

Replacement of Methylene Chloride in NVR and Paint Removal Applications

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Dan Pilson
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13. ABSTRACT (Maximum 200 words) Molecular film contamination is detected and monitored using a gravimetric laboratory process described in ASTM standard methods. These processes currently specify the use of methylene chloride as a rinsing and wiping solvent. Methylene chloride, however, is an organic solvent targeted for reduction by the Environmental Protection Agency. In this report, we describe a request for a change in the solvent specified by the ASTM standard procedure. We review the criteria for the suggested replacement, ethyl acetate, for use in nonvolatile residue (NVR) testing. The solubility criteria assembled for the replacement of methylene chloride are then used to evaluate the replacement of methylene chloride-based paint removers. It is found through an examination of the literature that paint removal is a complex procedure that cannot be described solely by solubility parameters. The general state of paint removal technologies that do not use methylene chloride is reviewed. The EPA survey of maximum achievable control technologies (MACTs) for paint removal suggests that flashlamp exposure followed by either wet or dry media blasting is the best alternative for paint stripping tasks.				
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Contents

1. Introduction.....	1
2. ASTM E1235-95 Request for Change.....	3
3. Replacement Rationale	5
3.1 Solvent Properties.....	5
3.2 Vapor Pressure.....	7
3.3 Flammability and Toxicity	7
3.4 Experimental Test Program	9
4. Application to Paint Removal.....	11
5. EPA Study of Maximum Achievable Control Technology (MACT) for Paint Removal.....	17
5.1 HAP Chemical Stripping.....	18
5.2 Non-HAP Chemical Stripping.....	19
5.3 Dry Media Blasting.....	19
5.4 Wet Media Blasting	19
5.5 Thermal Decomposition	20
5.6 Other Combined Approaches	20
5.7 EPA MACT Summary.....	21
6. Summary and Conclusions	23
References.....	25

Figures

1. Solvent rankings based on total Hansen solubility parameter, δ_t	6
2. Vapor pressures of solvents at 25°C	8
3. Percent recovery of deposited tetraphenyl dimethyl disiloxane from witness plates using three different solvents (two trials for each solvent).....	10

Tables

1. Proposed Rewrite of ASTM E1235-95 With Respect to the Usage of Methylene Chloride and its Replacement by Ethyl Acetate.....	4
2. Flammability and Toxicity Assessment for Various NVR Solvent Replacement Candidates From Reference 3.....	9
3. ASTM E1235 Test Results Using Methylene Chloride and Ethyl Acetate Solvents	9
4. Hansen Parameters and Gas-Phase Dipole Moments for Solvents.....	12
5. Hansen Solubility Parameters and Interaction Radius for Several Polymer Coatings	12
6(a). Effectiveness of Solvents Dissolving Polymers. Aggressive solvents.....	13
6(b). Effectiveness of Solvents Dissolving Polymers. Intermediate solvents.	14
6(c). Effectiveness of Solvents Dissolving Polymers. Weak solvents.	14

1. Introduction

The most important contaminants affecting space hardware are microscopic particles and molecular films. The particulate cleanliness of critical surfaces can be verified by microscopic inspection of tape lifts or witness plates. The quantitative measurement of molecular films, however, involves a gravimetric laboratory process. For the measurement and diagnosis of spacecraft processing facilities, the procedure uses the exposure of witness plates and subsequent rinsing with solvents.¹ Non-volatile residue (NVR) can be measured directly on surfaces by a process in which the surface is wiped with solvent-soaked cloths.² This procedure is described by ASTM E1235-95 "Standard Method for Gravimetric Determination of Non-volatile Residue in Environmentally Controlled Areas for Spacecraft."

The measurement described by ASTM E1235-95 utilizes a stainless-steel witness plate that is exposed to a facility environment for an extended time. The plate is then transported to a laboratory and rinsed with solvent. The solvent is filtered and deposited in a beaker of known tare. The solvent is then evaporated, leaving the nonvolatile residue (NVR). In early versions of this standard, the solvent used for rinsing the molecular film contaminant from witness plates was a mixture of ethyl alcohol and 1,1,1 trichloroethane. 1,1,1 Trichloroethane has since been categorized a Class I Ozone Depleting Substance (ODS) and is no longer used. As currently written, ASTM E1235-95 specifies the use of methylene chloride (dichloromethane) as the rinsing solvent. Methylene chloride is toxic and is targeted for reduction under Section 313 of the federal Emergency Planning and Community Right-To-Know Act (EPCRA). EPCRA 313 requires facilities to report releases of 650 toxic chemicals to the air, water, and land, as well as the quantities recycled, treated, burned, or otherwise disposed of. ASTM E1235-95 itself notes:

"Methylene chloride is toxic and is being phased out for many applications. Replacement solvents are under study and will be substituted when available. Use methylene chloride only in an exhausting workstation."

This report is composed of four parts.

- I. An official request for a change of solvents in the ASTM E1235-95 standard process is documented and described (Section 2.0).
- II. The rationale for choosing ethyl acetate as a replacement solvent is reviewed (Section 3.0).
- III. Possible extension of the methylene chloride replacement criteria to paint removal operations is discussed (Section 4.0).

IV. The EPA survey of maximum achievable control technologies (MACTs) for paint removal area is reviewed (Section 5.0). This EPA survey describes the current state of paint removal technologies that do not use methylene chloride-based paint removers.

2. ASTM E1235-95 Request for Change

ASTM E1235-95 was due for reconsideration in the year 2000 by the Subcommittee E21.05 on Contamination. Subcommittee E21.05 is part of the ASTM Committee E-21 on Space Simulation and Application of Space Technology. The process for consideration is outlined below:

1. *ASTM subcommittee receives request, proposal, and supporting data.*

This request was made in November 1999. The supporting data and reports are summarized in the following section.

2. *The committee members discuss proposal and data.*

For ASTM E1235-95, the committee members were in general agreement that the standard solvent was in need of change. Basic agreement was obtained in this meeting of the 21.05 subcommittee.

3. *Develop a proposal for a rewritten standard.*

The proposed rewriting of the standard was developed and submitted to the E21.05 subcommittee chairman on 28 April 2000. The proposed modifications are presented in Table 1.

4. *A new, draft ASTM standard will be prepared by the E21.05 subcommittee chairman.*

5. *A final vote will conclude the process.*

Currently, the E21.05 chairman is drafting a new ASTM standard (Step 4).

We note here as well that ASTM E1560M-95 “Standard Test Method for Gravimetric Determination of Nonvolatile Residue from Cleanroom Wipers” specifies an NVR solvent consisting of three parts 1,1,1 trichloroethane and one part ethanol, by volume. As noted earlier, 1,1,1 trichloroethane has been denoted a Class 1 ODS. The NVR solvent designated in E1560 should be modified in the future.

Table 1. Proposed Rewrite of ASTM E1235-95 With Respect to the Usage of Methylene Chloride and its Replacement by Ethyl Acetate

Line Number	Current Text Reads	Proposed Revision
4.2	The plate is rinsed with a high purity methylene chloride solvent.	The plate is rinsed with high-purity ethyl acetate solvent.
7.6	NVR <i>Solvent</i> consisting of HPLC (high-purity liquid chromatography) grade methylene chloride (dichloromethane). The solvent shall be certified to contain <1 ppm (<1 mg/L) NVR using the procedure in Section 10.	NVR <i>Solvent</i> consisting of HPLC (high-purity liquid chromatography) grade ethyl acetate. The solvent shall be certified to contain <1 ppm (<1 mg/L) NVR using the procedure in Section 10. Note: Burdick & Jackson cat. No. 100, B&J Brand Ethyl Acetate has been found to be satisfactory.
NOTE 5	Methylene chloride is toxic ¹⁷ and is being phased out for many applications. Replacement solvents are under study and will be substituted when available. Use methylene chloride only in the exhausting work station (6.3).	Ethyl acetate ¹⁷ is an organic solvent, and as such, presents some degree of physical and health hazard. Use of ethyl acetate should be according to the recommendations provided in the Material Safety Data Sheet
Footnote 17	Material Safety Data Sheet No. 310, Genium Publishing Corp., 145 Catalyn St., Schenectady, N.Y. 12303.	Material Safety Data Sheet No. 437, Genium Publishing Corp., 145 Catalyn St., Schenectady, N.Y. 12303.
10.2	The NVR of each bottle shall be determined upon opening in accordance with 10.3.	<i>Typo:</i> The NVR of each bottle shall be determined upon opening in accordance with 10.7.
10.4.1	Methylene chloride can be toxic. Handle with caution and observe appropriate precautions.	Handle ethyl acetate with caution and observe appropriate precautions.
11.2.1	Methylene chloride can be toxic. Handle with caution and observe appropriate precautions.	Handle ethyl acetate with caution and observe appropriate precautions.

Note the typo in the current standard in Subsection 10.2, erroneously referring to Subsection 10.3.

3. Replacement Rationale

In work performed by Arnold and Uht,³ potential solvent replacements were evaluated using a literature review of solvent properties together with a laboratory testing approach. The goal of the effort was not to find the best solvent for removing a particular NVR, but rather to maintain a connection with heritage results. A suitable “drop in” replacement would, therefore, have solvent properties that closely matched methylene chloride and the NVR mixture of 1,1,1 trichloroethane and ethanol.

Other chemical and physical properties also played a key role in the evaluation. The vapor pressure was important because the solvent must remain on the surface long enough to perform an effective wiping test. However, the solvent should not have too low a vapor pressure because the evaporation step in the NVR tests would take an unreasonably long time. The results of most NVR tests are desired in 24–48 h.

The replacement solvent would need to be readily available from more than one source. Ideally, it would be available routinely having a low level of impurities. Finally, it would have suitable safety, toxicity, and flammability properties and, of course, would be environmentally acceptable. All of these properties were evaluated to develop a “score” for a large number of replacement candidates.

3.1 Solvent Properties

The solvent properties are described successfully beginning with the cohesive energy density, c , given by

$$c = -U/V, \quad (1)$$

where U is the molar cohesive energy, and V is the molar volume, and where the units of c are the same as pressure. The Hildebrand parameter is given by

$$\delta = c^{1/2}. \quad (2)$$

δ has units of $(\text{MPa})^{1/2}$.^{*} According to Barton,⁴ two materials with similar values of δ gain energy on mutual dispersion to permit mixing. On the other hand, a material with a high value of δ requires higher energy for dispersal than can be obtained from a material with smaller δ and immiscibility results. These statements are similar to the rule-of-thumb often stated that “like dissolves like.”

Solvent properties are better described by multi-component parameters such as the three-component Hansen parameters shown in Eq. (3).

^{*} Pascal(Pa) = 1 N m⁻² = 7.5 x 10⁻³ Torr.

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2, \quad (3)$$

where δ_d describes dispersion forces, δ_p describes the polar forces, and δ_h corresponds to hydrogen bonding. The total Hansen parameter, δ_t , is equivalent to the Hildebrand parameter.

The replacement of methylene chloride or the NVR solvent blend begins by identifying those solvents with a similar δ_t . The results of that study are shown in Figure 1. Note in Figure 1 that several solvents have very large δ_t values, among them the solvents Freon 113 and methanol. However, the key is to identify those solvents that have the greatest similarity to methylene chloride and 1,1,1 trichloroethane, whose values of δ_t are between 18.5 and 20.5. The suitable candidates based on δ_t alone are methyl isobutyl ketone, n-butyl acetate, methyl acetate, ethyl acetate, and tetrahydrofuran. Further down-select based on vapor pressure, flammability, and toxicity are discussed in the following sections.

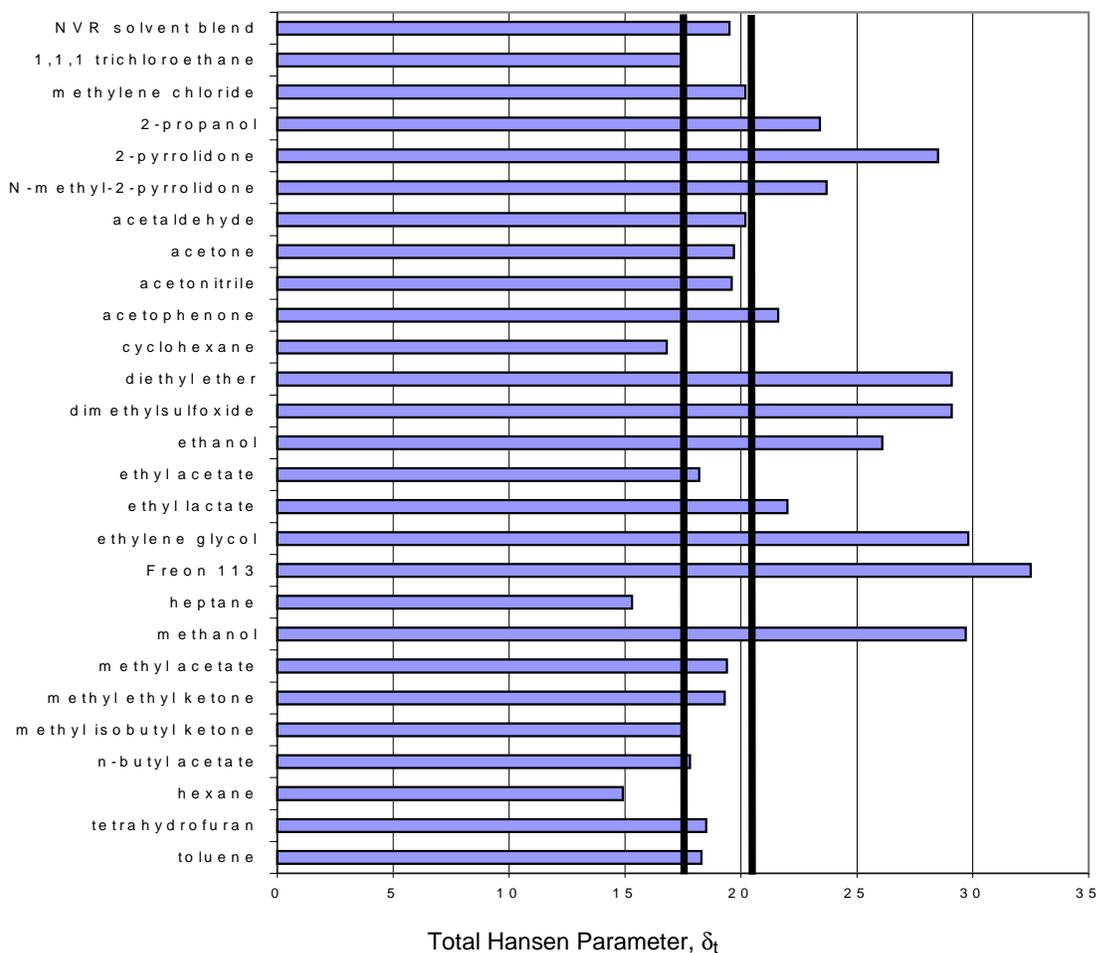


Figure 1. Solvent rankings based on total Hansen solubility parameter, δ_t . The desired replacement solvent for methylene chloride (dichloromethane) lies between 18.5 and 20.5, as indicated by heavy black lines.

For a three-component “vector” quantity such as the total Hansen parameter, the vector difference between, say, methylene chloride and any other solvent, designated by i , can be defined.

$$d_i^{\text{MC}} = [(\delta_{\text{dMC}} - \delta_{\text{di}})^2 + (\delta_{\text{pMC}} - \delta_{\text{pi}})^2 + (\delta_{\text{hMC}} - \delta_{\text{hi}})^2]^{1/2}, \quad (4)$$

where the vector difference, d , is made up of the individual differences between the dispersive, polar, and hydrogen bonding characteristics of methylene chloride and any other solvent. Though several solvents might have a total Hansen parameter near that of methylene chloride, ethyl acetate has the smallest vector difference. That is, ethyl acetate has the smallest difference between each of the forces: dispersive, polar, and hydrogen bonding.

3.2 Vapor Pressure

Vapor pressure plays a practical role in the selection of a replacement solvent. A solvent with a high vapor pressure reduces the residence time on the tested surface in a wiping test. A solvent with a low vapor pressure would extend the duration of the evaporation step in either of the NVR tests. Therefore, one seeks a solvent of moderate vapor pressure. Arnold and Uht examined the vapor pressures at 25°C for many of the solvents shown in Figure 1. Their results are shown in Figure 2. They concluded that diethyl ether would be the highest vapor pressure solvent one could use effectively. Isopropyl alcohol (2-propanol) was suggested as the lowest vapor pressure solvent. Ethyl acetate is near the low end of the vapor pressure scale, but higher than that of 2-propanol. The most practical range of vapor pressures lies between the two solid lines.

3.3 Flammability and Toxicity

Three figures of merit were examined concerning the flammability and toxicity hazards: the threshold limit value (TLV); the inhalation hazard ratio (IHR); and the “Flash Point.” The TLV represents the hazardous exposure level to the material given in ppm. Those replacement candidates with the highest TLVs received the highest scores. The IHR is the ratio of the saturated vapor concentration at 25°C to the TLV. A low IHR is desired, and those replacement candidates with the lowest IHRs received the highest scores. So-called open-cup (OC) and closed-cup (CC) flash point measurements give the temperature at which a solvent can be ignited by a hot wire. OC measurements address the possibility of ignition in an open environment (as would occur in a spill), while CC tests address the ignition in closed container. Since all potential replacements were both volatile and flammable, the flash point data were not given significant weight in the scoring. However, it is clear that the use of certain flammable replacements would likely be restricted in some areas where 1,1,1-trichloroethane and methylene chloride were allowed.

Most of the candidate solvents have a higher TLV and lower IHR than methylene chloride, warranting the toxic warnings concerning methylene chloride in the ASTM E1235-95. The exception is acetonitrile, with a TLV of 40 ppm versus 50 ppm for methylene chloride.

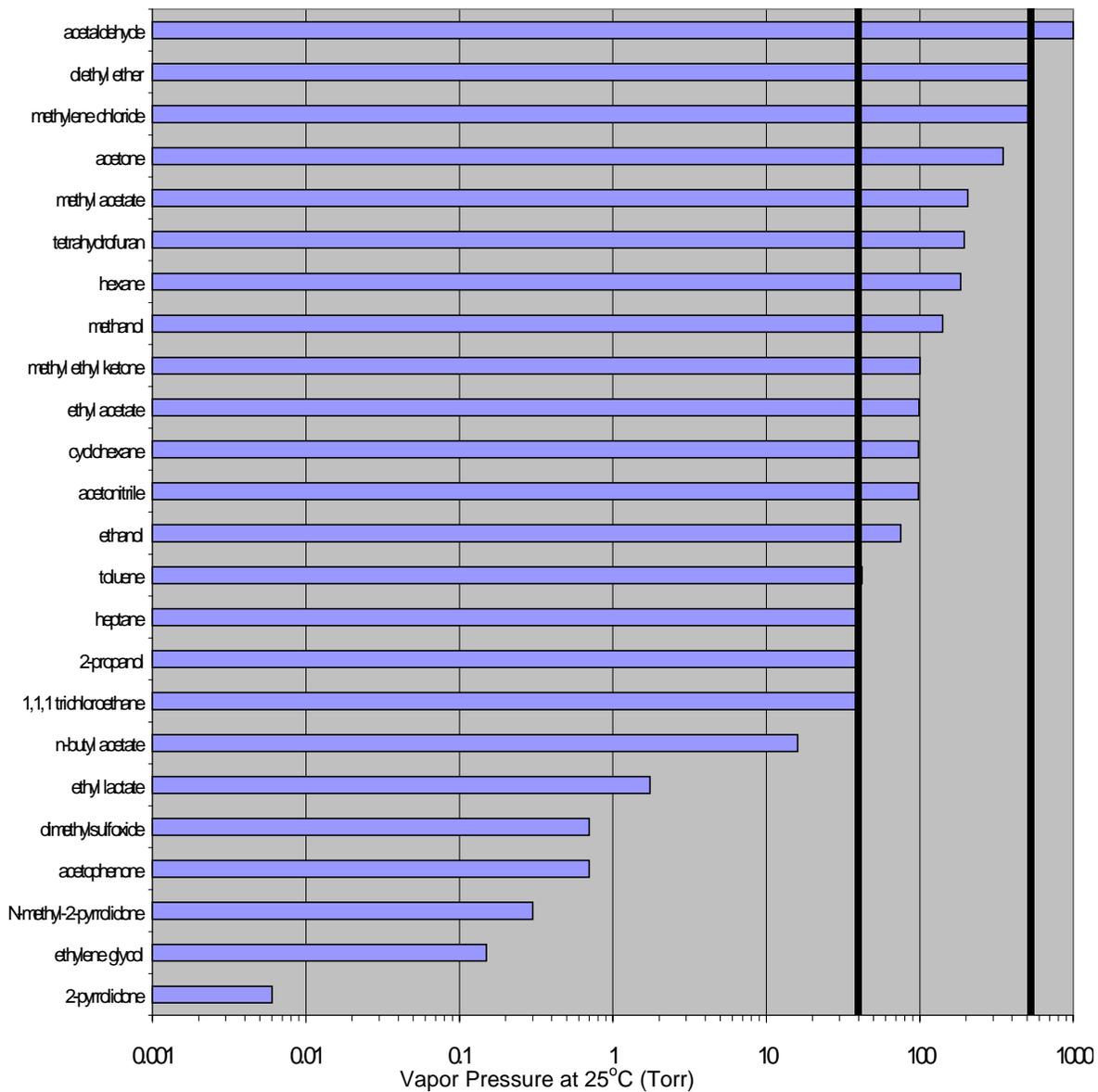


Figure 2. Vapor pressures of solvents at 25°C. The most practical vapor pressure for NVR testing lies between the two solid lines.

A summary of Flash Point, TLV, and IHR data for all solvents considered is shown in Table 2.

Table 2. Flammability and Toxicity Assessment for Various NVR Solvent Replacement Candidates From Reference 3

Solvent	Flash Point	TLV, ppm	Inhalation Ratio	Comments
1,1,1 trichloroethane	None	350	451	Class 1 ODS
2-propanol	12	400	140	
2-pyrrolidone	110			No TLV Data
Acetone	-19	750	386	
Acetonitrile	6	40	2888	
Cyclohexane	-18	300	396	
Diethyl ether	-45	400	1806	
Dimethylsulfoxide	88			Skin Penetrant, no TLV
Ethanol	12	1000	74	
Ethyl acetate	-4	400	288	
Ethyl lactate	49			No TLV data
Ethylene glycol	111	50	3	
Freon 113	48	1000	434	Class 1 ODS
Heptane	-4	400	141	
Hexane	-22	50	3816	
Methanol	11		796	
Methyl acetate	-16	200	1375	
Methyl ethyl ketone	-6	200	630	EPA 17*
Methylene chloride	None	50	11184	Carcinogen, EPA 17*
n-butyl acetate	22	150	112	
n-methyl-2-pyrrolidone	86			No TLV data
Tetrahydrofuran	-14	200	1086	Explosive hazard in distillation
Toluene	4	50	703	EPA 17*

*"EPA 17" refers to the voluntary reduced emissions of 17 chemicals as part of the EPA's Hazardous Air Pollutant Strategic Implementation Plan. EPA 17 has been concluded and has been replaced by EPCRA 313.

3.4 Experimental Test Program

A series of experimental results was conducted to evaluate the effectiveness of ethyl acetate compared to methylene chloride for use as an NVR solvent. The first test involved stainless-steel witness plates exposed for one month in a machine shop environment. The plates were then bagged together for about three months. The results of subsequent ASTM E1235 testing are shown in Table 3. The agreement is very good.

Table 3. ASTM E1235 Test Results Using Methylene Chloride and Ethyl Acetate Solvents

	Methylene Chloride	Ethyl Acetate
Sample Mass (g)	0.00093	0.00147
Blank (g)	0.00029	0.00072
NVR Mass (g)	0.00064	0.00075

A series of tests was performed in which known amounts of contaminants were deposited on stainless-steel witness plates having 1 ft² area. The witness plates were then rinsed with solvents to recover the deposited contaminant. The percent contaminant recovered, R_c , is given by:

$$R_c = (m_r - m_b)/m_c \times 100 \quad (5)$$

Where m_r is the contaminant mass recovered, m_b is mass of the solvent blank, and m_c is the known mass of the deposited contaminant. The results for one of the contaminants, tetraphenyl dimethyl disiloxane, a typical analog for silicone molecules, are shown in Figure 3. Ethyl acetate and methylene chloride were found to be equally effective in removing this contaminant. We note that methyl acetate was also effective. However, use of this solvent is not recommended because of its high vapor pressure and toxicity.

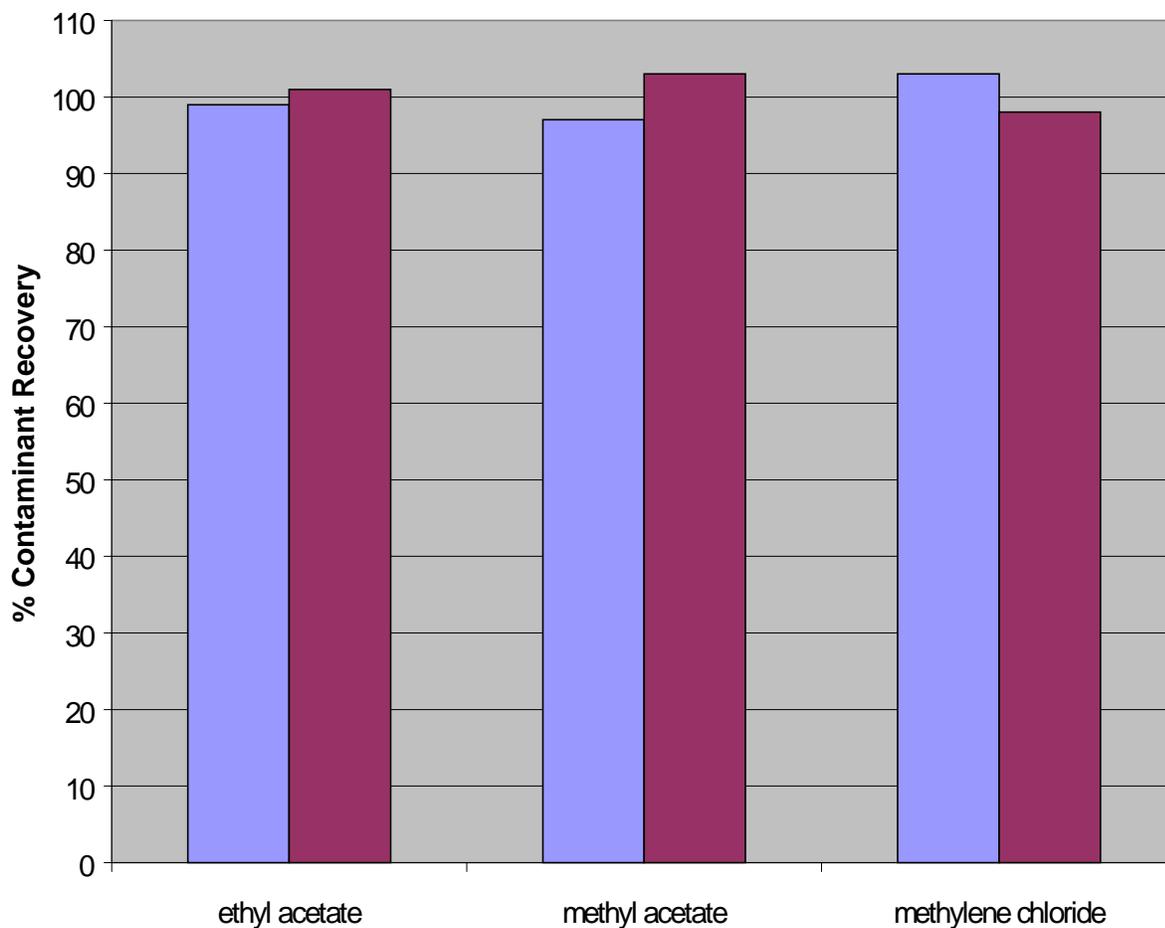


Figure 3. Percent recovery of deposited tetraphenyl dimethyl disiloxane from witness plates using three different solvents (two trials for each solvent).

4. Application to Paint Removal

Paint removal is performed frequently in the aircraft and aerospace industries, and a significant amount of methylene chloride is used for this purpose. As part of the effort to remove methylene chloride and other hazardous air polluting (HAP) chemicals, the solubility parameters compiled in the previous NVR study were used to identify potential replacements for methylene chloride-based paint removers or strippers.

Paint removal and NVR solvent replacements have similarities and differences. The development of a suitable NVR solvent replacement did not consider specific chemical interactions between solvent and NVR. It was not desired that the solvent replacement remove more NVR than the 1,1,1-trichloroethane/ethanol blend. Rather, the intent was to find a replacement most like the blend. Solubility parameters were, therefore, an ideal focus.

The removal of paint, however, is generally thought of as a more complicated process. The literature addressing paint removal technology describes a process in which the paint removal solvent penetrates the paint and attacks the adhesive bond. In this process, size of the molecule is important to enhance the transport through paint. Vapor pressure needs to be low to reduce the evaporation. The specific chemistry between the solvent and paint-substrate bond must be considered in detail. The interactions between the solvent and the pigment must also be considered. Thus, the formulation of methylene chloride paint removers involves the role of evaporation retardants, diffusion enhancers, and specific adhesive bond chemistry. Typically, paint removal literature describes a process in which swelling and blistering of the paint layer follows attack of the adhesive bond. The blistered paint layer is then removed by scraping or other mechanical means. Solubility is not often discussed except for small-scale specialty applications such as painting and furniture restoration.

A full listing of the dispersive, polar, hydrogen bonding, and total Hansen solubility parameters for the solvents considered as the replacement in the NVR test⁴ is shown in Table 4. The far right column also gives the molecular dipole moment measured in the gas phase.⁵ Dipole moments measured in the liquid phase are indicated in parentheses. (Reference 5 notes that dipole moments measured in the liquid phase are less reliable.)

Methylene chloride does not fall in an extreme range for any of the three Hansen parameters, but lies very near both the average and median values for the solvents listed. Similarly, the dipole moment for methylene chloride is less than the average and median values. Methylene chloride would, therefore, not be indicated as an effective paint remover based on solubility.

Using the rule-of-thumb that “like dissolves like,” an analysis was performed of solubility parameters and their vector differences for a number of polymeric coatings and solvents. A collection of solubility data for several polymeric coatings obtained from the literature⁶ is shown in Table 5. R is the radius of interaction can be thought of as a measure of similarity between the solvent and polymer.

Table 4. Hansen Parameters and Gas-Phase Dipole Moments for Solvents. Dipole moments in parentheses are measured in the liquid phase. NA = not available.

Solvent	Dispersive (MPa ^{1/2})	Polar (MPa ^{1/2})	Hydrogen Bonding (MPa ^{1/2})	Total (MPa ^{1/2})	Dipole Moment (Debye)
Toluene	16.4	8	1.6	18.3	0.36
Tetrahydrofuran	13.3	11	6.7	18.5	1.63
Hexane	14.9	0.0	0.0	14.9	0.00
n-butyl acetate	14.5	7.8	6.8	17.8	(1.9)
Methyl ethyl ketone	14.1	9.3	9.5	19.3	2.50
Methyl acetate	13.3	9.5	10.4	19.4	1.72
Methanol	15.1	12.3	22.3	29.6	1.70
Heptane	15.3	0.0	0.0	15.3	0.00
Ethylene glycol	17	11	26	32.9	2.28
Ethyl acetate	15.8	5.3	7.2	18.1	1.78
Ethanol	12.6	11.2	20	26.1	1.69
Dimethylsulfoxide	18.4	16.4	10.2	26.7	4.49
Diethyl ether	12.4	12.3	23.3	29.1	1.15
Cyclohexane	16.5	3.1	0.0	16.8	0.00
Acetonitrile	10.3	11.1	19.6	24.8	3.92
Acetone	15.5	10.4	7	20	2.88
N-methyl-2-pyrrolidone	16.5	10.4	13.5	23.7	2.66
2-pyrrolidone	19.4	17.4	11.3	28.4	(3.5)
2-propanol	14	9.8	16	23.4	1.66
Methylene Chloride	13.4	11.7	9.6	20.2	1.60
1,1,1-trichloroethane	17	4.3	2.1	17.7	1.78
Benzyl alcohol	14.7	12.2	15.6	24.6	(NA)
Average	15.0	9.3	10.9	22.1	1.8
Median	15.0	10.4	9.9	20.1	1.7

Table 5. Hansen Solubility Parameters and Interaction Radius for Several Polymer Coatings (Compiled by Burke)

Polymer/Coating	Dispersive (MPa ^{1/2})	Polar, (MPa ^{1/2})	Hydrogen Bonding (MPa ^{1/2})	Interaction Radius, R
Cellulose acetate	18.6	12.7	11	7.6
Chlorinated polypropylene	20.3	6.3	5.4	10.6
Epoxy	20.4	12	11.5	12.7
Isoprene elastomer	16.6	1.4	-0.8	9.6
Cellulose nitrate	15.4	14.7	8.8	11.5
Polyamide, thermoplastic	17.4	-1.9	14.9	9.6
Poly(isobutylene)	14.5	2.5	4.7	12.7
Poly(ethyl methacrylate)	17.6	9.7	4	10.6
Poly(methyl methacrylate)	18.6	10.5	7.5	8.6
Polystyrene	21.3	5.8	4.3	12.7
Poly(vinyl acetate)	20.9	11.3	9.6	13.7
Poly (vinyl butyral)	18.6	4.4	13	10.6

Polymer/Coating	Dispersive (MPa ^{1/2})	Polar, (MPa ^{1/2})	Hydrogen Bonding (MPa ^{1/2})	Interaction Radius, R
Poly (vinyl chloride)	18.2	7.5	8.3	3.5
Saturated polyester	21.5	14.9	12.3	16.8
Average	18.6	8.0	8.2	
Median	18.6	8.6	8.55	

Similar to Eq. (4), the vector solubility “distance” between solvent and polymer, D_{S-P} given by Ref. 6:

$$D_{S-P} = [4(\delta_{ds}-\delta_{dp})^2+(\delta_{ps}-\delta_{pp})^2+(\delta_{hs}-\delta_{hp})^2]^{1/2}, \quad (5)$$

where δ_{is} and δ_{ip} are the three Hansen parameters ($i = d$, dispersive; p , polar; and h , hydrogen) for the solvent and polymer, respectively. D_{S-P} differs from Eq. (4) by the leading factor of 4 for the dispersive term, which is included by Burke to create a spherical “solubility volume.” The results of the comparison are shown in Tables 6(a-c). If the vector difference, D_{S-P} , is less than R , the solvent and polymer are similar enough so that the solvent would be expected to dissolve the polymer. A “Yes” designation indicates that $D_{S-P} < R$ in Table 6. Table 6 has been divided into three parts. Those solvents that dissolve more than six of the polymers are termed “Aggressive” and are shown in Table 6(a). Table 6(b) lists “intermediate” solvents that dissolve between four and six of the polymers. Table 6(c) lists “weak” solvents that dissolve less than four polymers. It should be noted that these polymer coatings are not necessarily paints, although some paints might contain certain percentages of these polymers in their formulations.

Table 6(a). Effectiveness of Solvents Dissolving Polymers. Aggressive solvents.

Polymer	Ethyl Acetate	Acetone	N-Methyl-2- Pyrrolidone	Toluene	n-butyl acetate
Cellulose Acetate	No	No	Yes	No	No
Chlorinated polypropylene	Yes	Yes	No	Yes	No
Epoxy	Yes	Yes	Yes	No	No
Isoprene elastomer	Yes	No	No	Yes	No
Cellulose Nitrate	Yes	Yes	Yes	Yes	Yes
Polyamide, thermoplastic	No	No	No	No	Yes
Poly(isobutylene)	Yes	Yes	Yes	Yes	Yes
Poly(ethyl methacrylate)	Yes	Yes	Yes	Yes	Yes
Poly(methyl methacrylate)	Yes	Yes	Yes	Yes	No
Polystyrene	Yes	Yes	No	Yes	No
Poly(vinyl acetate)	Yes	Yes	Yes	Yes	Yes
Poly(vinyl butyral)	Yes	Yes	Yes	No	Yes
Poly(vinyl chloride)	No	No	No	No	No
Saturated polyester	Yes	Yes	Yes	Yes	Yes
Number Dissolved	11	10	9	9	7

Table 6(b). Effectiveness of Solvents Dissolving Polymers. Intermediate solvents.

	MEK	2-pyrrolidone	DMSO	Benzyl Alcohol	Iso-Propyl Alcohol	Methylene Chloride	1,1,1-Trichloroethane
Cellulose Acetate	No	Yes	No	No	No	No	No
Chlorinated polypropylene	No	No	No	No	No	No	No
Epoxy	No	Yes	Yes	Yes	No	No	Yes
Isoprene elastomer	No	No	No	No	No	No	No
Cellulose Nitrate	Yes	Yes	Yes	Yes	Yes	Yes	No
Polyamide, thermoplastic	No	No	No	No	No	No	Yes
Poly(isobutylene)	Yes	No	No	No	Yes	Yes	Yes
Poly(ethyl methacrylate)	Yes	No	Yes	No	Yes	Yes	No
Poly(methyl methacrylate)	No	Yes	Yes	No	No	No	No
Polystyrene	No	No	No	No	No	No	No
Poly(vinyl acetate)	Yes	Yes	Yes	Yes	No	No	No
Poly(vinyl butyral)	Yes	No	No	No	No	No	No
Poly(vinyl chloride)	No	No	No	No	No	No	No
Saturated polyester	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Number Dissolved	6	6	6	4	4	4	4

Table 6(c). Effectiveness of Solvents Dissolving Polymers. Weak solvents.

	Hexane	Acetonitrile	Ethylene Glycol	Methanol	Diethyl Ether	Ethanol
Cellulose Acetate	No	No	No	No	No	No
Chlorinated polypropylene	No	No	No	No	No	No
Epoxy	No	No	No	No	No	No
Isoprene elastomer	Yes	No	No	No	No	No
Cellulose Nitrate	No	No	No	No	No	No
Polyamide, thermoplastic	No	No	No	No	No	No
Poly(isobutylene)	Yes	Yes	No	No	No	No
Poly(ethyl methacrylate)	No	No	No	No	No	No
Poly(methyl methacrylate)	No	No	No	No	No	No
Polystyrene	No	No	No	No	No	No
Poly(vinyl acetate)	No	No	No	No	No	No
Poly(vinyl butyral)	No	No	No	No	No	No
Poly(vinyl chloride)	No	No	No	No	No	No
Saturated polyester	No	No	Yes	Yes	No	No
Number Dissolved	2	1	1	1	0	0

Table 6 illustrates that methylene chloride is only a moderate dissolver of a range of polymer coatings. Solvents that dissolve more than five polymers in the group, including toluene, MEK, N-methyl-2-pyrrolidone, 2-pyrrolidone, and acetone, are frequently mentioned as cosolvents with methylene chloride in commercial paint strippers. On the other hand, benzyl alcohol and methanol are also frequently mentioned as replacements for, or cosolvents with, methylene chloride, but are not indicated by this analysis. This wide variety of capability further demonstrates that the paint stripping process involves more complex parameters, and the effectiveness of a replacement cannot be assessed from solubility alone.

The aggressiveness of ethyl acetate in dissolving polymers is both surprising and somewhat of a concern. Ethyl acetate might be a good solvent for measuring NVR, but could damage painted surfaces and could give false high NVR results if the paints were of the right type. In other areas, the aggressiveness of ethyl acetate is well known. Ethyl acetate is currently available as an acetone-free finger nail polish remover.

Table 6(b) also shows that isopropyl alcohol (IPA) might not be as benign a solvent in all applications as previously thought. IPA dissolves as many polymers as 1,1,1-trichloroethane. Both solvents will dissolve poly(isobutylene) polymer systems as well as saturated polyesters.

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5. EPA Study of Maximum Achievable Control Technology (MACT) for Paint Removal

In previous sections of this report, the replacement of methylene chloride under EPCRA 313 regulations was discussed. In this section, we discuss the general operation of paint stripping, the use of methylene chloride in that operation, and the overall status of paint stripping technologies developed to reduce the emission of hazardous air pollutants (HAPs).

A preliminary survey of paint stripping technologies was initiated in 1998. This survey was mandated by Section 112(d) of the Clean Air Act and is part of the development of national emission standards for hazardous air pollutants (NESHAP). The objective of the survey was to produce maximum achievable control technology (MACT) standards for specific operations such as paint stripping. The MACT standards are important because they will define the allowable extent of HAP usage in future paint stripping operations. New paint stripping operations that do not meet MACT standards will require permits that limit HAP emissions. Alternatively, facilities that do not meet the MACT limits will be prohibited from operating.

To understand the scope of the effort, the constituent steps of the MACT survey are presented.

- Understand the paint stripping process.
- Identify typical emission points and the relative emissions from each point.
- Identify the range of emission reduction techniques and their effectiveness.
- Locate as many facilities as possible, both major and area sources.
- Identify and involve industry and regulatory agency representatives.
- Complete informational site visits.
- Identify issues and data needs and develop a plan for addressing them.
- Document results of the first phase of regulatory development.

The categories of different paint stripping technologies were assembled by the EPA MACT survey as follows:

Solvent Stripping

HAP Chemical Stripping

Non-HAP Chemical Stripping

Dry Media Blasting

- Plastic Media

- Wheat Starch and Walnut Hulls

- CO₂ Pellets

Thermal Decomposition

- Burn-off Systems

- Molten Salt Baths

- Laser Heating

Wet Media Blasting

- Medium- and High-Pressure Water

- Low-Pressure Sodium Bicarbonate Blasting

- Ice Crystal Blasting

We will briefly discuss the analysis and conclusions of the MACT survey in each of these categories.

5.1 HAP Chemical Stripping

The EPA MACT survey identified methylene chloride as the most widely used and most effective HAP in paint stripping applications. Typical paint stripping formulations will contain 60–65% methylene chloride, with the remainder consisting of activators, corrosion inhibitors, thickeners, and evaporation retarders. Methanol is the most common activator. A synergistic effect between methylene chloride and methanol is often cited.

Methylene chloride stripping formulations have been described as effective for virtually all paints on metallic substrates. As noted earlier in this report, methylene chloride strippers act by penetrating through the paint coating and causing the coating to swell away from the substrate. The penetration capability arises from the small size of the methylene chloride molecule. The EPA report notes that the intermediate solvency noted earlier is beneficial because it prevents the paint from dissolving and then redepositing when the methylene chloride evaporates. Thus, a paint coating treated by methylene chloride does not dissolve away. Rather, paint will wrinkle, bubble, and blister, whereupon it is washed or scraped away.

HAP emissions occur during the evaporation of the methylene chloride. Evaporation occurs during all phases of the paint stripping process, including the application and removal process, and possibly evaporates from the rinse water used to remove the swelled paint. Methylene chloride also evaporates readily when used in dip tanks that do not have vapor recovery capability.

5.2 Non-HAP Chemical Stripping

The EPA survey identifies N-methyl-s-pyrrolidone (NMP), benzyl alcohol, and dimethylsulfoxide (DMSO) as non-HAP paint strippers. The survey postulates that paint removal is achieved for these chemicals by dissolving the paint. It was shown in Table 4 that the dipole moments of both NMP and DMSO were very large (2.66 and 4.49, respectively, compared to 1.78 for methylene chloride). NMP and DMSO were also effective in dissolving more coating classes than methylene chloride, as shown in Table 6. Benzyl alcohol did not dissolve a large number of polymers in Table 6.

Benzyl alcohol is being evaluated as a HAP chemical and could be reclassified. NMP and DMSO were not classified by the EPA MACT survey as HAPs. However, NMP and DMSO are classified by the EPA as volatile organic chemicals (VOCs) and could come under the control of those regulations. Reference 3 notes that both NMP and DMSO could have toxic properties, but do not have TLV data. DMSO is known to be a skin penetrant.

Although the use of non-HAP chemicals eliminates the concern for HAP emissions, we anticipate that other regulatory issues will arise concerning VOCs. These regulations are likely to be the major reason for pursuing other paint stripping approaches.

5.3 Dry Media Blasting

Dry media blasting removes paint from the substrate via impact and abrasion. The media are entrained in a stream of compressed gas. Some dry media blasting techniques allow for control of the media stream such that topcoats of paint are removed while leaving the primer coat relatively undisturbed. The most commonly used dry media are plastic beads, wheat starch, walnut hulls, CO₂ pellets and sand. These media are attractive because they are recyclable and nontoxic.

HAPs or VOCs are emitted only if the paint contains appreciable amounts of either lead or chromium. Otherwise, dry media blasting presents no concerns for HAP or VOC emissions. Environmental controls are necessary to eliminate dangers arising from the resulting media dust clouds, especially from wheat starch, which is exceedingly fine-grained. The major disadvantages of dry media blasting arise from their relatively low efficiency in removing large volumes of paint. Although dry media blasting can be selective in the layers it removes, blasting has poor control in small crevices or corners. Additionally, the MACT survey suggests that dry media blasting might not be effective on all epoxies or polyurethanes, which are commonly used in the aerospace industry.

The MACT EPA survey reports that America West Airlines has offered third-party paint and coating removal services using dry blast media on aircraft. There is no reported data on how much of this work has been performed by America West.

5.4 Wet Media Blasting

Wet media blasting uses a high-pressure (15,000–55,000 psi) stream of water to remove paint. Sodium bicarbonate is sometimes added to the water stream to increase the abrasive effect. Wet media blasting is slower and less efficient than dry media blasting and can sometimes corrode metallic substrates. However, wet media blasting generates no dust cloud and produces no HAP or VOC

emissions other than heavy metals for certain paints, as described in the preceding section. Wet blasting requires no significant clean-up other than to filter solids from the water.

Paint removal from aircraft using robotic water blasting has been reported at Tinker Air Force Base in its efforts to reduce the use of methylene chloride.

Reports included in the appendices of the MACT survey indicate that blasting with ice crystals is not effective on typical aerospace coatings.

5.5 Thermal Decomposition

Removal of paint by thermal decomposition can be divided into two categories. First, thermal decomposition of painted parts can be performed using high-temperature baths of fluids or molten salt baths, or by using high-temperature ovens. Both approaches are impractical for fully assembled aircraft, but are used for removing paint from aircraft parts. Second, the paint can be heated and ablated using lasers or flashlamps.

Sames and coworkers⁷ have reported the removal of paint using lasers. Their study examines the use of a Nd:YAG laser to either directly remove the paint, or to destroy crosslinking in the topcoat, thereby allowing greater penetration by either NMP or benzyl alcohol. Sames et. al. report that benzyl alcohol is an effective stripper in either alkaline or acidic conditions but is ineffective in neutral formulations. Strongly alkaline or acidic conditions could damage the underlying substrate. They note further that NMP is an effective paint remover at elevated temperature, but is ineffective at room temperature.* The study showed that either solvent used alone was rendered ineffective when combined with a methylcellulose thickener. Certain laser pretreatments were found to cause damage to the crosslinked topcoat. The damage allows greater penetration by the solvent and results in attack of the adhesive bonds. Note that this is the same process envisioned for paint removal using methylene chloride.

The use of lasers for paint and coating removal is continuing. Workers in this area are receiving contracts from both DOD and commercial sources to develop laser techniques for specific applications. The laser approach is reportedly well suited to the removal of paint in small areas and from delicate materials. For example, lasers have been used to remove coatings in the art restoration area, and the US Navy has used lasers to selectively remove paint from around the rivets of torpedoes. Workers in the field concede that lasers are not yet competitive for large-scale applications, but improvements in laser technology tailored to large-scale paint and coating removal are in progress.

5.6 Other Combined Approaches

Success has been reported for the removal of paint using the combined approaches of flashlamp exposure followed by either wet or dry media blasting. This approach was developed by Boeing-MacDonnell Douglas Helicopters in 1991 for the Apache-Longbow conversion and has been named the FLASHJET[®] process. In this process, a pulsed, high-intensity lamp ablates the outer coating. A

* Note that listings of interaction radii in Table 6 make no reference to temperature effects.

high-pressure media stream is then used to easily remove the coating. Boeing-MacDonnell Douglas could not use methylene chloride because it would attack the resin in the composite structural material of the Apache helicopter. The flashlamp exposes a much larger area in a shorter time than a laser, increasing the process efficiency. Use of the FLASHJET[®] process on 232 aircraft is estimated to have saved about \$1M in materials and \$2.5M in labor costs. The FLASHJET[®] process is estimated to have reduced process waste by about 0.25 million pounds compared to other paint removal approaches. Currently, the FLASHJET[®] process is used world-wide for the maintenance of USAF Boeing-MacDonnell Douglas aircraft, including the F15, C5A, C130, and C141.

5.7 EPA MACT Summary

In summary, several approaches for the removal of paint have been examined since the EPA mandated the reduction of methylene chloride use in the early 1990s. Paint removal approaches that remain today are benzyl alcohol, currently a non-HAP, and dry and wet media blasting. By themselves, none of these methods is considered competitive with methylene chloride strippers, and some blasting methods have required the construction of totally new facilities. One procedure has been reported by Boeing-MacDonnell Douglas helicopters using both flashlamp thermal decomposition and wet or dry media blasting that compares well with chemical stripping and significantly reduces cost and waste matter.

The conclusions of the draft phase of the EPA MACT study are driven by the simple criterion that HAP emissions and potential HAP emissions must be reduced. Therefore, it is not surprising that the study rates dry and wet media blasting as the two alternatives of choice for the maximum effective technology and may be the technologies against which other methods are measured. It is likely, therefore, that any paint removal technique using organic solvents will require EPA permitting.

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6. Summary and Conclusions

As part of DOD programs to reduce the use of hazardous polluting materials, an effort has been made to identify and reduce the use of methylene chloride, among other materials. In previous work, a literature study of solubility parameters was used to determine a substitute for methylene chloride used as a solvent in ASTM and DOD tests for nonvolatile residue. Ethyl acetate was identified as the best replacement based primarily on the solubility parameter analysis. The results of toxicity and flammability analyses and a modest laboratory test program also contributed to this choice of a replacement solvent.

This year, a formal request was made to the ASTM E21.05 subcommittee to change the specified solvent from methylene chloride to ethyl acetate in ASTM E1235-95 "Standard Test Method for Gravimetric Determination of Non-Volatile Residue in Environmentally Controlled Areas for Spacecraft." A proposed rewriting of ASTM E1235-95 has been submitted and is now being formatted in preparation for a final vote.

The solvent solubility data were used to evaluate the replacement of methylene chloride for paint stripping applications. It was found that a much more detailed understanding of the paint removal mechanism is needed than for the NVR test process, and on the basis of solubility, methylene chloride itself is not identified as a good solvent of polymers. Rather, it is thought that methylene chloride has small molar volume and, therefore, diffuses well through many coats of paint. Several known additives to methylene chloride in commercial paint removers are identified by their solubility parameters. These include toluene, methyl ethyl ketone, tetrahydrofuran, N-methyl-2-pyrrolidone, 2-pyrrolidone, and acetone. Methanol, however, which is probably the most common cosolvent with methylene chloride in paint removers, is not identified on the basis of solubility parameters. Surprisingly, ethyl acetate is shown to dissolve paints aggressively. While ethyl acetate could see use as a paint remover, it could cause problems if used to measure NVR on painted surfaces. The results of this analysis show that, in addition to a more mechanistic understanding of paint removal, a supplementary laboratory testing program is essential to finding replacements.

The EPA has conducted a survey of paint removal technologies that replace the use of methylene chloride strippers. These technologies include the use of non-HAP chemical removers, dry and wet media blasting, and thermal decomposition. This survey was the first step in determining the maximum achievable control technology (MACT) against which future paint removal systems would be evaluated for HAP emissions. Future paint removal systems must be equal to the MACT or must undergo an EPA permitting process. The MACT survey identifies dry and wet media blasting as the most capable technology for removing paint while reducing HAP emissions. Flashlamp treatments appear to enhance the paint removal efficiency of wet or dry media blasting. The flashlamp/blasting approach is currently in wide use on large USAF aircraft.

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LABORATORY OPERATIONS

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