

**Center for
Emissions Control**

**SOLVENT CLEANING
(DEGREASING)**

An Assessment of
Emission Control Options

November 1992
Washington, D.C.



Printed on recycled paper.

This document is intended to serve as a general source of information on emission control options for various chlorinated compound applications. In publishing this document, neither the Center for Emissions Control, Inc. (CEC), the CEC member company representatives, nor the member companies —

- o endorse the performance, safety, or environmental acceptability of any of the technologies or products discussed. Those employing control technologies should consider the safety and proper disposal of contaminants and waste products generated from processes used.
- o purport to be an exclusive source of current information regarding control options. Over time more information may become available regarding the health and safety effects of the technologies or products described. Readers are encouraged to consult other sources.
- o make any warranty or representation, either express or implied, with respect to the accuracy, completeness, or utility of the information provided.
- o assume any duty or liability of any kind whatsoever resulting from the use of, or reliance upon, any information, material, or procedure contained in this document, including but not limited to any claims regarding health, safety, environmental effects or fate, efficacy, or performance, made by the source of the information.

Mention of any company or product in this document is for information purposes only, and does not constitute a recommendation of any such company or product, either express or implied, by CEC, CEC member company representatives, or member companies.

* * * * *



Contents

INTRODUCTION.....	1
DESCRIPTION OF PROCESS	3
Cold Cleaning.....	4
Vapor Degreasing.....	5
Immersion	7
Spray	7
Ultrasonics.....	7
Combining Cleaning Cycles	9
Precision Cleaning	9
SOURCES OF SOLVENT LOSS	11
Atmospheric Emissions.....	11
Losses in Hazardous Waste	15
VAPOR EMISSION REDUCTION.....	17
Housekeeping	17
Control Switches	18
Startup/Shutdown Procedures	19
Reduced Room Drafts/Enclosure	19
Down-Time Covers	21
Freeboard Height	21
Lower Primary Condensing Coil Temperature	23
Refrigerated Freeboard Chiller	24
Spray Containment	28
Transport Systems	28
Down-Time Sump Cooling	30

Drying Tunnel	31
Superheated Vapor Drying	31
VAPOR RECOVERY	33
Carbon Adsorption	33
Condensation.....	34
INTEGRATED CONTROL STRATEGY.....	39
SOLVENT RECOVERY FROM WASTE	43
Solvent Segregation	43
Microfiltration	44
On-Site Distillation.....	44
Off-Site Recycling	46
CHEMICAL SUBSTITUTION.....	47
Other Halogenated Solvents.....	47
Petroleum Solvents, Alcohols, and Ketones.....	48
Synthetic Aliphatic Hydrocarbons	49
Hydrochlorofluorocarbons.....	50
Alcohol Cleaning with Perfluorocarbon.....	51
Pentafluoropropanol	52
Perfluoroalkanes	53
Deionized Water	53
PROCESS SUBSTITUTION	55
Aqueous Cleaning	55
Types of Cleaners	56
Cleaning Processes.....	56
Drying.....	58
Wastewater Treatment.....	59
Semi-Aqueous Cleaning	63
Types of Cleaners	64
Cleaning Processes	65
Drying.....	65
Wastewater Treatment	66
Carbon Dioxide Cleaning	67
SUMMARY	69

REFERENCES	71
APPENDIX I: Cleaning Equipment Manufacturers	75
APPENDIX 11: Combined Control Efficiencies for Open-Top Degreasers	79
APPENDIX 111: Commercial Solvent Recyclers	81
APPENDIX IV: Solvent and Aqueous Formulation Manufacturers	85

List of Tables

Table 1. Estimate of Halogenated Solvent Use in Solvent Cleaning - 1991	4
Table 2. Effectiveness of Various Control Techniques for an Open-Top Degreaser	18
Table 3. Effectiveness of Control Technique Combinations Open-Top Degreasers	39
Table 4. Effectiveness of Control Technique Combinations In-Line Degreasers	40
Table 5. Characteristics of Selected Solvents	47

List of Figures

Figure 1. Basic Open-Top Vapor Degreaser Design	5
Figure 2. In-Line Cleaning System	6
Figure 3. Types of Vapor Degreasing Cleaning Cycles	8
Figure 4. Diffusion of Solvent Vapors from an Open-Top Degreaser	12
Figure 5. Diffusion Losses as a Function of Boiling Point for the Halogenated Solvents	13
Figure 6. Disturbance Losses Caused by Part Movement Through the Vapor Zone	14
Figure 7. Workshock Losses Caused by Introduction of a Large Workload	15
Figure 8. Part Orientation to Minimize Dragout	16
Figure 9. A Lip-Vent Exhaust System	20
Figure 10. Water Separator with Cooling Coil	24

Figure 11.	Convection Currents Created by a Refrigerated Chiller	26
Figure 12.	A Second Set of Low-Temperature Coils for Moisture and Vapor Control	27
Figure 13.	Automated Parts Handling Systems	29
Figure 14.	Carbon Adsorption and Desorption	35
Figure 15.	Solvent Recovery Using Recirculating Condensation	36
Figure 16.	Inert Carbon Bed Regeneration System - Process Schematic . . .	37
Figure 17.	Low-Emission Degreaser Design with Solvent-Saving Features	41
Figure 18.	Advanced Small Parts Degreasing Machine	42
Figure 19.	Inerted Alcohol Cleaner with Two Immersion Tanks	52
Figure 20.	Aqueous Cleaning Process	57
Figure 21.	Semi-Continuous Wastewater Treatment Process	60
Figure 22.	Water Recycling System Using Micro- and Ultrafiltration	61
Figure 23.	Tubular Membrane Ultrafiltration	62
Figure 24.	Semi-Aqueous Cleaning Process for an Immiscible Hydrocarbon Solvent	64
Figure 25.	Immersion Spray Zone in an In-Line, Semi-Aqueous Cleaning System	66

* * * * *





Introduction

Organic solvent cleaners use nonhalogenated or halogenated solvents, solvent blends, or their vapors to remove water-insoluble soils (i.e., grease, oils, waxes, carbon deposits, fluxes, and tars) from metal, plastic, fiberglass, and other surfaces. Solvent cleaning is performed prior to processes such as painting, plating, inspection, repair, assembly, heat treatment, and machining, and can reduce contamination in downstream production processes such as electroplating baths.

Examples of the nonhalogenated solvents typically used are mineral spirits, Stoddard solvent, and alcohols. Halogenated solvents commonly used are methylene chloride (dichloromethane or DCM), perchloroethylene (perc or tetrachloroethylene), trichloroethylene (tri or TCE), 1,1,1-trichloroethane (TCA, methylchloroform, or MCF), and trichlorotrifluoroethane (chlorofluorocarbon 113, or CFC-113).

Halogenated solvents have remained popular degreasing solvents for many years because of their good solvency for organic materials, low latent heat of

vaporization,¹ nonflammability,² noncorrosiveness, and relatively high stability (ASTM, 1989). They are particularly favored for vapor degreasing because they can be heated to their boiling point without the fear of fire or explosion (ASTM, 1989). In addition, because the vapors are heavier than air, they can be contained relatively easily.

The halogenated solvents also have a high degree of chemical compatibility with a wide range of materials (e.g., metals, glasses, plastics, and elastomers) that allows convenient cleaning of workloads consisting of mixed materials. Moreover, the development of stabilizing additives that prevent hydrolysis in the presence of water and inhibit the formation of oxidation products has enabled a more expanded use of the vapor degreasing process (ASTM, 1989).

Cleaning with halogenated solvents is a common practice in many diverse sectors of industry. About **445** million pounds (201,770 metric tons) of halogenated solvents are estimated to have been used for solvent cleaning in 1991 (*see Table*

1 The latent heat of vaporization is the heat required to convert a gram of liquid to vapor at the liquid's boiling point.

2 Used to describe solvents that have no fire or flash point when tested by standard test methods (ASTM, 1989). Methylene chloride, trichloroethylene, and 1,1,1-trichloroethane do exhibit a flammability range when high concentrations are mixed in air and exposed to a high energy source.

1). Organic solvent cleaning does not constitute a distinct industrial category, however, but is an integral part of many industries. The major manufacturing industries that use halogenated solvents for cleaning are furniture and fixtures (SIC³ code 25), fabricated metal products (SIC 34), electric and electronic equipment (SIC 36), and transportation equipment (SIC 37) (EPA, 1992a). Additional industries that use halogenated solvents in cleaning include primary metals (SIC 33), nonelectric machinery (SIC 35), and instruments and clocks (SIC 38). Several nonmanufacturing industries (e.g., vehicle maintenance and electric tool repair) also use halogenated solvent cleaners.

Production of two of the halogenated solvents, CFC-113 and 1,1,1-trichloroethane, will be phased out on January 1, 1996 in the United States under the stratospheric ozone protection provisions of the federal Clean Air Act.⁴ The international treaty on stratospheric ozone protection (the Montreal Protocol on Substances That Deplete the Ozone Layer) was revised in November 1992 to also require a phaseout of CFCs and 1,1,1-trichloroethane by the end of 1995.

The other three solvents (and 1,1,1-trichloroethane) are designated as hazardous air pollutants under Section 112 of the Clean Air Act and under a number of state "air toxics" regulations. Solvent cleaning with the halogenated solvents other than CFC-113 will be the subject of a national emission standard under Section 112 which is expected to be completed by mid-1994. Trichloroethyl-

ene and perchloroethylene have been considered photochemically reactive, and are subject to regulatory control as smog precursors under the ozone nonattainment provisions of the federal Clean Air Act.⁵ As a result, cleaning with trichloroethylene and perchloroethylene also has been subject to state regulations to comply with the national ambient air quality standard for ozone (smog). These regulations are based on control technique guidelines (CTGs) developed by EPA.

* * * * *

3 Standard Industrial Classification, as defined by the U.S. Department of Labor.

4 On February 11, 1992, President George Bush announced that the United States would phase out production of CFCs and 1,1,1-trichloroethane for all but feedstock and essential uses by December 31, 1995. Regulations implementing this accelerated phaseout will be issued by the Environmental Protection Agency (EPA) under the authority of Section 606 of the Clean Air Act.

5 EPA recently announced its intent to exempt perchloroethylene based on data indicating that it does not contribute to smog formation (EPA, 1983a; 1992b).



Description Of Process

The choice of a solvent for a specific cleaning task is complex. Various factors must be considered, including the type of surface to be cleaned, the soils to be removed, the degree of cleanliness required, the method of application, the temperature desired, the disposal of the contaminated solvent, and the cost of the complete cleaning operation (SRRP, 1992). Other factors, such as worker safety and regulatory compliance, also play a significant role in solvent choice.

Industrial contaminants can be classified into the following six common types (EPA, 1983b):

- o pigmented drawing compounds - usually oil-based materials to which a pigment such as lime, talc, chalk, sulfur, lithopone, or graphite is added to help overcome the frictional resistance of machining;
- o unpigmented drawing compounds - usually made from mineral oils and greases, vegetable or animal oils, or fats;

- o polishing and buffing compounds - composed of varying combinations of greases, metallic soaps, abrasives, and waxes, and (sometimes) fine metal particles;
- o cutting and grinding fluids - consisting of a variety of plain and sulfurized mineral and fatty oils, chlorinated paraffin oils, soaps, salts, and saturated fatty alcohols;
- o oxidation and scale fluids - including a variety of corrosion products such as rust, heavy metal salts, and assorted metallic oxides; and
- o miscellaneous surface contaminants - consisting of a broad range of common industrial soils such as metal chips, carbon deposits, and various salt deposits.

Generally, however, contaminants can be categorized into the following three groups: polar (i.e., salts), nonpolar (i.e., greases, oils and waxes), and particulate (i.e., dust and machining fragments).

Solvent cleaning can be classified into two major categories: cold cleaning and vapor degreasing. The solvent is maintained near room temperature in cold cleaning, while it is heated to its boiling point in vapor degreasing. Both halogenated and non-halogenated solvents have been used for cold cleaning. Non-halogenated solvents are not used in vapor degreasing because of their flammability. For the halogenated solvents, vapor degreasing is by far the more common cleaning method (**Table 1**).

Precision cleaning is a third type of cleaning that generally is defined by the type of part being cleaned (see below). It can be conducted at either room or elevated temperature.

Cold Cleaning

Cold cleaning generally is conducted at room temperature and at ambient pressure. In some cases, however, higher temperatures (lower than boiling point) may be employed. It is accomplished by dipping, wiping, or spraying, and is typically conducted in a batch process.

A number of different cold cleaning systems are used today. Pails and tanks, the simplest type of cleaning equipment, allow the work piece to be soaked and immersed. More sophisticated equipment may be employed, however, with vertical or ultrasonic agitation, spray cleaning, and/or automation. Mechanical agitation may be employed to enhance

. Table 1. Estimate of Halogenated Solvent Use in Solvent Cleaning - 1991 ¹		
	Vapor Degreasing	Cold Cleaning
Methylene Chloride	10.1	20.3
Perchloroethylene	46.0	--
Trichloroethylene	89.0	3.7
1,1,1-Trichloroethane (Methyl Chloroform)	162.2	95.4
Chlorofluorocarbon 113 (CFC-113)	8	2
Total	<u>323.3</u>	<u>121.4</u>
¹ Numbers are in millions of pounds. Estimates do not include solvent use in the electronics industry. Sources: IRTA, 1991b; EPA, 1992c.		

the dissolution and removal of soils. Spray washing machines with trays often are used for cleaning precision parts (Kirk-Othmer, 1979). Spray cleaning of large parts also is practiced. In these situations, however, an exhaust hood generally is required to collect the solvent fumes.

Vapor Degreasing

Vapor degreasing is conducted at the boiling temperature of the solvent and at ambient pressure. Vapor degreasing offers a more effective method for cleaning because the heated solvent vapors allow for a more thorough removal of dirt and insoluble soil and because the parts contact only distilled solvent (SRRP,

1992). In addition to metals, vapor degreasing can be used for cleaning glass, ceramics, plastics, elastomers, coated items, or a combination of these materials.

In general, a vapor degreaser is a steel tank with a steam or electrical heating coil below the liquid solvent level, and condensing coils located around the inner perimeter of the degreaser above the liquid level. Boiling solvent vapors rise inside the tank to the level of the condensing coils. The presence of these coils establishes a layer of relatively stagnant air in the freeboard zone of the machine that is sandwiched between 100 percent solvent vapor below the condenser and 100 percent air above it (**Figure 1**).

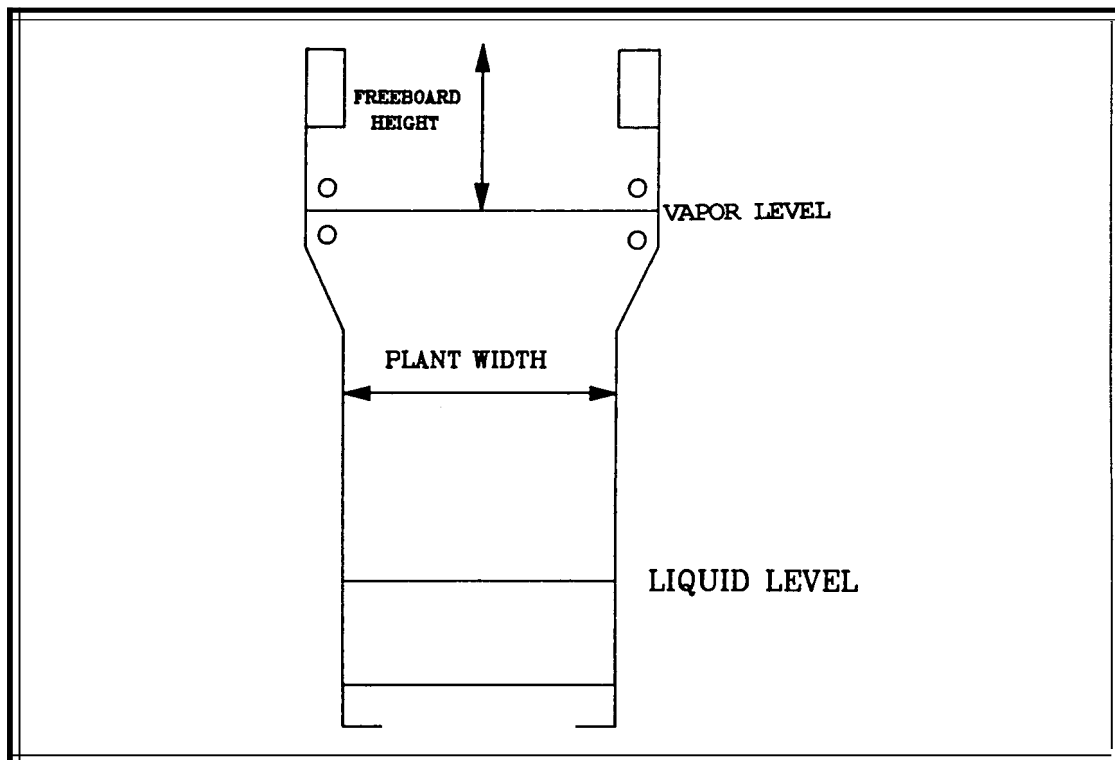
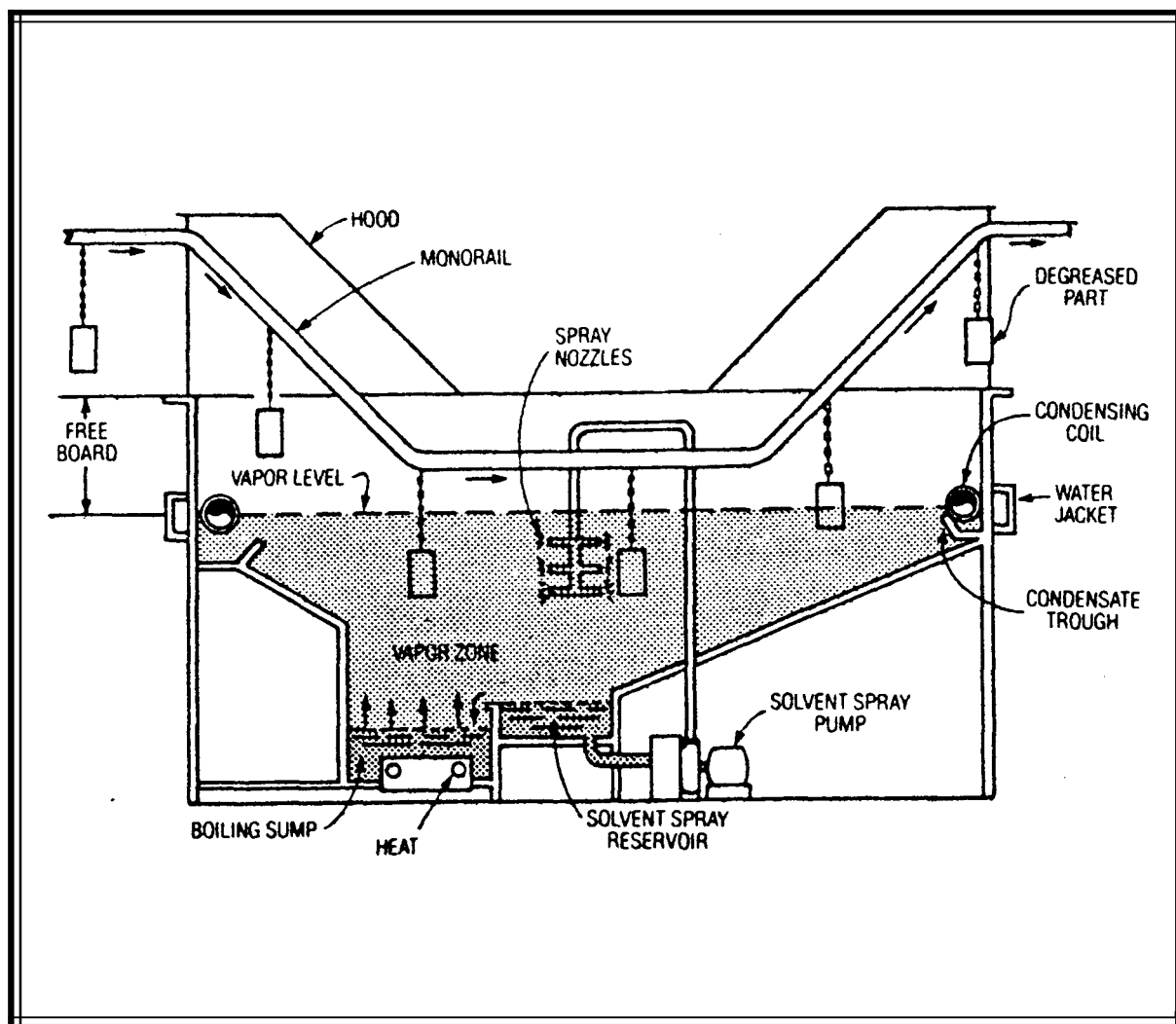


Figure 1. Basic Open-Top Vapor Degreaser Design (Weemes, 1990)



Vapor degreasers are usually classified as open-top or in-line (conveyorized).⁶ Open-top degreasers operate in the batch mode. The work piece is lowered (manually or mechanically) into the vapor zone and is similarly extracted after cleaning. In-line (conveyorized) degreasers are usually enclosed boxes, with openings only at entrance and exit ports, through which the parts to be cleaned are transported (**Figure 2**).

In-line degreasers are usually selected for large-volume production. Because these machines are only open to the ambient environment at the entrance and exit ports, solvent emissions are well controlled. Average emissions from in-line machines are greater than those from open-top machines, however, because in-line equipment generally is considerably larger (SRRP, 1992).

In the simplest form of degreasing, the

6 Of the estimated 20,000 vapor degreasers in operation in the United States, 70 to 90 percent are believed to be open-top machines (EPA, 1992c; SRRP, 1992).

work piece is placed in the vapor zone to allow solvent vapors to condense on it, dissolving the contaminants in the process and providing a continuous rinse with clean solvent. The piece remains in the vapor zone until it reaches the temperature of the solvent vapors, at which point cleaning stops, and the piece is then removed from the equipment. As the condensed solvent drains from the part, it carries off the soils and returns to the boiling liquid reservoir. Solvent in the liquid reservoir is sent to a recovery still, either continuously or in a batch process, to remove any grease, oil, or other contaminants and prevent the build up of these contaminants in the solvent sump.

This arrangement is usually satisfactory for the removal of oils and greases that are completely, or nearly completely, soluble in the degreasing solvent (ASTM, 1989). Only that amount of solvent that condenses on a part, however, is available for cleaning. To aid in cleaning, vapor treatment often is augmented by liquid immersion, spraying with liquid solvent beneath the vapor level, and/or ultrasonic agitation (**Figure 3**). In all cases, however, the work is held in the vapor zone for final rinsing. This ensures that no contaminants will remain on the part.

Immersion

If the amount of oils and greases is heavy in proportion to the condensing capacity of the work being cleaned, or if the contour of the parts is intricate, immersion in an adequate volume of solvent usually

is required to produce intimate solvent contact with the work (ASTM, 1989). The typical cleaning cycle includes: (1) immersion in boiling solvent, (2) immersion in a cool, relatively clean solvent, and (3) a final vapor rinse.

Spray

When insoluble soils (e.g., metal chips, polishing, buffing, and pigmented drawing compounds) are present on the surface of the work to be cleaned, or when the parts are too large to immerse, additional cleaning can be obtained using a spray cycle in which the work piece is sprayed with clean solvent (ASTM, 1989). Spraying can be accomplished with relatively small quantities of distilled solvent or, if necessary, larger quantities of solvent supplied by a separate sump circulating relatively clean solvent. In addition to removing soluble and insoluble soils, a large-volume, forceful spray can be used to break air pockets for cleaning in enclosed cavities. While effective, the use of a spray may increase overall solvent emissions by creating turbulence in the vapor zone (Gerard, 1989). This phenomenon is described in greater detail in Chapter 4.

Ultrasonics⁷

The addition of ultrasonics to a vapor degreaser can accelerate the cleaning process and provide a higher degree of cleanliness than normally obtained from any of the degreasing cycles described above (ASTM, 1989). Ultrasonic energy, at the proper frequency, can attack and remove strongly adherent soils on remote

7 Ultrasonics also can be used effectively in aqueous and semi-aqueous cleaning systems (see Chapter 9).

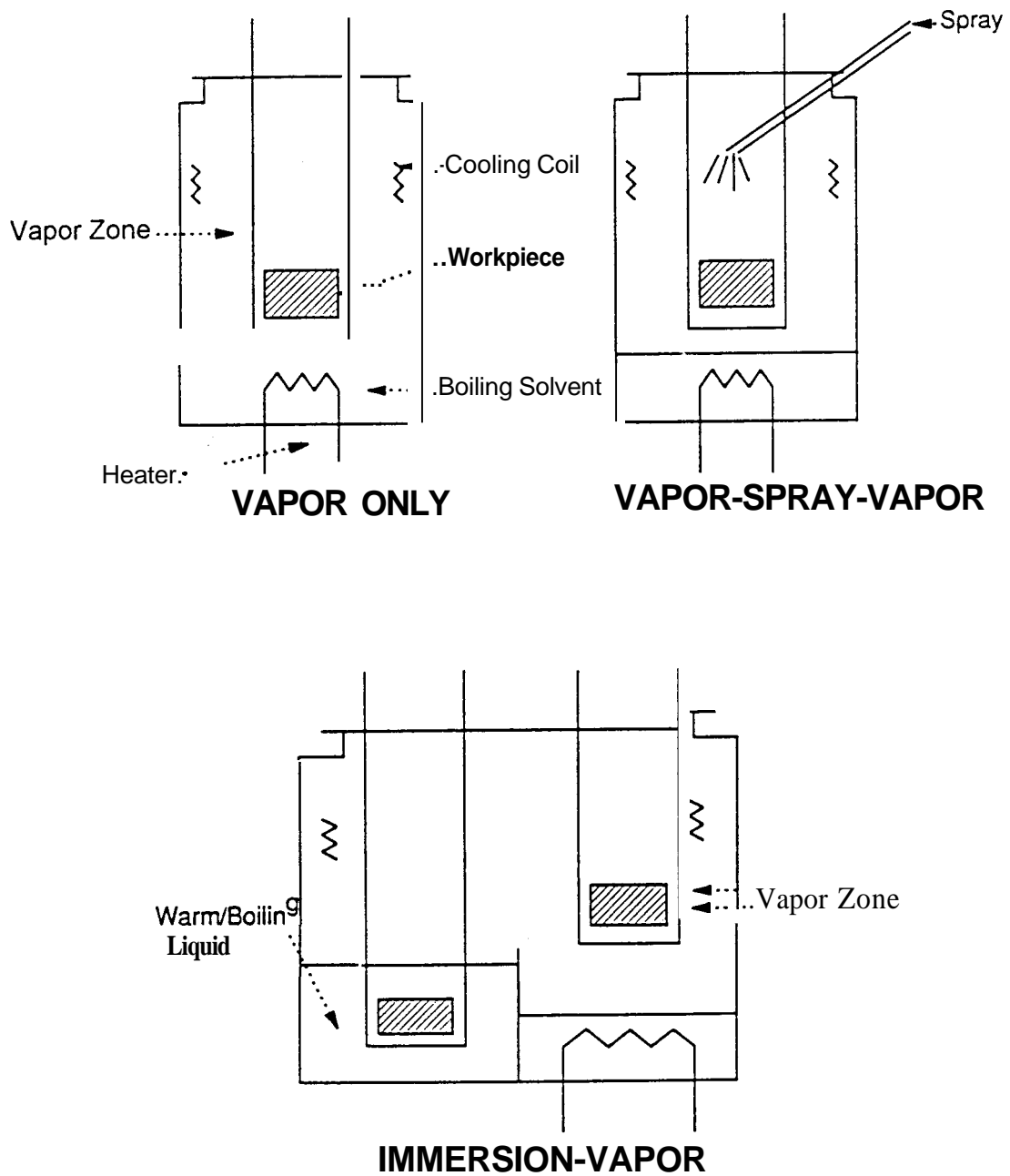


Figure 3. Types of Vapor Degreasing Cleaning Cycles (ChemSystems, 1990)

surfaces and in blind holes.

Ultrasonic energy is created within the liquid solvent by means of transducers bonded to the underside of the tank or immersed within the liquid. The effect of these transducers is to induce cavitation, a phenomenon caused by the implosion of millions of tiny bubbles. The bubbles are formed because of the inability of the liquid to transmit the high ultrasonic energy (Knaggs, 1974). The collapse of these bubbles causes a scrubbing effect on any objects immersed in the liquid, and is the basis of the ultrasonic cleaning process.

The transducers are energized by an electronic generator which is adjusted to produce mechanical vibrations of the desired frequency. Frequency affects cleaning efficiency by determining the cavity (bubble) size, and must be selected for each cleaning application. Low frequencies generate large, but relatively few, cavities with high cleaning power, while high frequencies generate a great number of small cavities with good penetrating capability.

Combining Cleaning Cycles

Degreasing equipment can be designed with any combination of these basic cleaning cycles to meet the specific cleaning requirement. To select the proper cycle for a specific cleaning application, consideration should be given to the nature and number of parts, the type of contaminant to be removed, the parts-handling method, and any physical limitations (e.g., floor space, ceiling

height).

In addition, specialized equipment has been developed for use with vapor degreasers. For example, when the work pieces are of a type or configuration that make proper cleaning and draining difficult, they can be rotated in immersion-type degreasing equipment. To protect the surface finish of the parts, trays can be used to hold each piece individually and the trays placed in fixtures that revolve. Moreover, wire mesh belt conveyors can be used to clean miscellaneous small parts in equipment employing the vapor, spray, or immersion cycles.

Precision Cleaning

Precision cleaning applications generally have been defined as those operations that satisfy the following criteria:

- o meet critical cleanliness standards for particulate or organic contaminants;
- o are used for cleaning components with sensitive compatibilities; and/or
- o are used to clean components that are costly.⁸

Industries considered to have a preponderance of precision cleaning uses are those involved in the manufacture of electronic, medical, aerospace, and defense system equipment and component ~ . ~

* * * * *

8 This definition is consistent with those outlined by the United Nations Environment Programme (UNEP, 1991a) and the U.S. Environmental Protection Agency (EPA, 1991a).

9 Precision cleaning is necessary in a variety of other industries where the geometry or composition of the component imposes special requirements on the cleaning process.



Sources *O*f Solvent *L*oss

There are two major loss mechanisms in solvent cleaning operations (SRRP, 1992). The first, emissions to the atmosphere, includes process and fugitive emissions that compose a significant fraction of total emissions. The second mechanism is the quantity of solvent lost in the disposal of waste materials. In addition, a small amount of solvent may be lost to water each year (SRRP, 1992).

Atmospheric Emissions

Solvent emissions occur both directly and indirectly from all types of solvent cleaning equipment. Major routes of atmospheric emissions include loss of solvent from the tank due to diffusion from, and disturbance of, the vapor layer, dragout of solvent and/or vapor with cleaned parts, fugitive emissions from equipment leaks, and losses during storage and handling of solvent and solvent waste. Increased solvent losses also can result from poor maintenance of the degreasing equipment. The quantity of these emissions depends on the solvent used, the type, design, and size of equipment, the number of hours of operation, the operating techniques, and the types of material

being handled. While the loss level is highly dependent on operator performance, emissions from vapor degreasers, both open-top and in-line, are caused primarily by diffusion, disturbance of the vapor zone, and solvent dragout.

Diffusion losses occur at the vapor/air interface of the cleaning system. They result from the tendency of the solvent vapor molecules to migrate from a region of high concentration at the air-vapor interface to a region of low concentration at the top of the machine (**Figure 4**). In general, diffusion losses can be minimized by reducing the vapor-/air interface where possible (Weemes, 1990). To further minimize these losses, the degreaser should be designed specifically for the solvent being used (**Figure 5**).¹⁰

Disturbance losses occur when a perturbation of the vapor zone within the degreaser causes air to enter the machine and to become saturated with solvent vapors. The solvent in the mixture generally cannot be condensed and is lost to the atmosphere as the vapor blanket is restored. Disturbance losses are caused by convection currents set up by tem-

¹⁰ The solvent's boiling point, vapor density, and latent heat of vaporization are important considerations in the thermal balance and other design aspects of the degreasing equipment.

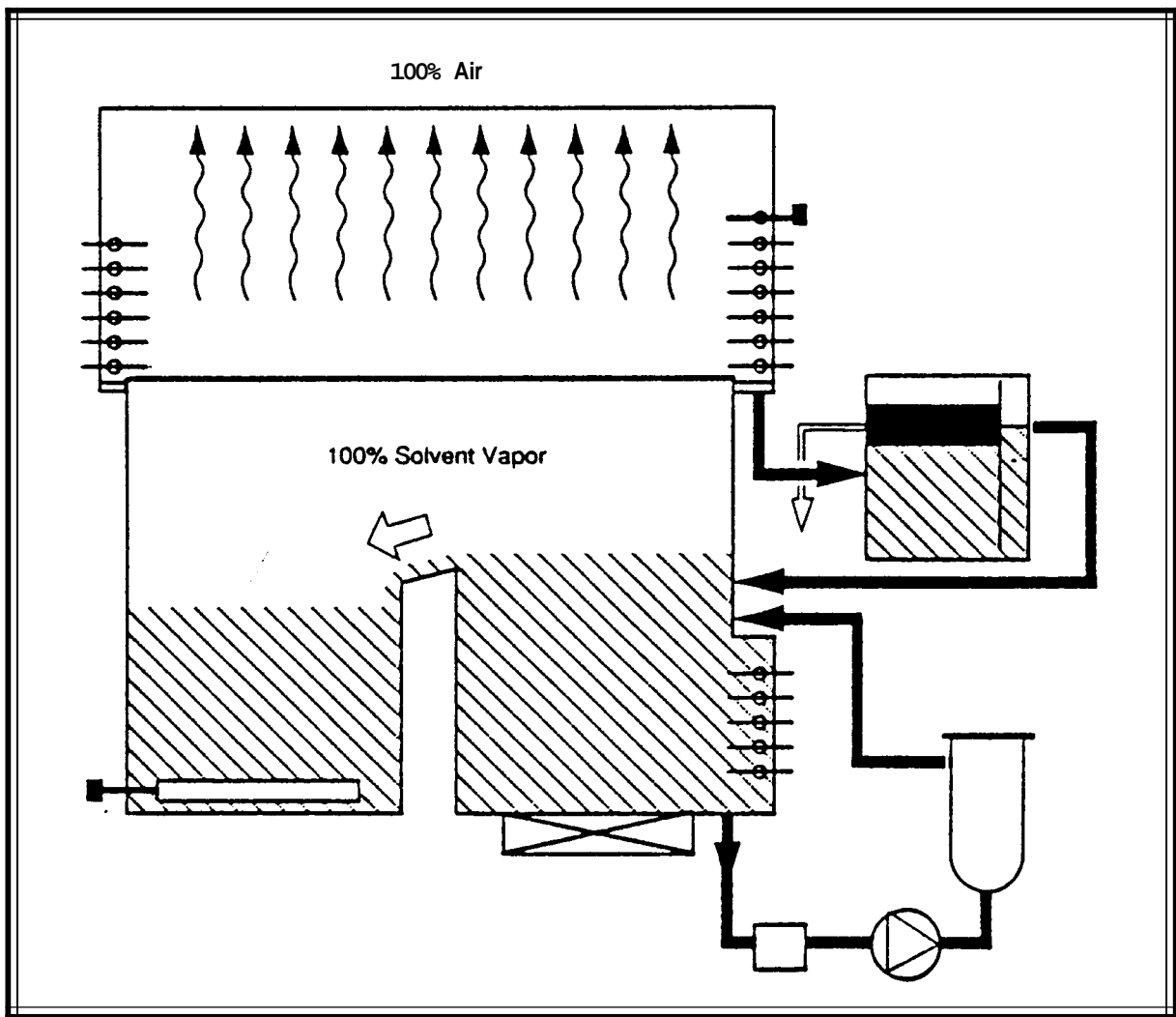


Figure 4. Diffusion of Solvent Vapors from an Open-Top Degreaser (Weemes, 1990)

perature differences within the freeboard zone of the degreaser, by excessive air currents across the top of the degreaser, and by the movement of the workload through the vapor zone (**Figure 6**).

Disturbance losses resulting from workshock (piston effect) also can be a significant contributor to emissions from open-top degreasers. Workshock occurs when the degreaser is used to clean

workloads that are larger than its design capacity." When the load is introduced into the machine, the vapor blanket at the level of the condensing coils collapses, increasing solvent losses as this blanket is restored (**Figure 7**).¹²

Solvent dragout is the third major contributor to solvent losses. If a part is not properly oriented while being carried through the cleaning system, it can cup

11 This phenomenon is a function of the rate of entry, the mass of the part, and the type of metal, as well as the surface area of the degreaser. It is most dramatic for high boiling-point solvents like perchloroethylene (Gerard, 1989).

12 Workshock emissions can be minimized by limiting the horizontal area of the load to be cleaned to 50 percent or less of the air/solvent vapor interface area (Ramsey, 1990; EPA, 1991b). This will mitigate the displacement and turbulence of solvent vapors as the load is lowered into the cleaner.

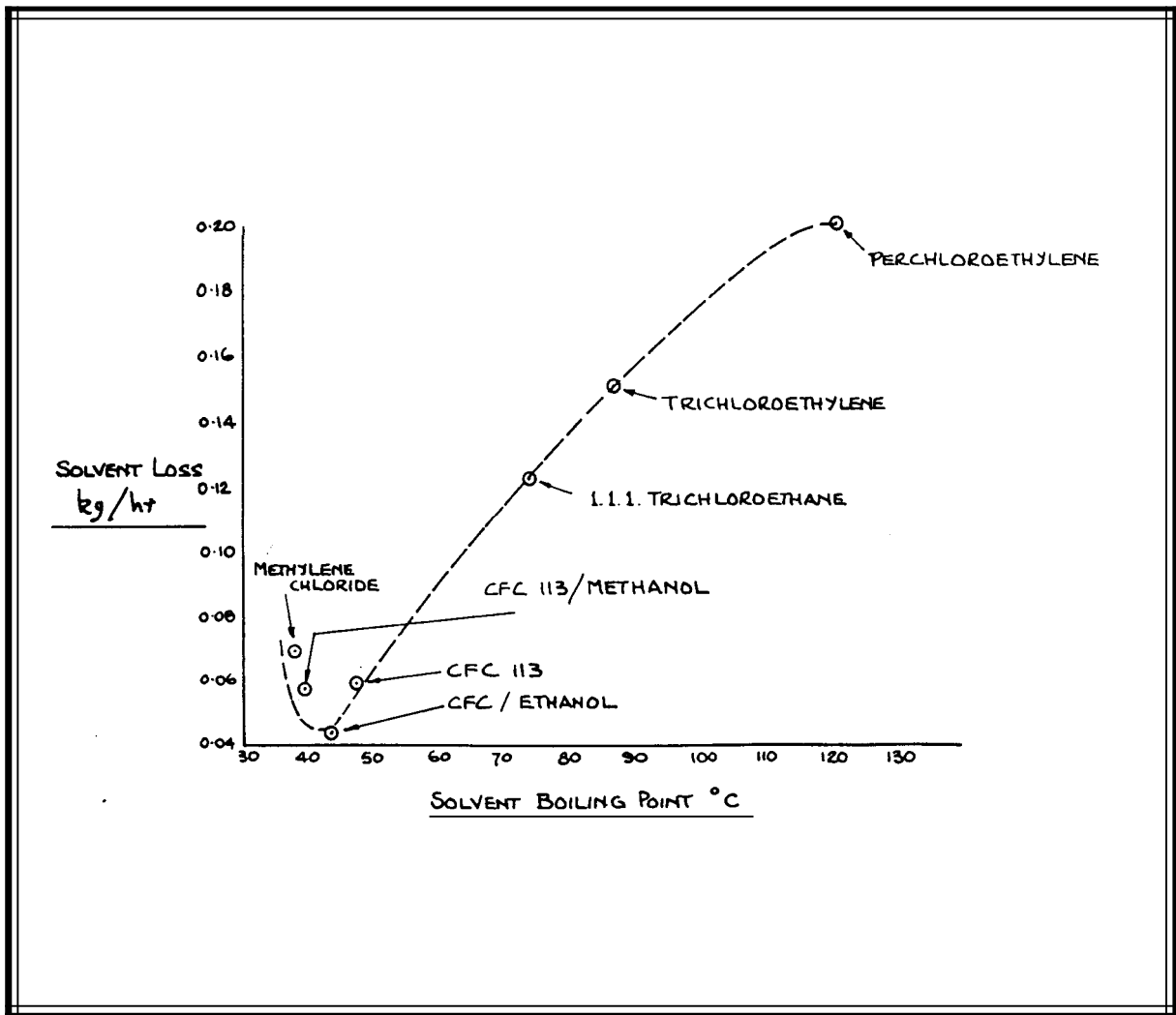
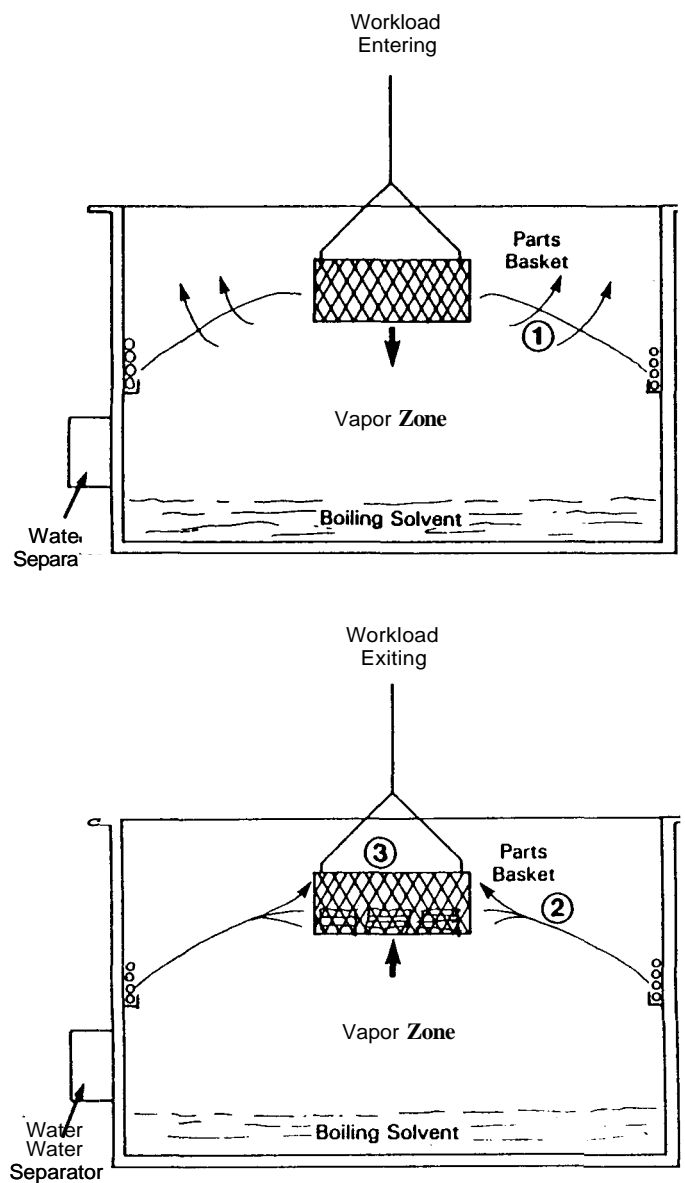


Figure 5. Diffusion Losses as a Function of Boiling Point for the Halogenated Solvents (Weemes, 1990)

or entrap liquid solvent (**Figure 8**). The part also will carry a thin film of solvent out of the equipment if it is moved too quickly through the vapor zone of the degreaser. In many cases, the parts can be oriented or rotated so that the solvent is not entrapped in pockets, recesses, and cavities. If drag-out cannot be overcome by proper orientation or rotation, methods exist to remove this solvent before it leaves the machine (see Chapter 5).

Leakage of solvent can be a problem in all systems and is compounded in large multi-stage cleaning systems that require complex piping arrangements for proper operation. In addition, extensive loss during transfer of solvent into and out of the degreaser can occur if solvent filling and draining are not performed using enclosed piping systems. Inadequate maintenance of the degreasing unit also can contribute significantly to solvent



1. Increased Diffusion and Mixing at Air/Solvent Vapor Interface due to Piston Effect, Disturbance of Vapor Layer, and Spraying
2. Vapor Entrainment and Increased Diffusion and Mixing due to Turbulence
3. Carryout of Solvent on Cleaned Parts

Figure 6. Disturbance Losses Caused by Part Movement Through the Vapor Zone (EPA, 1992b)

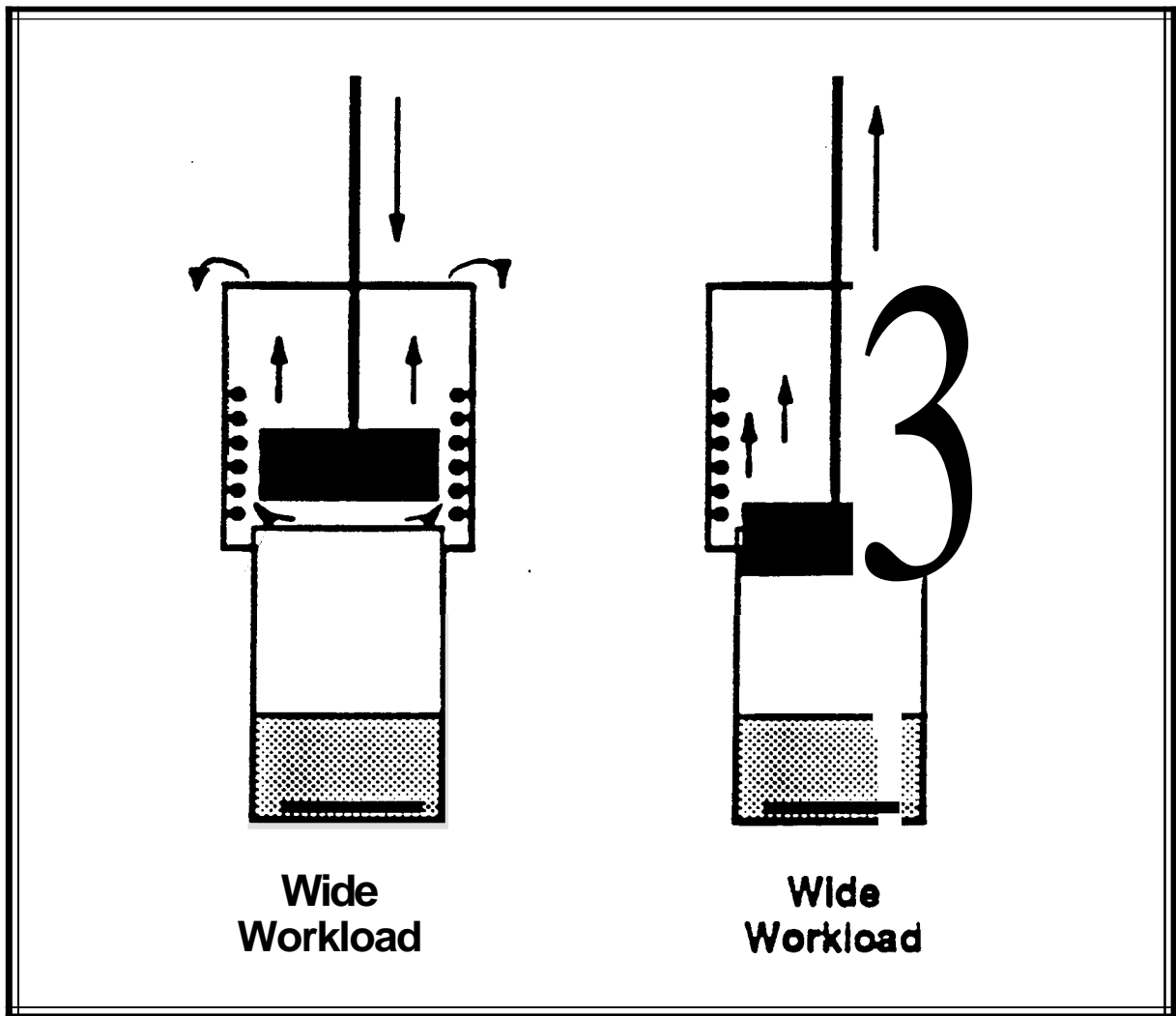


Figure 7. Workshock Losses Caused by Introduction of a Large Workload (EPA, 1991b)

losses. For example, if soils are allowed to build up on the solvent heating element, the element's thermal effectiveness will be lowered and a weak vapor blanket will be produced. In addition, the accumulation of scale in condenser coils can cause poor vapor control and can make it difficult to maintain the proper water flow rate and temperature of the cooling water.

Losses in Hazardous Waste

The hazardous waste generated in the cleaning process includes contaminated liquid solvent,¹³ residues from solvent stills (i.e., still bottoms) used for on-site recycling, and bottom sludge that occurs in cleaning degreaser tanks (SRRP, 1992). Much of this solvent can be reclaimed for reuse on-site or by a com-

13 The quantity of waste generated in a vapor degreasing operation is the sum of all soils removed from the parts plus a variable amount of solvent residue. The amount of residue will depend on the sophistication of the on-site reclamation system (see Chapter 7).

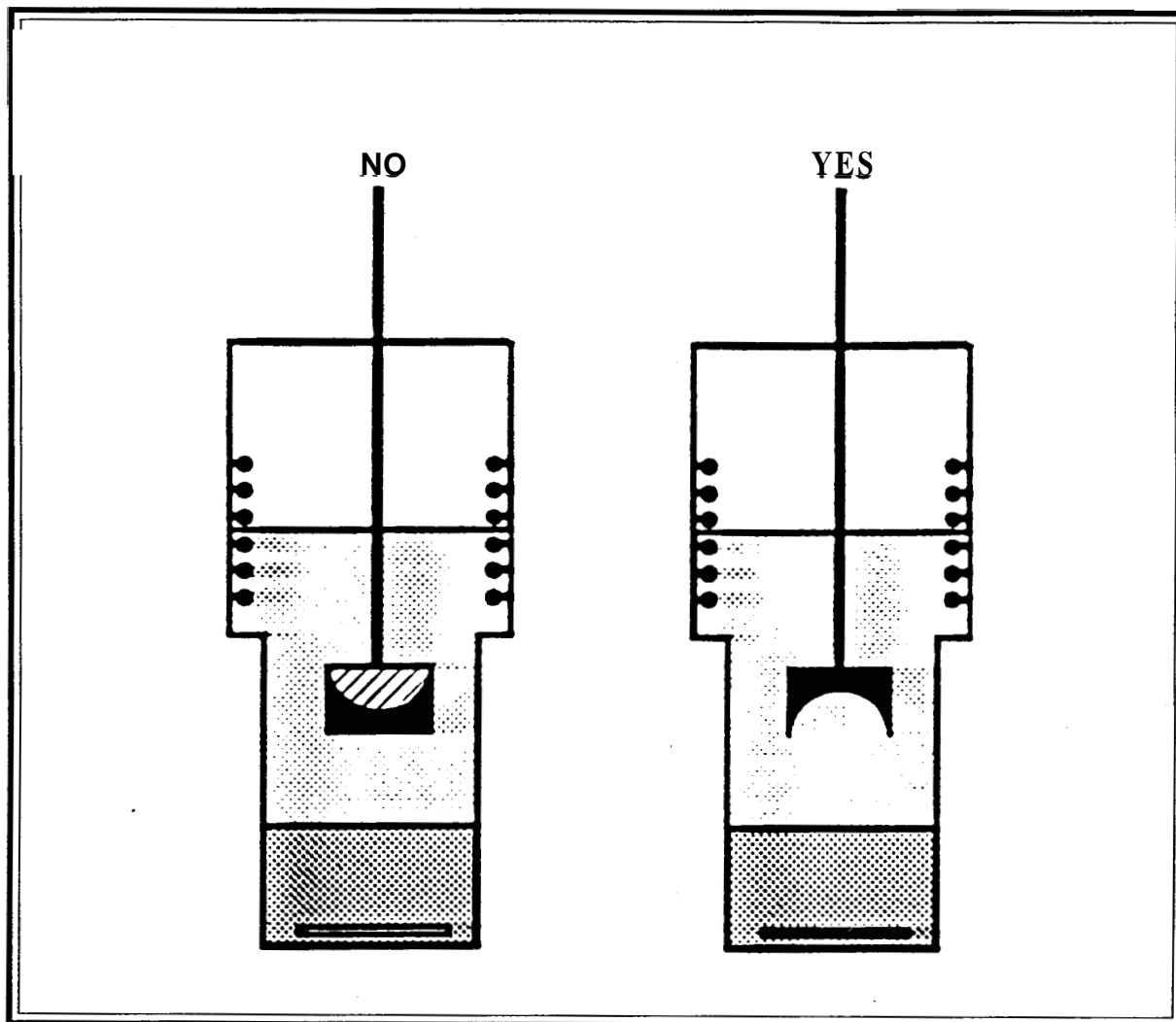


Figure 8. Part Orientation to Minimize Dragout
(EPA, 1991b)

mercial recycler, but some residual solvent will remain that requires disposal. Since the land disposal of solvent waste was prohibited in 1986,¹⁴ these residues generally are burned for energy recovery in cement kilns and industrial boilers (SRRP, 1992).

* * * * *

¹⁴ Land disposal of solvent residues from degreasing and recovery activities is prohibited unless the residue is treated to meet EPA treatment standards (40 CFR 268).



Vapor *E*mission *R*eduction

A variety of options are available for controlling solvent emissions to the ambient environment.¹⁵ These options can be classified as either one of two types: (1) those designed to minimize the release of solvent from the cleaning machinery and related equipment, and (2) those designed to recover or treat solvent emissions from the unit. While techniques designed to minimize emissions are most desirable, some solvent losses still occur. As less solvent is permitted to escape the degreasing unit, efficient recovery of that solvent may become more difficult (SRRP, 1992).

As described in Chapter 3, atmospheric losses from solvent cleaning operations can result from either process or fugitive emissions. Fugitive emissions generally can be addressed through housekeeping measures to ensure proper maintenance and operation of the equipment. To address process emissions, a number of techniques have been developed. These methods range from relatively simple changes like covers and freeboard extensions to new equipment designs.¹⁶ The potential emission reductions that can be

achieved with these methods are described in this chapter and are summarized in **Table 2**.

Housekeeping

The use of housekeeping and work practice techniques can help to prevent unnecessary solvent losses. These techniques include routine checks for leaks, proper handling and storage of solvent and solvent wastes, and regular maintenance of the cleaning system to ensure efficient operation.

Considerable progress has been made to minimize plumbing leakage problems through the use of special Teflon-based pipe dope, welded fittings, flanged and compression fittings, and solder joints for copper fittings (Gerard, 1989). In the event leaks do develop, however, a routine equipment inspection program will help locate them while they are still small.¹⁷ Potential solvent emissions then can be controlled by promptly repairing or replacing cracked gaskets, malfunctioning pumps, water separators, and steam traps.

15 Depending on the location of the facility, implementation of some of these control options may trigger local permitting requirements.

16 While many of these techniques may be applied to cold cleaning, the following discussion will focus on emission control for vapor degreasing with halogenated solvents.

17 Halide detectors can provide assistance in identifying small leaks.

Table 2. Effectiveness of Various Control Techniques for an Open-Top Vapor Degreaser ¹		
Control Technique	Control Efficiency (%)	
	Idling ²	Working
Manual Cover	40	--
FB Ratio 0.75 ==> 1.0	20	20
1.0 ==> 1.25	10	10
Reduced Condenser Temp.	40	40
Reduced Room Draft (100 ==> 50 fpm)	50	50
Refrig. FB above freez.	40	40
below freez.	40	40
Hoist	--	35
Dwell	--	30
Automated Cover	40	40

1 Operating schedule - 6 hrs working, 2 hrs idle, 16hrs downtime.
2 Breakdown of total solvent loss: working - 69%; downtime - 22%; idling - 9%
Source: EPA, 1992c.

Solvent losses during filling, draining, and transfer can be reduced by performing these operations with enclosed piping systems. Pumping the solvent directly from the drum to the cleaner can reduce spills and evaporative losses. Pumping the solvent into the cleaner with submerged fill piping will minimize splashing and reduce potential solvent losses. In addition, leak-proof connections can reduce transfer losses. Losses during transfer of contaminated solvent or sump bottoms from the degreaser sump to stills or waste solvent storage can be controlled by using leakproof couplings. Transfer to a vented tank or sealed containers will help reduce emissions.

Control Switches

Control switches are used routinely on vapor cleaners to prevent unsafe conditions such as vapor overflow and solvent decomposition. Although the effectiveness of these controls in reducing solvent losses has not been quantified, it is generally believed that they can protect against potentially significant emissions during upset conditions. Common types of control switches include: (1) vapor level control thermostat; (2) coolant flow switch and thermostat; (3) secondary heater switch; (4) sump thermostat; (5) liquid solvent level control; and (6) spray pump control switch (ASTM, 1989).

The vapor level control thermostat turns off the sump heat when the solvent vapor zone rises above the design operating level.¹⁸ The coolant flow switch and thermostat is designed to shut off the heat source if the coolant in the condensing coils becomes too warm or if the coolant is not flowing adequately to maintain the vapor blanket. The secondary heater switch, found on some machines, is activated when introduction of a large load causes the vapor level to fall (workshock). Secondary heaters reduce solvent loss from the resulting vapor level fluctuation.

As oils, greases, and other contaminants build up in the solvent, the boiling point of the solvent/contaminant mixture increases. Both the sump thermostat and liquid solvent level control prevent the solvent-decomposition that can occur if temperatures get too high. The sump thermostat cuts off the heat when the sump temperature rises significantly above the solvent's boiling point. The solvent level control turns off the heat when the liquid level of the boiling sump drops nearly to the height of the sump heater coils. While steam-heated units or heat-pump systems are less likely to produce solvent-decomposing temperatures, solvent level controls still can be useful for the higher boiling solvents (i.e., trichloroethylene and perchloroethylene) to prevent soils from baking onto the heating elements. The presence of these contaminants on the elements can impair heat transfer.

If the vapor level drops below a specific level, the spray pump control switch cuts

off the spray pump until the normal vapor level is resumed. While it is not used as often as the other safety switches, this control can prevent emissions that otherwise would occur. The spray pump control switch also may include a feature to cut off the spray pump if spraying is outside the vapor zone.

Startup/Shutdown Procedures

Significant solvent emissions have been found to occur if the condensing coils are not operating when the degreaser is first turned on and after the degreaser is turned off. Procedures for start-up of the solvent degreaser may include starting the condenser coolant flow prior to turning on the sump heater. This practice helps to prevent solvent vapors from escaping from the degreaser as the vapor blanket forms.¹⁹ Continued coolant flow after the sump heater is turned off can prevent solvent vapors from escaping before they condense. Cleaners that operate with a heat pump, however, may not be able to accommodate independent control of heating and cooling if the heat input and condensation are part of the same thermodynamic cycle.

Reduced Room Drafts/Enclosure

In industrial manufacturing settings, vapor degreasers often are operated in high draft areas. Such air movement over the degreaser can increase both diffusion and convection losses by creating turbulence in the degreaser. The available data indicate that reducing room drafts to calm conditions²⁰ over an

18 The following vapor thermostat settings are recommended (ASTM, 1989): methylene chloride - 95°F (35°C); CFC-113 - 105°F (41°C); 1,1,1-trichloroethane - 130°F (54°C); trichloroethylene - 160°F (71°C); and perchloroethylene - 180°F (82°C).

19 As described below, much larger savings can be achieved with the use of a below-freezing refrigerated chiller (Weemes, 1990).

20 Air flows of 50 feet per minute or less (EPA, 1989).

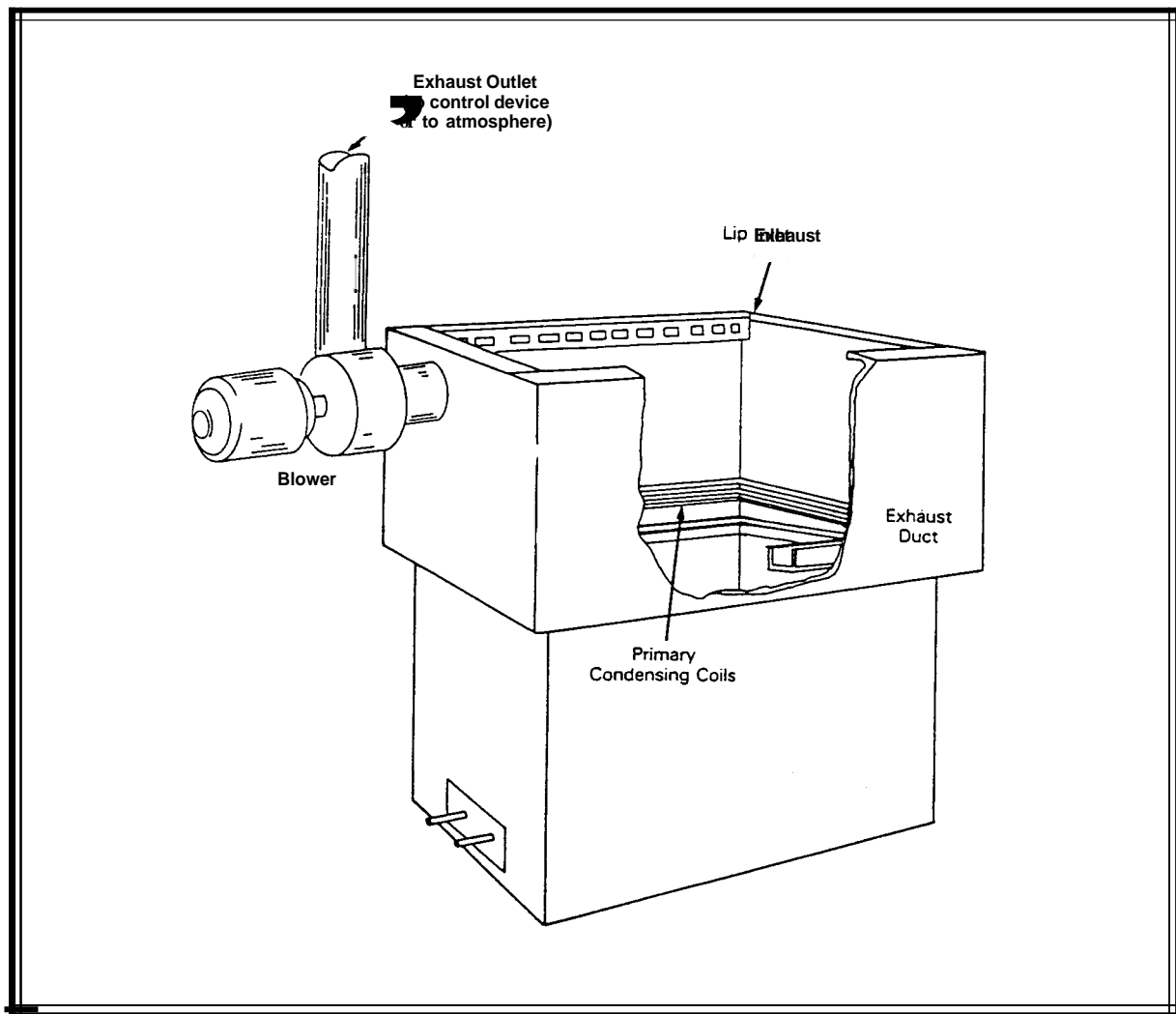


Figure 9. A Lip-Vent Exhaust System (SRRP, 1992)

open-top vapor degreaser corresponds to a 43-percent reduction in emissions during working conditions, when compared to operation in room drafts of 130 feet per minute (fpm), and a 58-percent reduction from working emissions under 160-fpm draft conditions (EPA, 1989). Many open-top degreasers in operation today employ lip-vent exhaust systems designed to capture solvent vapors from the degreasers and carry them away from operating personnel (**Figure 9**). These

exhaust systems act much like room drafts to disturb the vapor layer and to increase solvent losses. Available data indicate that a lip exhaust, even when properly operated, can double solvent consumption (EPA, 1989). If these solvent vapors are not recovered with vapor recovery equipment (described in Chapter 5), lip-vent exhausts can significantly increase overall emissions (EPA, 1989; SRRP, 1992).

Properly designed enclosures for the open-top area of a degreaser can effectively reduce idling and workload losses. By creating an enclosed environment, solvent diffusion is reduced and controlled. As with the effective use of covers discussed below, an enclosed design also minimizes the effects of room air drafts by allowing the equipment to be open to the ambient environment only when parts are being loaded or unloaded. EPA reports that such systems can reduce emissions by 42 to 67 percent (EPA, 1989). Enclosure can greatly reduce operator exposure to the solvent, without the use of a lip-vent system, but may require the use of hoists and remote spray control.

Down-Time Covers

Covers can minimize convection losses during idle periods and when the equipment is not in operation (i.e., down-time periods) in open-top degreasers by minimizing air drafts that disturb the air/solvent interface. Manual covers are normally provided as standard equipment, and can be flat-hinged, sliding, or roll-top. Hinged covers are not recommended because opening and closing these covers can disturb the vapor layer and unnecessarily expose the operator (EPA, 1989). Flat covers that slide horizontally off the machine have been found to reduce the disturbance to the vapor layer. It is generally recommended that manual covers fit well and should be handled carefully to ensure that they do not become bent or otherwise damaged (EPA, 1989).

Degreasers also can be retrofitted with electrically powered covers. For larger degreasers where covers can not easily be moved manually, it is generally desirable to have such powered (i.e., mechanically assisted) or automated covers. Powered, biparting covers can be designed to close around hoist cables that hold the parts inside the degreaser, providing virtually complete enclosure during the cleaning phase. These biparting covers can reduce both idling and working losses due to vapor disturbance by 38 percent under calm conditions and by 53 percent when room drafts are present (EPA, 1989). The most advanced biparting systems are automated to coordinate cover movement with the lowering of the parts into the degreaser. This design further minimizes the period of time that the cover is opened.

Although in-line degreasers are enclosed by design, additional emission control can be achieved by minimizing air drafts inside the cleaner. This is especially true for machines with openings at opposite ends (e.g., monorail cleaners). Designing the machine with a U-bend can help to eliminate air flow through the machine (Gerard, 1989). For many in-line cleaners, the addition of silhouette openings (providing only enough opening for the part to enter and exit), hanging flaps, and internal baffles also can prevent air flows (Gerard, 1989).

Freeboard Height

The freeboard height is the distance from the top of the solvent/vapor interface to

the top of the degreaser. Higher freeboards can reduce diffusion losses by lengthening the diffusion path or column, and can reduce convection losses by minimizing the effects of air currents (EPA, 1991b). Although simple, this method can be very effective in limiting solvent losses from open-top degreasers.

The absolute height of the freeboard is not the only factor, however, in determining the potential for convection losses. As the width of the degreaser increases, its susceptibility to air drafts also increases. To compensate for the increased width, the freeboard height must be proportionally increased. Consequently, it is common to refer to a degreaser's freeboard ratio, determined by dividing the freeboard height by the interior width of the equipment.²¹ In this way, two cleaners of differing sizes and widths, but having identical freeboard ratios, will be equally protected from drafts. While newer degreasers have freeboard ratios of 1.0 or greater, many existing units have ratios of only 0.5 or 0.75.

Under working conditions, the solvent emissions reduction associated with raising the freeboard ratio from 0.75 to 1.0 ranged from 19 to 21 percent (EPA, 1989). The emission reduction achieved by raising the freeboard ratio from 1.0 to 1.25 was somewhat lower, ranging from 6 to 10 percent (EPA, 1989). Using the above data, the efficiencies associated with raising the freeboard ratio from 0.75 to 1.25 can be expected to be about 25 percent. Little information is available to evaluate the effect of raising the free-

board ratio on solvent emissions under idling conditions. Based on the few tests that have been conducted, the control efficiency is estimated to be about the same as for working conditions (EPA, 1992c).

The freeboard ratio can be increased easily and inexpensively on existing equipment by fabricating a freeboard extension. Because it will be well above the vapor zone, the extension does not need to be welded to the existing freeboard (ASTM, 1989). On some machines, however, a higher freeboard may make it difficult for an operator to easily lower parts into the machine. In these cases, a hoist or an elevated work platform generally can be used to overcome the problem of machine height and reduce workload related losses.

For small open-top machines, the absolute freeboard height can be an important factor in solvent loss due to diffusion. Despite having a high freeboard ratio, very small machines may not have sufficient total freeboard height to prevent accelerated diffusion losses, even in calm environments. Industry tests show that solvent loss rates can increase substantially with absolute freeboard heights of less than approximately 12 inches (EPA, 1989).

Another strategy related to raising the freeboard for emission control is the design of narrower cleaners. For the same air/solvent vapor interface area, a square configuration is more susceptible to room drafts than a long narrow rectangular design. This is especially true if

21 The freeboard width is the largest width dimension of the air/solvent vapor interface that is directly exposed to the atmosphere.

the cleaner can be oriented in the room so that any drafts blow across the narrower dimension.

Lower Primary Condensing Coil Temperature

Although primary condenser coils are standard equipment on all degreasers, the temperature at which these coils are maintained has been shown to affect solvent losses during idling periods (EPA, 1989). A lower-temperature primary condenser, using chilled water or a refrigerant as opposed to tap water, may significantly lower diffusion losses. In addition to more effectively condensing the solvent vapors, a colder primary condenser temperatures may act to cool the air above the air/solvent vapor interface.

For 1,1,1-trichloroethane, a 41-percent reduction²² in emissions from an open-top degreaser under light working conditions was obtained by reducing the primary condenser temperature from 85°F to 50°F (EPA, 1989). Similarly, idling emissions of 1,1,1-trichloroethane were reduced by 39 percent (compared to uncontrolled idling emissions) by reducing the primary condenser temperature from 85°F to 50°F (EPA, 1989). These tests may overestimate the potential for emissions reductions since many 1,1,1-trichloroethane degreasers already employ refrigeration or chilled water systems operating at less than 85°F. However, even a 20° reduction in primary condenser temperatures (from 70°F to 50°F) achieves an emission reduction of 29 percent (EPA, 1989).

The effect of chilling or refrigerant systems will be particularly noticeable in the summer months, when the temperature of the tap, cooling tower, or well water that would otherwise be used can rise significantly. This can result in undesirable diffusion loss increases, the magnitude of which will vary by solvent. Reductions in trichloroethylene emissions would be expected to be comparable to those for 1,1,1-trichloroethane, while the temperature of the primary coils would not have as great an effect on perchloroethylene emissions. Reductions in CFC-113 emissions have been found to be more dramatic than those for 1,1,1-trichloroethane (EPA, 1989). The same dramatic reductions would be expected for methylene chloride.

One drawback to lowering primary condenser temperature is that it promotes condensation of ambient water vapor, especially in humid climates (EPA, 1989). Nearly all vapor degreasers are equipped with a water separator since water may enter the degreaser from the air and condense on the cooling coils along with solvent vapors. In the separator the lighter water floats on top of the denser solvent and can be easily decanted from the separator (**Figure 10**). The solvent flows from the bottom of the chamber back to the degreaser. Moisture control can be further improved by lowering the temperature of the solvent/water mixture in the water separator (ASTM, 1989).²³ It is important that machines employing low-temperature condensation contain adequately sized water separators to minimize water contamination.

22 Compared to emissions from an uncontrolled machine under the same working conditions.

23 Cooled condensate encourages better separation of water in the separator.

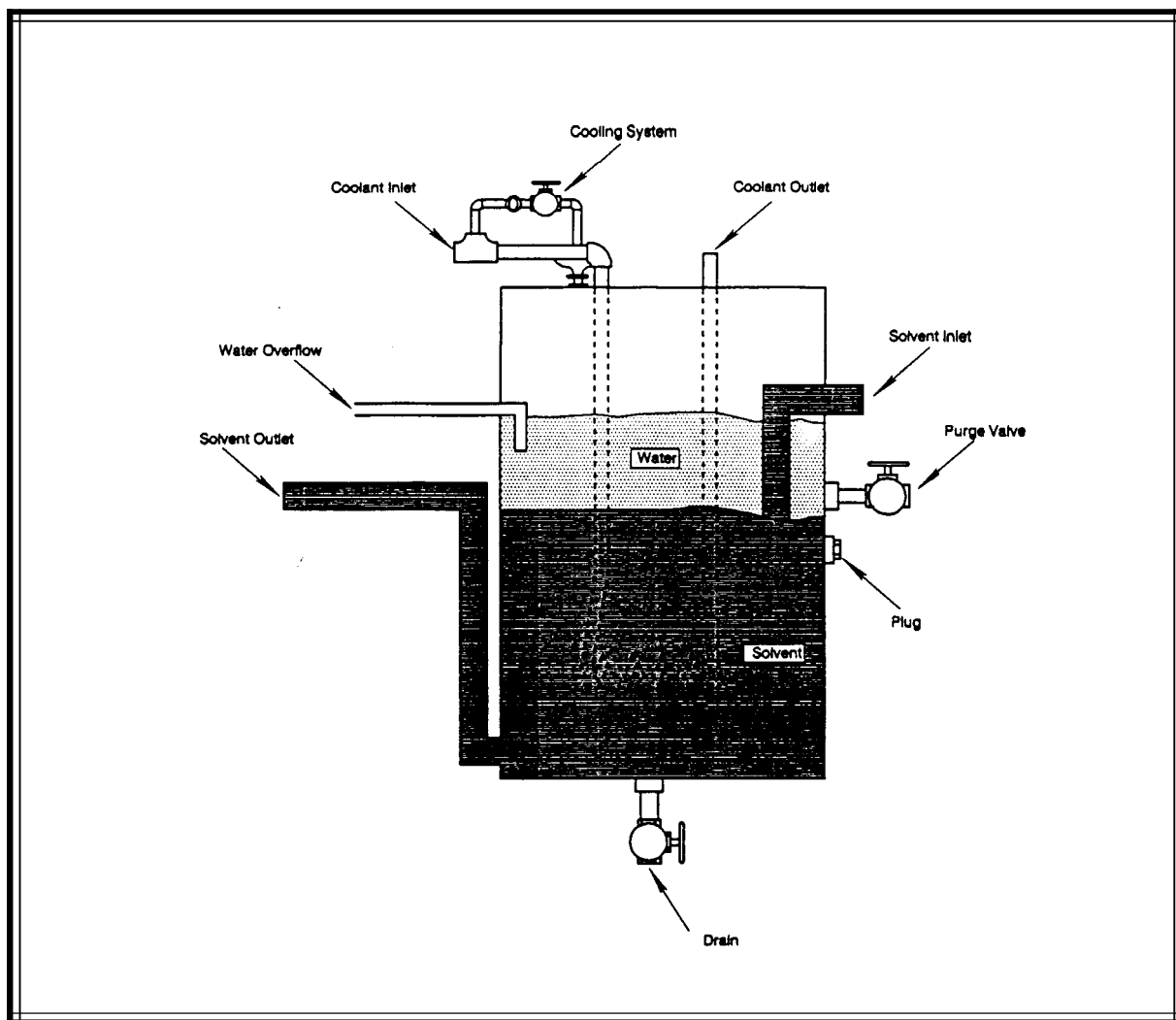


Figure 10. Water Separator with Cooling Coil (EPA, 1992a)

If the solvent formulation contains water-extractable components (e.g., aliphatic alcohols), they may be lost in the condensation of water vapors (SRRP, 1992). In such cases, it may be advisable to replace the water separator with a molecular sieve solvent dryer or to add a dryer. Water contamination also can have an adverse effect on water-soluble stabilizers present in many solvent formulations, particularly 1,1,1-trichloroethane formulations.

Refrigerated Freeboard Chiller

A refrigerated freeboard chiller controls diffusion losses from the degreaser with the addition of refrigerated condensing coils above the primary coils. While the primary condensing coils define the vapor zone, the freeboard chiller cools the air above the vapor zone and creates a second cold air blanket. As described above, such a cold air blanket suppresses solvent emissions. Freeboard chillers are

available on most new degreasers, and can be added to existing degreasers.

Two types of freeboard chillers are available: above-freezing refrigerated devices that operate at temperature ranges around 41°F (5°C); and below-freezing devices that operate with refrigerant temperatures usually in the range of -4°F to -22°F (-20°C to -30°C).

The positioning of the freeboard chiller coils also may affect the level of emission control achieved (EPA, 1992a). In a series of recent tests, the operation of the secondary condenser coils positioned either immediately above or overlapping the main condenser coils yielded lower diffusion rates (Ramsey, 1990). The greater the distance between the secondary coils and those of the main condenser, the lower the effectiveness of the chiller device. Other data suggest, however, that the relative position of the primary and secondary coils is not a significant factor, provided that measures are taken to prevent solvent losses resulting from convection currents established by the presence of the two sets of coils (**Figure 11**) (Weemes, 1992).

Several tests have been conducted on the effectiveness of below- and above-freezing freeboard chillers on open-top degreasers. For working conditions, above-freezing chillers achieved an average reduction of diffusion losses of 1,1,1-trichloroethane of about 37 percent (EPA, 1989) and up to 44 percent for trichloroethylene.²⁴ Tests using below-freezing chillers showed efficiencies of between 28 to 52 percent using 1,1,1-trichloroethane,

methylene chloride, or CFC-113. For idling conditions, the emission reduction was 18 percent for an above-freezing unit with CFC-113, and ranged from 11 to 58 percent for below-freezing chillers with CFC-113 or 1,1,1-trichloroethane (EPA, 1989).

Very few tests of the effectiveness of freeboard chillers in in-line degreasers have been conducted. The data available for CFC-113 and perchloroethylene indicate that below-freezing units can provide significant emissions reductions, while above-freezing units may only provide limited solvent savings (EPA, 1989).

The emission reduction achieved with the addition of a freeboard chiller may not be as significant in degreasers operating with a refrigerated primary condenser (EPA, 1989). In tests with CFC-113, the benefit of a below-freezing chiller was found to decrease as primary condensing temperature decreases. In fact, very little reduction was obtained by adding a freeboard refrigeration device to an open-top degreaser using CFC-113 that was operated with a primary condenser temperature of 40°F (EPA, 1989).²⁵ This effect is not nearly as pronounced for 1,1,1-trichloroethane, where the addition of a below-freezing freeboard refrigeration device to an open-top degreaser with a primary condenser temperature of 50°F still reduced emissions by more than 50 percent.²⁶ More recent data using CFC-11 as a surrogate for the hydrochlorofluorocarbons (see Chapter 8) indicated that operation of the primary condenser at 45°F, and the secondary chiller at 0°F,

24 Compared to uncontrolled emissions.

25 A similar effect can be expected with methylene chloride.

26 Similar reductions would be expected for trichloroethylene and perchloroethylene emissions.

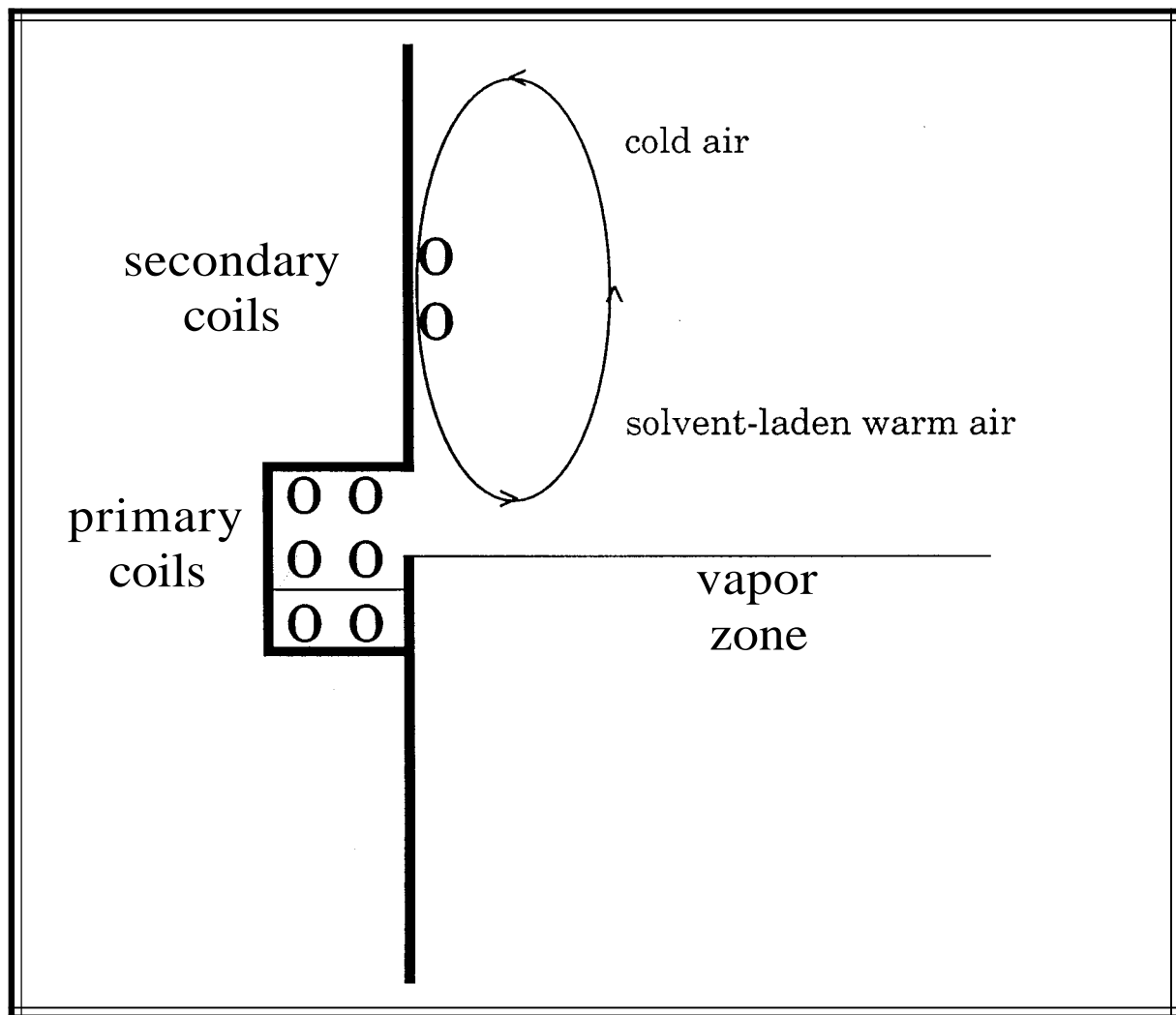


Figure 11. Convection Currents Created by a Refrigerated Chiller (Weemes, 1992)

decreased diffusion losses (Ramsey, 1990). In that case, however, the placement of the chiller coils in relation to the primary condenser coils was found to be the more critical factor.

Freeboard chillers also are effective in dehumidifying the air above the vapor line and, thereby, controlling the introduction of water into the degreaser. The water is collected in a condensation

trough located beneath the coils, and routed to a water separator to remove any accompanying solvent. To minimize the water contamination of the solvent, the solvent/water mixture generated from the freeboard chiller can be directed to a second water separator (distinct from the separator employed for the condensate from the primary condensing coils) for removal.

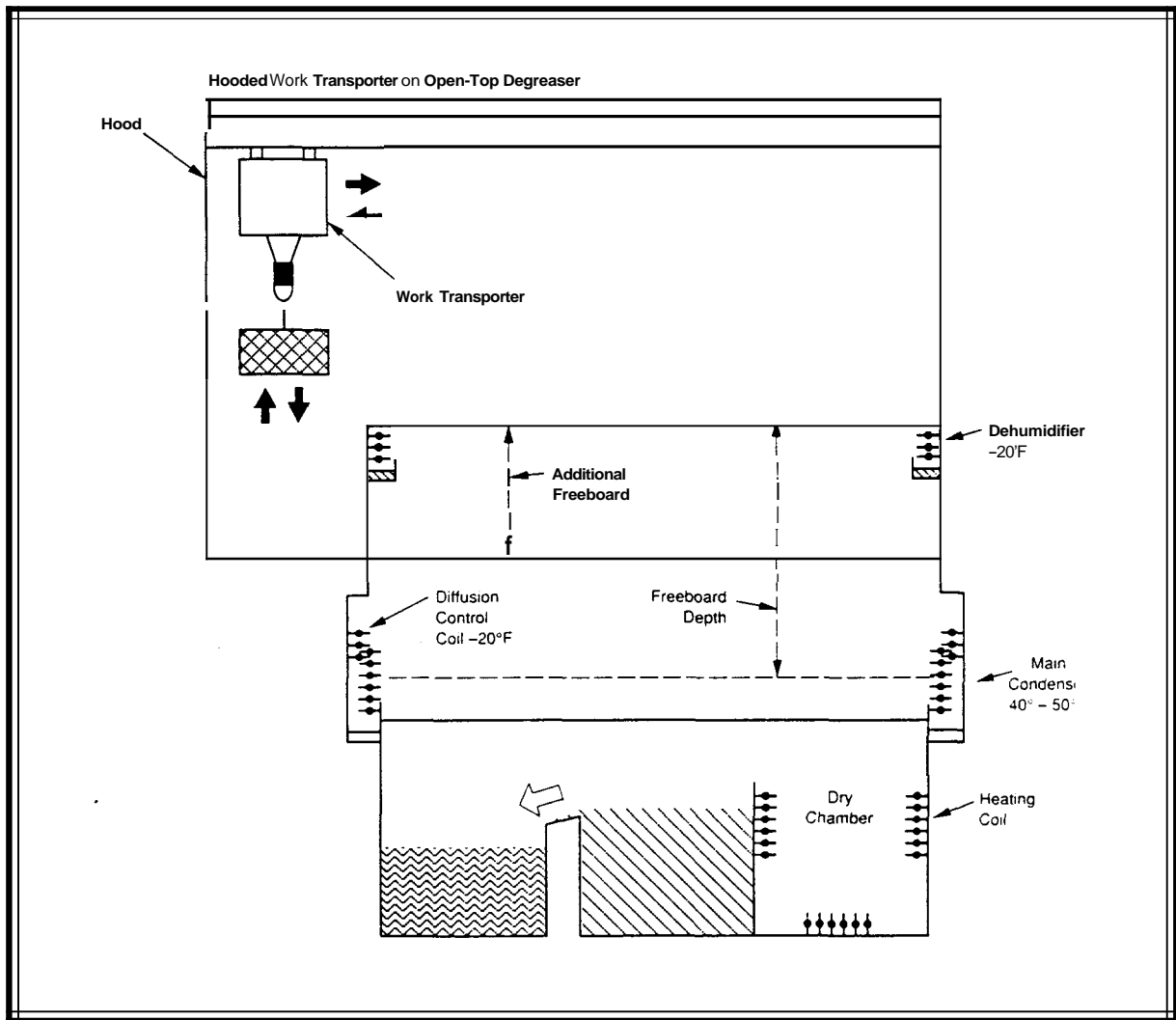


Figure 12. A Second Set of Low-Temperature Coils for Moisture and Vapor Control (Ramsey, 1990)

Due to the low operating temperatures of below-freezing refrigeration units, the water condensate from the surrounding air, along with some solvent, freezes on the chiller coils. If allowed to remain, this ice layer can reduce heat transfer efficiency. Consequently, provision is made for a timed defrost cycle to melt the water/solvent ice that may form on the coils. The melted water/solvent mixture drains to the trough located below the

freeboard refrigerated coils and is directed to a water separator. The need to periodically defrost a below-freezing freeboard refrigeration device can somewhat offset the performance advantage of below-freezing chillers (EPA, 1989; 1992c).

Placement of a second set of low-temperature peripheral coils above the freeboard chiller (**Figure 12**), however, was found

to provide an effective barrier to moisture infiltration (Ramsey, 1990). By preventing ice formation on the secondary condenser coils, periodic defrosting of this condenser may not be required and the resulting upset of the condenser equilibrium conditions may be avoided. The addition of a third set of condensing coils also was found to produce an overall decrease in the vapor concentration throughout the freeboard zone.

It should be noted that freeboard refrigeration devices primarily reduce diffusion losses.²⁷ During working conditions solvent losses are mostly due to dragout of solvent on parts. These dragout emissions usually exceed those caused by diffusion.

Spray Containment

The addition of solvent spray systems to degreasing units can create turbulence within the vapor blanket and result in higher solvent losses. If sprays are necessary, the following techniques can be employed to reduce potential turbulence: (1) the solvent should be sprayed beneath the vapor blanket; (2) the solvent temperature should be maintained as close to the boiling point as possible; and (3) spray unit systems should be contained with shields and baffles where possible (Gerard, 1989). With the availability of ultrasonics to enhance cleaning, however, the need for solvent sprays in cleaning operations often can be eliminated.

For open-top degreasers equipped with spray cleaning systems, excess solvent loss can be minimized by spraying within

the vapor zone and at a downward angle. Such a practice reduces liquid solvent forced out of the degreaser and minimizes turbulence which can increase convection and diffusion losses. The available data indicate that spraying five inches above the vapor line results in emissions that are ten times higher than when spraying four inches below the vapor line (EPA, 1989; Osterman, 1991). Machines equipped with permanently mounted spray nozzles eliminate the possibility of spraying outside the vapor zone. For in-line systems, shields and baffles can be used to minimize the turbulence created by a spray system (Gerard, 1989).

Recent data also indicate that the temperature of the solvent spray also can determine the potential for solvent loss. Spraying of cold solvent, which vaporizes upon contact with the hot work load, consumes heat from the vapor blanket, which increases the risk of its collapse. Spraying solvent near its boiling point minimizes the potential for vapor blanket collapse, and the loss of solvent that occurs when the blanket is reestablished (EPA, 1991b).

Transport Systems

Automatic or preprogrammed transport systems are commonly used in degreasing operations to move parts into and out of the cleaning system (**Figure 13**). Transport systems are the most effective method for controlling disturbance losses associated with work entering and leaving a degreaser and can reduce dragout losses significantly (EPA, 1989). Me-

²⁷ By drastically reducing the level of solvent saturated in the air in the vapor zone, below-freezing chillers also may help to reduce disturbance losses (Weemes, 1990).

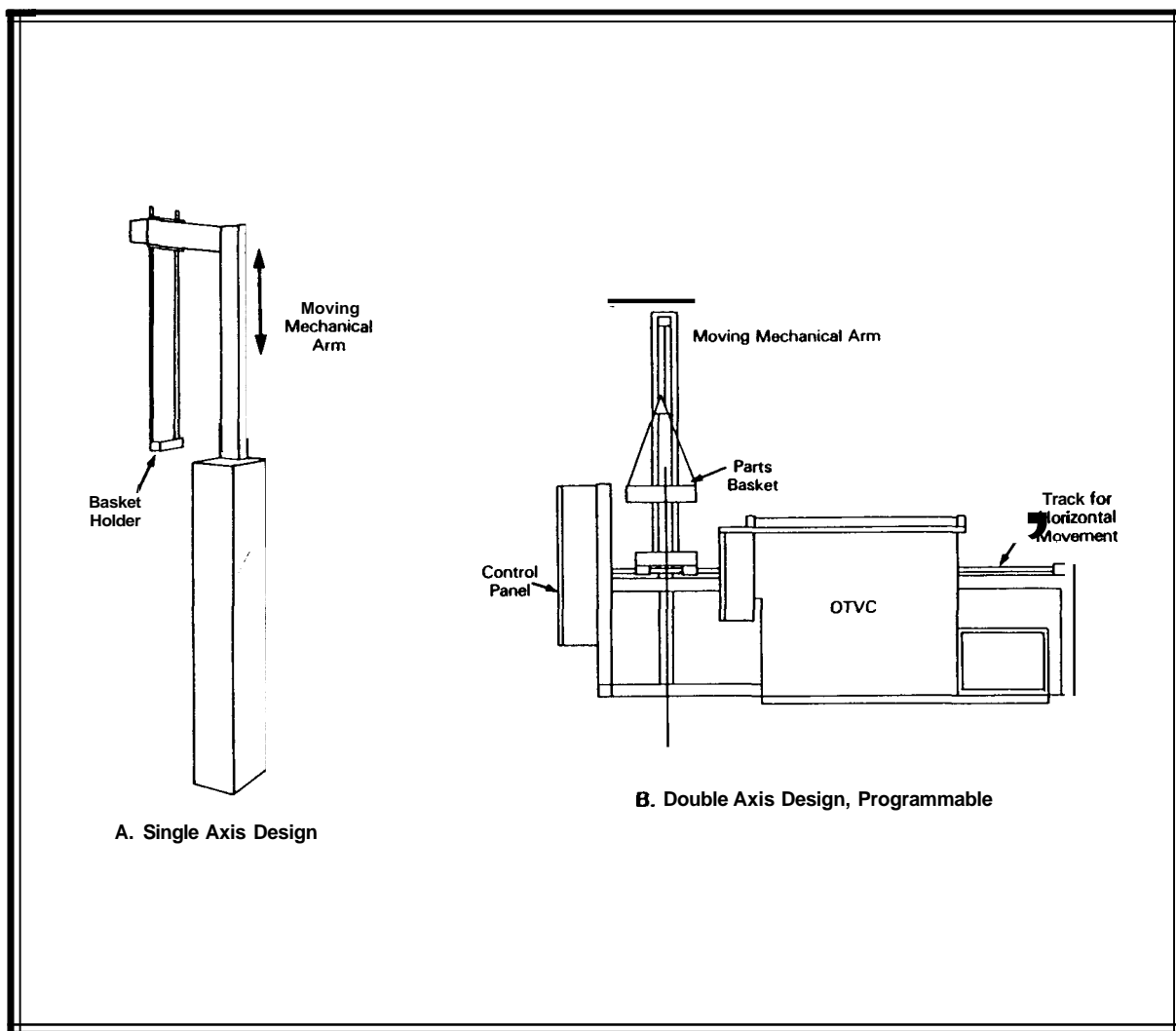


Figure 13. Automated Parts Handling Systems (EPA, 1989)

mechanical parts handling systems consistently move the parts through the degreaser at controlled speeds that are difficult to sustain manually. In addition to eliminating excess losses caused by manual operation, mechanical systems can reduce worker exposure by allowing the operator to work farther away from the cleaner (SRRP, 1992).

Mechanical parts-handling systems can

reduce the amount of dragout residue considerably by allowing the solvent to thoroughly drain from the parts before they are removed from the degreaser.²⁸ Moreover, powered rotating baskets can be installed in transport systems for in-line units to effectively limit solvent dragout on parts with recesses or blind holes that can trap solvent. In some instances, however, it may not be possible to completely eliminate dragout

28 Proper placement of parts in drainage racks to prevent the collection of solvent in depressions also can reduce dragout losses significantly.

through racking and rotating, and more elaborate control methods (described below) must be employed (Gerard, 1989).

Another advantage of mechanical parts handling is the potential for precise control of dwell time (the length of time the part remains in the vapor zone). Allowing an adequate dwell time decreases emissions by ensuring that the parts have reached the solvent vapor temperature before they are removed. Tests have shown that if a work piece has not reached the temperature of the solvent before leaving the vapor layer, a thin film of solvent remains on the surface. Hoists can be programmed to pause for a short period to allow the solvent to drain or evaporate from the parts. When the solvent has vaporized and the product is free of liquid solvent, the hoist raises the product out of the degreaser.

Although the emission reduction benefits of mechanically assisted parts handlers are generally not disputed, there are few data available to characterize the magnitude of the benefit. Test results indicate that a mechanical hoist operated at 10 fpm can reduce working losses by 28 percent, compared to a manual hoist operated at 20 fpm (EPA, 1989). Moreover, according to industry estimates, parts movement by typical human operators may be as high as 60 fpm or more (EPA, 1989). At these speeds, the working losses can be considerably higher.

In one series of tests to determine losses of 1,1,1-trichloroethane under actual working conditions, the addition of a hoist reduced losses by 38 percent (EPA,

1992a). Moreover, the addition of a 45-second dwell time decreased losses by an additional 10 percent.

The cost of purchasing, installing, and operating such devices varies widely. Both devices, however, have significant potential to reduce emissions over manual operation.

EPA guidelines and many state regulations specify a maximum vertical hoist speed of 11 fpm (EPA, 1977). Available data indicate, however, that substantial disturbance of the air/solvent vapor interface still occurs at this speed. An additional reduction in the hoist speed may reduce dragout and disturbance losses further. In one test that has been conducted, lowering the hoist speed from 11 to 3 fpm was found to result in an 81-percent decrease in total working losses of CFC-113 (EPA, 1989).²⁹

Down-Time Sump Cooling

Solvent evaporation during down time can be significant, especially for low boiling-point solvents like CFC-113 and methylene chloride. As described above, the use of downtime covers will reduce drafts and slow diffusion and convection, but will not stop losses completely. Several techniques can be used to further reduce these down-time losses. Among these techniques, cooling the solvent sump was shown in one test to reduce downtime losses considerably from an open-top degreaser (EPA, 1989).

To accomplish this, cooling coils are immersed in the solvent chamber to

29 Available data suggest that the addition of a dwell time to a transport system operated at 11 fpm can achieve comparable reductions (EPA, 1992a; 1992c).

lower the temperature of the solvent to the optimal vapor pressure for preventing diffusion losses. These coils also can drop the vapor line quickly at shutdown, lowering the losses that can occur, and can be easily installed in many cases (EPA, 1989).

To a lesser degree, solvent cooling during down-time periods can be achieved by continued operation of the refrigerated freeboard device to maintain the cool air blanket above the liquid solvent. Alternatively, down-time emissions can be reduced by pumping the solvent from the degreaser to an airtight storage drum. Of these three techniques, the use of cooling coils appears to be the most effective, reducing downtime losses by as much as 90 percent for CFC-113 and methylene chloride (EPA, 1989).

Drying Tunnel

Drying tunnels are add-on enclosures at the exit end of large in-line cleaning systems. The tunnel reduces dragout losses by containing solvent evaporating from the cleaned part before it mixes with air at the exit of the machine. Some of this solvent vapor may sink back into the vapor zone. For complete recovery, however, the drying tunnel can be connected to a vapor recovery device (see below), and the solvent vapor collected and recovered (EPA, 1989).

Drying tunnels primarily reduce dragout losses and worker exposure. Their effectiveness depends on the amount of solvent dragout that would otherwise occur and the dwell time of the parts in the

tunnel.

Superheated Vapor Drying

Superheated vapor drying is a relatively new development in cleaning machines that appears to have promise for both open-top and in-line degreasers. The technology was developed to address the problems of solvent entrapment created by cleaning certain products (e.g., printed circuit boards, heat exchange coils), and can drastically reduce or eliminate dragout losses (Ramsey, 1990). In this process, the items being cleaned are contacted with solvent vapor that is superheated to a temperature well above the normal boiling point (1.5 times or more) prior to their withdrawal from the freeboard zone. In this way, any solvent that remains on the surface of the parts is quickly evaporated.

There are two methods for creating a superheated vapor zone. The first, referred to as the static method, uses hot coils located in the vapor blanket of the cleaning system, below the condenser. These coils, heated by steam, hot water, or hot oil, radiate heat into the vapor blanket and superheat the vapor. They can be used in both open-top and in-line systems, but require that additional cooling be added above the vapor zone to absorb the excess heat (Gerard, 1989).

The second technique, the dynamic method, produces superheated vapors by recirculating the vapors through a heat exchanger (superheater) before they are blown through high velocity nozzles onto the parts. This technique also is referred

to as hot vapor recycle. Use of hot vapor recycle is generally limited to in-line systems, and requires the use of baffles to contain the turbulence created by the recirculating blower (Gerard, 1989).

While relatively common in new cleaning designs, superheated vapor drying may not be available as a retrofit option. This control method may be more cost-effective with low boiling solvents like methylene chloride and CFC-113 because of the lower heating requirements.

* * * * *





Vapor Recovery

While the control methods described above can be used to reduce emissions from degreasing equipment, some emissions will occur. In some cases, it may be possible to collect these solvent vapors with the use of carbon adsorption or vapor condensation systems. Some states have required the use of solvent vapor recovery systems and, as a result, hundreds of carbon adsorption units currently are in operation.

Carbon Adsorption

Activated carbon has been employed for many years to trap solvent vapors from air streams. As the solvent-laden air passes through the carbon bed, the solvent molecules adsorb to the surface of the carbon pellets, granules, or fibers. This technology can be used to recover low concentrations of solvent from the vapor stream of an open-top degreaser when used in conjunction with a lip-vent exhaust system. Solvent-laden air is pulled into the lip vents located at the top of the degreaser and channeled to a carbon adsorption unit. Lip-vent exhaust/carbon adsorption systems are

most commonly used on large solvent cleaners where the credit from solvent recovery helps to offset the high capital equipment cost (EPA, 1989; SRRP, 1992). As noted previously, carbon adsorbers also can be employed effectively in conjunction with drying tunnels in in-line equipment.

Like room drafts, the airflow created by the lip-vent exhaust or other system can disrupt the air/vapor interface, causing an increase in disturbance losses. Unless all of these emissions can be captured by the carbon adsorber, net solvent losses may increase. Available data indicate that a carbon adsorption system with lip-vent exhaust can reduce emissions by as much as 65 percent in an open-top degreaser. This level of vapor control, however, probably would not be achieved by most users (EPA, 1989). Because of the relative increase in emissions associated with adding a lip-exhaust, the overall effectiveness of control using carbon adsorption for open-top degreasers is likely closer to 40 percent (EPA, 1989).

Proper operation and maintenance procedures are important to maintaining the

efficiency of the carbon bed. Examples of operating procedures that have an effect on the operation of the carbon bed are:

- 1) dampers that do not open and close properly to allow the vapor-laden airstream to pass through the bed;
- 2) use of carbon that does not meet specifications; and
- 3) improper timing of the desorption cycles.

Desorption cycles must be frequent enough to prevent breakthrough of the bed, but not so frequent to cause excessive energy consumption (EPA, 1989).

Desorption of the solvent from the carbon is generally accomplished with steam (**Figure 14**). During the desorption cycle, the bed is initially heated with steam for 5 to 15 minutes, extracting the adsorbed solvent which is then separated from water contamination either physically or by distillation.

Depending upon the solvent mixture and the type of objects being cleaned, adverse effects may be encountered with carbon adsorption. Where solvent mixtures or stabilizers are used, the solvent vapor collected by the exhaust system may be richer in the more volatile components, and the recovered solvent mixture will not be identical to the fresh solvent. Also, some stabilizers or cosolvents used in solvent mixtures are water soluble and may remain in the water condensate derived from steam stripping (Higgins,

1989). This can be a particular concern with 1,1,1-trichloroethane degreasing formulations which contain relatively high quantities of acid-accepting stabilizers because of the solvent's tendency to hydrolyze in the presence of water.³⁰ The removal of these additives during the adsorption process may lead to equipment corrosion and can create a hazard for the degreasing personnel.

While carbon adsorption systems constructed from corrosion-resistant materials are available, the use of these materials can significantly increase the cost of the system. As a result, carbon adsorption with steam desorption generally has not been considered practical for use with 1,1,1-trichloroethane in the United States. Systems have been developed, however, to desorb the carbon with hot air instead of steam (see below). In addition, new adsorption materials have been developed with hydrophobic (water-rejecting) properties and higher adsorption capacity than carbon (Mertens, 1990; Hickman and Goltz, 1991; Hickman, 1992).

Condensation

As noted above, vapor condensation also can be used to directly collect solvent vapors from an air stream. Condensation traditionally has not been used in degreasing operations because of its generally lower efficiency, but is used in the state-of-the-art designs described below. In these systems, the recovery efficiency is increased by recirculating the air stream through the condenser several times (**Figure 15**). Efficiency

30 Methylene chloride also may hydrolyze in the presence of water.

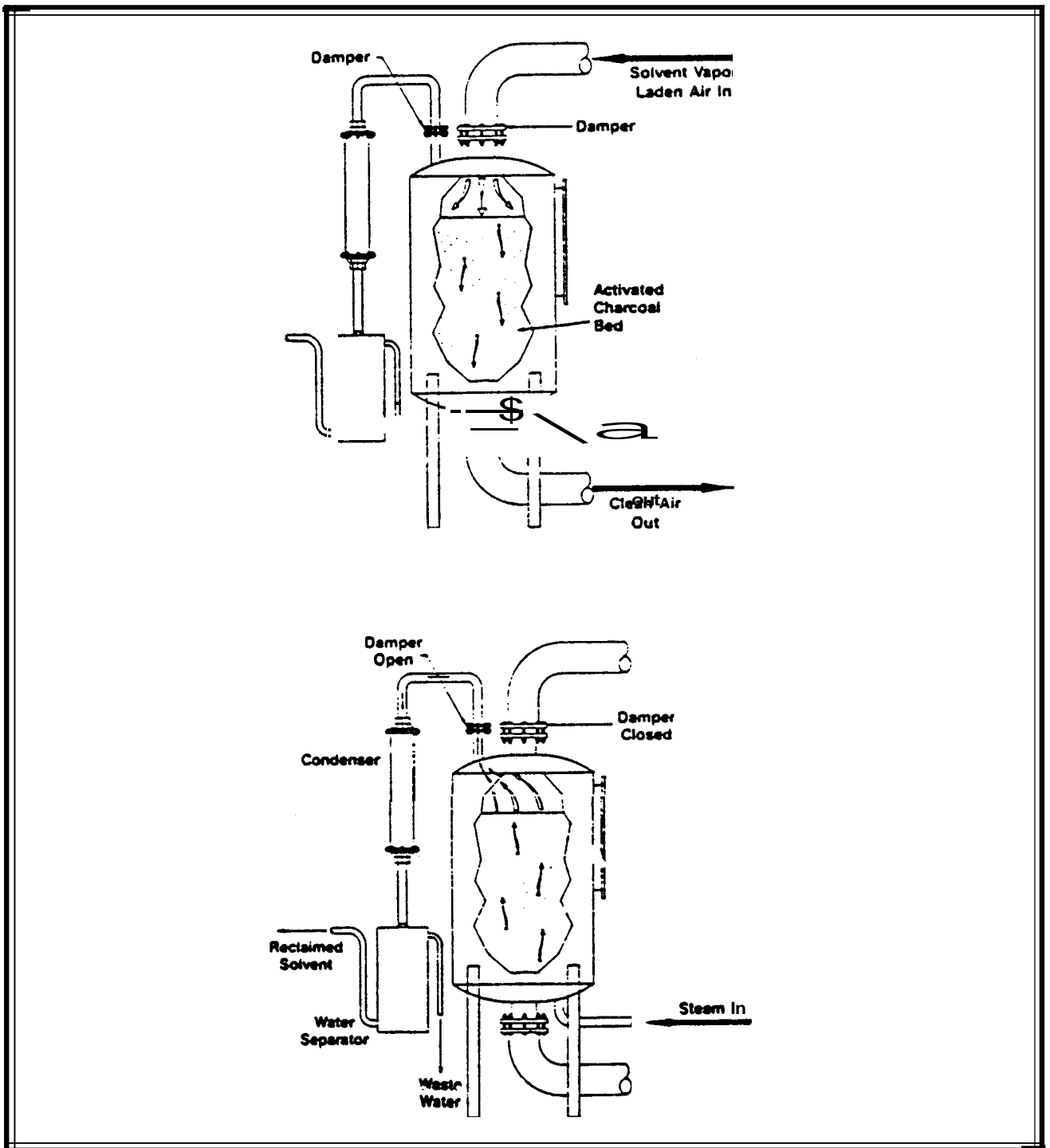


Figure 14. Carbon Adsorption and Desorption (Gerard, 1989)

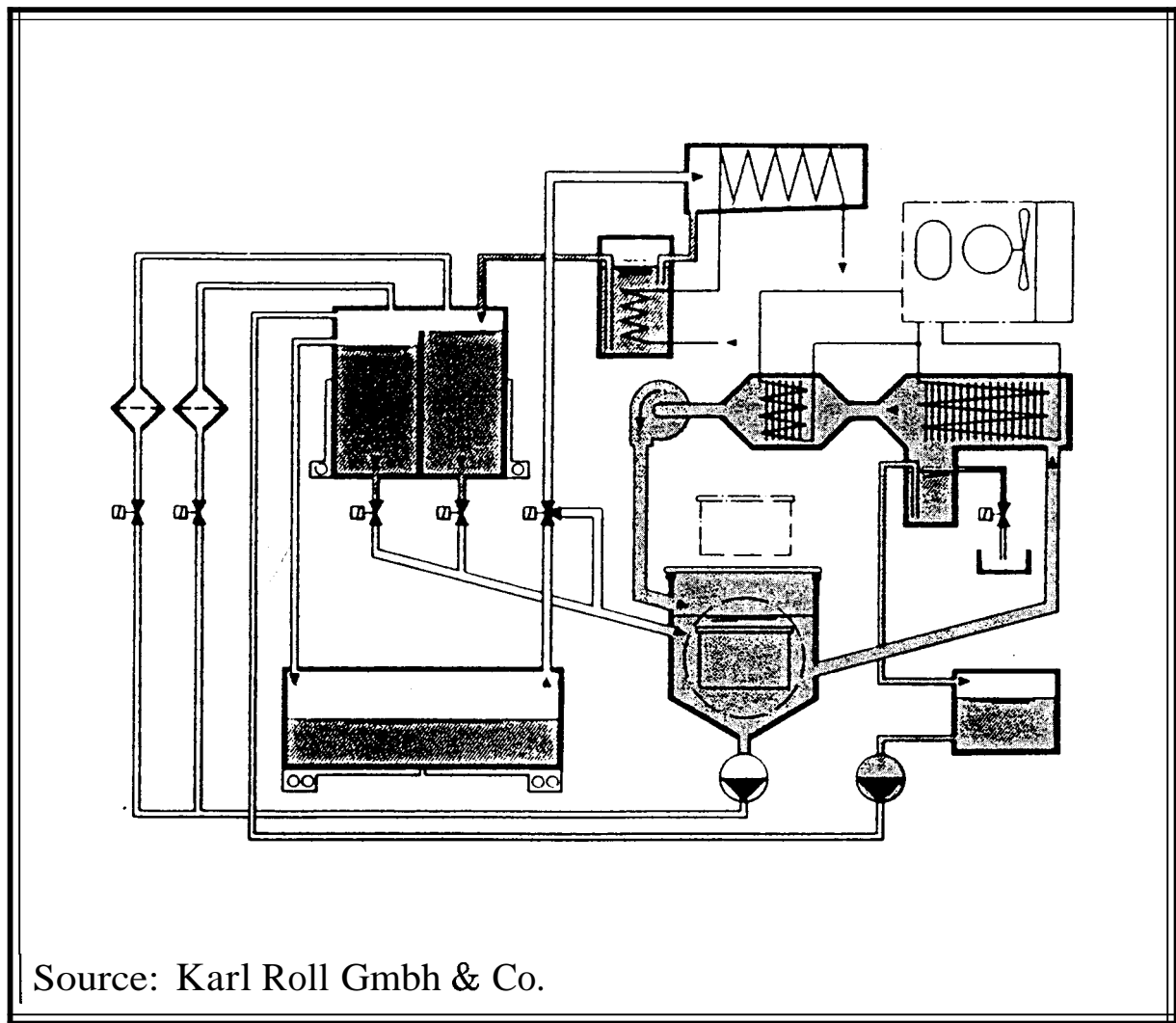


Figure 15. Solvent Recovery Using Recirculating Condensation

also can be improved by reducing the temperature of the air steam. In general, the lower the condenser temperature, the better the recovery efficiency (DOE, 1990; Hall, 1990).

Condensation technology also can be used in conjunction with standard carbon adsorption methods to remove emissions from a gas stream (**Figure 16**). In such a configuration, hot nitrogen replaces

steam for desorbing the organic solvent and regenerating the carbon bed. The solvent-laden inert gas is compressed and cooled to condense the solvent. The inert gas is then heated and returned to the carbon bed.

The coupling of the condensation system to carbon adsorption provides several advantages to traditional methods of solvent recovery for 1,1,1-trichloroethane

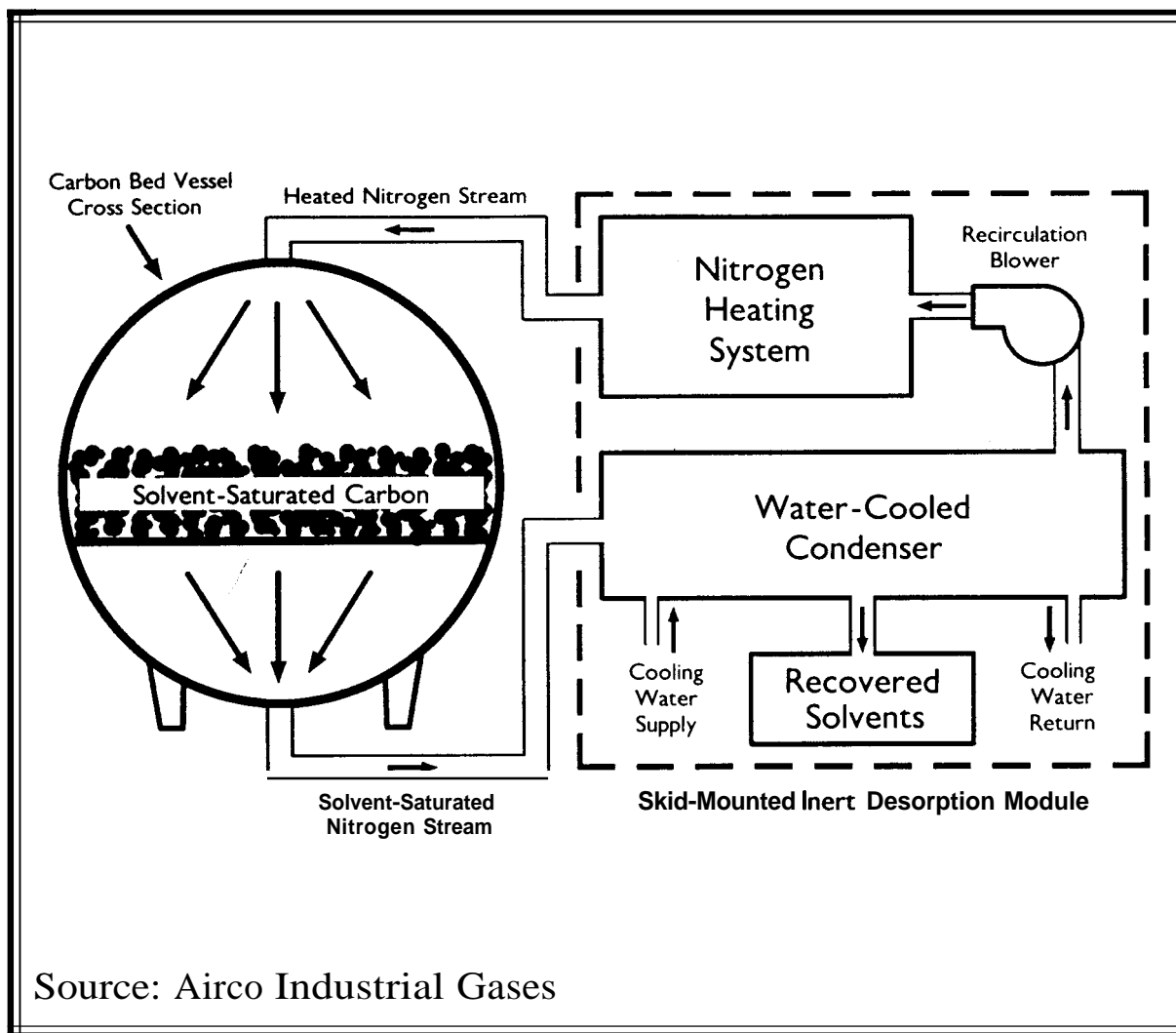


Figure 16. Inert Carbon Bed Regeneration System - Process Schematic

and methylene chloride. These advantages stem from the virtual elimination of water from the process, by removing the need for steam regeneration of the adsorption bed (Enneking, 1991; Whita l, 1991; Jefcoat and Heil, 1991). In addition, the use of regenerated inert gases at elevated temperature (>450°F) also may greatly reduce the amount of solvent remaining on the absorption medium after regeneration (Enneking, 1991), and

may permit a significant size reduction of adsorbent beds.

* * * * *



Integrated Control Strategy

The two main elements of a well controlled solvent cleaning operation are a good machine design and proper operating practice. In designing a solvent cleaning system, or when considering retrofit of an existing machine, it is important to consider the inclusion of

features to address the various types of emissions, including diffusion, convection, dragout, solvent transfer, and downtime.³¹ Proper operating practice will help to minimize losses from leaks, air drafts, spills, solvent transfer, waste handling, and dragout.

Table 3. Effectiveness of Control Technique Combinations - Open-Top Degreasers		
Control Technique	Achievable Reduction (%)	
	Schedule A ¹	Schedule B ²
FB Ratio = 1.0 ± Refrig. FB		
Hoist Speed = 11 fpm	40-50	50-70
Hoist Speed = 3 fpm ³	50-60	80
Enclosed Design ± Sump Cooling		
Hoist Speed = 11 fpm	70-80	70-80
Hoist Speed = 3 fpm ³	80-90	90
Automated Cover		
Hoist Speed = 11 fpm	30-40	50-60
Hoist Speed = 3 fpm ³	40-50	80
¹ Schedule A - 2 hrs working, 6 hrs idle, 16 hrs downtime. ² Schedule B - 12 hrs working, 4 hrs idle, 8 hrs downtime. ³ Similar reductions can be achieved with the addition of a dwell time (EPA, 1992c) Source: EPA, 1989;1992c.		

31 A partial list of cleaning equipment manufacturers is included in Appendix I.

Table 4. Effectiveness of Control Technique Combinations - In-Line Degreasers

Control Technique	Achievable Reduction (%)	
	Schedule A ¹	Schedule B ²
Refrig. FB	50	60
+ Sump Cooling	65	60
Carbon Adsorption	50	60
+ Sump Cooling	65	60
Superheated Vapor		
+ Sump Cooling	70	70
+ Refrig. FB	70	85

1 Schedule A - 8 hrs working, 16 hrs downtime for 260 days.
 2 Schedule B - 16 hrs working, 8 hrs downtime for 365 days.
 Source: EPA, 1989;1992c.

The discussion in Chapters 4 and 5 provides general information on the type of emissions each control technique or practice addresses and the level of control (compared to uncontrolled emissions) that can be expected. In retrofitting degreasing equipment, it is important to recognize that the effectiveness of any individual emission control technique or practice in reducing overall solvent emissions will depend on its ability to reduce the predominant emission type.

Moreover, the ability of any combination of control techniques to reduce overall solvent cleaner emissions depends upon the operating schedule and the specific techniques selected. The combined control efficiency of two or more techniques that act on the same type of emission will be less than the sum of their individual

efficiencies. EPA has developed estimates of the overall efficiencies associated with selected control technique options employed on uncontrolled machines. This information is provided in **Table 3** for open-top degreasers and in **Table 4** for in-line cleaners. A more detailed summary of the EPA review of control techniques for open-top degreasers is provided in Appendix 11.

To further reduce solvent emissions and workplace exposures, new state-of-the-art degreasing systems have been designed to incorporate all of the technology available to minimize solvent emissions (**Figure 17**). Such "low-emission" equipment is completely enclosed and automated and has been shown to reduce idling and working losses by as much as 90 percent (EPA, 1989; Weemes, 1990).

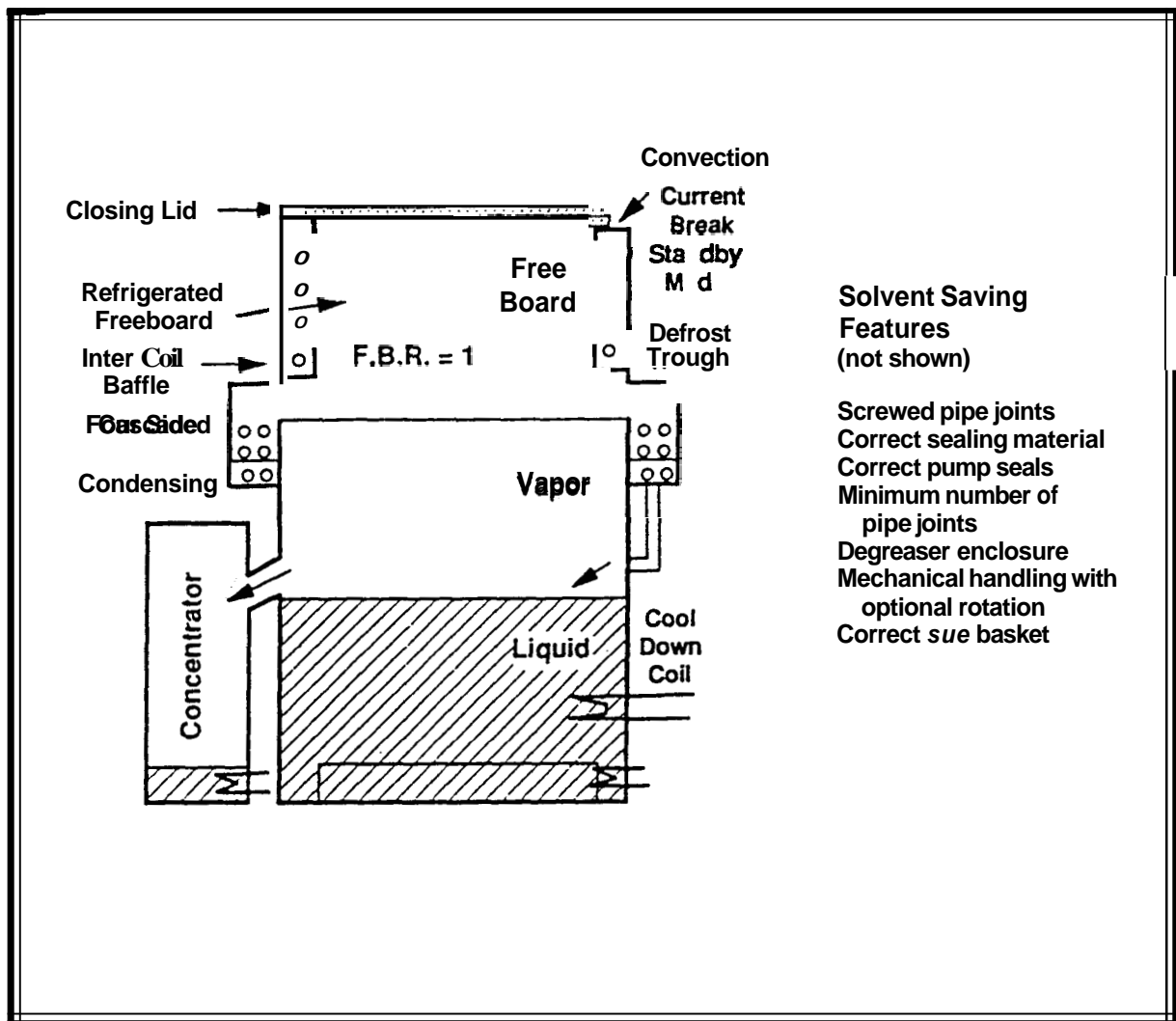


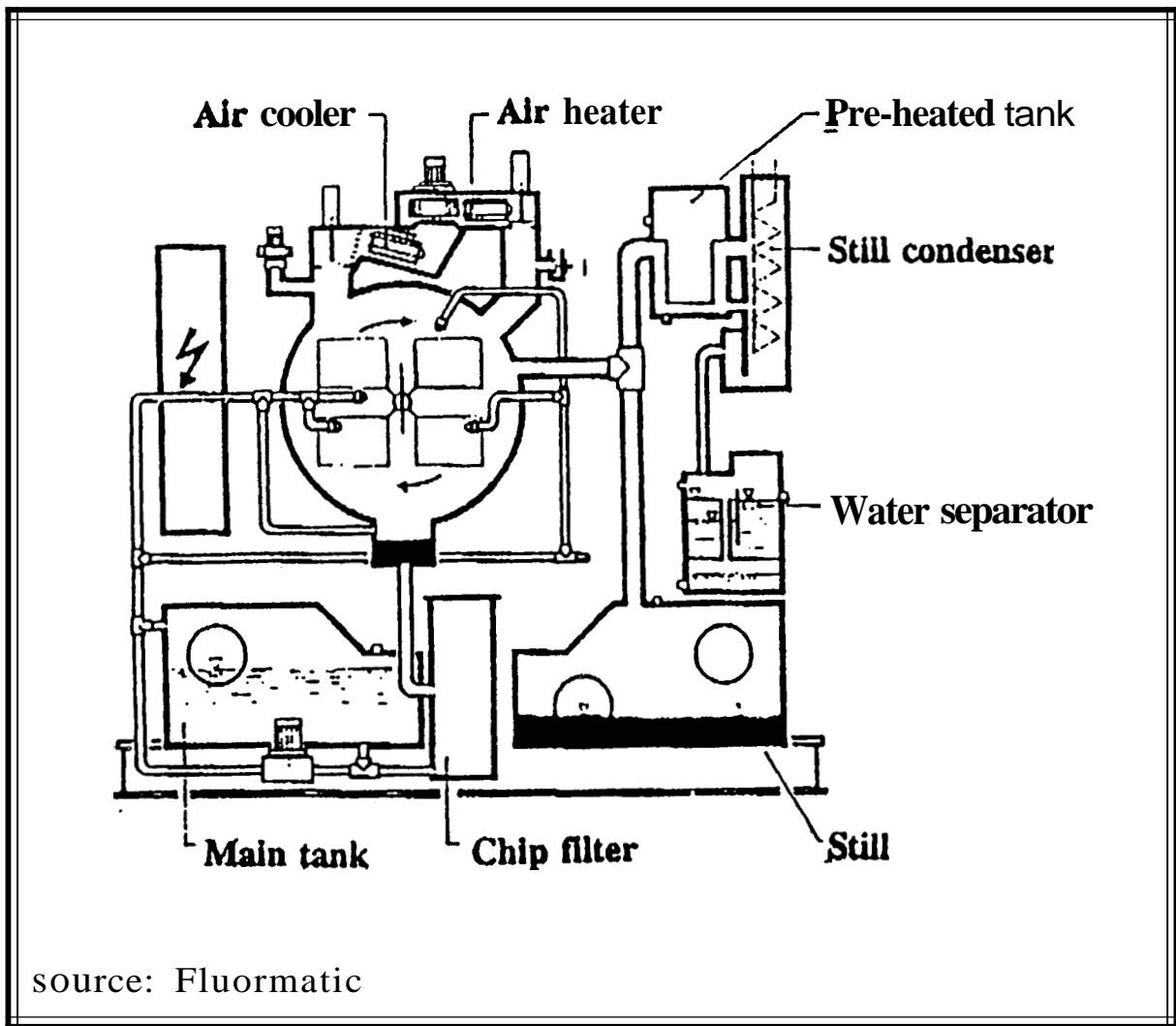
Figure 17. Low-Emission Degreaser Design with Solvent-Saving Features (Weemes, 1990)

Some of this new equipment is designed to bring the solvent to the parts to be cleaned rather than bringing the parts to the solvent as in traditional equipment (Mertens, 1990).³² In these systems, the basket of parts is placed in a chamber where all the cleaning takes place (**Figure 18**). The chamber is then sealed and hot solvent is pumped into it, while the basket is rotated. The solvent is then pumped out, and the process can be

repeated to produce a two-dip configuration. Solvent vapors are then introduced into the chamber, as the parts continue to rotate, to produce the vapor cycle. This cycle is followed with a hot-air cycle that blows hot air across the parts to completely dry them. The hot-air cycle continues until the chamber is completely denuded of solvent.

These designs employ a vapor condens-

32 These units are similar to the equipment used for dry cleaning clothes with perchloroethylene. They are designed to prevent exposure of the vapor zone to the atmosphere.



source: Fluormatic

Figure 18. Advanced Small Parts Degreasing Machine

ing, activated carbon, or other system to recover the solvent from the air stream leaving the cleaning chamber.³³ They generally have been developed for use with perchloroethylene, although the technology is applicable to the other solvents. Such systems tend to be relatively expensive, however, and may be limited in the size and capacity of parts that they can clean within a given cycle (Whitall, 1991).

* * * * *

33 One relatively new approach, temporary vapor storage or TVS, would store the solvent vapors on a synthetic adsorption media. The solvent then would be collected from the media, using hot air, and reintroduced into the machine (Hickman and Goltz, 1991; Hickman, 1992).



Solvent *R*ecovery

From Waste

The effectiveness of a vapor degreasing operation is dependent on the ability of the machine to produce a constant supply of clean solvent vapor for cleaning. To accomplish this, the contamination level in the solvent should be kept as low as possible. This is particularly true in immersion baths employed in some degreasing operations. Unnecessarily high contamination of a degreasing unit can result in lower cleaning efficiency, and can lead to solvent breakdown and increased solvent losses. Consequently, auxiliary distillation units, or stills, are frequently employed to maintain low contamination levels in the degreaser compartments.

The regular distillation of the contaminated solvent in the vapor degreasing process produces quantities of waste oils, greases, and other contaminant materials that require disposal. These sludges, collected in either the degreaser tank or the still, also contain a significant amount of solvent that can be recovered. In the absence of subsequent efforts to recover this solvent, losses of solvent in hazardous waste can compose as much as

30 percent of the total solvent losses. The percentage can be higher in cold cleaning operations where distillation is frequently not a part of the cleaning operations (SRRP, 1992).

There are several methods for reducing the quantity of solvent lost in hazardous waste. These include solvent segregation, microfiltration, on-site distillation, and off-site (commercial) recycling.

Solvent Segregation

A relatively simple method for reducing losses of solvent in waste materials is to avoid mixing solvents after their use. Recovery of the solvents from these mixtures, either on-site or off-site is more difficult and may prove uneconomic (Higgins, 1989). For example, separation of a mixture of CFC-113 and 1,1,1-trichloroethane requires intensive fractionation. A generator of a mixed solvent stream, therefore, likely will not be able to recover those solvents on-site and will incur additional costs to have it handled by a commercial recycler. Recovery is much easier if the spent solvents are kept

separate from the outset.

Microfiltration

Vapor degreasers are equipped with a filtration system to remove particulate matter from the solvent. The main types of filters typically used are bag, cartridge, and membrane. Cartridge filters can adsorb a considerable amount of solvent if not allowed to drain properly. While newer machines use bag filters that do not hold as much solvent, excessive solvent loss still can occur if the filters are not allowed to dry before handling (Gerard, 1989).³⁴

In addition, microfiltration systems may be placed off-line from a degreaser to maintain the solvent in an ultraclean condition for vapor spray, ultrasonic, and cold-cleaning applications. These systems can remove particles of 0.1 micrometers in size or less (SRRP, 1992). This helps to minimize particulate contamination of vapors and to remove undissolved organic and inorganic soils, thereby increasing the effective life of the solvent and improving product quality. These filters usually are connected to the rinse sump during the day, and are switched to the boil sump at night to ensure particulate-free solvent in both sumps for the next run (SRRP, 1992).

On-Site Distillation

Solvent reclamation is one of the most common methods for degreaser operations to handle waste solvents. On-site recycling of the halogenated solvent is relatively easy because of the stability of

these solvents, their relatively low latent heat of vaporization,³⁵ and their nonflammability. It involves boiling and vaporizing the solvent. In this process, the lower-boiling materials are distilled first, leaving the higher boiling impurities and sludges at the bottom of the still.³⁶ The contaminant-free solvent vapor is then condensed, and the distillate passed through a water separator.

Users of solvent recovery stills can realize substantial operating costs savings by reclaiming solvents rather than giving them to a commercial recycler (Schindler, 1990). Further significant cost savings result from the increased efficiency of production and reduced maintenance of degreasing operations.

In some operations, reclamation of the solvent is conducted by distilling the solvent within the degreaser's boiling sump and diverting the distillate to a separate tank or drum. This mode of solvent recovery has several limitations. The degreaser must be taken out of service for a number of hours, and the bottoms, after concentration, often contain over 50 percent solvent (ASTM, 1989; EPA, 1989). This practice also may increase emissions to the atmosphere (SRRP, 1992).

Stills specifically designed for solvent recovery are more efficient than degreasers, and are estimated to be used by about 50 percent or more of degreasing operations (Dow, 1988; SRRP, 1992). Dirty solvent is pumped from the most contaminated compartment of the degreaser, and the solvent distillate is

34 Many new machine designs connect the filter housing to a vent line so that air can be blown over the filter until it is dry (Gerard, 1989). The resulting air stream can then be vented to the condenser area of the degreaser or to a carbon adsorber.

35 Latent heats of vaporization for the chlorinated solvents (in BTU/lb) are as follows: CFC-113 • 63; perchloroethylene • 90; 1,1,1-trichloroethane • 102; trichloroethylene • 103; methylene chloride • 142.

36 These materials commonly are referred to as still bottoms.

returned to the degreaser rinse compartment or to a storage reservoir. The still may operate on a continuous basis, or the contaminated solvent may be collected regularly and reclaimed in a batch process. Continuous distillation allows constant cleanup of the solvent, and does not require that the degreaser be shut down as often. It is necessary to shut off the solvent supply periodically, however, to concentrate and dispose of the contaminants in the still. In batch distillation operations, direct connection of the still to the degreaser will avoid the need for manual transport and reduce potential emissions from this operation (ASTM, 1989).

In the distillation process, it is possible to concentrate the contaminants to a point where little (10 percent or less) solvent remains.³⁷ In addition, stills may be equipped with steam injection to recover all but the very last traces of the remaining solvent.³⁸ The technique forms an azeotropic mixture that boils at a lower temperature. The condensate of water and solvent is then separated by gravity. Microwave dryers also are available that can further reduce solvent levels in the still bottoms. The extent to which this waste is concentrated on-site may depend, however, on the cost of disposal (SRRP, 1992).

Single-plate distillation is the most commonly employed method of recovering solvent on-site. There are a variety of commercially available distillation systems, ranging in capacity from 0.5 to 100 gallons per hour. The smaller systems are self-contained, off-the-shelf units that

can be installed in any sheltered area with electrical power and cooling water, while the larger units are more complex and require steam (Higgins, 1989). The operating costs of the distillation apparatus include labor, energy, cooling water, and maintenance (Higgins, 1989).

The majority of distillation units used in degreasing operations are atmospheric stills. Because of their large vapor/air interfaces, they can be significant contributors to solvent losses (Gerard, 1989). Several newer designs (i.e., vacuum stills) exist, however, that eliminate the vapor/air interface and reportedly prevent solvent losses (Meier, 1986). These are closed systems in which the solvent is drawn into the evaporator of the distillation unit. A vacuum pump reduces the pressure to the point where the solvent starts to evaporate at room temperature. The solvent vapor is then drawn out of the evaporator and into a compressor/heat exchanger where it is condensed back into a liquid. The solvent then goes to a dryer to remove any water contamination.

Distillation under vacuum reportedly eliminates the problem of solvent decomposition due to overheating, and thereby can allow for a greater recovery efficiency (Meier, 1986). This is particularly important for a high boiling-point solvent like perchloroethylene. It also may minimize stabilizer losses (Meier, 1986).³⁹ Relatively low-boiling point solvents (<194°F) reportedly can be distilled in a single-stage operation, while higher boiling point solvents may require two stages.

37 Because of its low solvent content, commercial recyclers may charge degreaser operations more to pick up such waste.

38 Steam stripping generally is not recommended for use with 1,1,1-trichloroethane.

39 One study of the fate of stabilizers suggests that as much as 35 percent of these materials may be lost in an atmospheric distillation process (Higgins, 1989).

Another possible method for reducing the amounts of waste shipped off-site is to employ a mobile on-site solvent reclaim-er. In such a case, a mobile distillation system pays regular visits to the shop to perform the recycling operation. The recycled solvent is returned to the degreaser or to storage, while arrange-ment is made for the disposal of the still bottoms.

Off-Site Recycling

On-site recycling generally is considered economical if at least 8 gallons of solvent waste are generated'perday (EPA, 1991b). For generators that are not able to use in-house recovery techniques, however, off-site reclamation is a viable option. The recycler, under a contractual agreement, picks up the generator's contaminated solvent, recycles it, and delivers purified solvent back to the generator or sells it back to other users. While some users, particularly those under military contract, have questioned the quality of reclaimed solvent, reclaimers generally perform routine chemical analysis to assure customers that the solvent will meet their purity requirements.

Commercial recyclers also pick up still bottoms generated from on-site distilla-tion operations and, depending on the solvent content, may reclaim additional solvent from these materials. The slud-ges that result from the off-site reclama-tion contain small concentrations of solvents and are typically blended into fuel for destruction in cement kilns and industrial boilers.

In areas with large numbers of users, solvent reclamation services are readily available. In some rural areas, however, large distances may limit the availability of these services.⁴⁰

* * * * *

40 A list of active members of the National Association of Chemical Recyclers is included in Appendix 111.



Chemical Substitution

Several groups of substances have been used, or suggested, as alternatives to the halogenated solvents in degreasing operations. Two of these groups (petroleum solvents/alcohols/and ketones and synthetic aliphatic hydrocarbons) may have widespread applicability as alternatives to halogenated solvents for general metal cleaning.⁴¹ The other alternative substances described below are likely to have only limited applicability in precision

metal cleaning applications. In addition, the halogenated solvents considered in this document often can be substituted for one another without requiring significant equipment changes.

Other Halogenated Solvents

While their chemical and physical properties vary (**Table 5**), it often is possible to replace one of the halogenated solvents

Table 5. Characteristics of Selected Solvents

Solvent	Boiling Point (°F)	Flash Point (°F)	Surface Tension (dynes/cm)	KB Value'	TLV (ppm) ²
CFC-113	118		17.3	31	1000/1250
Methylene Chloride	104		28.2	132	50
Perchloroethylene	250		32.3	91	25/100 ^a
Trichloroethylene	188		31.6	124	50/100 ^a
1,1,1-Trichloroethane	165	-	25.5	130	350/450
HCFC-123	84		18.3	60-70	(10) ^b
HCFC-141b	89	-	18.3	57	(100) ^b
HCFC-225	124-133		16.3-17.7	30-34	n/a
Mineral Spirits	309-399	103	22.5	32	100
Ethanol	167-178	50	22.3	n/a	1000
Methanol	148	51	22.6	n/a	200/250

(continued on next page)

⁴¹ Some of the hydrocarbons included in the discussion of semi-aqueous cleaning systems in Chapter 9 also may have application as cleaning agents in their concentrated form.

**Table 5. Characteristics of Selected Solvents
(continued)**

Solvent	Boiling Point (°F)	Flash Point (°F)	Surface Tension (dynes/cm)	KB Value ¹	TLV (ppm) ²
Isopropanol	180	53	21.3	n/a	400/450
Acetone	133	15	22.3	n/a	750/1000
Methyl Ethyl Ketone	175	23	24.6	n/a	200/300
C10-11 Isoparaffins	320-340	107	n/a	29	
C10 Cycloparaffins	320-340	200	n/a	54	
C13 N-Paraffin	330-360	105	n/a	22	
N-Methyl Pyrrolidone	395	199	40.7	n/a	(100) ^b

1- Kauri-butanol (KB) value - measure of solvent strength.
 2- American Conference of Governmental Industrial Hygienists Threshold Limit Values (ACGIH, 1991).
 a- According to a recent notice of proposed change (ACGIH, 1992).
 b- Numbers in parentheses are manufacturer recommendations.
 n/a - not available.

with another. In the 1970s, for example, many companies substituted 1,1,1-trichloroethane for trichloroethylene to comply with state VOC regulations. More recently, as a result of the pending phaseout of 1,1,1-trichloroethane and CFC-113,⁴² there has been increasing interest in the use of trichloroethylene, perchloroethylene, and methylene chloride.⁴³ The properties of trichloroethylene and methylene chloride make them reasonable choices to replace 1,1,1-trichloroethane and CFC-113, respectively, in certain applications. In addition, although the high boiling point of perchloroethylene has limited its use for cleaning, the development of azeotropic formulations may broaden its applicability.

Switching to one of these other halogenated solvents may require companies to apply for a modification to an existing operating permit. As noted above, these three solvents may be regulated under state air toxics programs, and degreasing with these solvents will be subject, in time, to a national emission standard under Section 112 of the federal Clean Air Act. While trichloroethylene and perchloroethylene are regulated as VOCs, EPA has proposed to add perchloroethylene to the list of compounds exempt from regulation as volatile organic compounds, or VOCs (EPA, 1992b).

Petroleum Solvents, Alcohols, and Ketones

Petroleum solvents, alcohols, and ketones

42 On February 11, 1992, President George Bush announced that U.S. production of CFCs, halons, carbon tetrachloride, and 1,1,1-trichloroethane for emissive uses would be phased out by December 31, 1995.

43 Preliminary findings of EPA's review of alternatives to CFC-113 and 1,1,1-trichloroethane in cleaning indicate that these solvents will be viewed as acceptable, provided they are used in accordance with applicable regulatory controls (Bonnelycke, 1992). This review is being conducted as part of the requirements of Section 612 (Safe Alternatives) of the Clean Air Act.

presently are used in some sectors of manufacturing and repair industries for cold cleaning applications. Petroleum solvents (e.g., mineral spirits, kerosene, Stoddard solvent) show good solvency for most contaminants, are compatible with most rubbers, plastics, and metals, and have low surface tension. Alcohols (e.g., ethanol, isopropanol, and glycol ethers) have been used in certain applications requiring their high polarity and effective solvent power, including their use in azeotropic mixtures with halogenated solvents for defluxing operations in the electronics industry. Ketones (e.g., methyl ethyl ketone, acetone) are powerful solvents, but like alcohols are not compatible with many polymeric and elastomeric materials.

These solvents, however, have several limitations. Their flammability restricts their use in enclosed systems and in vapor degreasing applications. The common alcohols and ketones have flash points that are quite low, and are considered flammable (**see Table 5**). Flash points of the petroleum solvents generally are between 100°F and 140°F.⁴⁴ In addition, these solvents are photochemically reactive, and are regulated as ozone (smog) precursors in most urban areas of the country (EPA, 1991c).

Cleaning with these solvents is accomplished by immersion of the parts to be cleaned in one or more solvent baths. In most cases, the baths are operated at ambient temperature. For higher flash-point solvents, hot cleaning may be used to improve cleaning efficiency, but temperatures must be maintained well below

the flash point of the solvent. Spraying processes generally cannot be used with these solvents because the fine droplets produced can ignite at temperatures below the flash point of the bulk fluid. Because the parts are immersed in a solvent bath, the solvent must be maintained as free of contamination as possible. If contaminant oils and greases are allowed to build up, they may redeposit on the parts. In multistage wash processes, fluid from one bath is periodically transferred to the preceding bath as its soil level builds up. Fresh solvent is added only to the final bath to ensure the highest cleanliness of parts, and spent solvent is removed only from the first stage. Reclamation of these solvents can be accomplished using filtration and distillation, but flammability concerns may make distillation more difficult.

Many of these solvents, particularly the petroleum solvents, exhibit slower drying times than halogenated solvents. As a result, operations requiring a clean, dry part for the next step in the production process may need to add a drying step. Drying can be accomplished using forced air, but precautions must be taken to prevent combustion of the solvent. Solvent vapor recovery can be accomplished with carbon adsorption or condensation.

Synthetic Aliphatic Hydrocarbons

In addition to the hydrocarbons described above, several other synthetic products are available that offer favorable properties for metal cleaning. Commercially available products include those containing paraffinic or oxygenated hydrocar-

44 Stoddard solvent has a flash point of 103°F.

bons or aliphatic esters. While their properties vary, depending on the exact formulation, these products generally have lower flammability than petroleum fractions. In addition, they have relatively low surface tension allowing for good surface wetting and penetration (Miasek and Schreiner, 1991).

As with the hydrocarbons described above, the solvent bath must be kept relatively free of contaminants to ensure effective cleaning. While the lower volatility of these synthetic solvent formulations reduces their VOC emissions, it likely will further increase their drying times. Unlike those hydrocarbons used in the semi-aqueous processes described in Chapter 9, however, these aliphatic solvents reportedly can be dried from the surface without leaving a residual film (Miasek and Schreiner, 1991). This would eliminate the need for a water rinse and, thus, simplify any wastewater treatment requirements.

Hydrochlorofluorocarbons

Three of the hydrochlorofluorocarbons (HCFCs) developed to replace CFCs have been considered as potential cleaning alternatives. These three substances, HCFC-141b, HCFC-123, and HCFC-225 (ca & cb isomers), have stratospheric ozone depletion potentials (ODPs) considerably lower than the CFCs, although the ODP of 141b is comparable to 1,1,1-trichloroethane.^{45,46} The use of these HCFCs in applications other than refrigeration will be phased out in the United States after the year 2015 under the federal Clean Air Act, as amended, and

likely will be further restricted as a result of international and national regulation.⁴⁷

While 141b and 123 are being produced in commercial quantities, 225 may not be available for some time. Short-term toxicity testing of 123 and 141b has been conducted, and a preliminary assessment by EPA's Office of Toxic Substances in 1990 concluded that neither substance appears to present a significant health concern (EPA, 1990a). More recently, however, concern over positive results in a 2-year bioassay with 123 has prompted the manufacturers to lower the recommended worker exposure limit to 5 to 10 parts per million (ppm) for an 8-hour time-weighted average (IRTA, 1991a; Chemical Week, 1991; UNEP, 1991b). Results of a 2-year bioassay with 141b are expected by late 1992 (UNEP, 1991b).⁴⁸

Toxicity testing of 225 currently is underway (Kitamura and others, 1991; UNEP, 1991b). It appears that one of the isomers of the substance may exhibit some toxicity (IRTA, 1991a; UNEP, 1991a).

The solvent power of 123 and 141bis between CFC-113 and 1,1,1-trichloroethane, while that of 225 is very similar to CFC-113. HCFC-225 has a boiling point slightly above that of CFC-113 and could be used in existing equipment. In fact, it comes as close to a drop-in replacement for CFC-113 as any substance currently identified (Yamabe, 1989; Kitamura and others, 1991; UNEP, 1991a). Because of their considerably lower boiling points (89.6°F and 83.7°F,

45 ODP is an estimate of the compound's potential to deplete stratospheric ozone, relative to CFC-11 which is assigned a value of 1. The most recent review by the United Nations Environment Programme (UNEP) assigned ODPs as follows: CFC-113 - 1.07; 1,1,1-trichloroethane - 0.12; HCFC-141b - 0.11; HCFC-123 - 0.02; and HCFC-225 - 0.025-0.033 (UNEP, 1991b).

46 Because of concerns about the ODP of HCFC-141b, EPA is considering limiting its use for cleaning under the safe alternatives program required by Section 612 of the Clean Air Act (Bonnelycke, 1992).

47 On February 11, 1992, President Bush announced a review of the need for an accelerated phaseout of HCFCs.

respectively), 123 and 141b will tend to have higher emissions from existing machines.

The diffusivities of 123 and 141b are estimated to be 9 to 16 percent higher than that of CFC-113. As a result, they will require tighter equipment to achieve the same solvent mileage (Ramsey, 1990). In the case of 123 formulations, it may not be possible to achieve the recommended occupational exposure limits.⁴⁸ Mixtures of the two substances, developed to lower the ODP of 141b, have lower boiling points than either chemical, and will exhibit even higher solvent losses to the atmosphere.

All three substances are more expensive to produce than the other halogenated solvents, particularly 225 because of its complex three carbon structure, and will cost significantly more to use. While one or more of these HCFCs may be applied to certain electronics cleaning operations, their applicability to metal cleaning likely will be limited to a very few precision operations where their specific properties are necessary.

Alcohol Cleaning with Perfluorocarbon

To address the flammability concerns associated with alcohol cleaning, an "inerted alcohol" system has been developed for precision cleaning applications (Baxter, 1992). In a process that looks very much like traditional vapor degreasing with chlorinated solvents (**Figure 19**), the alcohol is combined with a suitable immiscible perfluorocarbon

(PFC). The two liquids evaporate together when heated to form a mixed vapor which is nonflammable. This allows the parts to be cleaned in alcohol vapors without the threat of explosion. The ability to continuously distill the alcohol improves its cleaning performance and reduces the amount required. In general, however, alcohols are not effective at removing nonpolar contaminants (e.g., greases). These contaminants can be addressed with the use of ultrasonic immersion and/or a precleaning tank filled with another solvent (Baxter, 1992).

Another inerting system has been developed that combines a more aggressive hydrocarbon solvent with an immiscible PFC (Hayes, 1992). This mixture is heated above the boiling point of the PFC to create an inert vapor zone, and the parts are cleaned by immersion in the bath containing the heated mixture of hydrocarbon and condensed PFC. After immersion, the part is rinsed by the PFC condensate in the vapor zone.

While both of these systems show significant promise for precision cleaning applications, PFCs have long atmospheric lifetimes and may contribute to global warming if released in significant quantities (EPA, 1991a; UNEP, 1991a). As a result, EPA is expected to limit the use of PFCs in cleaning systems (Bonnelycke, 1992). Other substances with short atmospheric lifetimes (e.g., certain hydrofluorocarbons) may be found to be effective inerting/rinsing agents, however, that can replace PFCs. The general high cost of these substances,

48 Preliminary results of this studies suggest only minor effects in laboratory animals exposed to high levels of 141b (Global Environmental Change Report, 1992).

49 Solvent cleaning formulations containing HCFC-123 have been withdrawn from commercial availability.

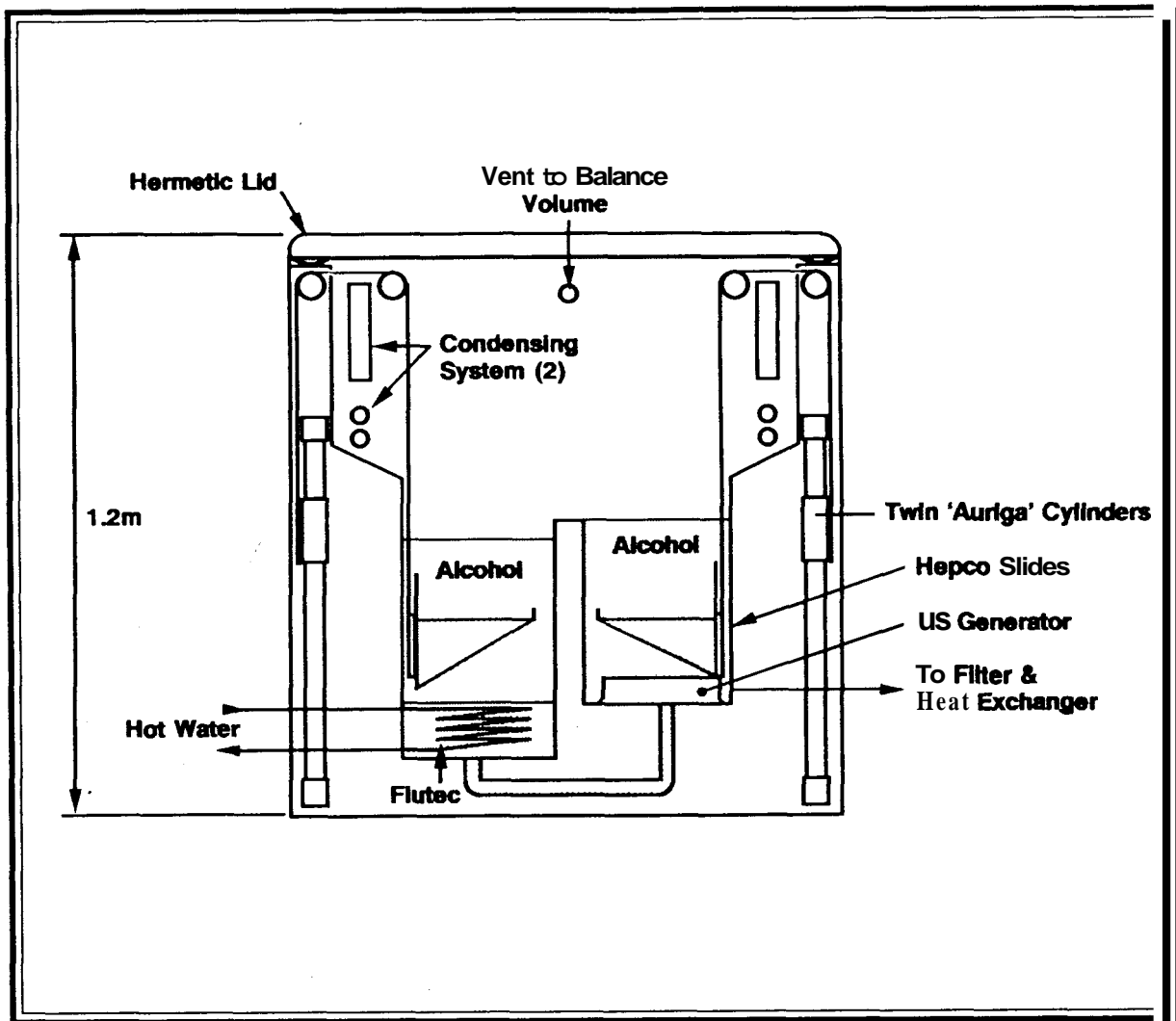


Figure 19. Inerted Alcohol Cleaner with Two Immersion Tanks (Baxter, 1992)

and the resulting need to tightly control emissions, likely will limit the use of these types of inerting systems to a very few specialized applications.

Pentafluoropropanol

Pentafluoropropanol (5FP) also has been suggested as an alternative to CFC-113, and may have some applicability in precision metal cleaning applications

(e.g., gyroscopes). This solvent is non-flammable, has similar solvent power to CFC-113, and has a significantly higher boiling point than CFC-113 (Naito, 1989). While 5FP has an ODP of zero, it has a long atmospheric lifetime and may contribute to global warming (EPA, 1991a; UNEP, 1991a; IRTA, 1991b). As with the HCFCs, the substance currently is undergoing toxicity testing (Naito, 1989).

Perfluoroalkanes

The perfluoroalkanes are a family of compounds produced by the substitution of all of the hydrogen atoms of a hydrocarbon with fluorine. The resulting virtual nonflammability and low toxicity of these substances, combined with the wide range of boiling points available, make them attractive candidates for specialized cleaning applications. They are weak solvents, however, and likely could not be used to remove oils (EPA, 1991a). Their high production cost may make them prohibitively expensive, even in precision cleaning applications, and their significant global warming potential is an environmental concern (EPA, 1991a).

Deionized Water

High-purity deionized water is effective for removing ionic contamination, has low surface tension, and can be used for certain cold (benchtop) cleaning applications of precision parts (Tourigny, 1991). It also can be mixed with alcohol for effective flux removal in electronics applications. It can lose its purity rapidly if stored in open containers, however, and evaporates slowly.

* * * * *



*P*rocess *S*ubstitution

A few alternative cleaning processes are available as substitutes to vapor degreasing with halogenated solvents. Some of these processes have been available for some time (aqueous cleaning), while others have been more recently developed (semi-aqueous cleaning with terpenes, dibasic esters, and n-methyl pyrrolidone). Other methods, including cleaning with carbon dioxide, remain primarily experimental.

Cleaning with aqueous and semi-aqueous formulations most often requires the replacement of the degreasing equipment. In cases where entirely clean and dry parts are not required, and/or where low volumes of parts are cleaned, it may be possible to convert an existing vapor degreaser into a filtered aqueous or semi-aqueous dip tank.

Aqueous Cleaning

Aqueous cleaning (often referred to as parts washing) has been widely used in industry for many years for the removal of salts, rust, scale, and other inorganic soils from ferrous metals, and has been more recently adapted to the removal of

greases and oils traditionally reserved for vapor degreasing. These water-based cleaning systems usually include synthetic detergents and surfactants, along with other additives (e.g., sequestering agents, saponifiers, emulsifiers, chelators, stabilizers, and extenders) in combination with mechanical, electrical, or ultrasonic energy. These various ingredients aid in the cleaning process by reducing surface or interfacial tension, by forming emulsions, and by suspension or flotation of insoluble particles.

Water-based cleaners typically are not as forgiving as solvent cleaning, and generally have poor solvent loadings (Harmon, 1991). Cleaning performance depends on several factors including the level of contamination, the concentration, pH (i.e., the degree of acidity or alkalinity), and operating temperature of the cleaning solution, the amount of mechanical agitation, and the ability to conduct effective rinsing. Good engineering and process control are more critical in preventing problems, and part design can have a significant influence on the level of cleanliness that can be achieved (EPA, 1991a). Aqueous cleaners tend to have

higher surface tension, and may not penetrate as readily into holes and capillary spaces. For complex parts, considerable engineering and experimentation may be required.

Types of Cleaners

Aqueous cleaning solutions typically are tailored to the requirements of the specific cleaning application, and generally are classified according to pH.⁵⁰ Acid cleaners contain inorganic (and sometimes organic) acids, acid salts, and wetting agents or detergents. While not commonly used, acidic aqueous cleaners are generally preferred for cleaning pigmented drawing compounds because of the chemical inertness and strong adherence of these contaminants (Chiarella, 1990).

Alkaline cleaners (pH>9) are the most common, and generally consist of the following three components: (1) alkaline salts, or builders;⁵¹ (2) organic and inorganic additives; and (3) surfactants. Alkaline cleaning baths generally are operated at temperatures of 130°F to 190°F to enhance cleaning, although some formulations can be operated at room temperature.

Builders typically are the largest percentage ingredient of an alkaline cleaner, and usually are derived from salts of phosphates, hydroxides, silicates, carbonates, bicarbonates, and borates. While phosphates generally are the best overall builders, the discharge of cleaning solutions containing them is subject to regulation (EPA, 1991c). Caustics and sili-

cates can be difficult to rinse, on the other hand, causing problems in subsequent operations if not completely removed (EPA, 1991c).

Organic or inorganic additives (e.g., glycols, glycol ethers, chelating agents, and polyvalent metal salts) provide additional cleaning or surface modification. They also can serve as chelating agents for softening water or binding with undesirable metal ions in solution.

Surfactants are organic compounds that provide detergency, emulsification, and wetting in alkaline cleaners, and generally compose about five percent of the aqueous cleaning solution. Surfactants have two distinct structural components: a hydrophobic half that has little attraction for the solvent (water) and is insoluble, and a hydrophilic half that has a strong attraction for water that carries the molecule into solution. Their unique chemical structure provides high affinity for surface adsorption. Surfactants used in alkaline cleaning formulations include sodium or potassium carbonates, phosphate, silicate, or borate soaps, and petroleum surfactants (Marinello, 1980).

Surfactants generally are classified as anionic, cationic, nonionic, and zwitterionic (amphoteric), based on the type of surface activity (EPA, 1991a). Anionic and nonionic agents are the most commonly used for metal cleaning.

Cleaning Processes

The principle stages in aqueous cleaning are washing, rinsing, and drying (**Figure**

⁵⁰ Appendix IV includes a partial list of aqueous and semi-aqueous solution formulators.

⁵¹ Somerecent formulations have replaced these alkaline salts with solvent micro-emulsions. This reportedly reduces the potential of the formulation to cause corrosion of aluminum and other reactive metals.

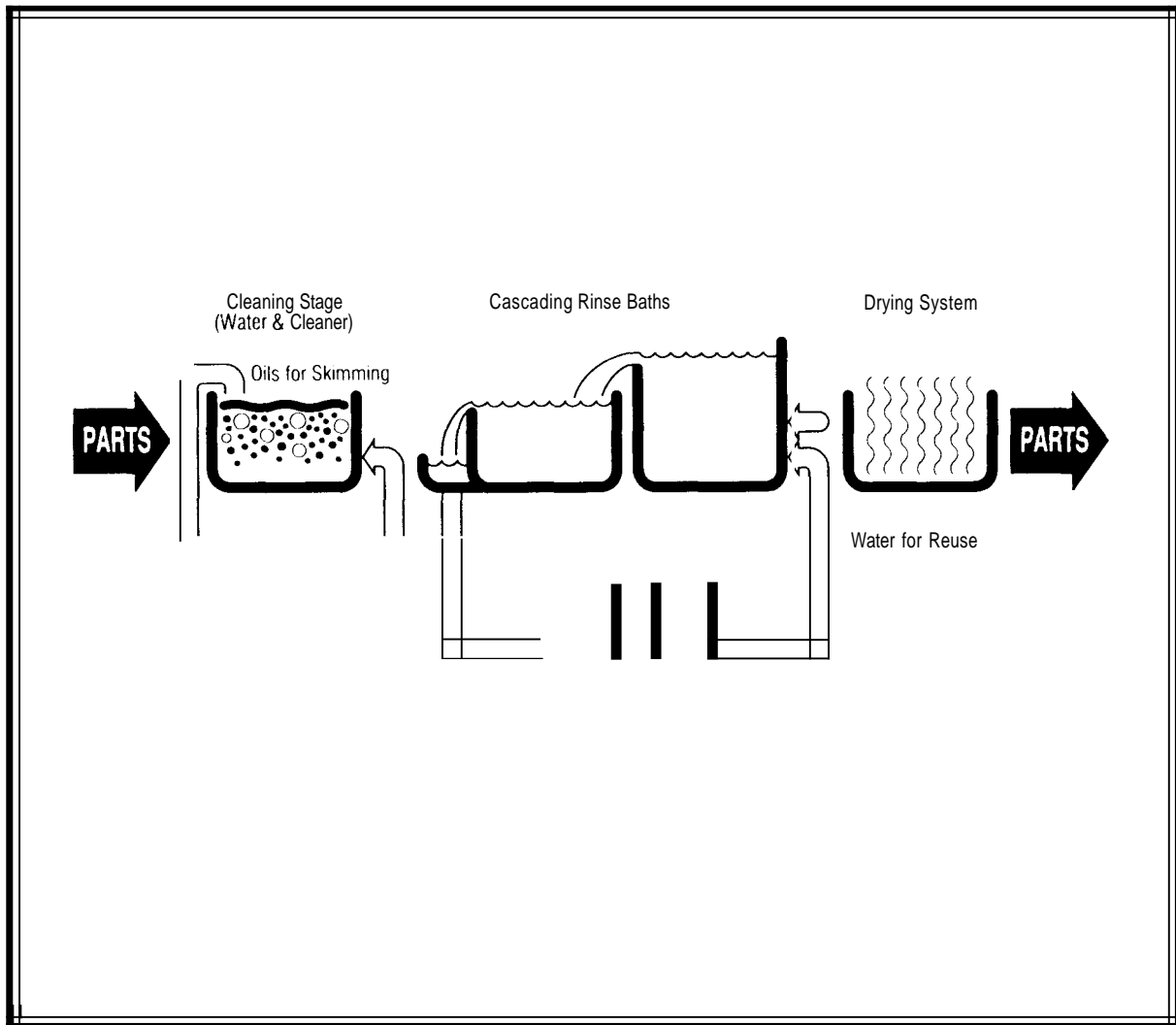


Figure 20. Aqueous Cleaning Process

20).⁵² Like vapor degreasing, aqueous cleaning equipment can be characterized as in-line, for high-throughput cleaning requirements, and batch for low-throughput applications. Each can be further subdivided into immersion, spray, and ultrasonic equipment.

Immersion aqueous cleaning typically employs temperature and/or mechanical agitation to remove the soil from the immersed part. The soil is removed by

convection currents in the solution created by heating coils and/or mechanical action. The simplest type of immersion cleaner consists of a single wash tank, but the demands of most cleaning jobs generally require more complex equipment (UNEP, 1991a). In most cases, rinsing of the part is required to remove any remaining contaminants and residual cleaning solution. Depending on the application and plant water quality, rinsing can be conducted with tap dis-

52 The requirement for a drying step will depend on the needs of the specific application.

tilled, or deionized water.⁵³

The addition of ultrasonic agitation to an immersion cleaning system can effectively clean complex parts and configurations that would otherwise provide a difficult cleaning challenge for aqueous systems. Ultrasonics also can be used to clean difficult-to-remove contaminants, like carbon and buffing compounds. In addition, ultrasonic agitation can be used to great advantage in rinsing.

Ultrasonics works well with aqueous cleaning systems because of the high cavitation efficiency of water.⁵⁴ Effective use of ultrasonic cleaning requires degassing of the aqueous cleaning solution, continuous filtration, and careful attention to the number and orientation of the parts to be cleaned (EPA, 1991c). Moreover, the addition of ultrasonics can make the process more corrosive, and caution should be used to ensure part integrity (UNEP, 1991a).

As an alternative to immersion, spray-wash systems use the mechanical energy associated with spraying the aqueous solution at medium to high pressures to clean the parts. Spray pressures can vary from 2 to 400 pounds per square inch (psi), or 14 to 2758 kilopascals (kPa), or more. In general, the higher the spray pressure, the greater the efficiency of soil removal. Spray cleaners are prepared with low-foaming detergents (i.e., nonionic surfactants) which are not as chemically active as those used in immersion cleaners, but are still effective because of the mechanical agitation.

Depending on the specific needs of the application, spray washers are available in the following three general types: batch, conveyORIZED, and rotary.⁵⁵ While spray cleaning is effective on flat surfaces and parts with simple geometries, parts with soiled areas that are inaccessible to the spray (i.e., blind holes, interior surfaces) are better cleaned with immersion cleaners.

A high-pressure (100 to 200 psi) spray system also can be used as an effective final rinse step, especially when filtered water is used. While optimization of the spray is important to the rinse effectiveness, spray rinsing uses less water and can provide cleaner surfaces since the final rinse water can be quite pure (UNEP, 1991a).

Drying

Drying can present a major challenge when switching to aqueous cleaning, particularly when dealing with complex parts in production processes.⁵⁶ Solvent equipment currently in use has no provision for drying, since the thermodynamics of the solvents are favorable to spontaneous evaporation. The addition of drying equipment will increase the amount of space required for the cleaning operation and the time required for cleaning, and will significantly increase its energy consumption (EPA, 1991a). The drying step may not be necessary, however, if the parts are not needed immediately and a rust inhibitor is used, or if the subsequent process (i.e., painting, electroplating) is water-based.

53 In some cases, a series of cascading rinse baths is used so that the part is rinsed with increasingly cleaner water to ensure that all residues are removed.

54 The principles of ultrasonic cleaning are described in Chapter 2.

55 ConveyORIZED and rotary units generally are used in high-throughput applications, and differ only in the way the parts are handled. While conveyORIZED systems are used to clean parts with flat surfaces, rotary spray washers are designed to clean large volumes of small parts that can withstand tumbling.

56 Flash rusting of parts due to incomplete drying is a common initial problem among companies switching to aqueous cleaning systems. Rust-prevention additives can be used to alleviate this problem.

Available drying techniques include compressed air blow-off, hot-air recirculation, drying ovens, infrared heating lamps, cloth wipe, centrifugal and vacuum drying, and displacement (Chiarella, 1991). Mechanical removal of 90 percent or more of the water can be achieved with the use of compact turbine blowers with filtered output to remove potential contaminants (EPA, 1991c; UNEP, 1991a). The use of high-velocity forced air can reduce drying times significantly, and can minimize the potential for water spotting and staining (Rowny and Temple, 1991). Subsequent evaporative drying can then be accomplished with drying ovens, infrared heating, or centrifugal drying. For parts with complex geometries, vacuum oven drying can be an effective secondary drying method for completely removing water (UNEP, 1991a)..

In some metalworking operations, water is displaced with oil by placing the wet part in an oil bath. The oil also serves to inhibit rust. Another displacement method, capillary drying, uses the surface tension of water to dry a hot part. In this method, the part is slowly extracted from a hot deionized water bath.

In addition, several features can be included in the overall design of the aqueous cleaning system to reduce the drying times and/or energy consumption (Maltby, 1991). These features include the following: (1) use of rinse agents that can speed drying; (2) improved surfactants to allow easier rinsing; (3) improved rinsing with ultrasonics and filtration to reduce overall water flow; (4)

use of multiple washtanks to reduce soil loading in the rinse tank; and (5) use of recirculating hot air dryers.

Wastewater Treatment

Wastewater treatment and disposal also may be an important consideration in aqueous cleaning. Wastewater generated from aqueous cleaning processes may contain detergents and surfactants that are not readily biodegradable, as well as oil and greases and other organic contaminants and dissolved or suspended metal derived from the cleaning process. In addition, alkaline cleaning systems may produce effluent that has unacceptably high pH.⁵⁸

As a result, this wastewater may require pretreatment prior to discharge to the sewer systems to meet local, state, or federal requirements. Moreover, facilities discharging to septic tanks may be subject to considerably more stringent discharge requirements. The level of contamination and the quantity of wastewater will depend on the specific cleaning application, and generally will determine the type of wastewater treatment required. In response to concerns about the effluent from aqueous cleaning, several "closed-loop" water recycling systems have been developed (**Figures 21 and 22**). These systems minimize the discharge of process water and the need to treat discharge water,⁵⁹ and concentrate the oils, metals, and other contaminants for disposal.

The application of aqueous cleaning systems to heavy oil and grease removal

57 The amount of organic matter in a waste stream generally is characterized by measuring the biological oxygen demand (BOD) and chemical oxygen demand (COD). BOD is a measure of the oxygen-consuming nature of the organic matter. COD measures oxygen-consuming pollutants in the wastewater (EPA, 1991c).

58 The alkalinity of the wastewater can be neutralized with the addition of an acidic solution (i.e., sulfuric or hydrochloric acid) in a mixing tank.

59 Closed-loop systems reportedly can reduce water and energy consumption, and can provide a source of water with low ionic content for rinsing (UNEP, 1991a).

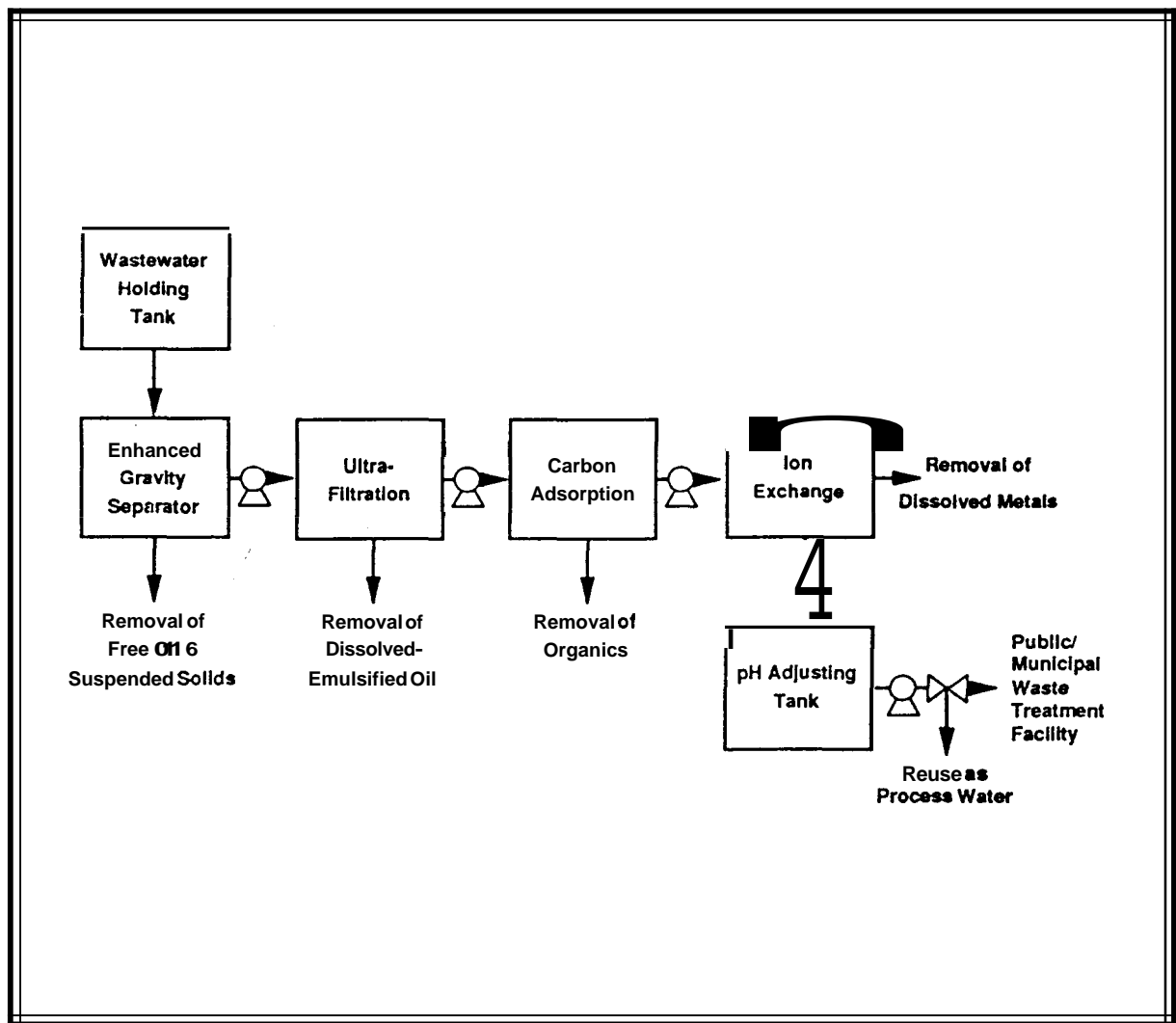


Figure 21. Semi-Continuous Wastewater Treatment Process (EPA, 1991a)

requires the inclusion of equipment to remove the high volumes of oils that can accumulate. This removal will not only serve to concentrate the oils for disposal, but reportedly can extend the effective life of the cleaning solution. Gravity separators are the most common devices employed to separate non-soluble oils, and can be included as an integral part of the wash solution holding tank (EPA,

1991c; Rowny and Temple, 1991). In these systems, the oil-laden overflow from the cleaning bath is directed to a decanting chamber where bulk separation of the oil and aqueous cleaner occurs (Temple, 1990). The oil is decanted from the top of the chamber, and the cleaner can be returned to the holding tank. The collected oil also may contain suspended soils, like metal fines and chips.

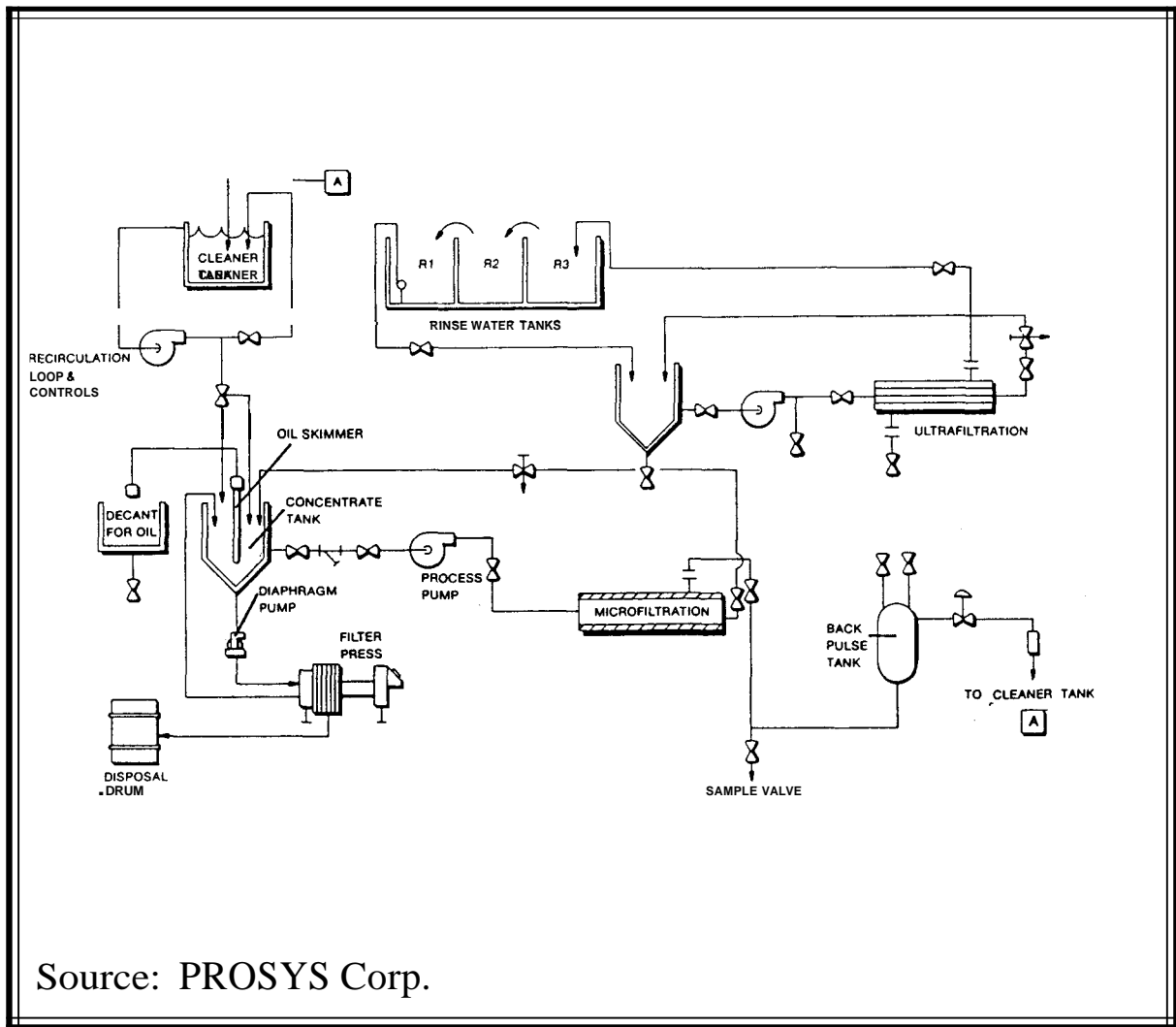


Figure 22. Water-Recycling System Using Micro- and Ultrafiltration

For additional separation of the non-soluble oils and greases, a coalescing medium (e.g., polypropylene or monofilament line, blankets, or pillows) can be used. Coalescing is a simple, but effective, method for removing the oil droplets. The droplets accumulate on the media and then rise to the surface of the solution as they combine to form larger particles.

The removal of emulsified oils may require chemical treatment or microfiltration (0.2 micron pore size).⁶⁰ Chemical treatment involves the addition of alum, ferric chloride, polymers, and/or organic compounds to break the emulsion and agglomerate the small oil droplets into larger ones. Microfiltration is accomplished by pumping the wastewater through a semi-permeable membrane

60 The selection of a non-emulsified aqueous cleaning solution will facilitate rapid oil separation, and may simplify treatment requirements (Rowny and Temple, 1991).

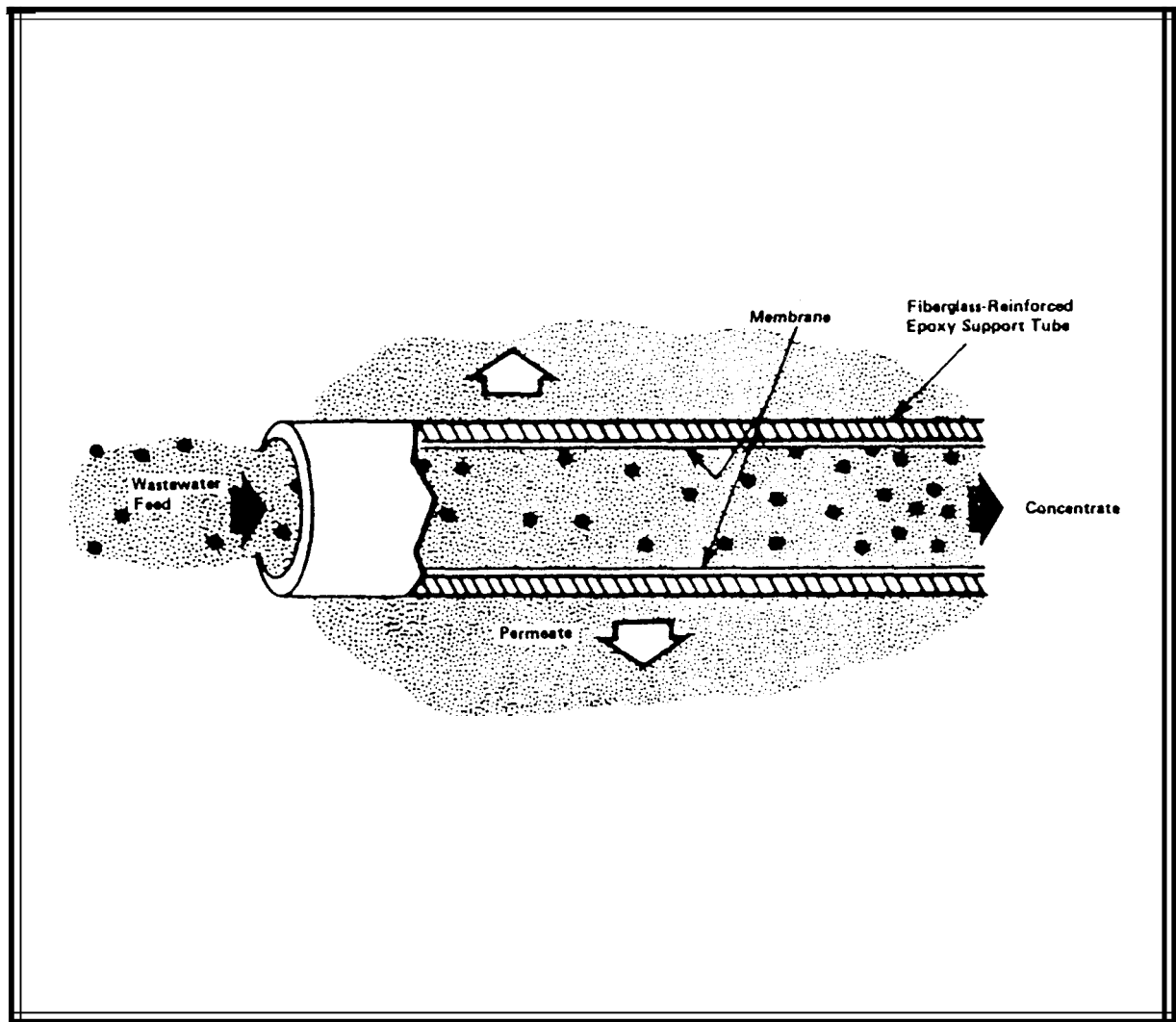


Figure 23. Tubular Membrane Ultrafiltration (Higgins, 1989)

that collects the emulsified oils and suspended soils, but allows the aqueous cleaner and dissolved contaminants to flow through as permeate. The wastewater flows through the membrane in a cross-flow pattern so that the concentrated oils and soils are prevented from building up on the membrane (**Figure 23**). This reportedly results in high filtration rates that can be maintained continuously (EPA, 1991c; Weaver,

1991).

Carbon adsorption or ultrafiltration (<0.2 micron pore size) can be used to effectively remove other organic contaminants from rinse water for discharge or reuse, including the hydrocarbon chemicals and surfactants used in the cleaners and any finishing and pigment compounds used in processing. Both techniques require that the water be relatively free of sus-

pended solids, oils, and greases, although ultrafiltration membranes do not clog as easily (EPA, 1991c).

Carbon adsorption provides cleaner water, but generally cannot remove dissolved metals and other ions, while membrane separation reportedly removes ions and organic material simultaneously (Weaver, 1991). The use of activated carbon requires periodic desorption/regeneration with steam to remove the accumulated organics. Ultrafiltration membranes, on the other hand, can be maintained continuously (EPA, 1991c).

While suspended metals generally are removed during gravity separation and filtration, the treatment of any dissolved metals in the effluent requires precipitation or ion exchange. Precipitation, the most common method, involves the addition of alkaline reagents such as lime and sodium hydroxide to the effluent to form a metal precipitate that can then be removed for disposal.⁶¹ The precipitation reaction can be conducted in a mix tank or in the sedimentation device or clarifier which, while more expensive to purchase and operate, can speed the sedimentation of the metal precipitate (EPA, 1991c).

An ion-exchange system uses the reversible interchange of ions between an exchange resin and the effluent to remove the dissolved metal from the solution.⁶² The resin bed then is recharged periodically, or replaced, to maintain its efficiency.

The cost of wastewater treatment can add significantly to the overall cost of

installing an aqueous cleaning system (Hood, 1991), and small users may find it more economic to contract with a reputable waste treatment company than to treat the wastewater on-site. In such cases, several methods exist for optimizing the cleaning process to minimize the quantity of wastewater produced, including prompt removal of sludge and soils, routine monitoring of the cleaning solution, regular maintenance of equipment, and the use of demineralized, deionized, or softened water to minimize unnecessary loading of the cleaner (EPA, 1991c).

Semi-Aqueous Cleaning

Cleaning systems using terpenes, dibasic esters, glycol ethers, n-methyl pyrrolidone, or other hydrocarbons, generally in combination with surfactants have been developed as alternatives to solvent degreasing. These hydrocarbon solvents are used in one of the following three cleaning processes: (1) emulsification in water, (2) application in concentrated form, followed by a water rinse, or (3) a combination of both. Because all of these techniques require water, the process generally is referred to as semi-aqueous.

The steps in a typical semi-aqueous cleaning process resemble those in aqueous processes - washing, rinsing, and drying (Figure 24). The only significant difference between the two cleaning processes is the primary cleaning tank. Because of their relatively strong solvency, semi-aqueous cleaning solvents exhibit good cleaning ability for heavy grease, tar, waxes, and hard to remove

61 The concentrated metals derived from either precipitation or ion exchange require disposal in accordance with federal, state, or local regulations.

62 Ion exchange can be performed in mixed-bed or dual-bed systems. Mixed beds combine the anion and cation exchange resins, while dual beds maintain them separately (Hood, 1991).

63 Surfactants are included in some semi-aqueous formulations to enhance the formulation's wetting, emulsification, and rinsing properties.

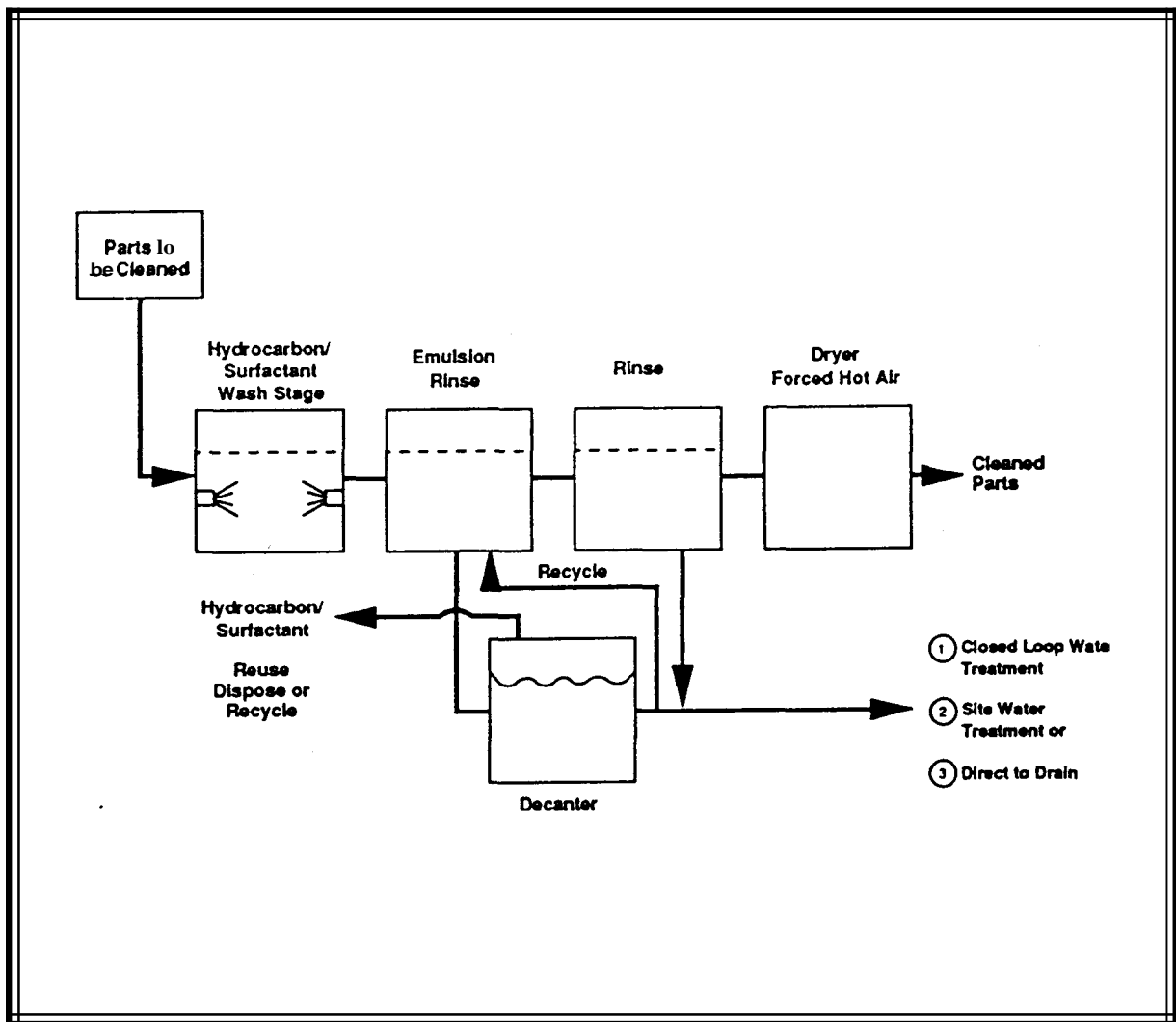


Figure 24. Semi-Aqueous Cleaning Process for an Immiscible Hydrocarbon Solvent (EPA, 1991a)

soils. In addition, hydrocarbon formulations used for semi-aqueous cleaning generally maintain their effectiveness through significantly higher soil loading than aqueous cleaners (Harmon, 1991).

Types of Cleaners⁶⁴

While this discussion will focus on cleaning systems that have been developed for use with terpenes, dibasic esters, glycol

ethers, and n-methyl pyrrolidone, the information generally can be extended to any such systems. Terpenes are a class of naturally occurring substances, derived from citrus and pine trees. Their chemical structures are similar to those of abietic acid and pimaric acid, the main components of printed circuit board flux residues. The most commonly used terpene in cleaning formulations to date is d-limonene, although many others

⁶⁴ Appendix IV contains a partial listing of companies offering semi-aqueous cleaners.

⁶⁵ EPA's Office of Pollution Prevention and Toxicology estimates that hundreds of terpenes could have potential use in cleaning formulations (Chemical Regulation Reporter, 1992). It has conducted an assessment of the health and environmental effects of eight terpenes including d-limonene, anethole, alpha- and beta-pinene, alpha- and beta-terpinene, terpinolene, and dipentene (EPA, 1990b).

exist.⁶⁵ Dibasic esters (DBEs) are refined dimethyl esters of adipic, glutaric and succinic acid, and have been shown to provide effective cleaning of many grimes and soils. Glycol ethers are effective solvents and have had a long history of industrial use, including their use in aqueous cleaning formulations. N-methyl pyrrolidone (NMP), an acetylene-based solvent, also appears to be an effective cleaning solvent in certain applications when combined with ultrasonics.

These four hydrocarbon solvents exhibit varying degrees of flammability,⁶⁶ and generally require that certain precautions be taken, especially if used in spray cleaning applications. All four have low vapor pressures, although they are still considered photochemically reactive and may be subject to VOC regulations in urban areas. This low volatility minimizes the potential for worker inhalation exposure.⁶⁷ While their low volatility means that emissions will be considerably lower than for vapor degreasing operations, these solvents do not dry quickly and require a water rinse to remove residues. As a result, rinsing is a particularly important step in the semi-aqueous process (EPA, 1991c).

Cleaning Processes

Semi-aqueous cleaning systems also can be configured as in-line or batch operations. Immersion equipment is the simplest and most common design that has been proposed. In these systems, the parts are dipped into the concentrated hydrocarbon/surfactant bath, an emul-

sion bath, or both. Additional energy (i.e., heating, ultrasonics, or spray under immersion) can be added to enhance the cleanliness, although the solvency of the hydrocarbon/surfactant often makes it unnecessary.

As noted above, caution must be taken in the use of sprays or in addition of heat, because of the solvents' combustibility. The use of high-pressure sprays below the surface of the liquid (**Figure 25**) prevents the formation of an atomized solution which can ignite at temperatures below the flash point (EPA, 1991c; Mouser, 1991). If heating is desired, it is recommended that the solution temperature be kept well below the flash point of the cleaner to avoid flammability concerns (EPA, 1991c; UNEP, 1991a).⁶⁸ In addition, because of the viscosity of the formulation, some ultrasonic equipment may not work properly with semi-aqueous cleaners.

The parts then are rinsed with clean water to remove residues left from the wash step. A water rinse may not be necessary if the operation includes an emulsion wash or rinse step and the application can tolerate some cleaner residue. For more demanding applications, a cascading rinse arrangement, or a final alcohol rinse, can be used to ensure the appropriate level of cleanliness. The rinse also may be used for the application of rust inhibitors or for other finishing processes.

Drying

Semi-aqueous cleaning processes gener-

66 Flash points for these solvents are as follows: terpenes - 100°F to >200°F; DBEs - 200°F to 225°F; glycol ethers - 100°F to 250°F; NMP - 199°F.

67 Some of the hydrocarbons used in semi-aqueous formulations have been found to have low toxicity, but others have not have been thoroughly tested (EPA, 1990b; UNEP, 1991a). Some cleaners (i.e., terpenes) exhibit objectionable odors, and may require local ventilation.

68 Dilute hydrocarbon emulsions formulated with water can be heated without a significant flammability concern (EPA, 1991c).

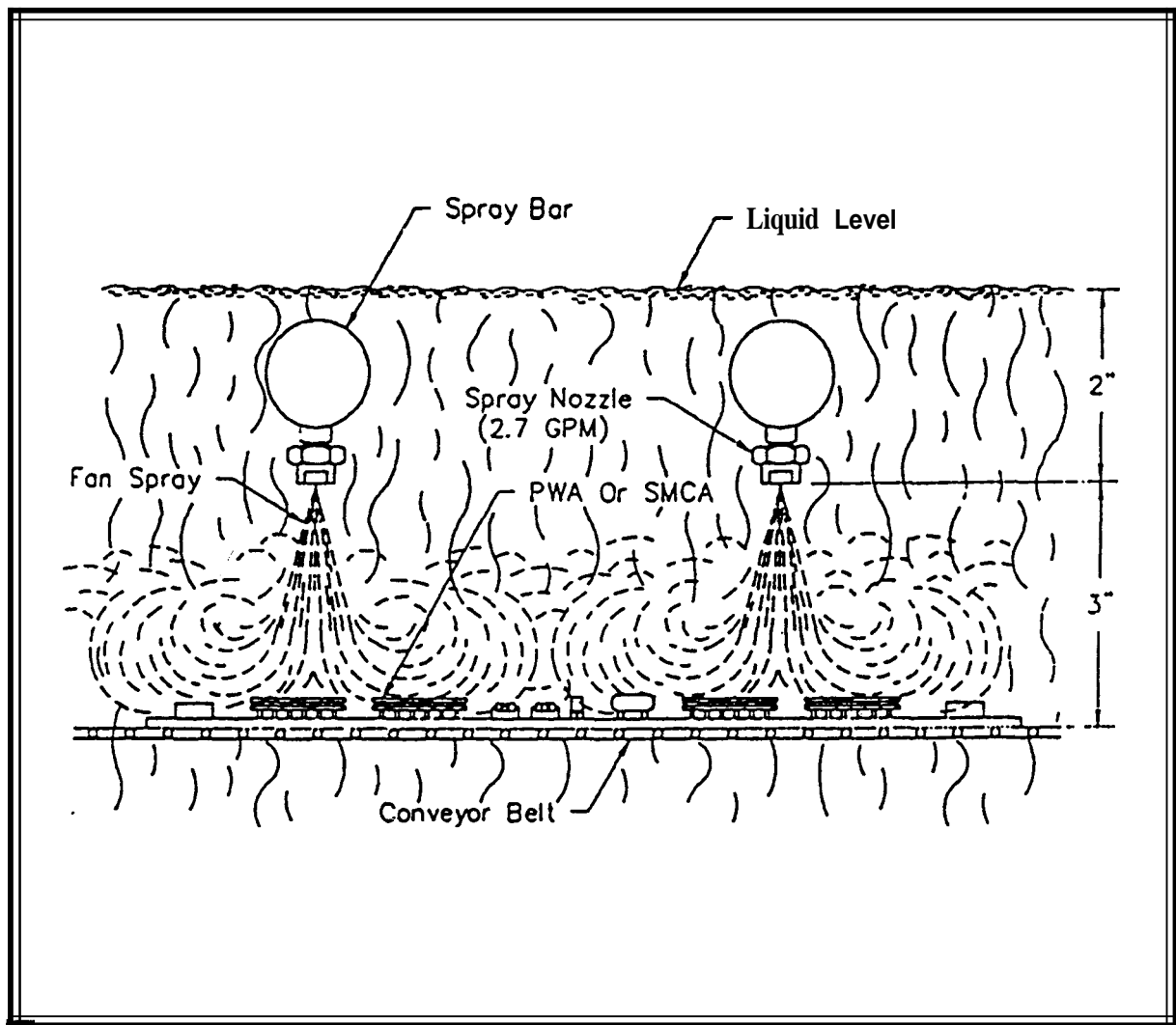


Figure 25. Immersion Spray Zone in an In-Line, Semi-Aqueous Cleaning System (Mouser, 1991)

ally require the addition of drying equipment to remove remaining water from the part for further processing or to prevent rusting. The available drying methods are the same as those for aqueous cleaning, and are described above. Hot-air recirculation and high velocity air blowers are the most common techniques (EPA, 1991c). As in aqueous cleaning, the drying step may not be necessary if the parts are not needed

immediately, and a rust inhibitor is used, or if the subsequent process (i.e., painting, electroplating) is water-based,

Wastewater Treatment

Because semi-aqueous cleaning generally demands water rinsing, the techniques available for treating semi-aqueous process effluent are the same as those for aqueous cleaning (see discussion above).

69 While most of these cleaners are biodegradable, they may not break down quickly into their constituent elements (EPA, 1991c). Moreover, while it may be possible to discharge effluent from semi-aqueous cleaners directly to the sewer in some parts of the country, interest in the closed-loop process is significant (Hood, 1991).

One additional problem that may be encountered with some semi-aqueous cleaners, however, is the inability of the solvent to separate quickly and completely from the rinse water and the resulting potential for significant organic discharge.⁶⁹ More recent, "second-generation" semi-aqueous formulations have been developed to separate more rapidly and completely, enabling the implementation of closed-loop recycling for rinse water.⁷⁰

As described above, some semi-aqueous systems include a two-stage rinse method consisting of both emulsion and water rinsing. In the emulsion section, the parts are given a preliminary rinse with an aqueous emulsion that contains a relatively high concentration of semi-aqueous cleaning agent dragged out from the wash tank. This emulsion rinse makes it possible to keep most of the cleaning agent and dissolved soils out of the water rinse baths (Fritz, 1991).⁷¹ The emulsion rinse is periodically discharged to a decanter where it separates into an aqueous layer and an organic layer (see **Figure 24**). The aqueous layer can be directly returned to the emulsion rinse tank without additional purification, while the organic layer, comprised of solvent and soil, can be collected for disposal.

If the soil can be removed, the cleaner can be returned to the cleaning bath. Recycling of these hydrocarbon solvents to remove dissolved oils and greases can be accomplished with vacuum distillation equipment (Harmon, 1992; SRRP, 1992). Depending on the quantity of waste

solvent generated, semi-aqueous cleaning operations may have to contract with a commercial recycler. Because of its relatively high BTU value, this solvent can be burned as fuel in an approved incinerator (EPA, 1991c).

Carbon Dioxide Cleaning

Cleaning with supercritical carbon dioxide (CO₂) and CO, snow are relatively new technologies that may have limited applicability for precision metal cleaning. Supercritical cleaning exploits the powerful solvent properties of CO₂, and other gases, when maintained at high temperature and pressure. CO, snow cleaning involves spraying pellets at the surface of the part to be cleaned to remove the contaminants through fracturing.

Above their critical temperature and pressure values,⁷² CO₂ and other gases exist as fluids with high diffusivity and low density and viscosity. This combination allows the fluid to effectively clean contaminants with medium molecular weight, but does not appear to be effective for removing ionic contaminants and particulate material (EPA, 1991a; IRTA, 1991b). The solvent power of the fluid can be varied by altering the temperature and pressure conditions. The technology is very specialized and relatively expensive, and may only be practical for the cleaning of precision parts that can withstand the extreme pressure and temperature conditions (Gallagher, 1991).

The use of CO₂ snow blasting to remove light organics and particulates from

70 Separation is complicated by the presence of surfactants, and surfactant-free formulations have been developed. Unlike other semi-aqueous hydrocarbons, NMP is miscible in water and requires distillation for separation (Lamm, 1991).

71 Carry out of solvent can be further controlled with the use of air knives to blow off excess cleaner from the parts as they exit the wash and emulsion rinse tanks (Fritz, 1991).

72 For CO₂, the critical temperature is 31°C and the critical pressure is 72.8 atmospheres.

metal surfaces has been adapted for use in certain specialized cleaning applications. Similar blasting techniques previously have been used to remove corrosion products, heat scale, and carbon deposits from metal parts. The use of CO₂ pellets is a relatively new development that minimizes the potential for damage to the part's surface and the amount of waste material generated (Schmitz, 1991). Upon contact with the surface, the CO₂ instantly sublimates and evaporates. Blasting is not effective for cleaning oil and greases, however, and can not effectively clean parts with crevices or blind holes (EPA, 1991b).

* * * * *



Summary

Cleaning of metal and other parts is an essential aspect of a variety of metalworking and other manufacturing processes. For many years, vapor degreasing using halogenated solvents has served as a versatile and dependable cleaning process for these applications.

Degreasing operations have been subject to several federal, state, and local regulations to control environmental releases of the halogenated solvents and to minimize worker exposure to these substances. These regulations have been designed to require the use of available technologies and services to minimize solvent losses. As a result, several emission control options are available to companies currently using the halogenated solvents for solvent cleaning.

The primary solvent loss mechanisms in degreasing operations are atmospheric emissions and losses in waste generated from the cleaning process. A variety of techniques have been developed in recent years for controlling atmospheric emissions from degreasers. These methods range from simple housekeeping practices to state-of-the-art equipment that can

drastically reduce emissions. Many of these techniques can be applied to existing degreasing machines.

Solvent losses in degreasing wastes have been reduced significantly through recycling activities, both on-site and off-site. In some cases, however, it may be possible to further reduce solvent losses through improved handling of these wastes.

Existing regulations also have encouraged some companies to replace their vapor degreasers with alternative cleaning solvents or processes. The pending phaseout of two of the halogenated solvents, 1,1,1-trichloroethane and CFC-113, has resulted in significant additional interest in alternatives to each in their various cleaning applications.

Several nonhalogenated substances have been available for some time as alternative cleaning solvents, while a few substances have been developed more recently. Traditional, flammable solvents have a long history of use in cleaning applications, but their applicability as vapor degreasing replacements

likely will be limited by technical and regulatory issues. Newer solvents or solvent systems have been developed to improve performance and to reduce regulatory considerations, but appear to have only limited application as replacements to halogenated solvents. The use of some of these newer solvents for cleaning may be limited, moreover, because of environmental concerns.

Alternative aqueous and semi-aqueous cleaning systems appear to offer significant potential for replacing vapor degreasing operations. Aqueous cleaning has been widely used in industry for many years, and recent developments have helped to improve cleaning performance and compatibility with waste treatment or closed-loop processes. While semi-aqueous systems present many of the same rinsing, drying, and wastewater treatment considerations as aqueous cleaning, they may offer superior cleaning performance and contaminant loading capacity.

Some existing degreasers may be retrofitted to accommodate simple water-based systems, but conversion to aqueous or semi-aqueous cleaning generally requires new equipment. The nature and cost of this equipment often will depend on the requirements of the specific cleaning operation. In evaluating these systems, it may be important to consider the particular requirements for cleanliness, drying, and wastewater treatment.

* * * * *

,



References

1. American Conference of Governmental Industrial Hygienists (ACGIH), 1991, Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices, Cincinnati, Ohio, 128p.
 2. _____, 1992, Report on 1992-1993 Proposed and Current Changes to TLV and BEI List, Report of the Chemical Substances TLV Committee to the ACGIH Membership, June 2.
 3. American Society for Testing and Materials (ASTM), 1989, Manual on Vapor Degreasing, ASTM Manual Series: MNL 2.
 4. Baxter, B.H., 1992, Developments in the Alcohol/PFC Cleaning Process, in Proceedings of the 1992 International CFC and Halon Alternatives Conference, Washington, D.C., September 29-October 1, p. 479-486.
 5. Bonnelycke, N., 1992, EPA's Safe Alternatives Program, Presentation to the Ozone Layer Protection Conference Addressing Metal Cleaning Alternatives, Sponsored by EPA Region V, Schaumburg, Illinois, October 27-28.
 6. ChemSystems, 1990, Methyl Chloroform Applications and Consumption - Outlook in the USA, Western Europe, and Japan, June.
 7. Chemical Week, 1991, HCFC-123 Hits a Snag in Toxicology Tests, 148(25): 10.
 8. Chemical Regulation Reporter, 1992, Hundreds of Terpenes Available as CFC Substitutes, More Data Needed, 15(43): 1575.
 9. Chiarella, W.J., 1990, Solvent Versus Aqueous Cleaning, American Machinist 134(6): 56-57 (June).
 10. _____, 1991, Alternatives for Solvent Cleaning, Presentation at Ozone Layer Protection Conference, U.S. Environmental Protection Agency Region I, Danbury, Connecticut, September 16-17.
 11. Dow Chemical Company (Chemicals and Metals Department), 1988, Waste Reduction Resources for Specialty Solvents, Form No. 100-6280-88R SMG.
 12. Enneking, J., 1991, Reverse Brayton Cycle Solvent Recovery, in Proceedings of the International CFC and Halon Alternatives Conference, Baltimore, Maryland, December 3-5, p. 122-135.
 13. Fritz, H.L., 1991, Waste Water Management for Semi-Aqueous Cleaning Processes, in Proceedings of the International CFC and Halon Alternatives Conference, Baltimore, Maryland, December 3-5, p. 96-104.
 14. Gallagher, P.M., 1991, Precision Parts Cleaning with Supercritical Carbon Dioxide, Presentation at Ozone Layer Protection Conference, U.S. Environmental Protection
-

- Agency Region I, Danbury, Connecticut, September 16-17.
15. Gerard, D.R., 1989, Solving Air Pollution by Reducing Emissions Losses from Solvent Vapor Cleaning Systems, *J. Testing Evaluation* 17(2): 106-117.
 16. Global Environmental Change Report, 1992, PAFT Finds Low Toxicity for HCFC-141b, Volume 4(21): 7.
 17. Hall, S.M., 1990, Predicting the Performance of VOC Condensers, *J. Air Waste Management Association* 40(3): 404-407.
 18. Harmon, J., 1991, Innovations in Chemical/Process Solutions to Metal Cleaning, in Proceedings of the International CFC and Halon Alternatives Conference, Baltimore, Maryland, December 3-5, p. 165-168.
 19. _____, 1992, Zero-Discharge Semi-Aqueous Cleaning Systems, in Proceedings of the 1992 International CFC and Halon Alternatives Conference, Washington, D.C., September 29-October 1, p. 349-364.
 20. Hayes, M., 1992, A New Process Alternative for Replacing CFC Solvents Cleaning, in Proceedings of the 1992 International CFC and Halon Alternatives Conference, Washington, D.C., September 29-October 1, p. 339-348.
 21. Hickman, J.C. and H.R. Goltz, 1991, Temporary Vapor Storage, in Proceedings of the International CFC and Halon Alternatives Conference, Baltimore, Maryland, December 3-5, p. 136-141.
 22. Hickman, J.C., 1992, Temporary Vapor Storage - A New Emission Control Technology, Presentation to the 85th Annual Meeting & Exposition of the Air and Waste Management Association, Kansas City, Missouri, June 21-26.
 23. Higgins, T.E., 1989, Hazardous Waste Minimization Handbook, Lewis Publishers, Inc., Chelsea, Michigan, 228p.
 24. Hood, C.C., 1991, Water Recycle in Semi-Aqueous Terpene Cleaning Processes, Presentation at Ozone Layer Protection Conference, U.S. Environmental Protection Agency Region I, Danbury, Connecticut, September 16-17.
 25. Institute for Research and Technical Assistance, (IRTA), 1991a, Printed Circuit Board Defluxing Without Chlorinated Solvents (unpublished).
 26. _____, 1991b, Metal and Precision Cleaning: Alternatives to Ozone Depleting Substances, March (unpublished).
 27. Jefcoat, I.A. and M.D. Heil, 1991, A Case Study of Waste Minimization by Process Change in Magnetic Tape Manufacture, Presentation at the 2nd Topical Pollution Prevention Conference, American Institute of Chemical Engineers, Pittsburgh, Pennsylvania, August 18-21.
 28. Kirk-Othmer, 1979, Encyclopedia of Chemical Technologies - Solvent Recovery, Volume 21.
 29. Kitamura, K., K. Ohnishi, S. Morikawa, and M. Yamabe, 1991, HCFC-225 As a Promising Substitute for Drop-In Replacement of CFC-113, in Proceedings of the International CFC and Halon Alternatives Conference, Baltimore, Maryland, December 3-5, p. 209-215.
 30. Knaggs, P., 1974, Ultrasonic Cleaning - Solvent Versus Aqueous, SubAssembly - Components - Fastening: 16-18 (March).
 31. Lamm, E., 1991, With New Water Miscible Chemistry, Semi-Aqueous Cleaning Has a New Twist, in Proceedings of the International CFC and Halon Alternatives Conference, Baltimore, Maryland, December 3-5, p. 307.
 32. Maltby, P., 1991, The Efficient Use of Aqueous Cleaning for Precision Components, in Proceedings of the International CFC and Halon Alternatives Conference, Baltimore, Maryland, December 3-5, p. 74-83.
-

33. Marinello, R.L., 1980, Metal Cleaning Solvents - Choices Available to Maintenance Shops, Plus Selection Guidelines and Safety Considerations, Plant Engineering.
 34. Meier, R., 1986, Technical Bulletin: Solvents Recovery - A Must, Phoenix International.
 35. Mertens, J.A., 1990, The Future of Solvent Cleaning: Steps to Emission Elimination, Presentation at the International Conference on CFC and Halon Alternatives, Baltimore, Maryland, November 27-28.
 36. Miasek, P.G. and J.L. Schreiner, 1991, Use of Advanced Hydrocarbon Fluids for Precision and Metal Cleaning, in Proceedings of the International CFC, and Halon Alternatives Conference, Baltimore, Maryland, December 3-5, p. 49-58.
 37. Mouser, W.L., 1991, Semi-Aqueous Cleaning in a High Production Environment, in Proceedings of the International CFC and Halon Alternatives Conference, Baltimore, Maryland, December 3-5, p.237-249.
 38. Naito, D., 1989, Non-Chlorofluorocarbon Type Cleaning Agent Pentafluoropropanol, in Proceedings of the International Conference on CFC and Halon Alternatives, Washington, D. C., October 10-11.
 39. Osterman, H., 1991, Setting Up a Test Protocol for Monitoring Solvent Loss Rates, Presentation at Meeting on Solvent Consumption Rating for New Cleaning Equipment, Washington, D.C., March 5.
 40. Ramsey, R.B., 1990, Vapor Degreaser Emission Control, Presentation at the International Manufacturing Technology Conference, Chicago, Illinois, September 11.
 41. Rowny, M.J. and S.D. Temple, 1991, Impingement: The Key to Effective Aqueous Cleaning, in Proceedings of the International CFC and Halon Alternatives Conference, Baltimore, Maryland, December 3-5, p. 174-183.
 42. Schindler, T., 1990, On-Site Solvent Recovery - Taking a Do-It-Yourself Approach to Waste Recovery, EI Digest (October),p. 23-28.
 43. Schmitz, W.N., 1991, CO₂ Pellet Blasting - Problems at First, but Worth a Second Look, Presentation at the Second Annual International Workshop on Solvent Substitution, Phoenix, Arizona, December 10-13.
 44. Source Reduction Research Partnership (SRRP), 1992, Source Reduction and Recycling of Halogenated Solvents in Parts Cleaning, 82 p.
 45. Temple, S.D., 1990, A New Era for Aqueous Cleaning, Products Finishing 54(6): 76-83.
 46. Tourigny, J.S., 1991, Alternative Cleaners and Methods for Benchtop Cleaning Electronics, in Proceedings of the International CFC and Halon Alternatives Conference, Baltimore, Maryland, December 3-5, p. 250-259.
 47. United Nations Environment Programme (UNEP), 1991a, Solvents, Coatings, and Adhesives Technical Options Report, December, 324p.
 48. _____, 1991b, Synthesis of the Ozone Scientific Assessment Panel, Environmental Effects Assessment Panel, and Technology and Economics Assessment Panel Reports, November, 33p.
 49. U.S. Department of Energy (DOE), 1990, The U.S. Department of Energy Brayton Cycle Solvent Recovery Heat Pump Project - Status Report, Office of Industrial Programs, February.
 50. U.S. Environmental Protection Agency (EPA), 1977, Control of Volatile Organic Emissions from Solvent Metal Cleaning, EPA-450/2-77-022 November.
 51. _____, 1983a, Photochemical Reactivity of Perchloroethylene, Environmental Science Research Laboratory, EPA-600/3-83-001, January, 61p.
-

52. _____, 1983b, Preliminary Analysis of Possible Substitutes for 1,1,1-Trichloroethane, Tetrachloroethane, Dichloromethane, Tetrachloromethane, Trichloroethylene, and Trichlorotrifluoroethane, Prepared by GCA Corporation for the Office of Policy and Resource Management, EPA-68-02-3168, May.
53. _____, 1989, Alternative Control Technology Document - Halogenated Solvents Cleaners, Office of Air Quality Planning and Standards, EPA-450/3-89-030 August.
54. _____, 1990a, Hydrofluorocarbons and Hydrochlorofluorocarbons - Interim Report, Office of Toxic Substances, November 15 (External Review Draft).
55. _____, 1990b, Aqueous and Terpene Cleaning - Interim Report, Office of Toxic Substances, November 15 (External Review Draft), 60p.
56. _____, 1991a, CFC-113 and Methyl Chloroform in Precision Cleaning Operations, Office of Air and Radiation, EPA/400/1-91/018, June, 100p.
57. _____, 1991b, Conservation and Recycling Practices for CFC-113 and Methyl Chloroform, Office of Air and Radiation, EPA/400/1-91/017, June, 78p.
58. _____, 1991c, Alternatives for CFC-113 and Methyl Chloroform in Metal Cleaning, Office of Air and Radiation, EPA/400/1-91/019, June, 94p.
59. _____, 1992a, Backg-round Information Document for Halogenated Solvent Cleaning/ Degreasing NESHAP, Chapters 3 and 4, Office of Air Quality Planning and Standards, October 1 (Draft).
60. _____, 1992b, Air Quality: Revision to Definition of Volatile Organic Compounds - Proposed Rule, Federal Register 57(207): 48490-48492.
61. _____, 1992c, Overview of Halogenated Solvent Cleaning/Degreasing NESHAP, Presented to the National Air Pollution Control Technology Advisory Committee, Office of Air Quality Planning and Standards, October 1.
62. Weaver, T.J.M., 1991, Recycling and Recovery of Cleaning Solutions, Presentation at Ozone Layer Protection Conference, U.S. Environmental Protection Agency Region I, Danbury, Connecticut, September 16-17.
63. Weemes, G.C., 1990, Design of Equipment for Use with HCFC Cleaning Fluids, Presentation at the International Conference on CFC and Halon Alternatives, Baltimore, Maryland, November 27-28.
64. _____, 1992, Memorandum to the Center for Emissions Control, June 15.
65. Whittall, K.L., 1991, Ultra Low Emission Solvent Vapor Degreasing, in Proceedings of the International CFC and Halon Alternatives Conference, Baltimore, Maryland, December 3-5, p. 116-121.
66. Yamabe, M., 1989, HCFC-225ca and 225cb as Alternatives to CFC-113, Presentation at the International Conference on CFC and Halon Alternatives, Washington, D. C., October 10-11.

* * * * *



Appendix I

Cleaning Equipment Manufacturers¹

- 1 - Vapor Degreaser**
- 2 - Aqueous**
- 3 - Semi-Aqueous**
- 4 - Other Hydrocarbon**
- 5 - Distillation Equipment**

ACCEL - 1, 2, 3
Plano, TX
214-424-3525

ACME-FAB - 2
Cincinnati, OH
513-489-3060

Advanced Curing Systems, Inc. - 2
Chicago, IL
312-247-3600

ADF Systems, Ltd. - 2
Humboldt, IA
515-332-5400

Advanced Deburring & Finishing - 2
York, PA
717-767-4843
800-553-7060

American Metal Wash, Inc. - 2
Canonsburg, PA
412-746-4203

Atcor Corp. - 2
Mountain View, CA
408-629-6080

Barnstead/Thermolyne Corp. - 5
Dubuque, IA
319-556-2241
800-446-6060

Baron Blakeslee Inc. - 1,3, 5
Long Beach, CA
310-491-1228

Barrett Centrifugals - 2
Worcester, MA
508-755-4306

Better Engineering Mfg., Inc. - 2
Baltimore, MD
410-931-0000
800-229-3380

Blackstone Ultrasonics Inc. - 1,2
Jamestown, NY
716-665-2340

Blue Wave Corporation - 1, 2
Davenport, IA
319-322-0144
800-373-0144

Bowden Industries Inc. - 2
Huntsville, AL
800-553-3637

Branson Ultrasonics Corp. - 1,2, 3, 5
Danbury, CT
203-796-0400

¹ This appendix is not intended to be a complete listing of available products and services.

Cincinnati Industrial Machinery - 2
Cincinnati, OH
513-769-0700

D.C. Cooper Company - 5
Chicago, IL
312-427-8046

Corpane Industries Inc. - 1,2, 3
Louisville, KY
502-491-4433

Crest Ultrasonics - 1,2, 3, 5
Trenton, NJ
609-883-4000
800-441-9675

Detrex Corp. (Equipment Mfg. Div.) - 1,2, 3, 5
Bowling Green, KY
502-782-1511

Disti, Inc. - 5
New York, NY
212-529-3989

DURR Automation, Inc. - 1,2
Davisburg, MI
313-625-5400

Electronic Control Designs, Inc. - 2
Milwaukie, OR
503-659-6100

Fentech - 1
Selbyville, DE
302-436-1780

Finishing Equipment Inc. - 1,2, 5
St. Paul, MN
612-452-1860

Forward Technology Industries Inc. - 2
Minneapolis, MN
612-559-1785

FMT, Inc. (Industrial Equipment Div.) - 2
Findlay, OH
419-422-0768
800-878-8011

FPI Systems - 2
North Haven, CT
203-281-6161

Giant Distillation & Recovery Company - 5
Toledo, OH
419-531-4600

Goff Corp. - 2
Seminole, OK
405-382-6900

Hotsy Corp. - 2
Englewood, CO
303-792-5200

Hotsy Equipment Company - 2
Boston, MA
800-544-7790

Jensen Fabricating Engineers, Inc. - 2
East Berlin, CT
203-828-6516

KEW Cleaning Systems, Inc. - 2
Carol Stream, IL
708-690-3000

Kleer-Flo Company - 2
Eden Prairie, MN
612-934-2555
800-328-7942

George Koch & Sons Inc. - 2
Evansville, IN
812-426-9600

L&R Manufacturing Company - 2
Kearny, NJ
201-991-5330
800-572-5326

Lenape Systems - 5
Manasquan, NJ
908-919-0405

Lewis Corp. - 1,2
Oxford, CT
203-264-3100

Mart Corp. - 2
Maryland Heights, MO
800-543-6278

Midwest Ultrasonics Co. - 2
Dearborn, MI
313-584-5616

NAPCO, Inc. - 2
Terryville, CT
203-589-7800

J.M. Ney Company - 3
Bloomfield, CT
203-286-6149

Oinni Finishing Systems, Inc. - 2
Ivyland, PA
215-953-1166

Proceco Inc. - 2
Jacksonville, FL
904-355-2888

Progressive Recovery Inc. - 5
Dupo, IL
618-286-5000

RAMCO Equipment Corp. - 1, 2
Hillside, NJ
908-687-6700
800-553-3650

Ransohoff Company - 2
Hamilton, OH
513-863-5813
800-248-9274

Safety Kleen Equipment System - 4
Des Plaines, IL
708-299-4060

Siva International, Inc. - 5
Ocala, FL
904-237-1220

S&K Products International - 1,2
Chestnut Ridge, NY
914-425-6200

SONICOR Instrument Corp. - 1, 2, 5
Copiague, NY
516-842-3344

Stoelting, Inc. - 2
Kiel, WI
414-894-2293
800-558-5807

Surface Dynamics Inc. - 1,2
Plymouth, MI
313-459-0010

Surf/Tran - 1,2
Madison Heights, MI
313-547-3133

Tally Cleaning Systems - 1,2
Attleboro Falls, MA
508-695-1007

Ultra-Kool Inc. - 1
Gilbertsville, PA
215-367-2019

Unit Design, Inc. - 2
Orange, CA
714-282-8100

Vapor Engineering - 1
Pensacola, FL
904-434-3191

Vitronics Corp. - 2, 3
Newmarket, NH
603-659-6550

Westek - 2
Vero Beach, FL
Arcadia, CA
407-388-5854
818-446-4444

Whitney Systems Inc.
Chelmsford, MA
508-937-7444

Zenith
Closter, NJ
201-767-1332

Wastewater Treatment Equipment Manufacturers

Aqualogic Inc.
North Haven, CT
203-248-8959

Golden Technologies Company
Golden, CO
303-239-7700

Haviland Engineering, Inc.
Grand Rapids, MI
800-456-1134

Hotsy Equipment Company
Boston, MA
800-544-7790

Ionics, Inc.
Watertown, MA
800-338-9238

Koch Membrane Systems Inc.
Wilmington, MA
508-657-4250
800-343-049.9

Leatherwood Plastics
Lewinsville, TX
214-221-7656

Memtek Corp.
Billerica, MA
508-667-2828

Napco Inc.
Terryville, CT
203-589-7800

Osmonics, Inc.
Minnetonka, MN
612-933-2277
800-351-9008

PROSYS Corp.
Chelmsford, MA
508-250-4940

Rosedale Products Inc.
Ann Arbor, MI
313-665-8201
800-821-3373

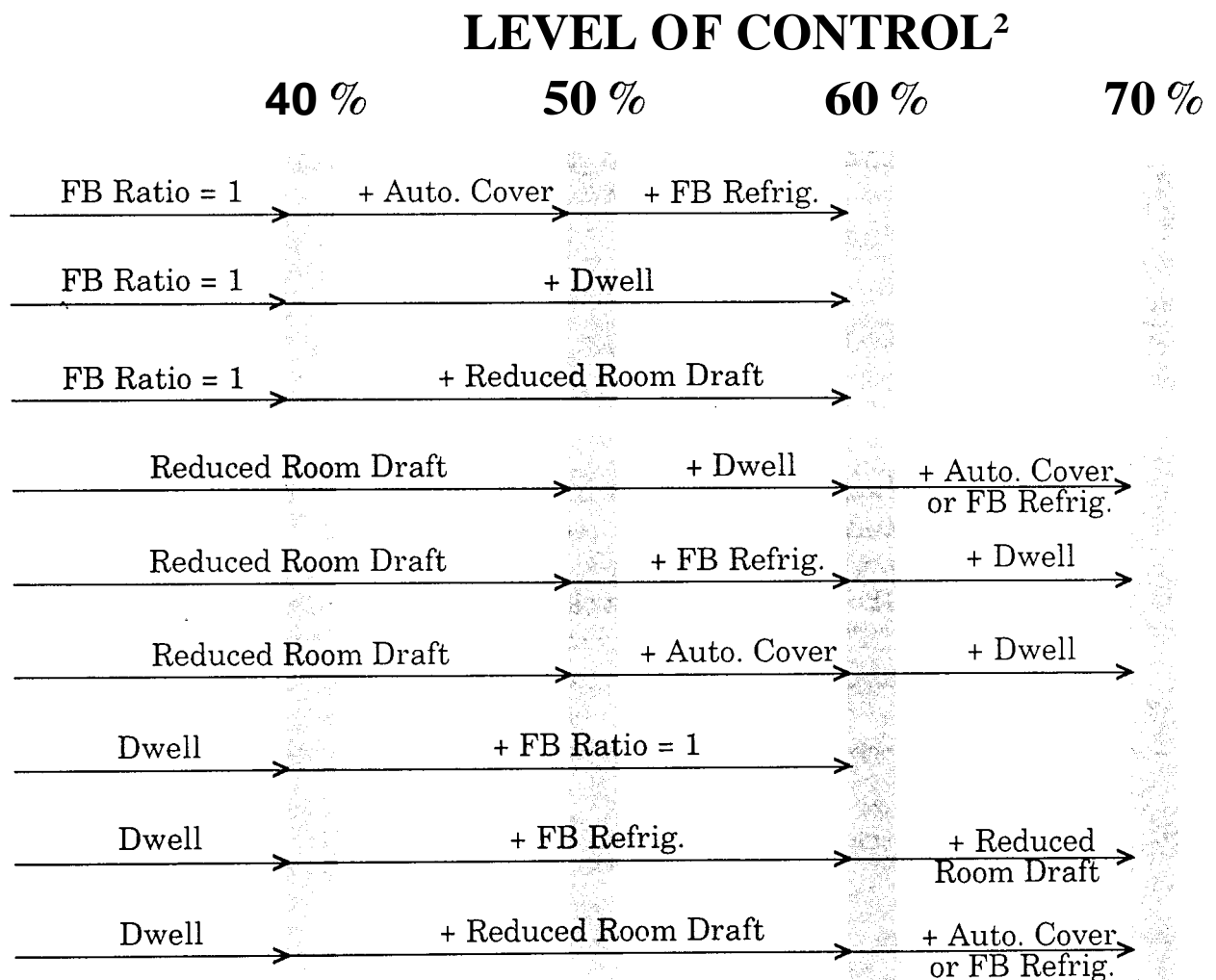
Separation Technologists
Metheun, MA
508-794-1170

* * * * *



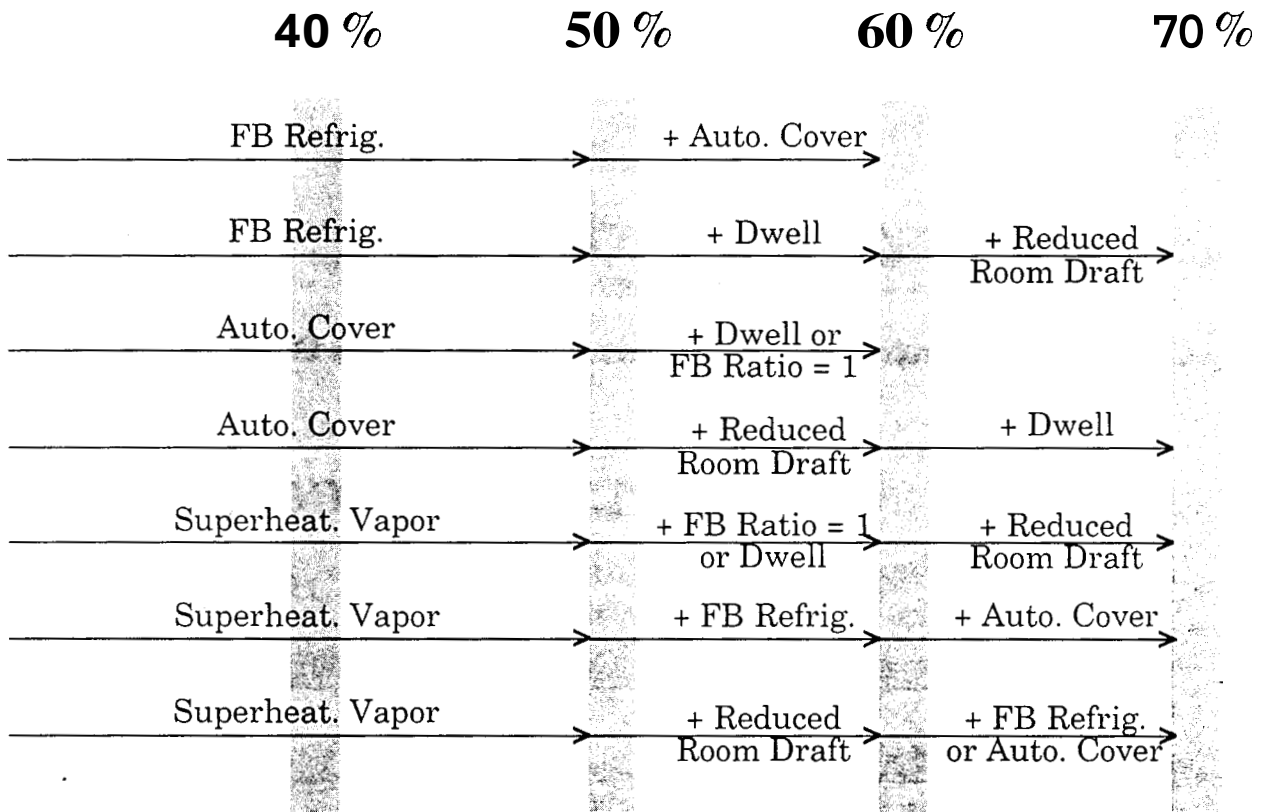
Appendix 11

Combined Control Efficiencies for Open-Top Degreasers¹



- 1 This chart summarizes information developed by EPA's Office of Air Quality Planning and Standards for its national emission standard for degreasing (EPA, 1992c). It is not intended as an evaluation of all available emission control options.
- 2 The level of control, as determined by EPA, is a measure of the potential reduction in solvent loss (compared to uncontrolled emissions), based on an operating schedule of 6 hours working, 2 hours idle, and 16 hours downtime for 260 days/year (EPA, 1992c). For the purposes of this chart, all degreasers are assumed to be equipped with a manual cover and a hoist operated at a vertical speed of 11 feet per minute (EPA, 1992c).

LEVEL OF CONTROL



FB Ratio = 1 -- Increase in freeboard ratio from 0.75 to 1.0

FB Refrig. -- Freeboard refrigeration device

Auto. Cover -- Automated (bi-parting) cover

Dwell -- Addition of a dwell time to the cleaning cycle during which the parts are held above the vapor zone

Reduced Room Draft -- Reduction in room drafts from 100 to 50 feet per minute

Superheat. Vapor -- Inclusion of a superheated vapor cycle

* * * * *



Appendix III

Commercial Solvent Recyclers¹

Alabama

M&M Chemical Corp.
Attala, AL
205-543-9721

Southdown Environmental Systems
Birmingham, AL
205-841-1707

Arizona

Romic Chemical Corp.
Chandler, AZ
602-377-2613

California

Detrex Corp.
Los Angeles, CA
213-588-9214

Oil and Solvent Process Company
Azusa, CA
818-334-9002

Romic Chemical Corp.
East Palo Alto, CA
415-324-1638

Safety Kleen Corp.
Reedley, CA
209-638-3010

Southdown Environmental Systems
Inglewood, CA
213-776-6233

Canada

Anacheinia Solvents
Mississauga, Ontario
416-279-5122

Colorado

Chemical Waste Management
Henderson, CO
303-289-4827

Florida

Laidlaw Environmental Services
Bartow, FL
813-533-6111

Georgia

M & J Solvents Company
Atlanta, GA
404-416-9692

Southeastern Chemical/Omni
Norcross, GA
404-449-1070
800-872-7003

¹ This appendix includes a list of active members of the National Association of Chemical Recyclers, as of March 30, 1992. It is not intended to be a complete listing of available products and services.

Illinois

Clayton Chemical Company
Sauget, IL
618-271-0467

Safety Kleen Corp.
Chicago, IL
Dolton, IL
Elgin, IL
312-247-2828
708-849-9475
708-697-8460

Indiana

Avganic Industries
Terre Haute, IN
812-232-5411

Detrex Corp.
Indianapolis, IN
317-241-9379

Industrial Fuels and Resources
South Bend, IN
219-234-0441

Reclaimed Energy Company
Connersville, IN
317-825-7101

Michigan

City Environmental
Roseville, MI
313-778-1414

Detrex Corp.
Detroit, MI
313-491-4550

Michigan Recovery System
Romulus, MI
517-326-3100

Nortru
Detroit, MI
313-824-5850

Missouri

Burlington Environmental
Kansas City, MO
816-474-1391

Industrial Fuels and Resources
Scott City, MO
314-651-3444

New York

Pride Solvents and Chemicals
Babylon, NY
516-643-4801

New Jersey

Marisol, Inc.
Middlesex, NJ
908-469-5100

Safety Kleen Corp.
Clayton, NJ
Linden, NJ
609-881-2526
908-862-2000

North Carolina

Detrex Corp.
Charlotte, NC
704-372-9280

Ohio

CWM Resource Recovery
West Carrollton, OH
513-859-6101

Hukill Chemical Corp.
Bedford, OH
216-232-9400

Safety Kleen Corp.
Hebron, OH
614-929-3532

Oklahoma

Hydrocarbon Recycling Services
Tulsa, OK
918-446-7434

Puerto Rico

Safety Kleen Corp.
Manati, PR
809-854-1740

Rhode Island

Chein Pak Corp.
Cranston, RI
401-467-3820

South Carolina

Safety Kleen Corp.
Lexington, SC
803-356-1250

Southeastern Chemical/Omni
Suinter, SC
803-773-1400

Texas

Detrex Corp.
Arlington, TX
817-640-6017

Gibraltar Chemical Resources
Winona, TX
903-877-3227

Safety Kleen Corp.
Denton, TX
817-383-2611

Chemical Reclamation Services
Avalon, TX
214-299-5043

USPCI
San Antonio, TX
210-490-9790

Washington

Burlington Environmental/Chempro
Wasougal, WA
206-835-8743

Wisconsin

Avganic Industries
Cottage Grove, WI
608-839-4571

Milsolv Company
Butler, WI
414-252-3550

* * * * *



Appendix IV

Solvent and Aqueous Formulation Manufacturers^{1,2}

- 1 - Halogenated Solvents**
- 2 - Aqueous Formulations**
- 3 - Semi-Aqueous Solvents**
- 4 - Other Hydrocarbon Solvents**

Aeromarine Corp. - 2
Brunswick, ME
207-729-0191

Alconox, Inc. - 2
New York, **NY**
212-473-1300

Allied Signal Inc. - 1
Morristown, NJ
201-455-2000

Alpha Metals - 1,2, 3
Jersey City, NJ
201-434-6778

Antrim, Inc. - 2
Greenville, SC
803-242-6152

Apex Alkali Products - 2
Pladefphia, PA
215-483-3939

Arco Chemical Company - 4
Newton Square, PA
215-359-2000

Ardrox - 2
Lake Bluff, IL *
708-295-1660

Ashland Chemical - 1,2, 3, 4
Columbus, OH
614-889-3333

BASF Corp. - 4
Parsippany, NJ
800-543-1740

Better Engineering Mfg., Inc. - 2
Baltimore, MD
800-229-3380

Biochem Systems - 3
Golden, CO
303-239-7700 (BIO TTM)

Blue Wave Corp. - 2
Davenport, IA
800-373-0144

BroCo Products Inc. - 2
Cleveland, OH
216-531-0880
800-321-0837

Brulin Corp. - 2
Indianapolis, IN
800-776-7149

Chargar Corp. - 2
Hamden, CT
203-562-9948

A.W. Chesterton Company - 2
Stoneham, MA
617-438-7000

1 This appendix is not intended to be a complete listing of available products and services.
2 Mention of companies or products is for information purposes only, and does not constitute a recommendation.

Chem Tech - 2
Alexandria, VA
703-549-1001

Cleaning Systems, Inc. - 2
Green Bay, WI
414-337-2175
800-225-2231

Cook Composites and Polymers - 2
Port Washington, WI
414-284-5541

Crest Ultrasonics - 2
Trenton, NJ
609-883-4000
800-441-9675

Delta-Omega Technologies - 2
Lafayette, LA
318-237-5091 (DOT™)

Dow Chemical - 1,2,3
Advanced Cleaning Systems
Midland, MI
800-447-4369 (PrimaClean™)

Dubois Chemicals - 1,2,3
Cincinnati, OH
513-762-6000
800-438-2647

Du-Lite Corp. - 2
Middleton, CT
203-347-2505

Dupont Company - 1,3
Chemicals & Pigments
Wilmington, DE
302-774-2099
800-441-9442 (AXAREL™)

3D Inc. - 2,3
Benton Harbor, MI
800-272-5326

Envirosolv - 3
Jacksonville, FL
904-724-1990 (RE-ENTRY™)

ETUS, Inc. - 2
Sanford, FL
407-321-7910

Exxon Chemical Company - 4
Houston, TX
713-870-6000
800-526-0749 (ACTREL™, EXXATE™)

EZE Products - 1,2
Greenville, SC
803-879-7100

Fine Organics Corp. - 1,2
Lodi, NJ
800-526-7480

Frederick Gumm Chemical Company - 2
Kearny, NJ
201-991-4171 (CLEPO™)

Fremont Industries - 2
Shakopee, MN
612-445-4121

Glidco Organics Corp. - 3,4
Jacksonville, FL
904-768-5800

W. R. Grace & Company - 2
Dewey and Almy Chemical Division
Lexington, MA
617-861-6600 (Daraclean™)

Graymills Corp. - 2,4
Chicago, IL
312-477-4100

Harry Miller Corp. - 2
Philadelphia, PA
215-314-4000

Haviland Products Company - 2
Grand Rapids, MI
616-361-6691
800-456-1134

Houghton Chemical Corp. - 2
Allston, MA
617-254-1010

Hubbard Hall Inc. - 1,2, 3
Waterbury, CT
203-756-5521
800-756-3412 (AquaEase™)

Hydrite Chemical Company - 2
Milwaukee, WI
414-354-3750

ICI Americas - 1,3
Wilmington, DE
302-886-3000

International Specialty Products - 3
Wayne, NJ
201-628-3000

Kester Solder - 1,2
Jamestown, NY
716-665-3438

Kyzen Corp. - 3
Nashville, TN
615-831-0888
800-845-5524 (IONOX™)

Magnuson Products - 2
Clifton, NJ
201-472-9292

McGean-Rohco Inc. - 1,2
Cleveland, OH
800-932-7006

Modern Chemical Inc. - 2
Jacksonville, AR
501-988-1311 (BLUE GOLD™)

Nalco Chemical Company - 2
Naperville, IL
708-305-1000

Novamax Technologies, Inc. - 2
Livonia, MI
313-464-4555
800-521-5770

Oakite Products, Inc. - 1,2, 3
Berkeley Heights, NJ
908-464-6900
800-526-4473

Occidental Chemical Corporation - 1, 4
Niagara Falls, NY
716-286-3000

OCS Manufacturing - 2
San Gabriel, CA
818-458-2471

Orange-Sol, Inc. - 3
Chandler, AZ
602-497-8822

Panther Chemical Company - 2
Fort Worth, TX
817-834-7164

Parker-Anchem - 2
Madison Heights, MI
313-583-9300

Penetone Corp. - 2
Tenafly, NJ
201-567-3000
800-631-1652

Petroferm - 3, 4
Fernandina Beach, FL
904-261-8286 (BIOACT™)

PPG Industries Inc. - 1,3
Pittsburgh, PA
800-243-6774 (Micro-Phase 3™)

Quaker Chemical Corp. - 2
Conshohocken, PA
215-832-4000
800-523-7010

Rochester Midland - 2, 4
Rochester, NY
716-336-2200 (Biogenics™, Neugenics™)

SWI International Inc. - 2
Boonton, NJ
800-334-2524

Shell Chemical Company - 4
Houston, TX
713-241-5383

Starlite Chemicals, Inc. - 2
Chicago, IL
312-772-2278

Storchem, Inc. - 3, 4
Toronto, Ontario, Canada
416-695-2877

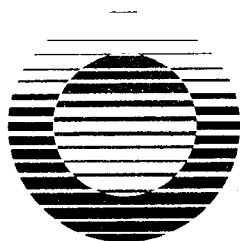
Turco Products - 2
Westminster, CA
714-890-3600

U.S. Polychemical - 2
Spring Valley, **NY**
914-356-5530
800-431-2072

Vulcan Chemicals - 1, 3
Birmingham, AL
800-873-4898 (HydroPer™)

Witco Corp. - 2
New York, NY
212-605-3800

* * * * *



Center
for
Emissions
Control

1025 Connecticut Avenue, N.W.
Suite 712
Washington, D.C. 20036
1-800-835-5520