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Prepsolv™: The Optimum Alternative to 1,1,1-Trichloroethane and Methyl Ethyl Ketone for Hand-Wipe Cleaning of Aerospace Materials

R. Scott Gallagher, Business Manager
Glidsafe® Terpene Cleaners and Solvents
Glidco Organics Corp.
P.O. Box 389, Jacksonville, FL 32201-0389
(904) 768-5800

Including data and case study by:
John A. Purvis, Process and Manufacturing Engineer
Wade W. Moran, Science and Technology Department
Hercules Aerospace Company
Bacchus Works, Magna, UT 84044-0098
(801) 251-3468

Introduction

Throughout the DOD and commercial manufacturing community, engineers are aggressively screening alternative solvents before the Clean Air Act mandated phase-out of methyl chloroform. Although virtually hundreds of products are being considered, the "short list" appears to include only the following:

- Terpenes (usually terpene hydrocarbons)
- Propylene glycol ethers and their esters (e.g. PTB, DPM, PM acetate)
- NMP and BLO (GBL)
- Esters (e.g. butyl butyrate, methyl lactate)
- Halogenated solvents (e.g. parachlorobenzo-trifluoride)
- Mineral spirits and paraffinic solvents

And although the criteria for acceptance is different for each user and each application, the following subset is generally common to all:

- Acceptable solvency for specific soils
- Ease of use
- Compatibility with contact materials
- Readily available
- Ability to clean to established specifications
- Low toxicity and ecotoxicity
- Acceptable odor
- Good storage stability
- Affordable and cost effective
- Regulatory acceptance (no ODP, low GWP, not considered a HAP)

The advantages and disadvantages of the various alternatives has been debated within the industry and there are misconceptions regarding the various alternatives. Extensive testing has shown that terpene hydrocarbons are among the most effective cleaning agents for dissolving and removing difficult surface contaminants. In addition, terpenes are desirable because they are safe (low toxicity) and biodegradable.

However, terpenes are so highly biodegradable that this has been a limitation as well as an asset. In the presence of air certain terpenes break down, forming much less volatile compounds that do not evaporate like the terpene solvents themselves. These residues can be left behind during the cleaning process unless another solvent, like alcohol, is used to rinse residues away. Unfortunately, the need to rinse makes cleaning large surfaces, like airplane wings and rocket motors, very difficult. And this has made the use of terpenes for hand-wipe cleaning virtually impossible.

Engineers at Hercules Aerospace, a rocket motor manufacturer in Utah, have worked closely with chemists at Glidco Organics to study the feasibility of using terpenes for zero-residue wipe cleaning. The result of this work is a technological breakthrough, in which the barrier to ultra-low non-volatile residue formation has been broken. After 2 years of development and testing, SCM Glidco Organics has announced the availability of Glidsafe® Prepsolv™: a state-of-the-art ultra-low residue terpene wipe cleaning agent that <u>does</u> <u>not</u> <u>require</u> <u>rinsing</u>. Prepsolv™ can successfully be used in simple hand-wipe cleaning processes without fear of leaving surface residues. Industry testing has confirmed that Prepsolv™ is not only highly effective, but can even be less expensive to use than traditional cleaning solvents like methyl chloroform.

This paper addresses the features and benefits of Prepsolv™, and presents performance and material compatibility data that characterizes this unique cleaning agent.

Since its commercialization, Hercules Aerospace has chosen Prepsolv™ as the optimum cleaning agent to replace ozone-depleting solvents in their weapons factory in Magna, UT. Likewise, Boeing has approved Prepsolv™ for cleaning components in the manufacture of commercial aircraft at their facilities in Seattle, WA and Wichita, KS. Additional approvals are forthcoming for this uniquely safe and effective solvent.

Solvency

Terpene hydrocarbons, because of their chemical structure, are highly effective in dissolving aliphatic and cyclic lubricating oils, greases, waxes, tape residues, silicone fluids, and similar soils likely to be found in the manufacturing industries. In those cases where they are not effective alone, they form the base for mixtures that closely approach the solvency of methyl chloroform (1,1,1-trichloroethane) and methyl ethyl ketone (traditional aerospace industry wipe solvents). Solubility parameters are a reasonable predictor of solvent performance, and although they do not take molecular size into consideration, they are certainly the most useful theoretical tool for solvent selection[1] :

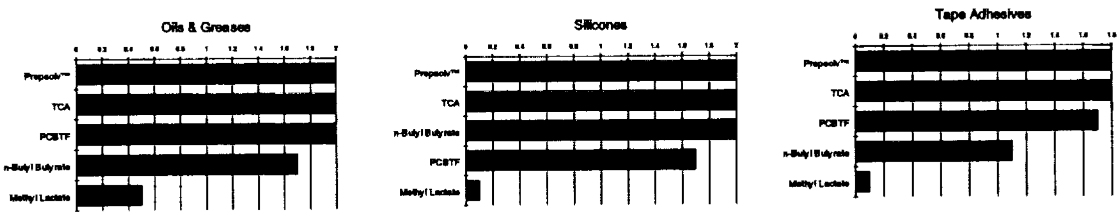
Hansen Solubility Parameter Comparison[2]

Target Solvents	δ_D **(Non-Polar)**	δ_P **(Polar)**	δ_H **(Hydrogen Bonding)**
Methyl chloroform (1,1,1-trichloroethane)	8.3	2.1	1.0
Methylene chloride	8.9	3.1	3.0
Acetone	7.6	5.1	3.4
Methyl ethyl ketone (MEK)	7.8	4.4	2.5
Alternative Pure Solvents			
Glidsafe® Prepsolv™ (Terpene hydrocarbon[3])	8.6	1.0	1.0
Stoddard solvent / mineral spirits	7.7	0.0	0.0
n-Methyl Pyrrolidone (Arco NMP)	8.8	6.0	3.5
n-Butyl butyrate[4]	7.9	2.0	3.6
Methyl lactate[4]	7.8	3.8	6.9
Propylene glycol t-butyl ether (Arco PTB)	7.3	2.1	6.0
Terpene alcohols (Glidco Glidsol® 90)	6.8	3.9	5.0
Water	7.6	7.8	20.7
Blended Solvent Systems			
Glidsafe® UTS-4B (Glidco Organics)	8.5	1.5	2.2
DS-104 (General Dynamics/Dynamold Solvents)	7.8	5.9	5.5

As can be seen, terpenes fall near methyl chloroform in solubility space. This property makes terpene solvents direct substitutes for 1,1,1 in many applications.

Tests performed at Hercules Aerospace Company confirm that solvent solubility can be reasonably predicted by solubility parameter modeling. The following graphical data shows that Glidsafe® Prepsolv™ is the most effective solvent against non-polar soils.

Solvent Solubility Test Results Against Various Soils[5]



Non-Volatile Residue

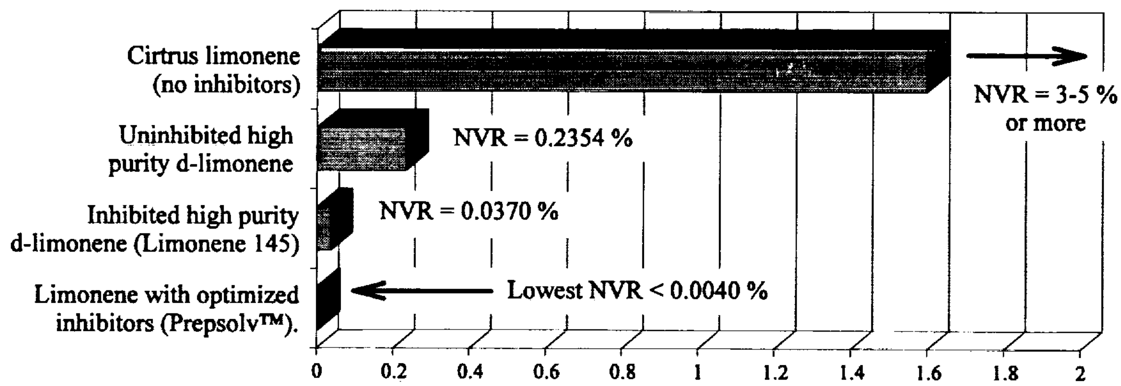
Traditional terpene solvents are not ideal wipe cleaning agents. In fact, many terpene solvents are actually poor choices for wipe cleaning because of their tendency to oxidize and polymerize, creating non-volatile organic surface residue (NVR). This polymeric residue is sometimes more difficult to remove than the original soil. The tendency has caused some researchers to conclude that terpenes are often not appropriate candidates for wipe cleaning solvents.

Antioxidants and inhibitors are added to terpenes much the same way that stabilizers have traditionally been added to chlorinated solvents. However, traditional development of terpene antioxidant and inhibitor technology was almost exclusively performed by the flavor and fragrance industry. Their needs and selection criteria were quite different from those of the aerospace industry, and their recommended inhibitors and antioxidant systems are not appropriate for precision cleaning applications.

A variety of commercially available terpene solvents were tested for NVR per ASTM D1353 (205°F in air). By this test, even the highest purity solvents left unacceptably high levels of surface residue (see graph on following page).

However, this problem has been solved. Hercules Aerospace and Glidco Organics initiated a development project to screen terpene systems and inhibitors to optimize a system that would adequately protect the terpenes from oxidation and polymerization, while not contributing themselves to surface residue. The resulting blend of terpenes and inhibitors leaves *virtually zero* NVR. This blend is available as Glidsafe® Prepsolv™. As you can see, proper choice of terpene solvent and inhibitor technology results in a truly "clean" terpene wipe solvent. It is no longer correct to assume or conclude that terpene solvents cannot be used as precision wipe cleaning agents.

Measured Non-Volatile Residue per ASTM D-1353 (weight %)



Inhalation Hazard and Workplace Safety

Because terpenes have low vapor pressure, they have low inhalation hazard. The ratio of the saturated vapor concentration of a solvent to its TLV is called the Inhalation Hazard Index (IHI) and is an indication of the relative danger from vapor exposure. The higher the ratio, the higher the vapor concentrations become in the workplace, and the quicker the TLV concentration is approached. Lower IHI ratios indicate that vapor concentrations will only slowly approach the TLV, which means that these solvents are safer to use in the workplace. High ratios indicate increased potential health risk. The following table compares the vapor pressure and Inhalation Hazard Index for common solvents. Note that Glidsafe® Prepsolv™ has the lowest IHI value and therefore is safest to use in the workplace:

Inhalation Hazard Index for Industrial Solvents[6]

	Vapor Pressure (mmHg @ 20°C)	TLV-TWA (ppm)	Inhalation Hazard Index @ 20°C
Glidsafe® Prepsolv™	1.6	100[7]	21.2
Stoddard Solvent / Mineral Spirits	2	100	26.3
2-Butoxyethanol (EB)	0.88	25	46.3
Perchloroethylene	13	50	342
Parachlorobenzotrifluoride (PCBTF)	5.3	20	349
1,1,1-Trichloroethane	100	350	376
Methyl Ethyl Ketone (MEK)	85	200	559
Trichloroethylene	59	50	1552
Methylene Chloride	340	50	8940

Vapor Pressure

Terpenes have relatively low vapor pressure. Low vapor pressure solvents have a number of advantages in wipe cleaning including:

- Reduced VOC emissions;
- Increased cleaning efficiency as a result of solvents remaining on the cloth longer before evaporation;
- Reduced evaporative losses translating into increased economy. Most experience indicates that terpene solvents are consumed at roughly 15-20% the rate compared to methyl chloroform in wipe cleaning.

In use, solvents are "consumed" not only by evaporation, but by disposal of unused material on cloths. In fact, disposal of unused material accounts for a major portion of the consumption. The evaporative losses alone from terpenes and conventional solvents have been compared in the lab:

Solvent Vapor Pressures and Estimated Evaporative Losses

	VAPOR PRESSURE (MMHG @ 20°C)	EVAPORATIVE LOSSES (LB/HR/SF @ 20°C)
Glidsafe® Prepsolv™	1.6	0.01
Methyl Ethyl Ketone	85	0.28
Methyl Chloroform	100	0.40

Regulatory Status of Prepsolv™

Terpenes like Prepsolv™ are non-toxic, biodegradable, and contain no reportable components. They are non-chlorinated, and therefore do not affect the Earth's Ozone Layer and are not regulated as a result of the Montreal Protocol. In addition, they are not classified as Hazardous Air Pollutants by the 1990 Clean Air Act Amendments. Furthermore, the U.S. EPA has endorsed terpenes as replacements for ozone-depleting solvents like 1,1,1-trichloroethane and CFC-113.

Water Solubility

As "zero discharge cleaning" becomes a goal, it is necessary to consider routes for release of solvents into the workplace and environment. Just as low vapor pressure restricts air emissions of terpenes, low water solubility can restrict release into water systems. This is not a strong consideration in wipe cleaning, but a consideration for solvent selection in general.

Terpene hydrocarbons are virtually insoluble in water. This is very different from alternatives like glycol ethers and NMP which are readily soluble in water. As water regulations tighten, this will become more and more important, and cleaning agents which can easily be separated from wastewater will become more desirable.

Relative Water Solubility of Terpenes vs. Other Solvents

	APPROX. SOLUBILITY IN WATER (WT % @ 20°C)
Glidsafe® Prepsolv™	0.02
Propylene Glycol Tert Butyl Ether (PTB)	14.5
2-Butoxyethanol (EB)	T
n-Methyl Pyrrolidone (NMP)	T

Material Compatibility

Glidsafe® Prepsolv™, being a blend of terpene hydrocarbons, is a non-polar, pH neutral, non-corrosive solvent. As such, it does not produce corrosion in any metals tested to date.

Metals Compatibility Data per SMI Testing

TEST	SPEC	RESULT
Hydrogen Embrittlement	ASTM F519	Conform (Type 1C)
Sandwich Corrosion	ASTM F1110	Conform
Titanium Stress Test	ASTM F945	Conform (AMS 4911)

Testing by Hercules Aerospace has confirmed that "no signs of corrosion or material degradation were noted in the immersion test" with the metals tested:

- Anodized 6061 Aluminum)
- Aluminum 7075
- Aluminum 6061
- Aluminum 1100
- Cadmium Plated 4140 Steel
- 304 Stainless Steel
- Lead Alloy (FLSC)

Conclusions

A terpene-based wipe cleaning agent is now available called Glidsafe® Prepsolv™ that combines the advantages of high solvency, environmental acceptability, regulatory compliance, low toxicity, with ultra-low non-volatile residue. All these advantages combine to suggest that this innovative material be considered as an alternative cleaning agent for replacing ozone-depleting and toxic solvents in hand-wipe cleaning.

No single solvent is likely to be a universal replacement for 111 and MEK. However, the state-of-the-art in terpene wipe-cleaning agents is advancing to the point that most all of the limitations of early terpene products no longer exist. Certainly, fear of non-volatile residue is no longer a reason to avoid consideration of terpenes for hand-wipe cleaning of aerospace materials.

Prepsolv™ Status Update - July '94

The latest NVR testing by Hercules Aerospace (June '94) documents in their final project report that Prepsolv™ leaves no visible or measurable NVR on evaporation.

Glidsafe® Prepsolv™ is now approved by Boeing per specification BAC 5750 for use in commercial aircraft fabrication and maintenance cleaning, and is preferred by Hercules Aerospace for cleaning during rocket motor fabrication and finishing as indicated below.

The following are excerpts from Hercules final report: "Test Report, 1,1,1 trichloroethane Replacement For Use in Cold Wipe Applications, June 1994".

CONCLUSIONS

The only solvent that produced any signs of corrosive attack on the alloys testes in immersion or galvanic couple testing was WS5B. No signs of corrosion were noted with any of the other candidate solvents. Testing performed for non-metallic surfaces showed that all solvents except DS104 performed equal to TCA. Laboratory input and actual use in operating areas reduced the viability of using IBIB due to its strong odor. Based on the material testing performed in test Series 2 Prepsolv, Iso-butyl Isobutyrate (IBIB), and Oxsol 100 perform as well as TCA on non-metallic surfaces in finishing operations. DS104 is not a top candidate because the tensile testing results showed significantly lower max. Stress values than TCA. In addition, input received from McDonnell Douglas suggest that other candidates would be more favorable due to the moderately strong odor of DS104.

Bonding tests showed that Prepsolv and WS5B were the best performers. RTV premold to aluminum bond compatibility was unfavorable using Prepsolv™, yet the surface preparation results for the same bond were different, but not unfavorable. Oxsol 100 and DS104 were the worst performers for bonding operations.

The overall performance of each of the solvents tested for finishing operations, based on meeting the established criteria, from best to worst are:

1. Prepsolv
2. WS5B
3. IBIB
4. Oxsol 100
5. DS104

RECOMMENDATIONS

Prepsolv should be qualified as the primary solvent for use in finishing operations because it is the best overall performer based on the laboratory testing which correlated very close to TCA. Although WS5B, IBIB, and Oxsol 100 did not perform overall as well as Prepsolv, the data generated should be considered valid in implementing the tested solvents for the appropriate operations in the event Prepsolv is not available in the future or does not remove abnormal soils.

Prepsolv can be handled safely in the finishing area with no additional protection required by the operators.

Case Study - John A. Purvis and Wade W. Moran, Hercules Aerospace Solvent Selection

Solvent Selection At Hercules Aerospace

Hercules Aerospace Corporation's Bacchus plant in Magna, Utah produces solid propellant rocket motors. Methyl chloroform, an ozone depleting compound, is used in a large number of manufacturing operations for these systems, mainly as a "wipe solvent" for cosmetic cleaning and for preparation of surfaces prior to bonding with adhesives or coatings. In this application, the solvent is applied to a clean cloth, which is then wiped on the surfaces to be cleaned. Remaining solvent is allowed to dry prior to bonding the components.

As an active participant in the Chemical Manufacturer's Association *Responsible Care®* program and to comply with legislation, Hercules is actively involved in eliminating ozone-depleting chemicals and minimizing use of hazardous air pollutants. In this effort, Hercules has achieved favorable results in selecting alternate solvents.

Of course, no single solvent identified can be used for all purposes. Rocket motor designs incorporate many different materials (aluminum, steel, graphite composite, elastomers, cork) and a large number of adhesive bonds utilizing a variety of adhesives. In addition, over 60 different "soils" are involved in the processes ranging from fugitive oils and greases and mold releases to epoxies, cyanoacrylates and urethanes in various states of cure. The solvents must remove these soils, but must not damage the substrates, react adversely with materials such as the propellant, nor weaken previously made bonds. One solvent blend developed was found superior to methyl chloroform for solvency power for the many soils but was incompatible with several of the substrates, requiring the identification of compatible, but less versatile solvents. Terpenes were found to be excellent solvents for oils, greases, certain resins, rubbers and tape residue (all major soils) but were reputed to be prone to oxidation and high in non-volatile residue. Hercules pursued the issue with Glidco Organics, a major manufacturer of both citrus and pine terpenes. The problem was eventually resolved by use of a refined citrus terpene and optimization of the antioxidant package. The resultant solvent is stable and has no significant non-volatile residue as measured gravimetrically or by infrared spectroscopy.

Hercules' strategy included thorough research of industry efforts and a careful examination of the process to determine if soils could be isolated, if steps could be re-ordered, or if soils needed to be removed from surfaces. If cleaning was required, mechanical and aqueous cleaning methods were considered. Where organic solvents were considered necessary, most important was the use of firm solvent selection criteria, *solubility parameter* technology and economical laboratory screening tests. Solvents identified for future qualification have been reduced from over 100 to 7 systems. These include parachlorobenzotrifluoride (PCBTF), an ester, a propylene glycol ether, a propylene glycol ether acetate, a lactate, a terpene (d-limonene) and blends of these materials.

Solvent Selection Criteria

Given the enormous number of solvents on the market, a set of firm criteria were developed. The solvent must be effective in removing the various soils. Solvents that have any known ozone-depleting potential, are hazardous air pollutants or are overly toxic were avoided. The inhalation hazard index (IHI) was used for comparison rather that the threshold limit value (TLV). Use of the TLV for comparison is often done but is normally misleading because of vapor pressure differences. The IHI takes into account the TLV and the vapor pressure. The higher the IHI, the more hazardous the material. For example, while d-limonene has a lower TLV than methyl chloroform, its IHI is less because of lower volatility. The IHI = $10^6*(P_v/P)/TLV$ where P_v is the vapor pressure and P the atmospheric pressure.

A flashpoint above 38°C (100°F) is required but volatility is also critical so components can be bonded soon after surface cleaning to prevent surface recontamination and minimize flowtime. Any solvents that contained measurable non-volatile residue with an ambient drying were not considered. Good stability in storage, a tolerable odor and compatibility with contact materials are also important attributes.

Given the costs incurred in qualifying new solvents and the importance of system reliability and consistency, the use of unknown or single-source formulations was avoided - a future formulation change or non-availability could not be tolerated. This criteria required selection of pure materials, which was beneficial in other ways. First, guarantee of supply is virtually assured since materials are typically available from a number of sources. Duplication of testing was also avoided since many proprietary tradename cleaners are similar in formulation. Toxicity information and solubility data are available and cost is less.

Use of Solubility Parameters to Select and Blend Solvents

The solubility parameter system is a practical and quantitative guide for selecting solvent candidates and for estimating the properties of a blended solvent. The system is well documented and accepted throughout the industry. Solubility parameters takes the like-dissolves-like logic by evaluating the mixing compatibility of materials by describing and quantifying the cohesive energy forces holding materials together (cohesive energy density). During dissolution, the intermolecular bonds of materials A and B are broken while new bonds between the different materials are formed. If A-A, B-B, and A-B bonds are similar, little energy is needed to replace the broken A-A and B-B bonds with the A-B bonds. But if the A-A bond is much stronger than the A-B and B-B bonds, breaking the A-A bond will be thermodynamically unfavorable[8] Solubility parameters can determine which situation will be favorable.

The Hildebrand parameter (δ) is the most commonly used and can be estimated for any material easily with a few physical constants. Hansen later modified the parameter to differentiate the contributions of dispersive (London) forces (δ_d), hydrogen bonding (δ_h), and polar forces (δ_p) through a semi-empirical process. These are in effect simultaneously, and can be resolved into a vector which describes the total Hansen solubility parameter, δ_t ($\delta_t^2 = \delta_p^2 + \delta_h^2 + \delta_d^2$). Hoy later modified the Hansen system by incorporating more theoretical considerations and provided the primary system used in our studies. References are readily available that provide detailed descriptions and also values for many solvents and other materials. A graphical representation of Hoy system δ_p vs. δ_h was found to be useful in the Hercules effort and is provided showing the dispersive parameter in parentheses. Note that these Hoy parameters differ in value from the Hansen parameters[9,10]

Hercules uses solubility parameter data in several ways. First, duplication of testing of similar solvents is easily avoided. For instance, NMP and BLO are very similar in all parameters, and therefore need not both be tested. Also, given the solubility parameter of a particular soil, it is easy to determine which solvents would function well. For soils with no solubility parameter data available, laboratory solubility tests can be run with a variety of different but known solvents to characterize the soil. The best solvent for the job can also be identified. Graphical examples of soil "mapping" are provided. To develop a more versatile solvent system, the solubility parameter data are also useful for predicting solvent blend properties that exhibit intermediate solubility parameters which can work for different soil types. The best hydrocarbon soil cleaners all share the attribute of having very low hydrogen bonding, while the solvents best for paints and adhesives tended to be moderate H bond with high polarity. d-Limonene, which was already quite versatile due to its moderate solubility parameter and Hoy polarity, was found to be a very useful base for blends which could also effectively remove the higher parameter soils such as paints, primers and epoxies. The solvent solubility parameter graph illustrates why d-limonene is in a position to form a wide variety of versatile cleaners by blending with various oxygenated solvents to get a parameter specific to one's needs.

Solvent Screening Testing

While solubility parameter technology is a useful system for solvent selection, it should only be used as a guide. Verification in the laboratory for solvency with the identified soils, and compatibility with the expected substrates is essential.

Solubility was tested in one of two methods. In one test, 0.1 gram of the soil was placed in a test tube with 4 ml solvent and agitated at 200 rpm for 5 and 40 seconds with the solubility and residue judged at the end of each interval (similar to ASTM D-3132). The second method consisted of coating a metal plate with the soil which was cured or "staged" for a certain amount of time and then cleaned with a solvent saturated wipe. Effectiveness in either case was judged by the speed in which the soil went into solution or could be visually removed from the plate. The general scoring is similar to the ASTM method with finer resolution provided by adjusting the numbers up or down by 0.3.

Solubility tests were very quick to perform and proved to be very useful in screening out mediocre candidates and helped characterize the soils for further testing.

Solubility Test Results - Relative Performance[11]

	Soil Group					
	E	P	S	U	T	O
1,1,1 TCA	1.8	1.7	2.0	1.4	1.8	2.0
Limonene (Prepsolv™)	0.7	1.4	2.0	0.9	1.8	2.0
PCBTF	1.5	1.6	1.7	1.9	1.7	2.0
Aliphatic/Terpene	NT	NT	1.7	NT	NT	1.7
n-Butyl Butyrate	1.4	1.9	2.0	1.4	1.1	1.7
Methyl Lactate	1.5	0.9	0.0	1.5	0.1	0.5
50/50 BLO/NMP	1.5	1.6	NT	1.7	0.0	NT
60/40 Limonene/NMP	1.8	2.0	1.5	1.9	1.1	1.9
90/10 PNB/PM	1.2	NT	0.9	1.2	NT	1.6

E = Epoxies (9 types) U = Urethanes (2 types) P = Paints/Primers (5 types)
T = Tape Adhesives (7 types) S = Silicones (2 types) O = Oils/Greases (3 composites)

0 = Insoluble with no solution or suspension and a large amount of residue.
1 = Partially soluble with a hazy or cloudy solution and/or varying amounts of residue.
2 = Completely soluble with a fully clear solution with no residue.
NT = Not tested.

Non-volatile residue (NVR) was also a value measured in the laboratory, being of concern for bond surface preparation. A solvent that leaves a low surface energy or low cohesive strength residue has the potential to produce a poor bond. NVR is measured in several ways. One method is ASTM 1353-90, where 100 ml of the solvent is evaporated to dryness on a steam table and then placed in a 205°F oven for a time. This test proved most of the solvents to be very clean. Some, however, had a significant amount of residue at the end of testing which was not expected from results of ambient dry observations. There was concern that the high temperature of the test may oxidize/polymerize some of the solvents, especially those with unsaturated sites, such as the terpenes. An alternate method was developed to help determine if the residue could be attributed to temperature/oxidation effects during testing. Approximately 0.1 g. of the solvents were placed on Germanium ATR crystals and evaporated at 205°F, 105°F, and 105°F in a vacuum. The ATR crystals were then analyzed by infrared spectroscopy, providing a semi-quantitative measurement of the amount of residue.

NON-VOLATILE RESIDUE ANALYSIS RESULTS

	ASTM D1353 WT% NVR	105°F FTIR ABSORBANCE[12]	AMB. FTIR ABSORBANCE	ATR NVR ANALYSIS
1,1,1 TCA	0.0000	0.00	0.00	-
Stoddard 140	0.0095	0.05	-	Hydrocarbon
Aliphatic/Terpene blend	0.0063	0.06	-	Ester
Limonene 145	0.0370	0.06	-	Ester/alc/AO
Limonene 145 w/o anti-ox	0.2354	0.00	0.00	-
Prepsolv™	0.0040[13]	0.00	0.00	-
NMP	0.0240	0.11	-	Ester/alc.
n-Butyl Butyrate	0.0046	0.04	-	Ester

Ambient testing of Glidco Limonene 145 and ATR/FTIR analysis showed that the bulk of the residue was attributable to the test environment, but residual anti-oxidant was present and led to study of a clean anti-oxidant package for bond surface preparation.

The potential for bond degradation from NVR was tested by treating smooth machined aluminum plates with various solvents before epoxy bonding. This configuration was estimated to be more sensitive to contamination than any bondline in our processes. 4-8 RMS milled 6061 plates were cleaned with toluene/ethyl acetate and rinsed with clean acetone and exposed to two treatments of streaming solvent over the plate and forcing off the excess with an inert aerosol dust chaser leaving only a thin film of solvent. The plates were then dried for 1.5 hours at ambient and placed in a desiccator overnight before bonding to grit blasted, stainless steel buttons with 3M EC2216 epoxy. The buttons were then pulled in tensile at 0.2 ipm. No degradation of the bondline was seen with the Glidco Limonene 145, Prepsolv™, or PCBTF compared to the methyl chloroform control.

The most critical bonds in the rocket motor are rubber-to-rubber, rubber-to-steel and rubber-to-composite. Therefore, compatibility of the solvents with the rubber is of great importance. The solvent affinity for the rubber and drying rate was tested simultaneously by exposing the rubber by a 30 second soak (simulating an accidental spill) and by a triple wipe with a solvent soaked cloth. The samples were dried at ambient lab conditions and gravimetrically tested over 5 days. Surprisingly, even methyl chloroform remained in the rubber for over 4 days due to its initial high absorption into the rubber. Apparently, a high evaporation rate is of little help since, once in the rubber, solvent transfer is diffusion limited. Effect on rubber mechanical properties were also measured. While solvents that soaked into the rubber had an immediate affect, in all cases the rubber returned to normal once dry.

Future Efforts

While Hercules' program to select solvents is explained, the criticality of rocket motor missions and designs demands rigorous qualification of any replacement solvent prior to its use in a production environment.

Qualification testing is currently in progress and will, in detail, examine the effect of selected solvents on material properties, corrosive effects, compatibility with bond lines and the effect of the solvents on long term properties of the motor.

Footnotes

[1] *Hansen solubility parameters differ from the Hoy solubility parameters in the Hercules case study.*

[2] *Source: Texaco Solvents Data, 1992 unless otherwise noted.*

[3] *John Van Dyk, Van Dyk Associates.*

[4] *Estimated from homolog data.*

[5] *Data per Purvis and Moran, Hercules Aerospace Case Study.*

[6] *Data for methyl lactate, n-butyl butyrate, n-methyl pyrrolidone, and gamma-butyrolactone not available.*

[7] *TLV/TWA not established for most terpenes. Assume 100, the established TLV for turpentine.*

[8] *Gardon, J.L., "Cohesive Energy Density", Ency. of Polymer Sci. and Tech, Vol. 3.*

[9] *Hansen, C., J. Paint Tech., Feb. 1967.*

[10] *Hoy, K.L., "Tables of Solubility Parameters", (Union Carbide).*

[11] *Shaded values indicate good performance relative to methyl chloroform.*

[12] *Absorbance for functional group of solvent or oxidation product.*

[13] *FTIR analysis showed only a trace of oxidation product. Most of the NVR was labware contamination (silicone). New sample used for ATR tests.*

ENVIRONMENTALLY SAFE FUELS, FIRE SUPPRESSANTS, REFRIGERANTS, AND INSULATIONS