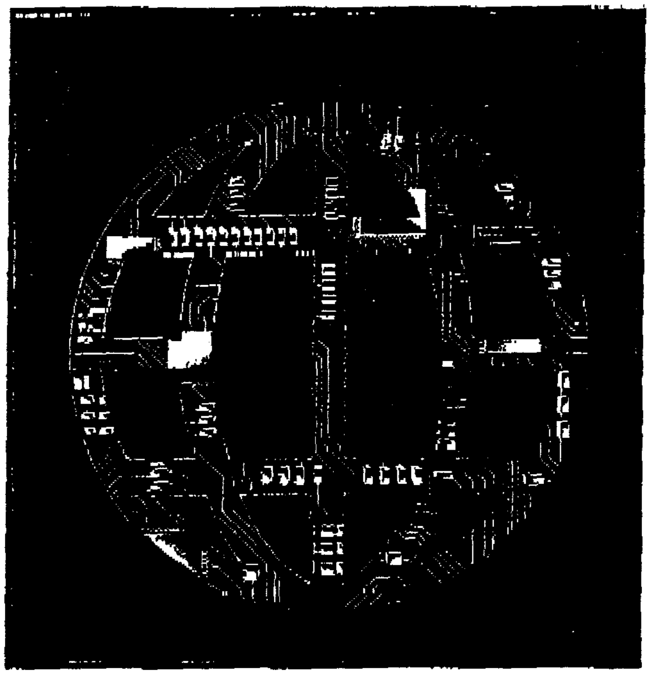

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HYDROFLUOROCARBON SOLVENTS IN PRECISION CLEANING

by

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I. BACKGROUND

The use of non-flammable "precision cleaning" solvents had its birth in the space age where mild, very low residue, safe solvents were required. The first solvent to meet these requirement was 1,1,2-trichloro-1,2,2-trifluoroethane better known as CFC-113. In the 1960's the use of this solvent and various azeotropic blends found increasing applications in electronics and metal working industry. CFC-113, being mild, stable, non-flammable, remained the workhorse of the precision cleaning industry as it brought together a combination of properties found nowhere else.

With the arrival of the ozone depletion issue in the late 1970s and 1980s [1], chemical manufacturers worldwide began searching for an acceptable alternative to CFC-113. In many of its areas of use, new technologies and processes were developed which were effective but the application of precision cleaning remains one of the most difficult for effective substitutes for CFC-113. The first series of volatile non-flammable solvents developed were hydrochlorofluorocarbons (HCFCs) [2]. These materials suffered one drawback in that they are low but non-zero ozone depleting. As a result these compounds can be considered as transitional substitutes.

This leads to the next generation solvents which are based on hydrofluorocarbons (HFCs). This class of compounds do not contain chlorine and therefore do not affect the ozone layer. These materials as a class are not excellent solvents but are fairly effective in various cleaning applications with additives such as alcohols, ketones, esters etc.

In this article we are going to discuss the development of hydrofluorocarbon solvents in various cleaning applications and also discuss HCFCs as transitional substitutes in precision cleaning.

II. HYDROFLUOROCARBONS (HCFCs) AS TRANSITIONAL SOLVENT SUBSTITUTES

Precision cleaning encompasses cleaning in electronics, semiconductors, gyroscopes, medical devices and other areas where a high degree of cleaning is required with very low residue left on the substrates. As a class HCFCs are effective solvents for various precision cleaning applications. Currently there are three materials in use or in development, these are 1,1-dichloro-1-difluoroethane (HCFC-141b), 1,1,2-difluoro-1,2-dichloroethane (HCFC-123) and 1,1,2,2,3-pentafluoro-1,3-dichloropropane (HCFC-225cb). A comparison of properties of these solvents are shown in Table 1.

(i) HCFC-141b

This material has been selected by a few chemical manufacturers in the late 1980s as a replacement for CFCs in solvent cleaning and as a foam expansion agent. HCFC-141b is presently manufactured by various companies worldwide and is also sold under various tradenames (e.g. Genesolv®2000 by AlliedSignal Inc.). HCFC 141b has been found effective in a large number of precision cleaning applications where CFC-113 is presently being used.

The solvent boils at a lower temperature than CFC-113 but is readily adoptable to existing open-top degreaser if relatively simple modifications are made to the system. Several equipment manufacturers offer these retrofit packages for the equipment. HCFC-141b also forms an azeotrope with methanol which can be used effectively in cleaning printed circuit boards.

The one single major disadvantage of HCFC-141b is its low but non-zero ozone depletion value of 0.11. Because of this, United States Environmental Protection Agency (EPA) intends to put restrictions on the use of the material in the area of precision cleaning. These restrictions as part of the Significant New Alternative Policy (SNAP) regulations (Section 612 of the Clean Air Act) are expected to be finalized late this year or early next year.

(ii) HCFC-123

HCFC-123 is similar in many respect to HCFC-141b. Similar to HCFC-141b, it was found to be an effective solvent in precision cleaning applications and can be used in today's equipment with minor modifications.

Extensive toxicological tests were carried out on both HCFC-141b and HCFC-123. These tests have shown that while HCFC-141b was of a very low order of toxicity (Permissible Exposure Limit (PEL) = 500ppm), however, HCFC-123 was found to have a relatively higher order of toxicity; PEL about 50ppm. While HCFC-123 could be used in non-solvent applications, this level of toxicity severely limited its use as a precision cleaning agent.

(iii) HCFC-225cb

HCFC-225cb is one of the two isomers being evaluated for solvent applications (HCFC-225ca being the other) This material has physical properties (Table-1) which makes it attractive for various precision cleaning applications. HCFC-225cb is currently in the development stage and their full commercial availability is still uncertain.

HCFCs are all mild ozone depleting materials with ODPs ranging from 0.03 to 0.11 and therefore, this class of materials can be looked at as transitional solvents leading to another generation of non-ozone depleting solvents which will be discussed in the next section.

Extensive toxicity studies of HCFC-225cb is being undertaken by the Program for Alternative Toxicity Testing (PAFT), a consortium of CFC producers in the world.

Table 1

Comparison of HCFC Solvents

Properties	CFC-113	HCFC-141b	HCFC-123	HCFC-225cb
Formula	$C_2Cl_3F_3$	$C_2H_3Cl_2F$	$C_2HCl_2F_3$	$C_3HCl_2F_5$
Molecular Weight	187.4	116.9	157.6	202.9
Boiling Point	47.8	32.0	27.8	56.0
Toxicity (PEL)	1000	500	10	-
Flammabilty	None	None	None	None
Ozone Depletion Potential	0.8	0.11	0.02	0.03
Viscosity	Low	Low	Low	Low
Surface Tension	Low	Low	Low	Low

III. HYDRFLUOROCARBON (HFC) SOLVENTS

Hydrofluorocarbon as the name suggests only contain carbon, hydrogen and fluorine. There are potentially a very large number of HFC compounds which are possible CFC alternates. Solvent selection among these large number of compounds is a difficult task. As a class, hydrofluocarbons remains to be the only ones which could be non-flammable, because it contain fluorine. Halogens make compounds non-flammable and among halogens chlorine and bromine are ozone depleting.

Solvent selection depends on a number of factors which include environmental acceptability, favorable toxicity, performance characteristics and available synthetic routes. The key environmental factors are ozone depletion, greenhouse warming, potential of contribution to smog in the lower atmosphere by the emission of volatile organic compounds (VOCs) and pollution to ground water by the way of water effluent. The solvent selection has to be done so as not to trade one environmental problem with another. There are Federal and State laws prohibiting the emission of VOCs which break down in the lower atmosphere and contribute to smog. Over and above these, the molecules have to be relatively non-toxic so that the work place remains safe.

Certain physical properties also have to be taken into considerations in the proper choice of solvents. Among physical properties, boiling point is perhaps the most important. Ideally the boiling point for most applications should be between 40 - 80°C, along with other properties, such as, low surface tension, viscosity and heat of vaporization. HFCs are the preferred choice because they have these key properties and are non-ozone depleting.

Using designed experiments and extensive computer modeling at AlliedSignal, the list has been narrowed and a few candidates were chosen to meet market needs. Synthesis routes, physical properties and environmental properties are all taken into consideration in candidate selection. Some of the more important physical properties of a typical HFC solvent as compared to CFC-113 is shown below.

Table 2
Physical Properties Comparison

Properties	Typical HFC Solvent	CFC 113
Boiling Point (°C)	50-70	47.6
Liquid Density(g/cc)	1.5-1.6	1.56
Solubility Parameter(cal/cc)1/2	7.6	7.3
Heat of Vaporization (Btu/lb)	65	63.1
Flash Point	None	None

IV. CLEANLINESS STUDIES

Our cleaning studies encompassed a wide variety of soils. Most of these were in the area of precision cleaning because the applications in this area are extremely diverse and in many of the applications no satisfactory alternate has been found. Precision cleaning encompasses cleaning oils, greases and particulate materials from various substrates, such as, metals, plastics, glasses and ceramics. Results of cleanliness studies of metal coupons are described in this section.

Cleanliness of coupons were tested using two methods. The first one is to determine cleanliness using carbon coulometer [2] which detects amounts of carbon physically adsorbed on the surface of the metals. Since most of the oils are hydrocarbon based this method detects the amount of oils left on the surfaces. The second method is the measurement of weight change of coupons using precision analytical balance. Weight change indicates residual oils left on the substrates.

Metal coupons soiled by various types of oils are degreased in a vapor degreaser machine using these solvents. The coupons are vapor rinsed for a short period of time depending upon the oils chosen. A short-period is selected so that the solvents can be compared easily. HFC solvents and their azeotropic blends are compared to CFC-113, HCFC-141b and methyl chloroform. The test results with various types of oils are shown below in Table 3. The numbers in the table show percent soil removal as measured by coulometry. The results show that HFC solvents have cleaning characteristics specific to soils.

These selected HFC solvents clean synthetic oils better than CFC-113 but could not clean the petroleum oils as well. They are not as good as methyl chloroform in cleaning these two types of oils. However, it has been shown [3] that azeotropic blends of these solvents do perform as good as methyl chloroform in cleaning both classes of oils and also clean the petroleum oil as good or better than CFC-113.

Table 3
Cleaning Results
Percent Soil Removed

\Solvents Soil \	Methyl Chloroform	CFC-113	HCFC-141b	HFC # 1	HFC # 2	HFC # 3
Petroleum oil	98	93	87	57	55	25
Synthetic oil	95	32	40	70	28	75

At the present time, various blends of HFCs, referred to as Genesolv®3000 series solvents are under development at AlliedSignal. These blends are being developed for use in different applications along with precision cleaning applications.

V. USE OF SOLVENTS IN PRECISION CLEANING OF GYROSCOPES

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 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. Beryllium metal parts preclude the use of aqueous based cleaning. processes.

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.

In an earlier paper [2], cleaning efficacy of HCFC-141b is compared to CFC-113. HCFC-141b was found to be comparable to CFC-113 in cleaning gyroscope components. That work examined a few of the aspects of testing the new HCFC solvents as replacement for CFC solvents in 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 of HFCs in this section.

Cleaning efficacy is determined by comparing the HFC cleaned surface to one cleaned with CFC using Fourier Transform Infrared Micro and Reflectance Spectroscopy, water break test or weight change of the coupon. FTIR with grazing angle measurements is a method to find details about surface chemistry and structure. Films less than 1 micrometer and down to a monomolecular layer on highly reflective metal surfaces can be analyzed by grazing angle reflection. The spectra can be analysed in FTIR and the composition of the films on the surfaces can be determined [4].

Analysis of surfaces before and after cleaning is done using Grazing Angle Fourier Transform Infrared spectra. The spectra (Figs. 1-3) show organic residues on coupons cleaned in CFC-113 and HFC solvents. The peaks here indicate the materials left after cleaning. The cleaning study used some of the soils normally cleaned in the manufacture of gyroscopes. The results have shown that bromotrifluoroethylene, a damping fluid used in gyroscopes, Krytox, a perfluorinated ether lubricant and a polyester lubricant is cleaned as good or better by the HFC solvent compared to CFC-113. For straight petroleum based fluids HFC solvents by themselves are found not to perform as good as CFC-113. Further studies are in progress to demonstrate the performance of the HFC solvents and their azeotropes in various precision cleaning applications.

VI. MATERIAL COMPATIBILITY

(i) Metals

Hydrolytic stability of HFCs are being tested by using sealed tubes containing HFCs in presence of various metals and water for a four(4) week period at an elevated temperature. The hydrolytic stability of the solvent compare very well with CFC-113. In these tests no chemical breakdown or hydrolysis of the solvent was observed. The metals used are stainless steel, cold rolled steel, aluminum, brass and copper.

(ii) Plastics and Elastomers

In commercialization of a new product for cleaning application another important property to study is its compatibility with various plastics and elastomers. Elastomers are used in pump seals, spray equipments etc. and both plastics and elastomers are present in various components to be cleaned. Compatibility studies were done where these plastics and elastomers are immersed in a solvent for a twenty-four (24) hour period at room temperature. Plastics used in the test are polycarbonates, acrylonitrile-butadiene-styrene (ABS), acrylic, polyvinyl chloride, high-impact polystyrene, nylon and extruded polypropylene. The elastomeric materials used are viton, neoprene, butyl rubber, silicone rubber, natural rubber and Buna N. The test results for plastics are shown below. All the elastomers tested except for viton are found to be compatible with HFC solvents.

Table 3
Plastics Compatibility

Plastics/Elastomers	CFC-113	HCFC-141b	HFCs
Acrylonitrile-Butadiene-Styrene	0	3	0
Acrylic	0	2	0
Polyvinyl Chloride	0	2	0
Nylon 46	0	0	0
High Density Polyethylene	0	0	0
Polypropylene	0	0	0
High Impact Styrene	0	3	0
Polycarbonate	0	2	0

Here 0 indicates no visible effect, 1 indicate slight effect, 2 indicates moderate effect and 3 indicate strong effect. Tests have shown that the solvent has no effect on these plastics at room temperature over a twenty four hour immersion period.

V. CONCLUSIONS

In this paper we have described the evolution of solvents in precision cleaning. The properties of HCFCs as transitional solvents and that of HFCs as future solvents as replacement for CFC-113 and methyl chloroform. Performance characteristics of HFCs are also shown here. AlliedSignal is currently developing Genesolv® 3000 series HFC solvents, these are non-ozone depleting, non-flammable substance which can perform by themselves or as azeotropic mixtures with various compounds better than or equal to CFC-113. The azeotropic mixtures of HFCs compare very well to methyl chloroform [3]. These chemicals are presently undergoing extensive toxicity evaluation and environmental impact studies. Measured lifetimes of these compounds have been found to be less than 30 years and the respective greenhouse warming is expected to be comparable to alternate technologies. AlliedSignal is planning to field test these materials by next year and commercialize in 1995.

VI. REFERENCES

[1] M.J.Molina and F.S.Rowland, "Stratospheric Sink for Chlorofluoromethanes: Chlorine Atom Catalyzed Destruction of Ozone", Nature, Vol. 249, 1974, pp. 810-812.

[2] R.S.Basu, P.B.Logsdon and E.M.Kenny-McDermott, "Precision Cleaning in Aerospace Industry with HCFC Based Blend - A Status Update", Proceedings of the International Conference on CFC and Halon Alternatives, Washington D.C., 1991, pp. 188 198.

[3] R.S.Basu and K.P.Murphy, "Novel Hydrofluorocarbon Solvents as Alternatives to CFC-113 and Methyl Chloroform in Cleaning", Proceedings of NEPCON EAST 93, Boston 1993, pp. 235-239.

[4] R.J.G.Greenier, "Infrared Studies of Adsorbed Molecules on Metal Surfaces by Reflection Techniques", Journal of Chemical Physics, 44 (1), pp. 310-15, 1966.

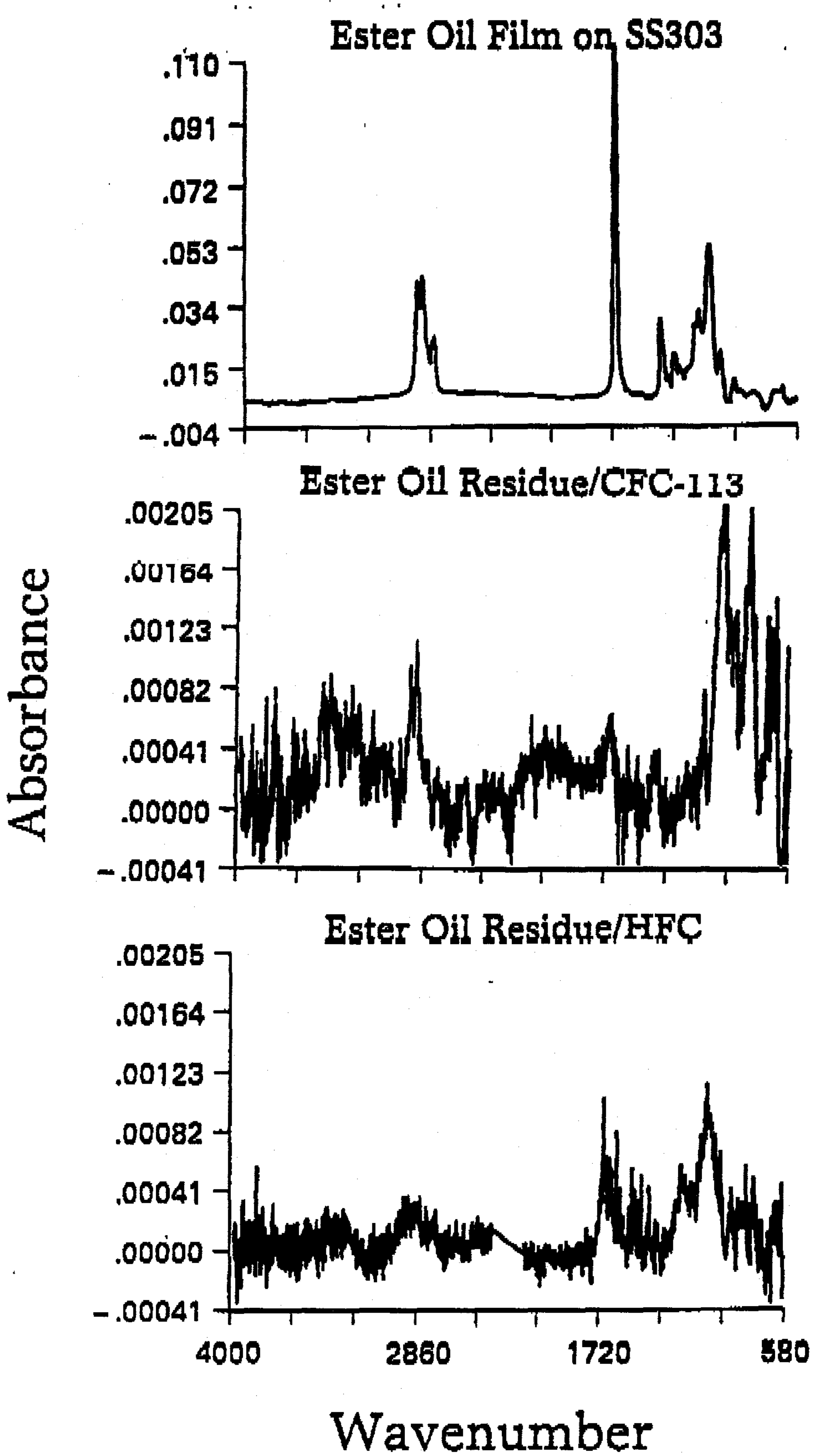
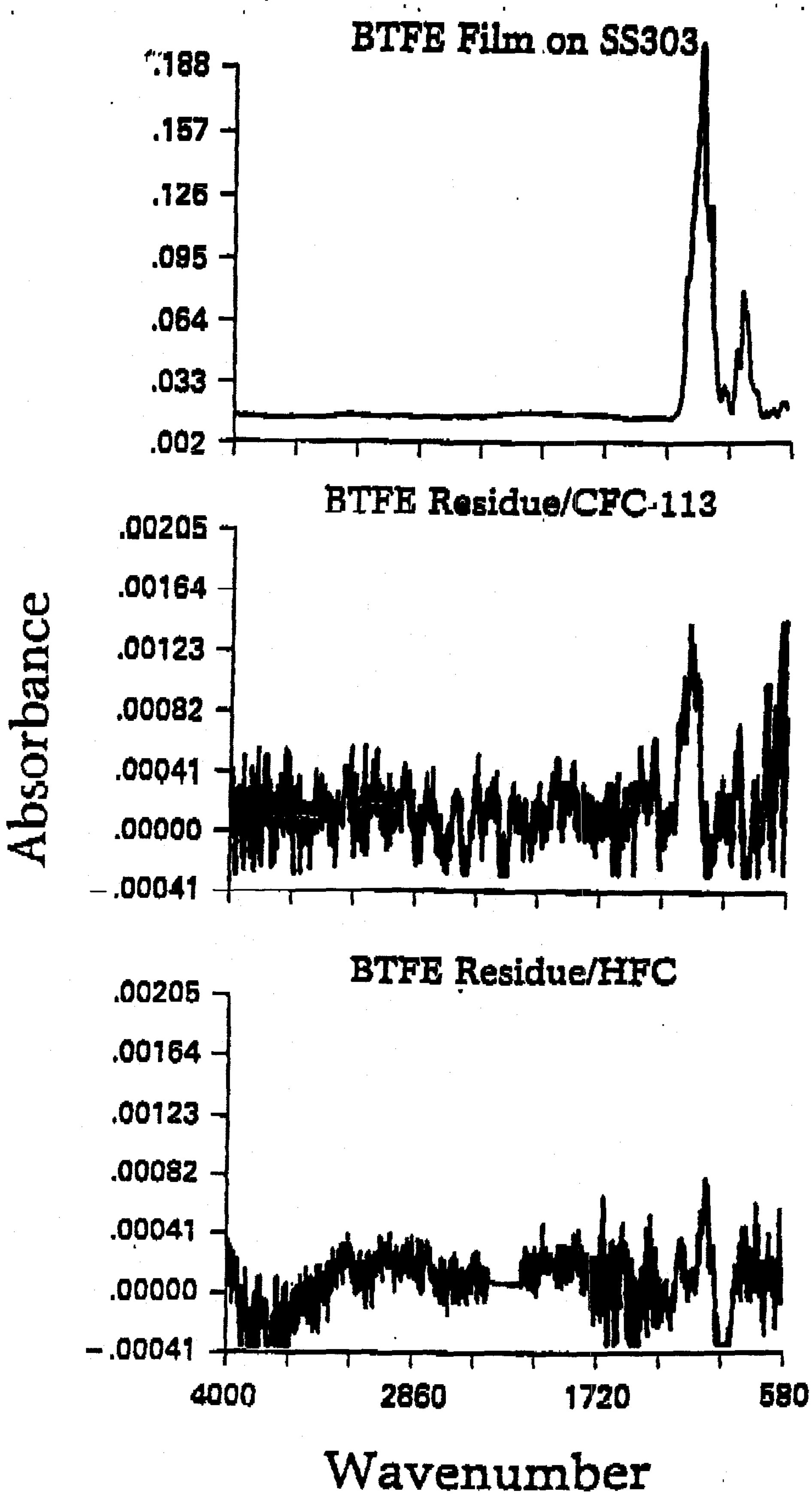

Ester Oil Film on SS303
.110
.091
.072
.053
.034
.015
-.004
Ester Oil Residue/CFC-113
.00205
.00164
.00123
.00082
.00041
.00000
-.00041
Ester Oil Residue/HFC
.00205
.00164
.00123
.00082
.00041
.00000
-.00041
Absorbance
4000
2860
1720
580
Wavenumber

FIGURE 1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.126
.095
.064
.033
.002
BTFE Residue/CFC-113
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.00164
.00123
.00082
.00041
.00000
-.00041
BTFE Residue/HFC
.00205
.00164
.00123
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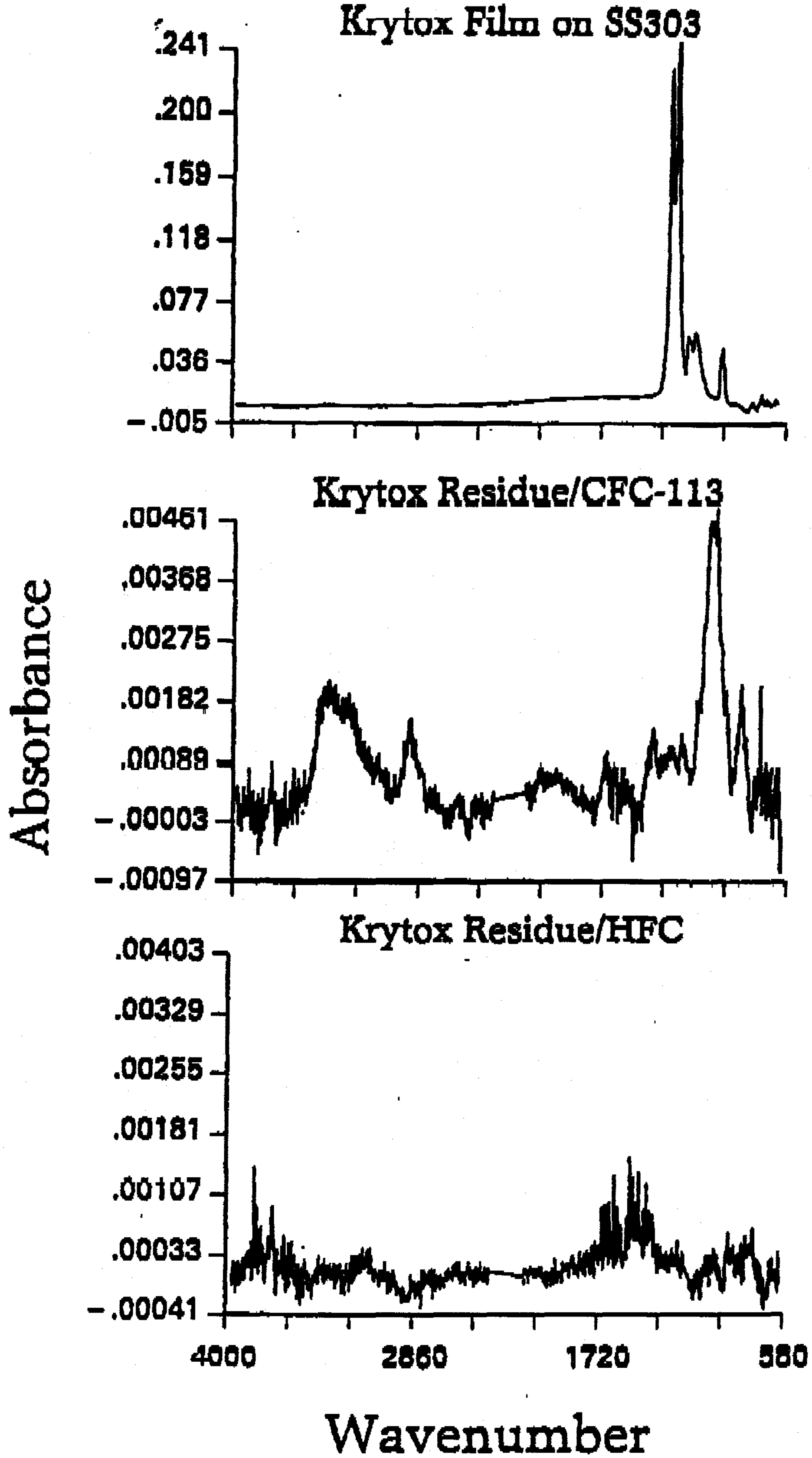
.00041
.00000
-.00041
Absorbance
4000
2860
1720
580
Wavenumber

FIGURE 2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.118
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.036
-.005
Krytox Residue/CFC-113
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.00275
.00182
.00089
-.00003
-.00097
Krytox Residue/HFC
.00403
.00329
.00255
.00181
.00107
.00033
-.00041
Absorbance
4000
2860
1720
580
Wavenumber

FIGURE 3