gases (ROG) emissions for each manufacturing subcategory (SIC code) included in the survey was performed in the following manner. First, the survey respondents were classified by SIC subcategory and by one of three size divisions (i.e., 1 to 20, 21 to 100, and greater than 100 employees). This classification is shown in Supplement B. Next, the respondents who used nonorganic degreasing solvents were identified. The amount and type of organic solvent reported as used for the base year 1976 were then noted for each positive respondent who performed organic solvent degreasing.

The emissions were determined for each positive respondent by subtracting from the total solvent used that amount of waste solvent reported as either recycled to supplier or picked up by solvent reclaimer. Where participants identified waste solvent disposed of by dumping or draining to sewer, such quantities were included in the total estimate of emissions. Respondent estimates of evaporation were accepted as representing the total emissions for those cases where the difference between the amount used and the amount evaporated was reasonably close to the amount of solvent reported as recycled, or when the evaporation estimate approached the total solvent reported as used for the year.

The total number of respondents, including both those who used and those who did not use organic solvents for degreasing, was calculated for each subcategory division (see Supplement B). The fraction of respondents that used organic solvents for degreasing was then determined. This fraction was multiplied by the estimated total number of manufacturers (shown in Supplement A) to obtain the number of degreasing users of that subcategory division within each county. The figures after the decimal point were rounded off to the nearest number. These numbers of degreasing users, together with the emission data provided by the respondents, were used to obtain the associated emission by county.

The method used can best be explained with the following example. Assume that the estimated total number of aluminum die casting firms in a certain county was nine with four responding to the survey questionnaire. Three of the four respondents indicated that they used solvents for degreasing in 1976. The amounts of solvents emitted were 250 gallons of solvent A from two firms and 2100 gallons of solvent B from the third one for the year 1976. Based on these responses, it was assumed that the medium size firms in the aluminum die casting subcategory of that county was made up of two firms (9 x 1/4 = 2.25 ≅ 2) which performed no solvent degreasing, five firms (9 x 2/4 = 4.5 ≅ 5) which emitted 250 gallons each per year of solvent A, and two firms (9 x 1/4 - 2.25 ≅ 2) who each emitted 2100 gallons of solvent B per year. The TOG emissions from this subcategory in that county would be approximately 5450 gallons per year.

In some cases, an industry had more than one degreasing operation

which used different solvents; therefore, the number of operations might exceed the actual number of manufacturers estimated for a particular county or for a particular SIC subcategory.

In developing this inventory, it was assumed that degreasing operations identified by the manufacturers surveyed were typical of degreasing operations carried on by manufacturers classified under the same size division of each subcategory. When operations varied among the respondents in the same subcategory division, the operations were kept separate. Since the number of manufacturers surveyed was usually less than the number of manufacturers determined (by the survey results and Chamber of Commerce statistics) to exist in a particular county, an average of the emissions for different operations under the same SIC subcategory was not generally required. But in some instances, the number of manufacturers determined to exist in a county was less than the number of respondents who performed solvent degreasing operations (for a particular subcategory division), and therefore the solvent emissions were averaged and the solvents listed as either of those solvent-types used.

It was further assumed that:

- The SIC categories surveyed represent all manufacturing industries which use organic solvent degreasing as a part of their manufacturing processes.
- The distribution of manufacturers on the mailing list was assumed to be representative of the remaining 49 percent of California manufacturers belonging to the same SIC subcategories in estimating the total number of manufacturing industries state-wide.
- The data provided by respondents were accurate and complete in most cases.

8.2.2 Automotive Repair Industry

Organic solvent degreasing operations conducted by the automotive repair industry are almost exclusively cold solvent degreasing operations using primarily petroleum solvents and are a large source of organic solvent emissions in California. As estimated in Section 5.0, the Safety-Kleen Corporation supplies parts washers to 37.6 percent of the automotive repair shops in California, and the number of degreasing units averages 1.3 units per shop.[2] Safety-Kleen consumption figures show an average emission value of 0.92 lbs. of solvent per day per unit. Therefore, an average emission factor was estimated as (0.92 x 1.3), or 1.20 lbs. per day for those dealers using Safety-Kleen washers. The Environmental Protection Agency (EPA) has estimated emissions from the average maintenance-type cold degreaser as 1.45 lbs. per day per unit.[3] Based on this figure, the emission factor of (1.45 x 1.3), or 1.89 lbs. per day was determined for dealers using non-Safety-Kleen degreasers. An average emission factor of 1.63 lbs. per day, based on the Safety-Kleen and EPA data, was used to determine solvent emissions from automotive repair dealers (including service stations). The calculations involved in determining these figures are summarized in Appendix D. The average emission factor, together with the number of dealerships in each county (as shown in Table 5-4), was used to obtain the solvent emission from automotive repair industries in each county.

The assumptions involved in this method were:

- All solvents used by automotive repair businesses are stoddard or mineral spirits with a density of 6.6 lb/gal.
- All solvent cleaning of parts is done with cold solvent in a parts

washer.

- There are 1.3 parts washers per auto repair business.
- All auto repair businesses that use "other" parts washers maintain their washers the same way by periodically replacing all of the contaminated solvent with fresh solvent.
- All solvents disposed of into a waste oil tank are 100 percent emissions.

8.2.3 Oil Well Maintenance Industry

Organic solvent emissions from the oil well mainteneance industry were significant in some counties with large numbers of active wells. As discussed in Section 5.0, a recent study shows an emission of 633.3 tons of solvents in 1976 from the maintenance sector of oil production industry that included 12,768 active wells (which are 30 percent of all the oil wells in California). Based on this information, an emission factor of 0.05 tons/well/year was calculated. The total solvent emissions from oil well maintenance in each county was estimated by multiplying the total number of active wells in that county by the above emission factor (as shown in Table 5-5).

The major assumptions involved in this method were:

- Degreasing data provided by the five major oil companies in Kern County were representative of all the active oil wells in California.
- Unless it was indicated by an oil company that some of the solvent was recovered, all solvents used were considered to have evaporated into the air.
- All solvents used were classified as reactive.

In respect to the first assumption, it should be pointed out that

Kern County emission factors for oil wells probably are not representative of state-wide oil well degreasing. Oil production in Kern County includes advanced recovery techniques and results in predominantly high viscosity crude oil. Because the efficiency of solvent degreasing is partially a function of the viscosity of "soil" being removed, there may be substantial differences in the state-wide averages and those factors generated for Kern County.

8.2.4 Other Maintenance Industries

Organic solvent emissions from the railroad maintenance industry are minimal due to the large amount of alkaline cleaners that are used by the industry. Degreasing emissions from the railroads in California were calculated from use data listed in Table 5-6, and were made with the following major assumptions:

- All railroad degreasing maintenance performed in California is done at specific maintenance depots.
- Mixtures of chlorinated solvents used are 50/50 mixtures with an average density of 12.2 lb/gal.
- Rinsing oil is assumed to be kerosene with a density of 6.8 lbs/gal.
- The 21 minor railroads in California have negligible emissions from organic solvent degreasing.

Degreasing emissions inventory data for the civilian aircraft maintenance industry consists of data obtained from recent CARB inventory data for some airlines located in Los Angeles and San Diego Counties.

Organic solvent emissions from the military aircraft maintenance industry were partly obtained from recent CARB emissions inventory data and partly from calculations based on use data listed in Table 5-7. The calculations were made with the assumption that PD-680 Type II dry cleaning solvent is a stoddard solvent with a density of 6.5 lbs/gal.

8.3 1976 Degreasing Solvents Emission Inventory

The detailed inventory of organic solvent emissions, solvent type, and number of operations according to employment size and SIC subcategory are shown by county in Supplement C for all manufacturing industries. Many of the counties in the less populated regions of the state were estimated by the above method to not have manufacturing industries performing organic solvent degreasing operations; thus these counties are not included in the detailed table in Supplement C. Furthermore, those SIC subcategories not using organic solvents or performing degreasing operations were also not included.

There are several counties in the state that have been divided up into two air basins. In estimating emissions for these air basins, the population distribution in these counties was used as a basis to obtain the proportional factors[5] (see Appendix E). These proportional factors were used to develop for each air basin an inventory of emissions resulting from manufacturing auto repair dealers and oil well maintenance degreasing operations.

A summary of the total estimated organic solvent emissions (ROG and TOG) for 1976 from manufacturing industries which perform degreasing is illustrated in Table 8-1. As indicated in the table, approximately one fourth of the manufacturers in these SIC subcategories (254-382) used solvent degreasing in 1976. Organic degreasing emissions from manufacturing industries are estimated as prevalent in only six of the state's fourteen air basins. The San Diego, San Francisco Bay area, and South Coast air basins are estimated to contain degreasing operations which are responsible

Table 8-1. ESTIMATED ORGANIC SOLVENT EMISSIONS FROM MANUFACTURING INDUSTRY DEGREASING OPERATIONS IN CALIFORNIA FOR THE YEAR 1976

Air Basin	County	Total Number of Manufacturing Industries (SIC 254-382)*	Estimated Number of Manufacturing Degreasing Operations (SIC 254-382)	Total Solvent Emissions Tons/Day** ROG	Total Solvent Emissions Tons/Day** TOG
Great Basin Valleys	All	---	Negl.	Negl.	Negl.
Lake County	"	---	Negl.	"	"
Lake Tahoe	"	---	Negl.	"	"
Mountain Counties	"	---	Negl.	"	"
North Central Coast	"	---	Negl.	"	"
North Coast	"	---	Negl.	"	"
Northeast Plateau	"	---	Negl.	"	"
Southeast Desert	"	---	Negl.	"	"
Sacramento Valley	Sacramento	89	10	"	.09
San Diego	San Diego	499	128	0.27	8.30
San Francisco Bay Area	Alameda	921	210	0.29	3.36
	Contra Costa	145	36	0.05	0.19
	Marin	45	7	0.01	0.04
	San Mateo	355	87	0.25	1.00
	Santa Clara	778	238	0.41	2.61
	San Francisco	260	39	0.09	0.34
	Sonoma	151	9	0.01	0.04
		2655	626	1.11	7.58

Table 8-1. Continued

Air Basin	County	Total Number of Manufacturing Industries (SIC 254-382)*	Estimated Number of Manufacturing Degreasing Operations (SIC 254-382)	Total Solvent Emissions Tons/Day** ROG	TOG
San Joaquin	Fresno	87	23	0.06	0.23
	Kern	64	18	0.02	0.15
	San Joaquin	90	10	0.02	0.69
	Stanislaus	61	8	Negl.	0.03
	Tulare	42	8	Negl.	0.06
		344	67	0.10	1.16
South Central Coast	Santa Barbara	85	20	0.06	0.75
	Ventura	64	20	0.02	0.78
		149	40	0.08	1.53
South Coast	Los Angeles	7841	1930	3.02	54.90
	Orange	1288	402	0.64	11.03
	Riverside	171	23	0.03	0.21
	San Bernardino	191	11	0.07	0.40
		9491	2366	3.76	66.54
TOTAL		13,227	3,237	5.32	85.20

* Does not include manufacturing industries for those SIC codes which did not perform degreasing operations based on survey response

** Per calendar day

for about 97 percent of the total degreasing solvent emissions in the state. Manufacturing industry degreasing operations in Los Angeles County alone are estimated as 54.9 TPD (TOG), or 64 percent of the total state-wide emissions from manufacturing operations. The aircraft parts manufacturing industry (SIC #372) in Los Angeles County is estimated to generate approximately 68 percent of the estimated 54.9 TPD.

Estimated organic solvent emissions by solvent type for the manufacturing industry degreasing operations are presented in Table 8-2. As indicated in the table, 1,1,1-trichloroethane and perchloroethylene made up approximately 61 percent of the manufacturing solvent emissions statewide in 1976. The reactive organic solvents, trichloroethylene, petroleum solvents, and alcohols made up 6.2 percent of the total manufacturing degreasing emissions. This figure should be the same as the ROG/TOG ratio (5.32/85.20 = 6.2%) shown in Table 8-1.

The estimated organic solvent emissions from the manufacturing industry degreasing operations by SIC subcategories are presented in Table 8-3. The aircraft parts manufacturing industry contributed the majority of emissions resulting from manufacturing solvent degreasing operations in California in 1976.

The estimated total solvent emissions from automobile repair dealers (including service stations) for each county and air basin in the state are given in Table 8-4. The solvents used were assumed to be reactive organic compounds.

The organic solvent emissions from oil well maintenance operations for each county and air basin are presented in Table 8-5. These emissions were classified as ROG emissions.

Table 8-2. ESTIMATED ORGANIC SOLVENT EMISSIONS
BY SOLVENT TYPE FOR MANUFACTURING
INDUSTRY DEGREASING OPERATIONS FOR 1976

Air Basin County	Total Organic Solvent Emissions (Tons/Day)*									
	A	B	C	D	E	F	G	H	I	TOTAL
Sacramento Valley										
Sacramento	0.05		0.02						0.02	0.09
San Diego										
San Diego	3.23	0.15	1.84	0.05	0.03	0.07	1.89	1.00	0.04	8.30
San Francisco Bay Area										
Alameda	2.00	0.15	0.36	0.14	0.22		0.36		0.13	3.36
Contra Costa	0.06	0.03	0.03	0.01	0.01	0.01	0.02		0.02	0.19
Marin	0.02			0.01					0.01	0.04
San Mateo	0.23	0.09	0.27	0.12	0.17	0.04	0.02		0.06	1.00
Santa Clara	1.07	0.19	0.62	0.13	0.06	0.09	0.13	0.02	0.30	2.61
San Francisco	0.14	0.01	0.08	0.06		0.02			0.03	0.34
Sonoma	0.02	0.01							0.01	0.04
	3.54	0.48	1.36	0.47	0.46	0.16	0.53	0.02	0.56	7.58
San Joaquin Valley										
Fresno	0.03	0.02	0.04	0.04	0.04				0.06	0.23
Kern	0.10		0.01	0.02					0.02	0.15
San Joaquin	0.23		0.44	0.02						0.69
Stanislaus	0.01								0.02	0.03
Tulare	0.04				0.01				0.01	0.06
	0.41	0.02	0.49	0.08	0.05				0.11	1.16

Table 8-2. Continued

Air Basin County	Total Organic Solvent Emissions (Tons/Day)* A	B	C	D	E	F	G	H	I	TOTAL
South Central Coast										
Santa Barbara	0.23	0.01	0.42	0.05	0.02				0.02	0.75
Ventura	0.22		0.42	0.02	0.06				0.06	0.78
	0.45	0.01	0.84	0.07	0.08				0.08	1.53
South Coast										
Los Angeles	17.04	1.35	15.88	1.38	2.63	0.29	9.06	5.98	1.29	54.90
Orange	4.14	0.26	2.54	0.27	0.38	0.11	1.93	1.01	0.39	11.03
Riverside	0.09	0.01	0.04	0.01	0.03	0.01			0.02	0.21
San Bernardino	0.11	0.02	0.11	0.05	0.08				0.03	0.40
	21.38	1.64	18.57	1.71	3.12	0.41	10.99	6.99	1.73	66.54
TOTAL**	29.06	2.30	23.12	2.38	3.74	0.64	13.41	8.01	2.54	85.20
Percentage	34%	3%	27%	3%	4%	1%	16%	9%	3%	100%

*Rounded to nearest 0.05 TPD
**Rounded to nearest 0.1 TPD

Solvents: A-1,1,1-trichloroethane
B-Trichloroethylene
C-Perchloroethylene
D-Petroleum (Stoddard) solvents
E-Ketones
F-Alcohols
G-Freons
H-Methylene Chloride
I-Other

Table 8-3. ESTIMATED ORGANIC SOLVENT EMISSIONS
BY DIFFERENT MANUFACTURING INDUSTRY IN CALIFORNIA

SIC	Industry	ROG		TOG	
		TPD	%	TPD	%
372	Aircraft and Parts	0.21	4.0	52.29	61.3
347	Metal Services	0.56	10.6	4.63	5.4
376	Guided Missiles, Space Vehicles, Parts	0.10	1.9	4.34	5.1
356	General Industrial Machinery	0.10	1.9	2.98	3.5
359	Misc. Machinery, except Electrical	0.32	6.1	2.96	3.5
366	Communication Equipment	0.68	12.9	2.42	2.8
342	Cutlery, Hand Tools, and Hardware	0.40	7.6	2.19	2.6
371	Motor Vehicles and Equipment	0.68	12.9	1.97	2.3
367	Electronic Components and Accessories	0.11	2.1	1.65	1.9
349	Misc. Fabricated Metal Products	0.01	0.2	1.47	1.7
344	Fabricated Structural Metal Products	0.00	0.0	1.39	1.6
339	Misc. Primary Metal Products	0.01	0.2	1.11	1.3
357	Office and Computing Machines	0.34	6.5	1.02	1.2
364	Electric Lighting and Wiring Equipment	0.06	1.1	0.72	0.8
343	Plumbing and Heating, except Electric	0.00	0.0	0.57	0.7
354	Metalworking Machinery	0.32	6.1	0.52	0.6
353	Construction and Related Machinery	0.48	9.1	0.49	0.6

Table 8-3. Continued

SIC	Industry	ROG TPD	ROG %	TOG TPD	TOG %
345	Screw Machine Products, Bolts, etc.	0.29	5.5	0.36	0.4
254	Partitions and Fixtures	0.00	0.0	0.34	0.4
361	Electric Distributing Equipment	0.16	3.0	0.30	0.4
382	Measuring and Controlling Devices	0.13	2.5	0.25	0.3
362	Electrical Industrial Apparatus	0.02	0.4	0.20	0.2
346	Metal Gorgings and Stampings	0.17	3.2	0.18	0.2
358	Refrigeration and Service Machinery	0.00	0.0	0.16	0.2
352	Farm and Garden Machinery	0.00	0.0	0.14	0.2
259	Misc. Furniture and Fixtures	0.00	0.0	0.13	0.2
351	Engines and Turbines	0.06	1.1	0.10	0.1
355	Special Industrial Machinery	0.00	0.0	0.09	0.1
335	Nonferrous Rolling and Drawing	0.00	0.0	0.08	0.1
336	Nonferrous Foundries	0.06	1.1	0.08	0.1
381	Engineering and Scientific Instru.	0.00	0.0	0.04	0.0
332	Iron and Steel Foundries	0.00	0.0	0.03	0.0
348	Ordnance and Accessories	0.00	0.0	0.02	0.0
369	Misc. Electrical Equipment & Supplies	0.00	0.0	0.02	0.0
379	Misc. Transportation Equipment	0.00	0.0	0.01	0.0
	Total	5.27		85.25	

Table 8-4. STATE-WIDE ORGANIC SOLVENT EMISSIONS FROM AUTOMOTIVE REPAIR DEALERS AND SERVICE STATIONS

Air Basin	County	No. of Automotive Repair Dealers	Reactive Organic Solvent Emissions Tons/Day*
Great Basin Valleys	Alpine	2	.001
	Inyo	61	.05
	Mono	22	.02
			.07
Lake County	Lake	89	.07
			.07
Lake Tahoe	El Dorado	66	.05
	Placer	17	.01
			.06
Mountain Counties	Amador	43	.04
	Calaveras	35	.03
	El Dorado	108	.09
	Mariposa	15	.01
	Nevada	97	.08
	Placer	196	.16
	Plumas	57	.05
	Sierra	5	.004
	Tuolumne	81	.07
			.53
North Central Coast	Monterey	424	.35
	San Benito	37	.03
	Santa Cruz	259	.21
			.59
North Coast	Del Norte	35	.03
	Humboldt	249	.20
	Mendocino	159	.13
	Sonoma	60	.05
	Trinity	25	.02
			.43
Sacramento Valley	Butte	288	.23
	Colusa	35	.03
	Glenn	55	.04
	Sacramento	1105	.90
	Shasta	230	.19
	Solano	77	.06
	Sutter	95	.08
	Tehama	87	.07
	Yolo	184	.15
	Yuba	89	.07
			1.82

Table 8-4. Continued

Air Basin	County	No. of Automotive Repair Dealers	Reactive Organic Solvent Emissions Tons/Day*
San Diego	San Diego	2259	1.84
San Francisco	Alameda	1538	1.25
	Contra Costa	788	.64
	Marin	362	.30
	Napa	155	.13
	San Mateo	866	.71
	Santa Clara	1654	1.35
	San Francisco	727	.59
	Solano	257	.21
	Sonoma	442	.36
			5.54
San Joaquin	Fresno	922	.75
	Kern	578	.47
	Kings	152	.12
	Madera	97	.08
	Merced	221	.18
	San Joaquin	500	.41
	Stanislaus	384	.31
	Tulare	447	.36
			2.68
Northeast Plateau	Lassen	50	.04
	Modoc	25	.02
	Shasta	16	.01
	Siskiyou	115	.09
			.17
South Central Coast	San Luis Obispo	315	.26
	Santa Barbara	527	.43
	Ventura	613	.50
			1.19
South Coast	Los Angeles	9928	8.09
	Orange	2315	1.89
	Riverside	665	.54
	San Bernardino	1046	.85
			11.37

Table 8-4. Continued

Air Basin	County	No. of Automotive Repair Dealers	Reactive Organic Solvent Emissions Tons/Day*
Southeast Desert	Imperial	133	.11
	Kern	110	.09
	Los Angeles	100	.08
	Riverside	272	.22
	San Bernardino	230	.19
			.69
TOTAL FOR STATE			27.05

*Per calendar day

Table 8-5. ESTIMATED STATE-WIDE ORGANIC SOLVENT EMISSIONS FROM OIL WELL MAINTENANCE OPERATIONS

Air Basin	County	Number of Wells	ROG Emissions Tons/Day*
North Central Coast	Monterey	958	0.13
	San Benito	35	Negl
			0.13
San Francisco Bay Area	Alameda	10	Negl
	Contra Costa	45	Negl
	San Mateo	13	Negl
	Sonoma	1	Negl
			Negl
San Joaquin Valley	Fresno	2553	0.35
	Kern	24568	3.37
	Kings	138	0.02
	Tulare	31	Negl
			3.74
South Central Coast	San Luis Obispo	253	0.03
	Santa Barbara	1849	0.25
	Ventura	2613	0.36
			0.64
South Coast	Los Angeles	5988	0.82
	Orange	3158	0.43
	Riverside	15	Negl
	San Bernardino	42	Negl
			1.25
TOTAL			5.76

The estimated total solvent emissions from the railroad maintenance industry in California are given by county and air basin in Table 8-6.

Table 8-6. ESTIMATED STATE-WIDE ORGANIC SOLVENT EMISSIONS FROM RAILROAD MAINTENANCE OPERATIONS

Air Basin	County	Railroad and Depot	ROG Emissions Tons/Day*	TOG Emissions Tons/Day*
Sacramento Valley	Sacramento	Southern Pacific Trans. Co.		
		Roseville	0.07	0.09
		Sacramento	---	0.22
		Western Pacific R.R.		
		Sacramento & Stockton	---	0.08
South Coast	Los Angeles	Southern Pacific Trans. Co.		
		Los Angeles	0.07	0.09
		Union Pacific R.R.		
		Los Angeles	0.00	0.00
			0.07	0.09
TOTAL FOR STATE			0.14	0.48

*Per calendar day

Estimated organic solvent emissions from the civilian aircraft maintenance industry are detailed in Table 8-7. As can be seen by the individual degreasing solvent emission estimates for each airline listed, the degreasing practices for the industry are diverse. Consequently, to determine the extent of solvent degreasing emissions originating from each airport where maintenance is performed will require surveying each airline and private maintenance facility.

Table 8-7. ESTIMATED STATE-WIDE ORGANIC SOLVENT EMISSIONS FROM CIVILIAN AIRCRAFT MAINTENANCE OPERATIONS[1]

Air Basin	County	Airline	ROG Emissions Tons/Day*	TOG Emissions Tons/Day*
San Diego	San Diego	PSA	0.01	0.13
South Coast	Los Angeles	American Airlines	0.01	0.02
		Continental Airlines	0.01	0.02
		Flying Tiger Airlines	0.02	0.02
		Western Airlines	---	0.06
			0.04	0.12
TOTAL FOR STATE			0.05	0.25

---

[1] Estimated emissions taken from recent CARB emissions inventory data.

The estimated organic solvent emissions from the military aircraft maintenance industry are detailed in Table 8-8. The estimates given for each military installation are unique and cannot be extrapolated to the other military installations. Therefore, it is recommended that each base be surveyed individually to provide an accurate assessment of military aircraft maintenance degreasing in California.

Table 8-8. ESTIMATED STATE-WIDE ORGANIC SOLVENT EMISSIONS FROM MILITARY AIRCRAFT MAINTENANCE OPERATIONS[1]

Air Basin	County	Military Installation	ROG Emissions Tons/Day*	TOG Emissions Tons/Day*
Sacramento Valley	Sacramento	McClellan AFB	0.30	0.97
		Mather AFB	0.02	0.03
		Sacramento Army Depot	0.01	0.02
TOTAL FOR STATE			0.33	1.02

---

*Per calendar day

[1] Estimated emissions for McClellan and Army Depot are from recent CARB inventory data.

On a state-wide basis it should be noted that although the manufacturing industry contributed to the majority of total solvent emission in 1976, it contributed only a relatively small amount of the reactive organic emissions. The oil well maintenance and automotive repair dealers contributed most of the reactive organic emissions. The distribution of organic solvent emissions among solvent degreasing users in California is summarized in Table 8-9.

A comparison of the total solvent degreasing emissions derived from this study (including manufacturing, automotive repair, and oil well maintenance), along with the total emissions for 1973 reported by CARB, is provided in Table 8-10. As indicated in the table, the estimated emissions are significantly less than that reported for 1973 for the Sacramento Valley and Bay Area Air Basins, and significantly greater for the South Coast Air Basin.

The differences between the degreasing emissions reported by the CARB for 1973 and those calculated under this project may in some instances be due to the fact that some large nonmanufacturing sources were not included in the project survey or that manufacturing operations may have changed significantly since 1973. For example, the CARB-reported emissions for Sacramento County of 11.9 TPD in 1973 are twice as high as those reported for Orange County even though Sacramento County has approximately 7 percent of the estimated total number of manufacturing industries located in Orange County. Communication with Sacramento County APCD personnel[6] indicates that organic solvent degreasing operations at two large military installations in the county were responsible for the major part of the 11.9 TPD figure for 1973. Since then a major reduction in military de-

Table 8-9. DISTRIBUTION OF ORGANIC SOLVENT EMISSIONS AMONG SOLVENT DEGREASING USERS IN CALIFORNIA IN 1976

Industry	ROG		TOG	
	TPD	%	TPD	%
Manufacturing	5.32	13.8	85.20	71.1
Automotive Repair	27.05	70.0	27.05	22.6
Oil Well Maintenance	5.76	14.9	5.76	4.8
Railroad Maintenance	0.14	0.4	0.48	0.4
Civilian Aircraft Maintenance	0.05	0.1	0.25	0.2
Military Aircraft Maintenance	0.33	0.8	1.02	0.9
	38.65	100.0	119.76	100.0

Table 8-10. SUMMARY OF ESTIMATED AND REPORTED ORGANIC SOLVENT EMISSIONS FROM DEGREASING OPERATIONS IN CALIFORNIA

Air Basin County	Estimated Total Emissions*** for the Year 1976 Tongs/Day		Reported Total Emissions for the Year 1973* Tons/Day	
	ROG	TOG**	ROG	TOG
Sacramento Valley				
Sacramento	1.30	2.40	2.0	11.9
Other Counties	0.92	0.92	0.7	3.4
	2.22	3.32	2.7	15.3
San Diego				
San Diego	2.13	10.27	6.7	9.5
San Francisco Bay Area				
Alameda	1.54	4.61	---	10.0
Contra Costa	0.69	0.83	---	5.4
Marin	0.31	0.34	---	1.8
San Mateo	0.95	1.71	---	5.4
Santa Clara	1.76	3.96	---	11.0
San Francisco	0.67	0.93	---	6.3
Sonoma	0.37	0.40	---	2.3
Other Counties	0.34	0.34	---	2.7
	6.63	13.12		44.9
San Joaquin Valley				
Fresno	1.16	1.33	0.6	3.3
Kern	3.86	3.99	---	---
San Joaquin	0.43	1.10	0.4	2.4
Stanislaus	0.31	0.34	0.3	1.6
Tulare	0.36	0.42	0.2	1.5
Other Counties	0.38	0.40	0.1	1.6
	6.50	7.58	1.6	10.4
South Central Coast				
San Luis Obispo	0.28	0.28	0.1	0.8
Santa Barbara	0.74	1.43	0.3	2.1
Ventura	0.88	1.64	1.2	6.0
	1.90	3.35	1.6	8.9
South Coast				
Los Angeles	12.04	64.02	1.6	24.0
Orange	2.96	13.36	1.2	5.3
Riverside	0.57	0.74	---	0.1
San Bernardino	0.92	1.25	---	3.3
	16.49	79.37	2.8	32.7
ALL OTHER AIR BASINS	2.73	2.73	1.3	12.3
TOTAL	38.60	119.74	16.7	134.0

*Emission Inventory-1973, Air Resources Board, August 1973

**Per calendar day

***Rounded to nearest 0.1 TPD

greasing operations has taken place, and their 1976 update of the emission inventory is anticipated to reflect this change.

A second reason for the differences in some of the reported county emissions and those calculated here may be the various methods used by local APCDs to determine degreasing emissions. For instance, for many years the South Coast Air Quality Management District Metropolitan Zone has used solvent-consumption information contained in permit files to determine degreasing emissions.[7] Permits have been required on all vapor-type degreasing equipment and cold-type degreasers larger than one square meter. But since most cold-type degreasing units such as those used by automobile repair dealers would not require permits, they would not be included in district estimates; thus at least 9.0 TPD (as shown in Tables 8-4 and 8-5) from automobile repair dealers and oil well operators is probably not included in reported emission inventory values for Los Angeles County.

On the other hand, the total emissions calculated for the San Francisco Bay Area (Table 8-5) are approximately one-third that reported by CARB for 1973. Discussions with Bay Area APCD personnel[8] indicate that their estimate of degreasing emissions is based on a survey of solvent manufacturers undertaken in 1963, which provided the district with estimated quantities of solvents sold in the Bay Area for degreasing purposes. Since 1963 the solvent consumption estimates have followed population growth figures. Some information on the largest degreasers has been obtained since district regulations require operating permits for sources of air pollution that emit over 25 TPY. However, it may be possible that use of solvent sales figures could result in overestimating degreasing emissions.

A third major reason for differences between degreasing emission estimates and those actually reported for 1973 may be the limitations of the project surveys. Approximately 1500 firms (representing about 10 percent of the total manufacturing industries that include potential degreasing operations) were sent survey questionnaires of which 44 percent did not respond, and of those who did respond, 68 percent stated that they performed no degreasing. Therefore, estimates of the number of degreasing operations and associated quantities and types of solvents used are based on information from less than 6 percent of the total manufacturing industries in California with potential degreasing operations (SIC #254-382).

8.4 Projected Emission Reduction

Based on replacing organic solvent usage with alkaline and emulsion degreasing processes (as recommended in Section 6.0 for those SIC categories given in Tables 6-4 and 6-7), the total potential reduction in degreasing emissions and percent reductions are given in Table 8-11. As shown in the table, an estimated 63 percent reduction in emissions state-wide would result from the conversion of degreasing operations using organic solvents to alkaline and emulsion cleaners, as recommended in Section 6.0. More important is the estimated average reduction of 75 percent in total organic degreasing emissions that would occur as a result of solvent conversion in the South Coast Air Basin. In this basin, photochemical air pollution problems are most serious and the quantities of organic solvent emissions are the highest for the state.

The South Coast Air Quality Management District has proposed a rule for degreasing operations installed prior to October 8, 1976, that would limit total organic emissions from any single source to 600 lbs/day. New

Table 8-11. POTENTIAL REDUCTION IN ESTIMATED TOTAL ORGANIC EMISSIONS FROM SOLVENT SUBSTITUTION FOR DEGREASING OPERATIONS

Air Basin	County	Potential Reduction in Estimated Emissions for 1976 Tons/Day		Remaining Estimated Emissions Tons/Day		Percent Reduction in TOG
		ROG	TOG	ROG	TOG	
Sacramento Valley	Sacramento	---	0.1	1.3	2.3	10
	Others	---	---	0.9	0.9	---
		Negl	0.1	2.2	3.2	3
San Diego	San Diego	0.2	8.1	1.9	2.2	79
San Francisco Bay Area	Alameda	0.3	2.9	1.2	1.7	63
	Contra Costa	---	0.2	0.7	0.6	25
	Marin	---	0.1	0.3	0.2	33
	San Mateo	0.2	0.8	0.8	0.9	47
	Santa Clara	0.3	2.3	1.5	1.7	58
	San Francisco	0.1	0.2	0.6	0.7	22
	Sonoma	---	0.1	0.4	0.3	25
	Others	---	---	0.3	0.3	
		0.9	6.5	5.8	6.4	50
San Joaquin	Fresno	---	---	1.2	1.3	---
	Kern	---	0.1	3.9	3.9	3
	San Joaquin	---	0.7	0.4	0.4	64
	Stanislaus	---	---	0.3	0.3	---
	Tulare	---	---	0.4	0.4	---
	Others	---	---	0.4	0.4	---
		Negl	0.8	6.6	6.7	11

Table 8-11. Continued

Air Basin	County	Potential Reduction in Estimated Emissions for 1976 Tons/Day ROG	Potential Reduction in Estimated Emissions for 1976 Tons/Day TOG	Remaining Estimated Emissions Tons/Day ROG	Remaining Estimated Emissions Tons/Day TOG	Percent Reduction in TOG
South Central Coast	Santa Barbara	---	0.7	0.7	0.7	50
	Ventura	---	0.6	0.9	1.0	38
		Negl	1.3	1.6	1.7	43
South Coast	Los Angeles	2.3	49.1	9.7	14.9	77
	Orange	0.4	9.6	2.6	3.8	72
	Riverside	---	0.1	0.6	0.7	13
	San Bernardino	---	0.4	0.9	0.9	31
		2.7	59.2	13.8	20.3	75
ALL OTHER AIR BASINS		Negl	Negl	2.7	2.7	---
TOTAL		3.8	76.0	34.6	43.2	63

degreasing equipment is limited to 250 lbs/day of organic solvent emissions. This regulation would primarily affect the aircraft industry (SIC #372) since degreasing emissions for this industry are the largest in the district, and individual operations are known to exceed this value. Based on the inventory developed under this project, the new regulation (600 lbs/day) could reduce organic solvent emissions within the aircraft industry by as much as 20 TPD (as shown in Supplement C). The reduction of ROG emissions by applying alternative measures would be achieved at a much lower level (3.8/38.6 = 9.8%) compared to the reduction of TOG emissions (63%).

However, data presented in Table 8-11 was based on the assumption that no alternatives had been applied to the automotive repair and oil well maintenance industry; thus the solvent emission reduction shown in the table are the result of replacing the conventional degreasing operations in the manufacturing industry with alkaline and emulsion cleanings. The actual emission reduction which could be achieved for manufacturing industry degreasing operations would be 89 percent (76/85) for TOG and 72 percent (3.8/5.3) for ROG.

8.5 Conclusions and Recommendations

By analyzing the data from the emission inventory and the projected emission reduction, several conclusions can be made:

- Trichloroethylene was the most widely used vapor degreasing solvent before its use was regulated (the national consumption of trichloroethylene then accounted for 50 percent of the market). In 1976, only 3 percent of the degreasing solvents emitted by manufacturing operations in California was trichloroethylene. Most manufacturers selected either 1,1,1-trichloroethane (34%) or perchloroethylene (27%) as alternatives to trichloroethylene.

- In 1976 out of the 85.2 TPD TOG emitted from the manufacturing industry degreasing operations in California, only 5.3 TPD (6.2%) can be classified as ROG (trichloroethylene, petroleum products, and alcohols).
- In 1976 Los Angeles County had the highest solvent emission 54.9 TPD (or 64%) from solvent degreasing operations conducted by the manufacturing industry in the state. The aircraft parts manufacturing industry (SIC #372) in Los Angeles County contributed 68 percent of the total in the county.
- In 1976 the aircraft industry contributed 61 percent of the total solvent emissions from manufacturing industries as a result of degreasing operations.
- The manufacturing industry contributed most of the TOG emissions in the state (85.2 TPD, or 71%). The maintenance industry (automotive repair, oil well, railroad, civilian and military aircraft maintenance) contributed most of the ROG emissions (33.3 TPD, or 86%). For all degreasing operations in California, the ROG emissions were about 32 percent (38.6/119.7) of the TOG emissions.
- By using solvent degreasing alternatives to replace the conventional degreasing operations in the manufacturing industry, the solvent emission reduction would be 89 percent for the TOG and 72 percent for the ROG.

Based on data and conclusions presented, two recommendations are made:

- The maintenance industry (automotive repair and oil well maintenance) contributes large amounts of ROG emissions. The potential, however, for this industry to switch from cold solvent degreasing to other alternative systems is relatively unknown. Therefore, a demonstration study to compare cold degreasing with emulsion cleaning is recommended.

- From photochemical air pollution standpoints, degreasing solvent emission regulations should be concentrated on those degreasing operations that use reactive solvents. For the less reactive solvents, however, other factors, such as occupational health, should be considered.

8.6 References

1. Emission Inventory, 1973. California Air Resources Board, August 1976.

2. Data provided by Safety-Kleen Corporation.

3. Control of Volatile Organic Emissions from Solvent Metal Cleaning, EPA, November 1977, EPA 450/2-77-022.

4. Personal communication with Mr. Larry Landis of Kern County Air Pollution District (1976) on the subject of organic solvent use, Kern County Oil Fields.

5. Statistics from California Department of Finance.

6. Personal communication with Mr. Bruce Nixon, Sacramento County Air Pollution Control District, Feb. 27, 1978.

7. Personal communication with Mr. George Rett, South Coast Air Quality Management District--Metropolitan Zone, on Feb. 23, 1978.

8. Personal communication with Mr. Nat Flynn, San Francisco Bay Area Air Pollution Control District, Feb. 27, 1978.

APPENDIX A

CARB REACTIVITY CLASSIFICATION OF ORGANIC COMPOUNDS

CARB REACTIVITY CLASSIFICATION OF ORGANIC COMPOUNDS

Class I (Low Reactivity)	Class II (Moderate Reactivity)	Class III (High Reactivity)
C_1-C_2 Paraffins	Mono-Tert-Alkyl-Benzenes	All Other Aromatic Hydrocarbons
Acetylene	Cyclic Ketones	All Olefinic Hydrocarbons (including partially halogenated)
Benzene	Alkyl Acetates	Aliphatic Aldehydes
Benzaldehyde	2-Nitropropane	Branch Alkyl Ketones
Acetone	C_3+ Paraffins	Cellosolve Acetate
Methanol	Cycloparaffins	Unsaturated Ketones
Tert-alkyl Alcohols	N-alkyl Ketones	Primary & Secondary C_2+ Alcohols
Phenyl Acetate	N-methyl Byrrolidone	Diacetone Alcohol
Methyl Benzoate	N,N-dimethyl Acetamide	Ethers
Ethyl Amines	Alkyl Phenols*	Cellosolves
Dimethyl Formamide	Methyl Phthalates**	Glycols*
Perhalogenated Hydrocarbons		C_2+ Alkyl Phthalates**
Partially Halogenated Paraffins		Other Esters**
Phthalic Anhydride**		Alcohol Amines**
Phthalic Acids**		C_3+ Organic Acids + di acid**
Acetonitrile*		C_3+ di acid anhydrides**
Acetic Acid		Formin** (Hexa methylene-tetramine)
Aromatic Amines		Terpenic Hydrocarbons
Hydroxyl Amines		Olefin Oxides**
Naphthalene*		
Chlorobenzenes*		
Nitrobenzenes*		
Phenol*		

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* Reactivity data are either non-existent or inconclusive, but conclusive data from similar compounds are available; therefore, rating is uncertain but reasonable.

** Reactivity data are uncertain.

APPENDIX B

SURVEY COVER LETTERS AND QUESTIONNAIRES

STATE OF CALIFORNIA
EDMUND G. BROWN JR., Governor

AIR RESOURCES BOARD
1102 Q STREET
BOX 2815
RAMENTO, CA 95812

(916) 445-0753

RE: Manufacturers' Literature

Dear Sir:

The California Air Resources Board has contracted with Eureka Laboratories, Inc. of Sacramento, California to conduct a study of emissions of organic solvents from degreasing operations in California. In order to become familiar with the materials, processes and equipment used for solvent degreasing, we are requesting relevant technical literature from your company.

Should your company manufacture non-organic solvent cleaning materials or equipment for utilizing such products, we are also requesting relevant technical literature.

Please send the literature to:

Eureka Laboratories, Inc.
401 N. 16th Street
Sacramento, CA 95814

In accordance with the California Public Records Act (Government Code Section 6250 et seq.), the information you provide will be released to the public upon request unless Trade Secret classification is requested in writing and accompanied by a justification, as specified in Section 91010, Title 17 of the California Administration Code. In addition, such information may be forwarded to the Environmental Protection Agency, which protects trade secrets in accordance with federal law. Further information regarding the Air Resources Board procedures for protecting trade secrets may be found in Section 91010, Title 17 of the Code or by contacting the Board's Legal Affairs and Enforcement Division, (916) 322-2884.

Thank you for your cooperation.

Sincerely yours,

John R. Holmes

John R. Holmes, Ph.D.
Chief, Research Division

STATE OF CALIFORNIA
EDMUND G. BROWN JR., Governor

AIR RESOURCES BOARD
1102 Q STREET
P.O. BOX 2815
RAMENTO, CA 95812

(916) 445-0753

RE: Source Questionnaire

Dear Sir:

The California Air Resources Board has contracted with Eureka Laboratories, Inc. of Sacramento, California to conduct a study concerning emissions of organic solvents from degreasing operations in California. This survey is designed to determine the types and quantities of organic solvents being used and the processes in which they are employed. From the information you provide, the approximate emissions can be determined.

In accordance with the California Public Records Act (Government Code Section 6250 et seq.), the information you provide will be released to the public upon request unless Trade Secret classification is requested in writing and accompanied by a justification, as specified in Section 91010, Title 17 of the California Administration Code. In addition, such information may be forwarded to the Environmental Protection Agency which protects trade secrets in accordance with federal law. Further information regarding the Air Resources Board procedures for protecting trade secrets may be found in Section 91010, Title 17 of the Code or by contacting the Board's Legal Affairs and Enforcement Division, (916) 322-2884.

We would appreciate your cooperation in completing this questionnaire. This is a formal request made pursuant to Section 41511 of the California Health and Safety Code and Section 91100, Title 17 of the California Administrative Code which authorize the Air Resources Board to require the submission of information from owners and operators of emission sources. Please return the completed questionnaire in the enclosed, self-addressed envelope as soon as possible.

Any questions regarding the questionnaire should be directed to the Eureka Laboratories, 401 N. 16th Street, Sacramento, CA 95814, (916) 443-3932. Your cooperation in providing the requested information within two weeks from receipt of this letter will contribute materially to the Air Resources Board's accurate assessment of the hydrocarbon emissions from organic solvent degreasing operations in California. Thank you for your assistance.

Sincerely yours,

John R. Holmes

John R. Holmes, Ph.D.
Chief, Research Division

ORGANIC SOLVENT DEGREASING EMISSIONS

DETERMINATION QUESTIONNAIRE

GENERAL INFORMATION

A. Company Name ______________________________

Address ______________________________

B. Person to contact about questionnaire ______________

Title ______________ Telephone ______________

C. Nature of Company ______________________________

D. Are volatile organic or solvent-containing materials manufactured and/or used by your Company?

Manufactured _______ Used _____ No _____

If no, sign form and return.
If yes, complete the applicable section of the questionnaire, sign, and return.

E. Type(s) and amount(s) of solvent cleaner manufactured

Solvent type (Generic)	______________	Amount	__________	gal/yr. Cost $__________ /gal
	______________		__________	__________
	______________		__________	__________
	______________		__________	__________

F. What reasons are there for selecting the particular solvent cleaner(s) you use?

Solvent	Reason for selection
______________	______________________________
______________	______________________________
______________	______________________________
______________	______________________________

G. Have any other solvents previously been used by your Company for degreasing? If yes, identify the solvent and give the reason(s) it is no longer used.

____

____

d. Type(s) and amount(s) and use(s) of solvent cleaner purchased in base year 1976.

PRODUCT DEGREASED	How many times degreased	Degreasing Method(s) Used	Step in manufacturing when degreased	Solvent type used	COMMENTS

d., Cont.

PRODUCT DEGREASED	Amount solvent used (gal/yr) Base year 1976	Cost of solvent ($/gal)	Energy consumption for degreasing product (KWH)	Type of emission control used	COMMENTS

I. Supplier of solvent cleaner(s)

(Name and City) ____________________

____

J. If non-volatile substitutes are required, what are your recommendations? ____________________

____

Cost $__________ /gal.

K. Do any of your products listed in Section H of this questionnaire require special degreasing utilizing only organic solvents?

No ______ Yes ______

If yes, give details. ____________________

____

____

____

L. Does your Company utilize alkaline washing or other non-solvent cleaning for degreasing? If so, please describe. __________

____

____

____

____

M. Waste solvent disposal method. ____________________

____

____

N. Quantity of solvent disposed of in base year 1976 __________ gal

Signature ____________________

DEGREASING EMISSIONS DETERMINATION QUESTIONNAIRE

A. Company Name ______________________________

Address ______________________________

B. Person to contact about questionnaire ______________________________

Title ______________________ Telephone ______________________

C. Nature of company ______________________________

D. Are organic solvent, aqueous (alkaline or detergent) or any other type of degreasing processes used by your company? Yes ____ No ____

If no, sign form and return.

If yes, complete the questionnaire, sign and return.

E. Waste solvent disposal method. (Check appropriate box)

( ) Picked up by solvent reclaimer ( ) Dumped ( ) Sewer ( ) Incinerated ( ) Evaporation

( ) Picked up by supplier ( ) Other, please describe ______________________________

____

If solvent is returned to supplier, is it reclaimed ( ) or disposed of ( ) by the supplier? ( ) Do not know.

F. Do any of your products you listed on the second page of this questionnaire require special degreasing utilizing only organic solvents? No ____ Yes ____

If yes, please give details ______________________________

____

____

G. If your company utilizes volatile organic solvents for degreasing, what would be the difficulties in changing your current degreasing process to a less volatile or non-solvent system?

Please describe ______________________________

____

____

____

H. What are your recommendations if substitutes are required for volatile organic degreasing solvents?

____

____

Signature ______________________________

Degreasing Practice in Base Year 1976

Product Degreased				
How Many Times Degreased?				
Step in Manufacturing when Degreased				
Degreasing Method(s) Used				
Solvent or Chemical Used				
Reason for Selecting the Particular Solvent or Chemical				
Amount of Solvent or Chemical Used in Base Year 1976 (gal/yr, lb/yr)				
Cost of Solvent or Chemical ($/gal)				
Energy Consumption for Degreasing Product (KWH)				
Type of Emission Control Used				
Amount of Solvent Disposed of in Base Year 1976 (gal/yr)				
Manufacturer of Solvent or Chemical				

APPENDIX C

DEDUCTION OF COST FACTORS

DEDUCTION OF COST FACTORS

1. Estimated Costs for Wastewater Treatment[a] ($/1,000 gal)

Process	Without In-Plant Treatment[b]	With In-Plant Treatment[b]
Primary with Flocculation[c]		0.19
Activated Sludge (including primary)[d]	0.09	0.07
Chemical Coagulation and Sedimentation[d]	0.05	0.05
TOTAL COST (1972)	0.14	0.31
TOTAL COST (1978)[e]	0.22	0.49

a. Data derived from "Wastewater Reclamation, State of the Art," Bulletin No. 189. California Department of Water Resources.

b. If the wastewater is large in amount or heavily loaded with organics and inorganics, in-plant primary treatment is generally required before discharging to the sewer.

c. Based on 1 MGD facility size.

d. Based on 100 MGD facility size.

e. Based on 8 percent annum inflation rate.

2. Estimated Cost for Building Space[a] (\$/ft^2)

Shell (M & L) Cost	4.09
Lighting and Electrical	1.75
Heating and Ventilating	1.50
Plumbing	1.70
Fire Prevention	1.10
Total Cost (1968)[b]	10.14
Total Cost (1978)[c]	21.90
Sub-contract Cost[d]	28.50
Contingency[e]	32.80

a. Data derived from "Modern Cost-Engineering Techniques," by H. Popper.

b. Including maintenance cost.

c. 8 percent annual inflation rate.

d. 30 percent charge.

e. 15 percent.

APPENDIX D

DEGREASING EMISSIONS DETERMINATION FOR AUTOMOTIVE REPAIR INDUSTRY

DEGREASING EMISSIONS DETERMINATION
FOR AUTOMOTIVE REPAIR INDUSTRY

1. Safety-Kleen Parts Washer

- Safety-Kleen Data: $\frac{\text{3.4 gal/mo-unit} \times \text{6.6 lb/gal} \times \text{12 mo/yr}}{\text{365 days/yr}}$

$$= 0.74 \text{ lb/day-unit}$$

- Dow Report: $\frac{\text{8,200,000 gal/yr} \times \text{6.6 lb/gal}}{\text{150,000 unit} \times \text{365 days/yr}}$

$$= 0.99 \text{ lb/day-unit}$$

- EPA Report: $\frac{\text{380 lb/yr-unit}}{365}$

$$\approx 1.04 \text{ lb/day-unit}$$

Average Emission for Safety-Kleen Parts Washer:

$$(0.74 + 0.99 + 1.04)/3 = 0.92 \text{ lb/day-unit}$$

2. "Other" Parts Washer

- Dow Report: $\frac{\text{160 gal/yr-unit} \times \text{6.6 lb/gal}}{\text{365 days/yr}}$

$$= 2.9 \text{ lb/day-unit}$$

Average Emission for "Other" Parts Washer:

$$(2.9 + 1.45) \div 2 = 2.18 \text{ lb/day-unit}$$

The Dow figure is generally regarded as too high because it includes those manufacturing sectors that used cold degreasers; therefore, the EPA figure is used in this study.

3. Emission Factors

- Safety-Kleen Washer Users

  0.92 lb/day-unit x 1.3 unit/dealer = 1.20 lb/day-dealer

- "Other" Washer User

  1.45 lb/day-unit x 1.3 unit/dealer = 1.89 lb/day-dealer

- Average

  1.20 lb/day-dealer x 0.376 + 1.89 lb/day-dealer x (1 - 0.376)

  = 1.63 lb/day-dealer

APPENDIX E

PROPORTIONAL FACTORS FOR DIVIDED COUNTIES

PROPORTIONAL FACTORS FOR DIVIDED COUNTIES

1. El Dorado County: 38.4% in Lake Tahoe AB
   61.6% in Mountain Counties AB
2. Kern County: 83.9% in San Joaquin Valley AB
   16.1% in Southeast Desert AB
3. Los Angeles County: 98.9% in South Coast AB
   1.1% in Southeast Desert AB
4. Placer County: 92.1% in Mountain Counties AB
   7.9% in Lake Tahoe AB
5. Riverside County: 71.1% in South Coast AB
   28.9% in Southeast Desert AB
6. San Bernardino County: 82.5% in South Coast AB
   17.5% in Southeast Desert AB
7. Shasta County: 93.6% in Sacramento Valley AB
   6.4% in Northeast Plateau AB
8. Solano County: 76.9% in Bay Area AB
   23.1% in Sacramento Valley AB
9. Sonoma County: 87.9% in Bay Area AB
   12.1% in North Coast AB