ALTERNATIVES TO CFCs IN PRECISION CLEANING: A NEW HCFC BASED SOLVENT BLEND

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INTRODUCTION

Recent findings of ozone layer depletion has prompted United Nations Environmental Program (UNEP) to amend the Montreal Protocol, for an accelerated phase-out of chlorofluorocarbons (CFCs), carbon tetrachloride and halons by the year 2000 and phase-out of methyl chloroform by the year 2005. In addition, U.S. Congress has passed the Clean Air Act which puts similar phase-out dates for CFCs and methyl chloroform. Because of these regulations, a search for replacements for all the regulated CFC molecules has been intensified. In addition, global warming is also emerging as another major environmental problem making the search more and more complex.

In this article, we are going to discuss the performance characteristics of a new stratospherically safe alternate to trichlorotrifluoroethane (CFC-113) as a precision cleaning solvent. The alternates are based on hydrochlorofluorocarbons, the selected ones are 1,1-dichloro-1-fluoroethane (HCFC-141b) and 1,1-dichloro- 2,2, 2-trifluoroethane (HCFC-123) with blends based on these compounds. These compounds are formed by the addition of hydrogen to CFCs to make them shorter lived in the troposphere and therefore less harmful to the stratospheric ozone. The Montreal Protocol has also put restrictions on the use of these substances because of their low but non-zero ozone depletion potential. HCFCs are considered interim replacements with phaseout dates starting from 2020 and complete phaseout no later than 2040. The U.S. Clean Air Act assigns earlier phase-out dates for HCFCs, starting with a freeze in production in the year 2015 with complete phase-out by 2030.

SOLVENT SELECTION

In this section we are going to discuss how the solvent for precision cleaning application is selected. Precision cleaning encompasses manufacturing aerospace components, gyroscopes in missile guidance systems, medical devices, computer disks, silicon wafers, etc. These parts to be cleaned contain various metals and plastics and CFC-113 is the universal choice in these applications. CFC-113 is non-flammable, non-toxic, stable, has good solvency characteristics and is compatible with these materials.

Solvent selection depends on a number of environmental factors, along with the ozone depletion and greenhouse warming potential mentioned before. The potential of contributing to smog in the lower atmosphere

Table 7. ECONOMIC ANALYSIS

Capital Expenditures

Item	Cost
Ultrasound with heater	$1425
5 gallon stainless steel rinse vessel	38
Immersion heater	105
Heat Gun	75
DI water system installation	150
TOTAL	$1793

Annual Operating Costs

Item	Gal/Yr	Cost
DuSQUEEZE usage	7.8-11.8	$150
DI Water usage	1825-2920	700
TOTAL		$850

Annual Cost Savings

Item	Amount	Cost
Avoided TCA Purchases	330 gal/yr	$1650
Avoided Methanol Purchases	120 gal/yr	1000
Avoided Waste Disposal	6 barrels/yr	3000
TOTAL		$5600

Net Cost Savings $4800

Payback Period: $1793/$4800 = 0.37 year, 4.5 months

TABLE 4. RESULTS OF ANALYSES FOR RESIDUAL LIMONENE ON PARTS CLEANED WITH 100:1 DILUTE SOLUTION DUSQUEEZE

Test	limonene concentration Total Ug/sample
Rinse Sample, Fresh Bath	ND(<0.3)
Rinse Sample, Mid-life Bath	ND(<0.65)
Rinse Sample, End-life Bath	ND(<0.3)
BLANK	ND(<0.2)

TABLE 5. RESULTS OF ANALYSES OF 100:1 DILUTE DUSQUEEZE SOLUTION FOR CONTAMINANTS

Test	Fresh Bath mg/L	Dump#1 mg/L	Dump#2 mg/L
Dissolved solids	3650	3010	887
Suspended solids	ND*	ND*	19
Oil and Grease	37.0	30.8	15.1
Metals			
Cobalt	0.019	0.18	0.081
Titanium	ND#	ND#	1.65

* Method detection limit is 2
# Method detection limit is 0.047

TABLE 6. TENSILE STRENGTH TEST RESULTS FOR IN-PLANT OPERATIONS

Coating/Substrate	Cleaning Agent	Tensile Strength (psi)
titanium / titanium	methanol	5560+/-600
titanium / titanium	DuSQUEEZE	7180+/-610
titanium / cobalt-moly	TCA	5820+/-370
titanium / cobalt-moly	DuSQUEEZE	5330+/-1560

TABLE 1. TENSILE STRENGTH TEST RESULTS FOR BENCH SCALE EXPERIMENTS

Test Buttons	Cleaning Agent	Tensile Strength (psi)
titanium	methanol	6300+/-1260
titanium	DuSQUEEZE*	7000+/-570
cobalt/molybdenum	TCA	5150+/-1990
cobalt/molybdenum	DuSQUEEZE*	5400+/-1290

* Tensile strengths measured for test button cleaned with various dilutions of DuSQUEEZE showed no trends or statistical differences, so values shown include all measurements.

TABLE 2. RESULTS OF ANALYSES OF SOLVENT SAMPLES FOR CONTAMINANTS

Test	Methanol (mg/l)	TCA (mg/l)
Dissolved solids	1	29
Suspended solids	33	9
Oil and Grease	911	141
Metals		
Cobalt	-	ND*
Titanium	0.021	-

* Method detection limit is 0.01

TABLE 3. RESULTS OF ANALYSES FOR OIL & GREASE ON PARTS CLEANED WITH 100:1 DILUTE SOLUTION DUSQUEEZE

Test	Oil and Grease Total Mg
Wipe Sample, Fresh Bath	1.0
Wipe Sample, Mid-life Bath	0.4
Wipe Sample, End-life Bath	1.2
BLANK	ND*

* Method detection limit is 0.3

and pollution to ground water by way of water effluents are also important considerations. The objective of solvent selection is not to trade one environmental problem with another. There are federal and state laws prohibiting the emission of volatile organic compounds (VOCs). These materials break down in the lower atmosphere and contribute to smog pollution. Over and above these, the molecules have to be relatively non-toxic so that the workplace remains relatively safe. Effluents from plants may also pose a problem which is of a lesser concern for solvents than for aqueous systems. The energy requirement is in general lower for solvent cleaning as compared to aqueous cleaning. However, energy consumption also has to be considered in detail because of its contribution to the greenhouse effect.

Among hydrochlorofluoroethanes HCFC-123 (1,1-dichloro-1,2,2-tri-fluoroethane) and HCFC-141b (1,1-dichloro-1-fluoroethane), with boiling points between 80 and 90 F, are being considered as alternates to CFC-113 in solvent applications. The rest of the hydrochlorofluoroethanes are not found to be suitable because of their toxicity, flammability or other undesirable characteristics. These two HCFCs are far less ozone depleting than the current CFCs. Molecular structure of these compounds are shown in Figure 1. The lifetimes, ozone depletion potentials (ODP) of these chemicals and also the greenhouse warming potentials (GWP) are given in Table 1. The ODP and GWP are measured relative to CFC-11 which is assigned a value of 1.0. The ODP and the GWP numbers for the molecules are still being revised by AFEAS and values are expected to be finalized by the end of the year. These two HCFCs are not considered VOCs by US Environmental Protection Agency and therefore, they do not come under that regulation.

Our tests have shown that since HCFC-141b or HCFC-123 alone are not equivalent to CFC-113, a blend of the two is required. HCFC-123 lowers both the ODP and the flammability characteristics of the blend. HCFC-123 is more aggressive towards the plastics and the presence of HCFC-141b makes the blend more compatible to plastics. So blends are preferred to the pure components both from an environmental and performance standpoint.

The preferred blend for precision cleaning is a new azeotrope-like non-segregating blend consisting of HCFC-141b and HCFC-123. The composition of the blend is 80 percent by weight HCFC-141b and 20 percent by weight of HCFC-123. Some of the physical properties of the blend as compared to CFC-113 are shown in Table 2. The blend is commercially available from Allied-Signal under the tradename Genesolv®2020.

As we compare the properties we find that the major difference in physical properties between the CFC-113 and HCFC based blend is their boiling point. This would normally indicate that Genesolv 2020 would evaporate faster than CFC-113 resulting in higher loss rates of the solvent but in reality the evaporation rates of the solvents at room temperature are equivalent. This is due to the fact that Genesolv 2020 has higher heat of vaporization. This property makes it an acceptable substitute for CFC-113 despite its lower boiling point.

Another important use of CFC-113-based blend is in printed circuit board cleaning. The azeotrope- like blend containing HCFC-141b, HCFC-123 and methanol marketed by Allied-Signal under the tradename Genesolv 2010 is the solvent of choice for that application. We are not going to discuss that application in this article. However, we would like to refer the readers to several other articles detailing the use of this blend in defluxing [2,3,4].

SOLUBILITY AND CLEANLINESS STUDIES

In selecting a new solvent, solvency and boiling point are chosen as major physical properties. The solvency of various light oils is determined by measuring their solubility in these solvents. A boiling point range of 25° to 75°C has been chosen as the range for these solvents and various solubility models are used as a tool to select solvents on the basis of solvency. Cleaning tests were performed to finalize the selection.

In the cleaning tests, metal coupons are soiled by various types of oils and heated to 200°F. This is done to partially simulate the temperature attained while machining and grinding in the presence of these oils. The metal coupons thus treated, are degreased in a vapor phase degreaser machine. The coupons are held into the vapor and are vapor rinsed for a period of 15 seconds to 2 minutes depending upon the oils chosen. A short time period is selected so that the solvents can be compared easily. The blend mentioned here is compared to CFC-113 in cleaning performance. Cleanliness of the coupons after cleaning is determined by carbon coulometer which detects amounts of carbon physically adsorbed on the surface of the metals. Since most oils are hydrocarbon-based this method detects the amount of hydrocarbon left on the surfaces.

The overall cleanliness test results with various types of oils are shown in Table 3. The results show that the performance of azeotrope-like blend Genesolv 2020 is equal to or better than CFC-113 in cleaning various oils. The cleaning results shown in Table 3 are in percentages of oils removed from various substrates.

PRECISION CLEANING STUDY OF GYROSCOPE COMPONENTS

High precision gyroscopes contain some mechanical assemblies with tolerances on the order of 1-5 micrometers. As a result, they are extremely sensitive to particulate contamination as well as to very low levels of foreign fluids and polymeric films. Accuracy, precision and reliability of gyroscopes used for military and aviation applications depend on a cleaning process being able to remove these deleterious contaminants without degrading the materials of construction. Gyroscope components are fabricated using a variety of materials, including light metals (i.e. beryllium and aluminum), plastics, adhesives and elastomers. CFC solvents and blends have been eminently suited for this application. Finding a suitable alternative cleaning agent or process will be a difficult task. Extensive material compatibility and cleaning efficacy studies must be conducted on any new solvent system to ensure product integrity. Beryllium metal parts preclude the use of aqueous based cleaning or 1,1,1-trichloroethane which hydrolyzes easily and may cause corrosion. Also, any new solvent system must not attack the polymeric materials in the device.

Present cleaning processes include vapor degreasing, pressure cooking, soxhlet extraction, cold spraying in enclosed booths, cold cleaning in ultrasonics and gyroscope flushing with CFC solvents and blends. Parts and sub-assemblies are typically cleaned several times during assembly in order to remove handling and processing contaminants. Typical soils include particulates, silicones, hydrocarbons, finger oils, bromofluorocarbon balancing fluids, flux and excess adhesive.

This work examines a few of the aspects of testing the new HCFC solvents replacement for CFC solvents for precision cleaning of gyroscope parts and assemblies. It is only the beginning of the extensive research program required to implement these new solvents into the manufacturing mainstream. We are going to talk about the cleaning studies in this section. Cleaning efficacy is determined by comparing the HCFC cleaned surface to one cleaned with CFC using Fourier Transform Infrared Micro and Reflectance Spectroscopy, water break test or weight change of the coupon.

Fourier Transform Infrared reflectance spectra of the surfaces of the coupons cleaned in

CFC-113 and Genesolv 2020 are shown in Figures 2 and 3. The spectra show peaks of various heights indicating materials left on stainless steel coupons after cleaning with CFC-113 and Genesolv 2020. The soils used are phenyl methyl silicone and silicone grease. In case of both of these soils, coupons degreased in Genesolv 2020 show fewer peaks indicating better cleaning compared to CFC-113.

TOXICITY AND MATERIAL COMPATIBILITY

Introduction of new compounds in the marketplace requires extensive toxicity studies. Presently both HCFC-123 and HCFC-141b are undergoing thorough toxicological studies. A Program for Alternative Fluorocarbon Toxicity (PAFT) has been set-up by a consortium of a large number of current CFC manufacturers all over the world. Repeated dose toxicity studies have been completed and no significanct adverse effects have been found. Allied-Signal has been given permission by the US Environmental Protection Agency to manufacture and sell HCFC-141b for solvent use. Of the two HCFCs, HCFC-141b has been found to be less toxic. At this point with available information, an interim PEL of 500 ppm is assigned to HCFC-141b and 50-100 ppm is assigned to HCFC-123. These are interim values, final PELs are expected to be assigned following completion of the chronic studies, which are underway.

Due to lower boiling points, loss of HCFC solvent vapors from older degreasers may be too great for reasons of health and safety and also effect the processing costs. This requires tighter or low emission machines. Existing equipment should, therefore, be evaluated in this respect and be either upgraded to new equipment, or perhaps, be retrofitted to maintain safe and healthy work environment.

Hydrolytic stability of the solvent blend is tested by refluxing the solvent in the presence of various metals and water for a two (2) week period. The solvent even without any stabilizer, showed excellent stability in presence of water. Its stability compares very well with CFC-113 and it seems far superior to 1,1,1-trichloroethane. It appears the presence of a fluorine in the molecule and stronger carbon-fluorine bonding has increased the stability of HCFC-141b over 1,1,1-trichloro- ethane. One important point to note is that, HCFC-141b, HCFC-123 and Genesolv 2020 are all compatible with beryllium metal which makes the solvent blend extremely attractive to clean gyroscopes. As mentioned before, various components in a gyroscopes are fabricated using beryllium and its alloys which makes beryllium compatibility a very important factor in solvent selection.

In commercialization of a new product for precision cleaning another important property to study is its compatibility with various elastomers. These elastomers are present in various components cleaned. The elastomer compatibility is done where the elastomers are refluxed in solvent for a two week period. The solvent blend seemed to have reasonable compatibility with a large number of elastomers. A detailed account of material compatibility appears on references [5,6] and is also available from Allied-Signal upon request.

CONCLUSIONS

In this paper we have shown that a substitute for CFC-113 has been found with a much lower ozone depletion potential for use as a solvent in precision cleaning applications. This is an azeotrope-like blend of HCFC-141b, HCFC-123 (Genesolv 2020) and is presently in the process of commercialization. Solubility measurements with various oils have shown that this blend has a very good potential to be used as a solvent for these applications. This is further confirmed by metal cleaning studies where the blend showed equivalent or better performance compared to

CFC-113. Finally application results were done to demonstrate that Genesolv 2020 performs very well in field applications of cleaning gyroscope components. In this application FTIR reflectance spectroscopy has been used and is found to be an excellent method for cleanliness measurement.

The solvent is currently being produced in pilot quantities in the pilot plant working at Buffalo and is marketed under the tradename Genesolv 2020. The actual commercial production will start by the end of 1991 or by early 1992.

REFERENCES

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Table 1: ODP and GWP Values for Selected Compounds

Solvents	Formula	B.P.(°F)	Lifetime	ODP	GWP
CFC-11	CCl_3F	75	60	1.0	1.0
CFC-113	$C_2Cl_3F_3$	118	102	0.8	1.3
HCFC-123	$C_2HCl_2F_3$	82	1.5	0.02	0.02
HCFC-141b	$C_2H_3Cl_2F$	89	10	0.12	0.12

Table 2: Physical Properties Comparison

	Genesolv 2020	CFC-113
Ozone Depletion Potential	0.1	0.8
Greenhouse Warming Potential	0.1	1.3
Flash Point	None	None
Boiling Point (°F)	87.8	119
Liquid Density(g/cc)	1.38	1.56
Kauri-Butanol Value	58	31
Solubility Parameter$(cal/cc)^{1/2}$	7.6	7.3
Evaporation Rate(ether=1)	1.2	1.2
Surface Tension (dynes/cm)	18.4	17.8
Heat of Vaporization (Btu/lb)	91.0	63.1

Table 3: Cleaning Results

OIL	SOLVENT	% Oil Removed		
		Substrates		
		Aluminum	Stainless Steel	Mild Steel
Petroleum Based	CFC-113	100.0	100.0	100.0
	Genesolv®2020	88.8	97.9	98.3
Semi-synthetic	CFC-113	94.5	94.5	98.3
	Genesolv®2020	99.2	99.2	99.0
Synthetic	CFC-113	19.5	14.6	7.6
	Genesolv®2020	40.1	38.1	54.4

HCFC Solvents Comparison

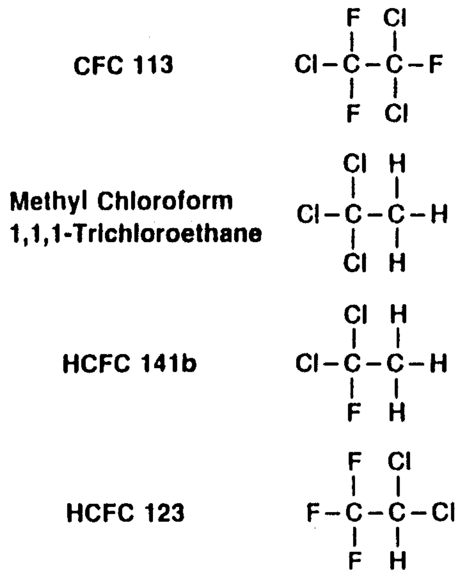


Fig. 1

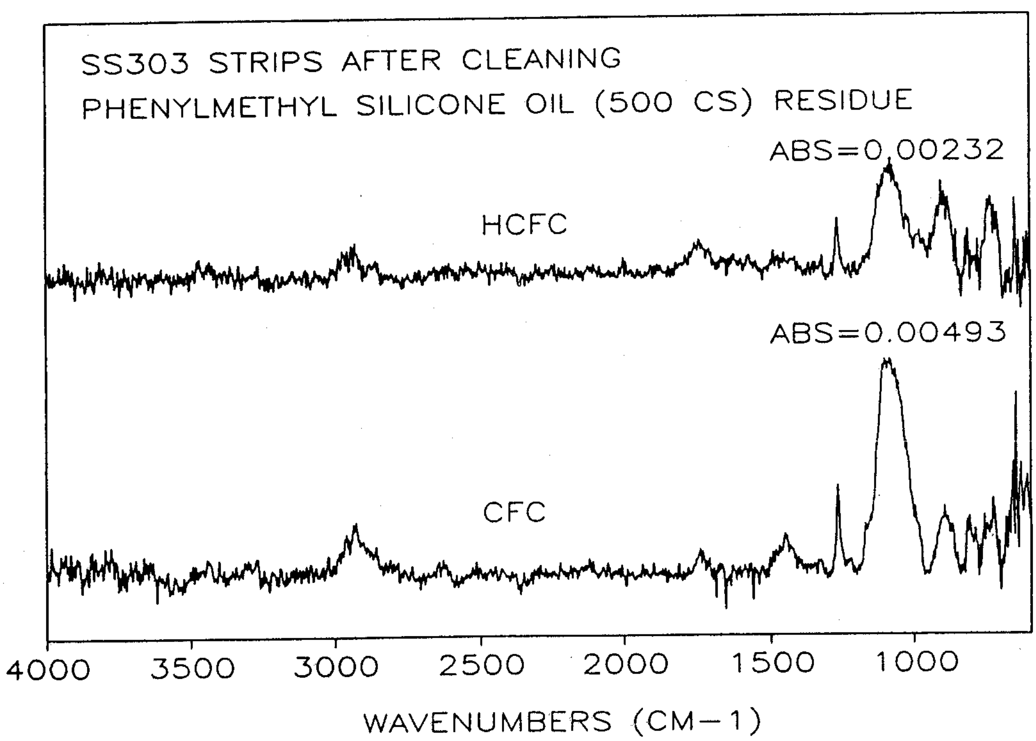
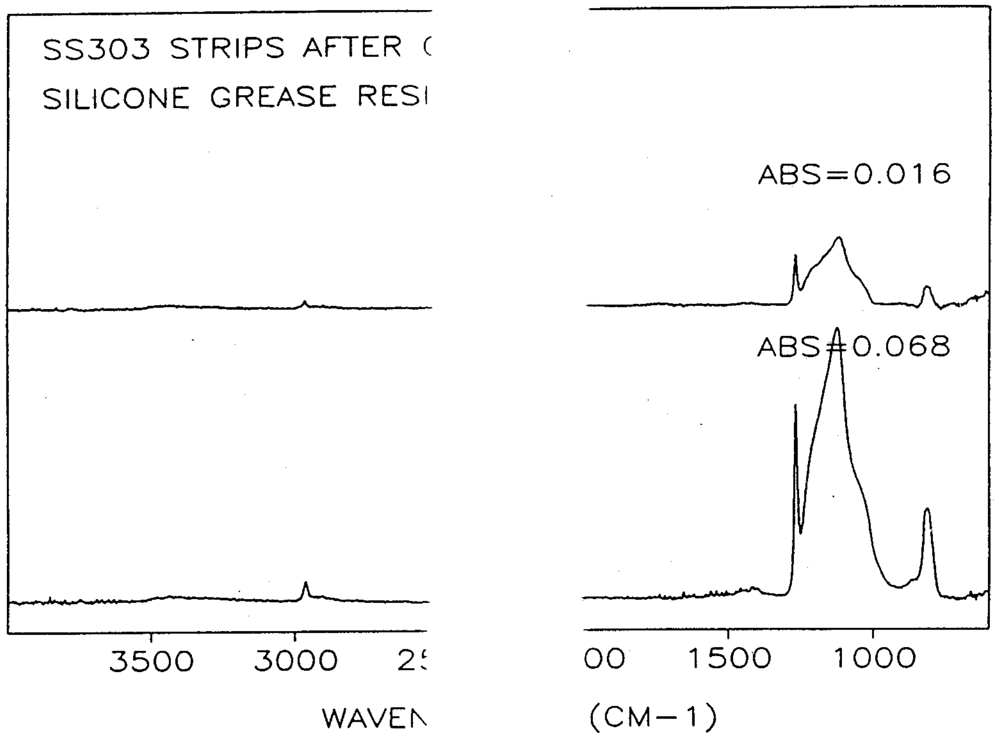


Fig. 2



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