A COMPARISON OF CFCs, HCFCs AND SEMI-AQUEOUS AGENTS FOR PRECISION METAL CLEANING

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ABSTRACT

CFC-113-based cleaning agents, once considered "ideal" for metal cleaning applications, will soon be phased out under provisions of the Montreal Protocol. As a result, CFC-113 users are examining alternative technologies for metal degreasing. HCFC and semi-aqueous cleaning represent two major classes of alternative technologies.

This paper compares the properties, performance and ecology of an HCFC blend (consisting of 34.9% HCFC-141b, 64.8% HCFC-123 and 0.3% stabilizer), HCFC-123 and a hydrocarbon-based, semi-aqueous agent to those of CFC-113.

Both the HCFC blend and HCFC-123 are superior to CFC-113 for removing heavy grease and water-soluble oil residues. They are equivalent to CFC-113 for removing light oils, but slightly less effective for removing waxes and buffing compounds. The hydrocarbon-based agent for semi-aqueous cleaning is more effective than CFC-113 for removing light oil, heavy grease and when heated, wax.

This paper also discusses the equipment and process design considerations for these CFC alternatives. Generally, these alternative technologies require new equipment vs. CFC-113 vapor degreasers; although some existing equipment may be retrofitted for HCFC use.

INTRODUCTION

Cleaning is required in the metal-working industry to remove oils, greases, metal-working fluids, abrasive polishing compounds and particulate contamination, such as metal fines and shop soils.

Over the last 30 years, cleaning agents based on CFC-113 and chlorocarbon solvents, such as 1,1,1-trichloroethane, have been used successfully in vapor degreasing processes. CFC-113 gained widespread acceptance due to its numerous desirable characteristics. It is nonflammable, chemically and thermally stable and low in toxicity. In addition, CFC-113 operates at low temperatures, provides selective solvency, is easily recovered and, most importantly, is an extremely effective cleaner. Used in the time-proven vapor degreasing process, CFC-113 achieves the highest levels of cleanliness for spot-free cleaning of precision metal parts.

However, because of its high ozone depletion potential (ODP) and global warming potential (GWP), CFC-113 is no longer considered an "ideal" cleaning agent. In fact, under the provisions of the Montreal Protocol, CFC-113-based cleaning agents will be phased out by the year 2000. In the interim, supplies will diminish and costs will increase significantly. Therefore, CFC-113 users are examining more environmentally acceptable alternatives, such as HCFC and semi-aqueous cleaning agents.

This paper compares an HCFC blend and HCFC-123 for use in a modified vapor degreasing process and a hydrocarbon-based agent for use in the semi-aqueous cleaning process to traditional CFC-113 cleaning.

HCFCs VS. CFCs: A PROPERTY COMPARISON

Comparative Properties

HCFC alternatives can be designed to retain many of the desirable characteristics of CFCs. In 1989, an HCFC blend, consisting of 34.9% HCFC-141b, 64.8% HCFC-123 and 0.3% stabilizer, was introduced by Du Pont for precision metal cleaning. Recently, Du Pont also introduced another effective, environmentally compatible cleaning agent, HCFC-123. The properties of these HCFCs compared to those of CFC-113 are shown in Table 1.

These HCFC alternatives have lower boiling points, and hence, higher vapor pressures at comparable temperatures than the CFCs they would replace. Thus, they necessitate using new vapor degreasing equipment or modifying existing equipment, as discussed in the following section (HCFC Equipment and Process Design Considerations). However, the low surface tension and viscosity of these products prove extremely helpful in cleaning metal parts.

Since they are constantly boiling, the HCFC blend and HCFC-123 exhibit azeotrope-like behavior under the conditions used in a vapor degreaser for cleaning metals. In addition to compositional stability, they are extremely chemically stable. In reflux corrosion tests, they exhibited excellent chemical stability.

Comparative Environmental Impact

From an environmental standpoint, both the HCFC blend and HCFC-123 offer advantages over CFCs in both ODP and GWP. The presence of hydrogen atoms on the HCFC molecule dramatically reduces its atmospheric life, and hence the ODP of these compounds. The atmospheric life of CFC-113 is approximately 90 years, compared to 12 years for HCFC-141b and only two years for HCFC-123. The shorter atmospheric life of these compounds translates into an order of magnitude decrease in the ODP of the HCFC alternatives compared to CFCs.

Both the HCFC blend and HCFC-123 have significantly lower GWPs than CFCs -- 0.08 and 0.02, respectively, compared to 1.35. Even though CFCs are responsible for less than 10% of the GWP, substituting shorter life HCFCs for CFCs will reduce the concentration and contribution of these compounds to the earth's warming.

TABLE 1. Comparative Properties of an HCFC Blend,[a] HCFC-123 and CFC-113

Property	Units	HCFC Blend[a]	HCFC-123	CFC-113
Boiling Point	°F (°C)	84.6 (29.2)	82.2 (27.9)	117.6 (47.6)
Vapor Pressure at 77° F (25° C)	psia	13.0	14	6.5
Liquid Density at 77° F (25° C)	lb/gal g/cc	11.43 1.37	12.16 1.46	13.06 1.57
Latent Heat of Vaporization at Boiling Point	BTU/lb	79.2	74.9	63.1
Surface Tension at 77° F (25° C)	dynes/cm	17.3	16	17.3
Viscosity at 77° F (25° C)	cp	0.42	0.45	0.68
Estimated Ozone Depletion Potential (CFC-11=1)	--	0.07	0.02	0.80
Global Warming Potential	--	0.07	0.02	1.35
Flammability	--	No	No	No
Estimated Toxicity	ppm by vol	150 (AEL)[b]	100 (AEL)[b]	1,000 (TLV)[c]

[a] This HCFC blend consists of 34.9% HCFC-141b, 64.8% HCFC-123 and 0.3% stabilizer.

[b] An Acceptable Exposure Limit (AEL) is the recommended time-weighted average concentration of an airborne chemical to which nearly all workers may be exposed during an 8-hr day, 40-hr week without adverse effect, as determined by the Du Pont Company for compounds that do not have a Threshold Limit Value (TLV®).

[c] A Threshold Limit Value (TLV®), established for industrial chemicals by the American Conference of Governmental Industrial Hygienists, is the time-weighted average concentration of an airborne chemical to which nearly all workers may be exposed during an 8-hr day, 40-hr week without adverse effect.

HCFC EQUIPMENT AND PROCESS DESIGN CONSIDERATIONS

One trade-off of HCFC-141b/123-based products used in vapor degreasing equipment is their relatively low boiling points compared to CFC-113. To minimize solvent losses, new equipment or retrofitted existing equipment must incorporate provisions for controlling emissions due to leaks, dragout and diffusion, as discussed below.

Controlling Leaks

To minimize solvent emissions due to leakage, the equipment itself should be fabricated from materials that are chemically compatible with the cleaning agent. Type 304 and Type 316 stainless steel are the preferred materials of construction for equipment. Copper and brass may be acceptable for valves and piping in degreasers, if they are compatible with the soils being removed. Seals and gaskets should also be chemically compatible with the cleaning agent. (Refer to the HCFC Compatibility with Plastics and Elastomers section.)

Controlling Dragout

Dragout can be minimized by designing work baskets and methods of handling parts that minimize solvent entrapment and maximize solvent drainage during cleaning. In addition, the flow of parts through the degreaser should be controlled to avoid disturbing the vapor/air interface during part insertion and removal. The recommended maximum speed for part entry and removal is 10 ft/min.

However, even with these measures, parts removed from a degreaser contain a thin liquid film that evaporates, resulting in vapor emission. One way to minimize or even eliminate this dragout is to dry the part in the vapor zone, using superheated vapor drying. This technology subjects the part to solvent vapor heated above its normal boiling point in the vapor zone. This superheated vapor evaporates any entrapped solvent and the liquid film, allowing the part to emerge dry.

Controlling Diffusion

In a vapor degreaser, relatively stagnant gas in the freeboard zone is sandwiched between a layer of 100% solvent vapor (extending from the condenser downward) and a layer of 100% air (extending upward from the top of the machine). This causes diffusion to occur as the solvent vapor migrates from an area of high vapor concentration to an area of low vapor concentration. To minimize the rate of diffusion, deeper freeboards and lower condenser temperatures compared to CFC-113 equipment are needed.

HCFC COMPATIBILITY WITH PLASTICS AND ELASTOMERS

In general, the HCFC blend and HCFC-123 are more aggressive than CFC-113 and less aggressive than chlorinated solvents, such as 1,1,1-trichloroethane. They are compatible with a wide range of plastics, elastomers and metals. Typically, they are gentle enough for cleaning metal assemblies having components made of many common plastics. Table 2 shows the compatibility of the HCFC blend and HCFC-123 with various plastics.

Elastomeric gaskets and seals used in the construction of cleaning equipment are exposed to the cleaning agent for long time periods. Table 3 shows the compatibility of the HCFC blend and HCFC-123 with various elastomers. Specific recommendations are available for suitable gasket and seal materials for operating equipment.

TABLE 2. Plastic Compatibility of an HCFC Blend[a] and HCFC-123 under Typical Cleaning Conditions[b]

Plastic	Tradename	HCFC Blend[a]	HCFC-123	CFC-113
ABS	Kralastic®	3	3	0
Acetal	DELRIN®	1	1	0
Acrylic	LUCITE®	3	3	0
Cellulosic	Ethocel™	3	3	3
Epoxy	--	1	1	0
Fluorocarbon	TEFLON® TFE, FEP, PFA	1	1	0
Ionomer	SURLYN®	0	0	0
Nylon	ZYTEL®	0	0	0
Polycarbonate	Tuffak®	3	3	0
Polyester	RYNITE®, Valox®	0	0	--
Polyetherimide	Ultem®	0	0	--
Polyethylene	ALATHON® HDPE	0	0	0
Polyphenylene Oxide	Noryl®	2	2	0
Polyphenylene Sulfide	Ryton®	0	0	--
Polypropylene	--	0	0	0
Polystyrene	Styron™	3	3	0
Polysulfone	--	0	0	0
Polyvinyl Chloride	--	0	0	0

[a] This HCFC blend consists of 34.9% HCFC-141b, 64.8% HCFC-123 and 0.3% stabilizer.

[b] Test Conditions: Samples immersed in boiling liquid for 5 min.

Key:
0 = Compatible
1 = Probably Compatible
2 = Probably Incompatible
3 = Incompatible

TABLE 3. Elastomer Compatibility of an HCFC Blend[a] and HCFC-123 under Typical Cleaning Conditions[b]

Elastomer	Common/ Tradename	Extractables (%) HCFC Blend[a]	HCFC-123	CFC-113
Polyurethane	ADIPRENE®	3	8	0.2
Acrylonitrile-butadiene	Buna N	21	3	20
Styrene-butadiene	Buna S	12	15	8
Isobutylene-isoprene	Butyl	7	12	7
Chlorosulfonated Polyethylene	HYPALON®	13	7	3
Polyester TPE	HYTREL®	1	7	0.2
Natural Polyisoprene	Natural	4	7	5
Polychloroprene	Neoprene	19	20	17
Ethylene/Propylene Terpolymer	NORDEL®	31	35	30
Polysiloxane	Silicone	3	5	2
Polysulfide	Thiokol FA	0.3	4	0.3
	Thiokol ST	2	7	0.4
Fluoroelastomer	VITON® A	4	8	0.4
	VITON® B	0.3	3	0
Perfluoroelastomer	KALREZ®	0.4	8	--

[a] This HCFC blend consists of 34.9% HCFC-141b, 64.8% HCFC-123 and 0.3% stabilizer.
[b] Test Conditions: Samples immersed in boiling liquid for at least 8 hrs.

SEMI-AQUEOUS VS. CFCs: A PROPERTY COMPARISON

Comparative Properties

A hydrocarbon-based agent for semi-aqueous cleaning of precision metals, commercially available from Du Pont, combines polar and nonpolar components to yield a proper balance of selective solvency, high flash point, low toxicity, maximum biodegradability and other important characteristics. Its hydrocarbon base component is non-aromatic. In addition to low toxicity, high flash point and mild odor, the hydrocarbon base was selected for its ready and abundant availability and for its consistent quality on a large-volume basis and for its quick separation from water.

Hydrocarbon blends used in the semi-aqueous process are compositionally more flexible than CFC-113-based azeotropes. This allows their solvency to be adjusted to match the soils to be removed. Table 4 compares the physical properties of a hydrocarbon-based agent for semi-aqueous cleaning to those of CFC-113. In contrast to CFC-113-based cleaners, the hydrocarbon-based, semi-aqueous agent has a very low vapor pressure. It also has slightly higher viscosity and surface tension, differences that are exploited by agitation and heating to ensure good cleaning.

Comparative Environmental Impact

Semi-aqueous cleaning agents have zero ODP and GWP, making them attractive for replacing CFC-113 and other ozone-depleting solvents, such as methylchloroform, which will be phased out by the year 2005.

Additionally, the semi-aqueous process has several advantages over aqueous cleaning. Since the organic soils dissolve in the semi-aqueous agent, they can be separated from the aqueous effluent, minimizing the load on treatment facilities. The hydrocarbon-based cleaning agent and the soils can be incinerated as fuel. And since the hydrocarbon-based, semi-aqueous process operates at a neutral pH, it does not dissolve metals and is considered a non-hazardous waste under RCRA standards.

The aqueous effluent, which contains very low levels of biodegradable components, can be recycled in a closed loop system or sent to the drain in most parts of the world. Furthermore, waste water treatment using existing technologies can reduce organic output by more than 95%.

Rinse water containing the hydrocarbon-based agent is non-toxic and non-inhibitory to bacteria. As with all organic fluids, however, it should not be a major portion of the feed to a biological waste treatment plant.

TABLE 4. Comparative Properties of a Hydrocarbon-Based Agent for Semi-Aqueous Cleaning and CFC-113

Property	Units	Hydrocarbon-Based Agent for Semi-Aqueous Cleaning	CFC-113
Boiling Point	°F (°C)	464 (240)	117.6 (47.6)
Vapor Pressure at 77° F (25° C)	mm-Hg	<0.1	334
Flash Point (TCC)	°F (°C)	210 (99)	None
Viscosity at 77° F (25° C)	cp	2.9	0.68
Surface Tension at 77° F (25° C)	dynes/cm	26	17.3
Specific Gravity at 77° F (25° C)	--	0.83	1.6
Estimated Ozone Depletion Potential (CFC-11 = 1)	--	0	0.80
Global Warming Potential	--	0	1.35
Estimated Toxicity	ppm by vol	None established	1,000 (TLV)[a]

[a] A Threshold Limit Value (TLV®), established for industrial chemicals by the American Conference of Governmental Industrial Hygienists, is the time-weighted average concentration of an airborne chemical to which nearly all workers may be exposed during an 8-hr day, 40-hr week without adverse effect.

SEMI-AQUEOUS EQUIPMENT AND PROCESS DESIGN CONSIDERATIONS

To obtain optimum performance requires equipment designed for semi-aqueous cleaning. Figure 1 shows a schematic of an early semi-aqueous system, which involved dissolving the soil in the solvent; rinsing the solvent/soil mixture from the surface with water; and drying the parts. Generally, an air knife was used after the solvent stage to remove the excess solvent/soil mixture from the parts. This limited the contamination introduced to the rinsing system, and hence, to the aqueous effluent.

Several improvements to this process have adapted semi-aqueous cleaning to the modern industrial environment. The first improvement establishes consistent, stable process control, while the others improve the ecology of the process.

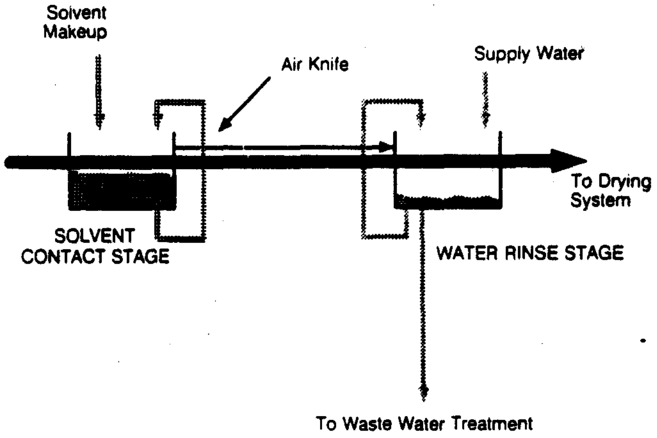
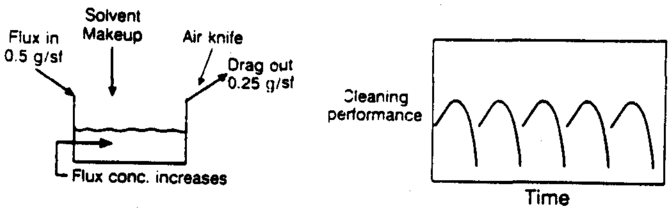


FIGURE 1. Early Semi-Aqueous Cleaning Process.

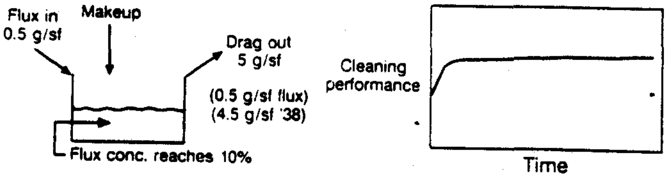
Achieving a Steady-State Solvent Stage

In early semi-aqueous equipment designs, the air knife used in the solvent stage reduced the organic loading in the water effluent. However, it introduced an unsteady state in the bath. More soil was added to the bath than removed. Hence, the soil concentration constantly increased and the bath eventually became too contaminated to clean. This made cleaning performance dependent upon the bath's life cycle. In fact, cleaning efficiency initially increased with small concentrations (approximately 10%), but eventually decreased as flux concentrations became very high (40% to 50%). Hence, cleaning efficiency of a new bath rose, tapered off and eventually fell substantially. This meant that contaminant concentration required monitoring and that the bath had to be dumped periodically (Figure 2a).

The preferred situation is to equalize the dragout of the contaminants with the amount of contaminants being introduced. This can be accomplished by controlling the effectiveness of the air knife. In this case, the contaminant concentration reaches an equilibrium condition at a low contaminant concentration, where the bath is at an enhanced state of cleaning effectiveness. Stable process control is established and the need for bath changes is eliminated (Figure 2b).



(a) Use of an Air Knife Produces Unsteady State.



(b) Natural Dragout Produces Steady State.

FIGURE 2. Use of an Air Knife vs. Natural Dragout in the Semi-Aqueous Cleaning Process.

Reducing Organics in the Effluent

If the air knife is controlled, reducing organics in the aqueous effluent can be accomplished by establishing an emulsion in the first rinse stage, where the dragout from the solvent stage is removed with water (Figure 3). Since the organic concentration of the cleaning agent/soil is relatively low in the emulsion, the organic dragout to subsequent rinse stages is reduced by 80% to 95%. As the organic concentration increases in the emulsion stage, it can be removed to a decanter and allowed to separate into two layers. Once separated, the decanter water can be recycled into the emulsion stage.

This approach separates the contaminants generated in the cleaning process from the aqueous effluent. Contaminants collect in the hydrocarbon layer separated in the decanter. The organic in the water is primarily entrapped cleaning agent.

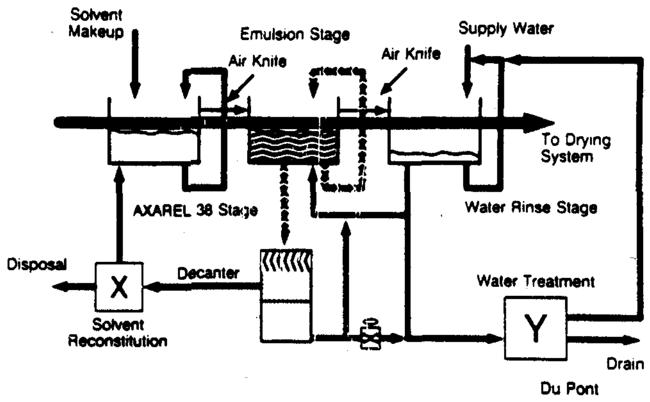


FIGURE 3. Reducing Organics by Establishing an Emulsion in the First Rinse Stage by the Dragout from the Solvent Stage.

Recycling Rinse Water

To make the semi-aqueous cleaning process even more environmentally attractive, two well-known technologies are currently being evaluated for their effectiveness in removing contaminants from the rinse water.

Tests with membrane technology have provided very positive results. Mixtures of 1% hydrocarbon-based agent for semi-aqueous cleaning (containing flux residues) have been evaluated by ultraviolet (UV) spectroscopy, chemical oxygen demand (COD) and conductivity after treatment with three different membranes. Each of the three membranes resulted in water that was greater than 95% clean.

The effectiveness of these same membranes in treating decanter water, a worst case situation, has also been evaluated. After treatment, the decanter water was greater than 70% clean. Tests with two commercially available membranes are underway, and to date have yielded waste water that is more than 95% clean after two weeks of processing.

Another approach, involving carbon treatment/ion exchange technology, is under evaluation as well. In initial tests, it shows promise for removing 90% of the organics.

Since 100 ppm organics in the water can be obtained with both water-cleaning technologies, other factors, such as equipment and operating costs, will determine which system is best for a given application.

SEMI-AQUEOUS COMPATIBILITY WITH PLASTICS AND ELASTOMERS

In general, the hydrocarbon-based cleaning agent is more aggressive than CFC-113 and less aggressive than chlorinated solvents, such as 1,1,1-trichloroethane. It is compatible with a wide range of plastics, elastomers and metals.

Generally, it is gentle enough for cleaning metal assemblies having components made of many common plastics (Table 5). It is also compatible with most elastomers used for gaskets and seals in semi-aqueous equipment (Table 6). Specific recommendations are available for suitable gasket and seal materials for operating equipment.

TABLE 5. Plastic Compatibility of a Hydrocarbon-Based, Semi-Aqueous Cleaning Agent Under Typical Cleaning Conditions[a]

Material	Tradename	Hydrocarbon-Based, Semi-Aqueous Cleaning Agent	CFC-113
ABS	Kralastic®	0	0
Acetal	DELRIN®	0	0
Acrylic	LUCITE®	0	0
Cellulose	Ethocel™	3	3
Epoxy	--	0	0
Fluorocarbons			
PTFE	TEFLON®	0	0
PVDF	KYNAR®	0	0
Ionomer	SURLYN®	3	0
Nylon	ZYTEL®	0	0
Polyarylate	Arylon®	0	--
Polycarbonate	Tuffak®	0	0
Polyester			
PBT	Valox®	0	--
PET	RYNITE®	0	--
Polyetherimide	Ultem®	0	--
Polyethylene	ALATHON®	0	0
Polyimide	KAPTON®	0	--
Polyphenylene Oxide	Noryl®	0	0
Polyphenylene Sulfide	Ryton®	0	--
Polypropylene	--	2	0
Polystyrene	Styron™	3	0
Polysulfone	--	0	0
Polyvinyl chloride	--	0	0
Chlorinated Polyvinyl Chloride	--	0	--

[a] Test Conditions: Hydrocarbon-based, semi-aqueous samples immersed at 50° C (122° F) for 1 day; CFC-113 samples immersed in boiling liquid for 5 min.

Key: 0 = Compatible; 1 = Probably compatible; 2 = Probably incompatible; 3 = Incompatible

TABLE 6. Elastomer Compatibility of a Hydrocarbon-Based, Semi-Aqueous Cleaning Agent[a]

Material	Hydrocarbon-Based, Semi-Aqueous Cleaning Agent % Wt. Change	% Linear Swell
SBR	15	6
Butyl	100	30
Natural	150	40
EPDM NORDEL®	30	10
ADIPRENE®	2	0
NBR	70	20
HYPALON®	15	6
Neoprene	30	9
ALCRYN®	10	5
HYTREL®	4	1.4
Silicone	50	15
Thiokol FA	-0.1	0
Thiokol ST	1.3	0.3
VAMAC®	40	15
VITON® A	0.6	0
VITON® B	0.4	0
KALREZ®	0	-0.9
VITON® GF	0.3	0.9
VITON® VT-R-6186	0.3	0.9

[a] Test Conditions: Samples immersed at 50° C (122° F) for 1 week.

HCFCs AND SEMI-AQUEOUS VS. CFCs: COMPARATIVE CLEANING EFFECTIVENESS

The HCFC blend, HCFC-123 and the hydrocarbon-based, semi-aqueous agent (followed by water rinsing) are all excellent alternatives to CFC-113 for precision metal cleaning. They are superior to CFC-113 for removing heavy grease and equivalent to, or slightly better than, CFC-113 for removing light oils.

The HCFC blend and HCFC-123 provide more effective removal of water-soluble oil residues than CFC-113; however, they are less effective for removing waxes and buffing compounds. On the other hand, slightly heating the hydrocarbon-based, semi-aqueous agent results in faster removal of waxes than CFC-113. In fact, it approaches the speed and effectiveness of 1,1,1-trichloroethane. In addition, the semi-aqueous agent incorporates a rust inhibitor that protects metal parts during the rinsing step by coating them with a monomolecular layer.

Numerous tests were conducted to compare the cleaning effectiveness of these alternatives to CFC-113 and 1,1,1-trichloroethane. The results of these tests are presented here.

Removing Light Oil

To determine the effectiveness in removing light drawing oil, assemblies were dipped for 15 seconds and drained for 15 seconds prior to cleaning. Each assembly was then suspended for the desired cleaning time in boiling cleaning agents in four-liter beakers, equipped with condensing coils. The assemblies cleaned in the hydrocarbon-based, semi-aqueous agent were agitated by stirring and rinsed in water for 60 seconds.

After air drying, cleaned assemblies were inspected under UV light. The oil fluoresced strongly, while the cleaning agents did not. Removing light oil is relatively easy, and the performance of these agents was essentially the same.

Removing Heavy Grease

The ability to remove heavy grease was measured by determining the cleaning rate for a steel ball-bearing packed with high-filler Shell Alvania Grease No. 2. The bearing had an outside diameter of 1 1/2 inches, and contained 24 balls, each 7/32 inch in diameter. In the tests performed for each agent, the bearing was packed with 1.10 grams of the grease, and then cleaned by suspending in beakers for the desired cleaning time. The assemblies cleaned in the hydrocarbon-based, semi-aqueous agent were then rinsed for two minutes. After each cleaning time increment, the bearing was allowed to dry and the amount of grease remaining was determined by weighing.

Figure 4 shows the results of these tests in which the HCFC blend, HCFC-123 and the hydrocarbon-based, semi-aqueous agent removed grease significantly faster than CFC-113 and essentially as fast as 1,1,1-trichloroethane.

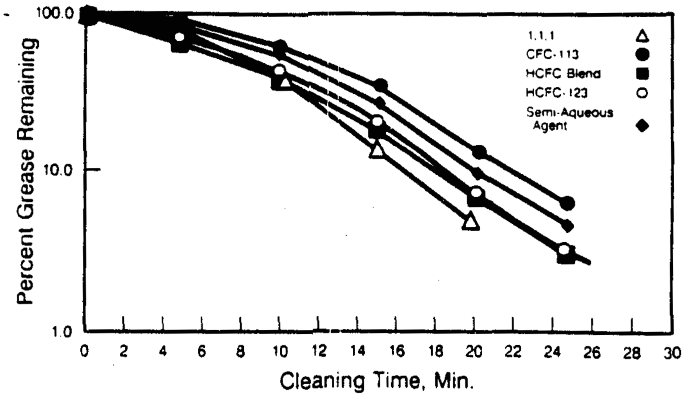


FIGURE 4. Removal of Heavy Grease by Cleaning with an HCFC Blend (Consisting of 34.9% HCFC-141b, 64.8% HCFC-123 and 0.3% Stabilizer); HCFC-123; a Hydrocarbon-Based, Semi-Aqueous Cleaning Agent; CFC-113; and 1,1,1-Trichloroethane.

Removing Buffing Compounds and Waxes

Buffing compounds are very difficult to remove. Their abrasive particles are bonded together with fatty acids and tallows. After buffing, the compound also contains metal fines and metallic soaps, formed by the reaction of the fatty acid with the metal surface.

Waxes are most easily removed at temperatures that are high enough to soften or even melt them. Unfortunately, when removing waxes, the enhanced solvent power of the HCFCs is offset by their lower boiling (operating) temperatures. In contrast, heating the hydrocarbon-based, semi-aqueous agent above the melting point of the wax speeds up the cleaning process, resulting in performance close to 1,1,1-trichloroethane, as shown in Figure 5. These data were obtained from a test in which parts were dipped in Carnauba wax and cleaned as described previously. The parts cleaned in the hydrocarbon-based, semi-aqueous agent were then rinsed for two minutes.

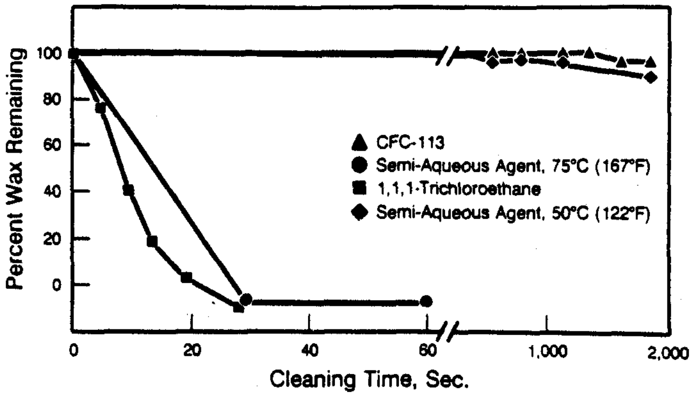


FIGURE 5. Removal of Carnauba Wax by Cleaning with a Hydrocarbon-Based, Semi-Aqueous Agent; CFC-113; and 1,1,1-Trichloroethane.

Removing Water-Soluble Oil Residues

Water-soluble oils contain 15% to 20% surfactant and form milky emulsions when diluted with water to cool and lubricate cutting tools. Dried, water-soluble oil residues consist of the oil, plus the surfactant.

To study the ability of the HCFC blend, HCFC-123, CFC-113 and 1,1,1-trichloroethane to remove these residues, known amounts of undiluted Safety Cool 4165 oil were added to these cleaning agents at room temperature. The surfactants in the oil formed floating solids in CFC-113 solutions, while the concentrated HCFC blend and HCFC-123 solutions were clear, indicating good solubility for the surfactants (Table 7).

TABLE 7. Solubility of Undiluted Safety Cool 4165 Water-Soluble Oil in Room-Temperature Cleaning Agents

	Appearance of Solutions			
Weight Percent Oil in Cleaning Agents	0.25	0.99	2.44	4.76
Cleaning Agent				
HCFC Blend[a]	Slight Solids	Clear	Clear	Clear
HCFC-123	Slight Solids	Clear	Clear	Clear
CFC-113	Increasing Flocculent Solids -----------------→			
1,1,1-Trichloroethane	Clear	Clear	Clear	Clear

[a] This HCFC blend consists of 34.9% HCFC-141b, 64.8% HCFC-123 and 0.3% stabilizer.
NOTE: All cleaning agents became increasingly yellow with increasing oil concentration.

SUMMARY

The HCFC blend, HCFC-123 and the hydrocarbon-based, semi-aqueous agent discussed in this paper are all viable alternatives to CFC-113 for precision metal cleaning. In numerous tests, they have demonstrated cleaning effectiveness that is equivalent or superior to CFC-113. Additional tests are being conducted to further evaluate the performance of HCFC-123, the newest of the three alternative cleaning agents.

Like CFCs, both HCFCs and hydrocarbon-based, semi-aqueous agents employ a very effective cleaning strategy; they dissolve the soils in a solvent. In the semi-aqueous process, however, subsequent rinsing and drying steps are required. To protect the metal parts during the rinsing step, the semi-aqueous agent incorporates a rust inhibitor that coats the parts with a monomolecular layer.

In general, these CFC alternative technologies are more aggressive than CFC-113 and less aggressive than chlorinated solvents. Tests have shown that the HCFC blend, HCFC-123 and the hydrocarbon-based, semi-aqueous agent discussed in this paper are compatible with a wide range of plastics and elastomers used in the metal-working industry.

Due to their relatively low boiling points compared to CFC-113, HCFC-based cleaning agents require new or retrofitted vapor degreasing equipment. In contrast, hydrocarbon-based, semi-aqueous cleaning agents require new equipment that is specially designed for semi-aqueous cleaning.

From an environmental standpoint, these CFC alternatives differ. The HCFCs offer significantly reduced ODP and GWP compared to CFC-113. Though it is widely agreed that HCFCs will fill many immediate needs and represent an essential part of the solution to the CFC/ozone issue, it is recognized that they will have a limited life cycle. A non-binding resolution to the Montreal Protocol calls for phasing out HCFCs by 2040, and possibly by 2020. In addition, like CFCs, HCFCs require disposal as a hazardous waste.

Semi-aqueous cleaning with a hydrocarbon-based agent offers significant long-term ecological advantages over currently available vapor degreasing agents. Unlike CFC-113-based cleaners, semi-aqueous cleaners have zero ODP and GWP, and do not require disposal as a hazardous waste. In addition, soils removed in the semi-aqueous process are easily separated from water rinses, greatly reducing treatment requirements. The aqueous effluent can be recycled in a closed loop system to reduce water consumption or it can be sent to the drain. In addition, the spent cleaning agent can be disposed of by incineration to generate energy for other operations.

Recently, the Environmental Protection Agency (EPA) recommended that CFC alternatives featuring the lowest ODP and the required cleaning effectiveness be used for precision metal cleaning applications. This means that CFC-113 users must carefully evaluate their application needs vs. both the performance and ODP of alternative cleaning agents. For some users, semi-aqueous agents, which have zero ODP, may be the best choice. For others, the HCFC blend with its broad range of applicability may offer the solution. Still others may decide that HCFC-123, with a lower ODP than the HCFC blend, is best suited for their needs.

Table 8 provides a brief overview of the three metal cleaning technologies discussed in this paper -- CFCs, HCFCs and semi-aqueous.

TABLE 8. Alternative Metal Cleaning Technologies vs. Vapor Degreasing with CFC-113

	Vapor Cleaning with CFC-113	Vapor Cleaning with an HCFC Blend[a]	Vapor Cleaning with HCFC-123	Semi-Aqueous Cleaning with a Hydrocarbon-Based Agent/Water
Overall Cleaning Effectiveness vs. CFC-113	--	Better Than or Equal To	Better Than or Equal To	Better Than or Equal To
Cleaning Strategy	Soils dissolved in solvent	Soils dissolved in solvent	Soils dissolved in solvent	Soils dissolved in solvent and rinsed away
Drying Step	No	No	No	Yes
Process Control	Easy	Easy	Easy	Easy
New Equipment vs. CFC-113	--	Yes	Yes	Yes
Aqueous Waste	None	None	None	Does not contain soils or hydrocarbons; can be recycled
Non-aqueous Waste	Requires disposal as hazardous waste	Requires disposal as hazardous waste	Requires disposal as hazardous waste	Is separated from aqueous waste; ready for incineration (15,000 BTU/lb fuel value)
Estimated Toxicity (ppm by vol)	1,000 (TLV)[b]	150 (AEL)[c]	100 (AEL)[c]	None Established
Estimated Ozone Depletion Potential (CFC-11=1)	0.80	0.07	0.02	0
Global Warming Potential	1.35	0.07	0.02	0

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[a] HCFC blend consisting of 34.9% HCFC-141b, 64.8% HCFC-123 and 0.3% stabilizer.

[b] A Threshold Limit Value (TLV®), established for industrial chemicals by the American Conference of Governmental Industrial Hygienists, is the time-weighted average concentration of an airborne chemical to which nearly all workers may be exposed during an 8-hr day, 40-hr week without adverse effect.

[c] An Acceptable Exposure Limit (AEL) is the recommended time-weighted average concentration of an airborne chemical to which nearly all workers may be exposed during an 8-hr day, 40-hr week without adverse effect, as determined by the Du Pont Company for compounds that do not have a Threshold Limit Value (TLV®).

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