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ENVIRONMENTALLY FRIENDLY THINNERS FOR CHEMICAL AGENT RESISTANT COATINGS

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ABSTRACT

MIL-T-81772 Type I and Type II is a volatile organic hazardous air pollutants (VOHAP) containing, high volatile organic compound (VOC) thinner. It is the only specification for thinning chemical agent resistant coatings (CARC). As CARC evolves to become completely VOHAPs free and contain lower VOC, a VOHAPs-free with low or no VOC must be deployed. A new environmentally friendly solvent blend must be universal and must work in all applications that MIL-T-81772 Type I or Type II would have been used including thinning, flushing, and cleaning. The U.S. Army Research Laboratory in coordination with Sustainable Painting Operations for the Total Army (SPOTA) is evaluating new formulations that are environmentally friendly and that can be used for both solvent-borne polyurethanes and solvent-borne epoxies that are specified by The U.S. Army Research Laboratory and The Naval Air System Command. The ultimate objective of the process is to demonstrate that a VOHAPs-free, low VOC or zero VOC thinner can provide a “drop-in” solution to the environmental issues associated with specified material MIL-T-81772 Type I and Type II currently in use, providing equal or better corrosion and weathering performance, involving no significant changes to procedures currently used in the field.

Key Words: VOHAPS, Volatile Organic Compound, Army, Corrosion

INTRODUCTION

The Army Research Laboratory (ARL), under a Sustainable Painting Operations for the Total Army (SPOTA) program, has conducted a research effort on the development of a hazardous air pollutant (HAP) free and low volatile organic compound (VOC) paint thinner as an alternative to MIL-T-81772. The military specification MIL-T-81772, “Thinner, Aircraft Coating”, has been the standard throughout the industry and government for the thinning of chemical agent resistant coating (CARC) coatings and aircraft primers and topcoats. The paint thinners conforming to this specification are used in the majority of the painting applications at military locations that use polyurethane and epoxy coatings. The use of paint thinners accounts for a significant amount of HAP and VOC emissions from Army surface coating operations. Thinners conforming to MIL-T-81772 contain solvents that have a high percentage of HAPs are 100% VOC. These solvents are not only being used to thin the various military coatings, but are also being used to clean and flush the application equipment, which contributes significantly to the HAP and VOC emissions.

The Army's solvent borne CARC, MIL-DTL-53039 topcoat and MIL-DTL-53022 primer, have been revised to be HAP-free and to significantly lower the applied VOC. Due to this, alternative thinners are required to prevent Army installations from reintroducing HAPs and VOC into the CARC system. The present thinner, MIL-T-81772, is being added to the CARC coatings by as much as 20% by volume to thin these coatings for application. This solvent is also being used as a paint gun cleaner and a hand wipe substrate cleaner. A universal solvent blend will significantly reduce the emitted HAP and VOC in all three operations.

MIL-T-81772 is supplied in three types of paint thinners. For the CARC coatings, only the first two types are used. These are type I, which is polyurethane thinner and contains up to 12% of toluene and 8 % xylene, and type II, which is an epoxy thinner and contains up to 20% methyl isobutyl ketone. All of these solvents are declared HAPs. The type I can be used to thin both the polyurethane and epoxy coatings, while the type II can only be used with the epoxy primers. The goal of this effort is to develop a universal thinner that can be used with both the CARC topcoats and primers. Although this program was established primarily as an Army effort, it was agreed upon with NAVAIR that this solvent blend would also be applicable for use with the Navy aircraft topcoats and primers. The Navy coatings to be evaluated for thinning and cleaning with this alternative thinner are MIL-PRF-85285 topcoats; which include types I, II and IV; and MIL-PRF-23377 primers, classes C and N.

ARL will work to develop, demonstrate and qualify a HAP-free and low VOC solvent blend that is proven to be compatible with all products qualified under its coating specifications regardless of the coating manufacturer. Besides the ability to thin, clean and flush, ARL will evaluate the affect of these thinners on storage stability, spectral and specular reflectance, adhesion and weathering of the referenced topcoats and primers. ARL will work with the affected stakeholders to choose the most efficient option for implementing and maintaining the composition requirements for the universal solvent blend, either in an existing specification or the development of a new one. The ultimate goal is to coordinate with the General Services Administration (GSA) to establish new National Stock Numbers (NSN) for procurement.

APPROACH

It is of the upmost importance that a HAPs-free thinner blend has no adverse effects on the coating prior to application and the finished coating. It is also important that a HAPs-free thinner blend is able to perform the entire set of tasks that is currently asked of the MIL-T-81772[1] thinner. Not only will the new blend be used to thin CARC materials, it will also be used to flush and clean spray guns in the field. It is important to validate all of these aspects in the lab work.

The first set of testing included viscosity, spraying properties, cleaning properties, and pot life. Because the spraying properties and cleaning properties of a material tend to be very subjective, three technicians worked on these tasks. Also, results for spraying properties and cleaning properties were listed as a comparison to the current specified material, MIL-T-81772. Viscosity was taken at intervals of 2 hours during a 6 hour period using a Brookfield model KU-2 viscometer. All of the readings were taken in Krebs units (KU).

The second set of testing included dry time, adhesion, and flexibility of the coating on a substrate. Dry-to-touch was determined using a mechanical recorder as detailed in ASTM D5895[2]. Adhesion was tested in accordance with ASTM D3359, method B[3] and verification requirements detailed in MIL-DTL-53072[4] listed in paragraph 4.2.3.6.1. Flexibility was tested in accordance with ASTM D522[5] using a 1/4" mandrel.

Finally, performance was tested for the thinned coatings. For primer samples, ASTM B117[6] salt fog exposure and GMW 14872[7] cyclic corrosion testing was completed. For the topcoat samples, ASTM G154[8] UV light apparatus exposure using criteria outlined in MIL-DTL-53039D[9].

PRODUCTS

Three blends are being tested as possible replacements for the current specified thinner. Blend A contains t-butyl acetate, methyl acetate, and parachlorobenzotrifluoride. Blend B contains t-butyl acetate, and methyl-n-amyl ketone. Blend C consists of t-butyl acetate, and methyl acetate. All three of the blends are HAPs-free. Blends A and C contain only content VOC exempt solvents. The methyl-n-amyl ketone in Blend B is not a VOC exempt solvent. Table 1 denotes the exact formulation for each blend.

TABLE 1
CONTENTS OF BLENDS A, B, AND C

Solvent	Percent of Formulation		
	Blend A	Blend B	Blend C
t-Butyl Acetate*	70%	75%	75%
Methyl Acetate*	20%		25%
Parachlorobenzotrifluoride*	10%		
Methyl-n-Amyl Ketone		25%	

(* denotes VOC exempt solvent)

MIL-T-81772 type I material was used as the control for polyurethane topcoat testing and MIL-T-81772 type II material was used as the control for epoxy primer testing. Table 2 shows the formulation for MIL-T-81772 type I and type II. MIL-DTL-53039 type III and type IX CARC polyurethane topcoats were used. MIL-DTL-53039 type III contains a maximum of 1.5 lb/gal of VOC and is flattened with polymeric agents. MIL-DTL-53039 type IX contains a maximum of 3.5 lb/gal of VOC and is flattened with polymeric agents. The color Green 383, 34094 was selected for each of these products. MIL-DTL-53022 Type II was used as the CARC epoxy primer. MIL-DTL-53022 is a high solids, lead and chromate-free formulation with a maximum VOC of 3.5 lb/gal.

TABLE 2
CONTENTS OF MIL-T-81772 MATERIAL

Solvent	Percent of Formulation	
	MIL-T-81772 type I	MIL-T-81772 type II
Methyl ethyl ketone	30%	50%
Methyl isobutyl ketone	-	20%
Butyl acetate	10%	-
Propylene glycol methyl ether acetate	40%	-
Propylene glycol methyl ether	-	30%
Toluene	12%	-
Xylene	8%	-

Cold rolled steel panels pretreated with zinc phosphate coating B-952 with P60 chrome rinse, 0.032 inches (0.8128 mm) thick, were used for all testing except for flexibility. Flexibility was completed on tinplated steel, 0.010 inches (0.254 mm) thick. These panels are consistent with test panel requirements in specifications MIL-DTL-53039 and MIL-DTL-53022.

RESULTS

The viscosity of the topcoats and primer were tested with 10% thinner by volume. Results for the primer can be seen in Table 3 and the topcoats can be seen in Tables 4 and 5. The control sample in this test was a sample that contained no thinner. Results show that all of the thinners reduce the viscosity of the primer and topcoats.

These samples were aged to determine pot life with the thinner. All of the thinners kept the viscosity below the viscosity of the controls. Also, there were no signs of skinning or curing in the container. The material was in a condition that it could be properly sprayed after 8 hours.

TABLE 3
MIL-DTL-53022 WITH 10% THINNER

Products	0 hour	2 hours	4 hours	6 hours
81772 T II	53.4 KU	53.6 KU	53.3 KU	57.8 KU
A	56.3 KU	60.4 KU	63.1 KU	69.2 KU
B	55.9 KU	58.9 KU	60.4 KU	64.0 KU
C	55.3 KU	60.4 KU	64.7 KU	68.4 KU
Control	57.0 KU	65.6 KU	67.7 KU	77.8 KU

TABLE 4
MIL-DTL-53039 TYPE III WITH 10% THINNER

Products	0 hour	2 hours	4 hours	6 hours
81772 T I	47.2 KU	47.6 KU	47.8 KU	47.9 KU
A	48.1 KU	48.5 KU	50.1 KU	50.3 KU
B	49.1 KU	49.1 KU	49.1 KU	48.8 KU
C	46.8 KU	47.5 KU	47.5 KU	47.5 KU
Control	52.3 KU	52.7 KU	52.7 KU	54.2 KU

TABLE 5
MIL-DTL-53039 TYPE IX WITH 10% THINNER

Products	0 hour	2 hours	4 hours	6 hours
81772	49.4 KU	50.0 KU	50.0 KU	51.8 KU
A	49.0 KU	49.1 KU	49.3 KU	53.3 KU
B	50.0 KU	50.3 KU	50.0 KU	52.1 KU
C	49.4 KU	49.4 KU	50.8 KU	52.1 KU
Control	59.9 KU	61.4 KU	61.6 KU	64.7 KU

Spraying properties were tested next. The three experimental thinners and the MIL-T-81772 Type I and Type II were mixed with the primer MIL-DTL-53022 and topcoats MIL-DTL-53039 Type III and Type IX. Because spraying properties can be very subjective, three technicians were asked to spray all of the materials. Comparisons were all based on the sprayability of the primer and topcoats that were thinned with MIL-T-81772 material. All three technicians commented that the primer thinned with the experimental thinners performed at the same level as the material thinned with MIL-T-81772. Comments were made with experimental thinner C with both topcoats. The topcoats thinned with C sprayed thick and did not provide the same wet edge that the other thinners did. Experimental thinners A and B behaved like the MIL-T-81772 type I material.

The thinners were then used to flush and clean the spray guns. Clean comparisons were performed by all three technicians. The experimental thinners were compared to the MIL-T-81772 material. For the epoxy primer, experimental thinners A and B performed better than MIL-T-81772 Type II material. There was less effort to get the gun clean with these two thinners and less thinner was used. Experimental thinners A and B performed as well as MIL-T-81772 Type I with the topcoats. Experimental thinner C did not clean the gun. The thinner seemed to aide in curing the moisture cure topcoat in the gun very rapidly. More aggressive techniques had to be used to clean the gun after thinner C was used.

Dry times for the thinned coatings were tested. The primer samples dried very evenly with all of the thinners. The samples were all dry-to-touch in about the same time. For the topcoats, experimental thinners A and C caused the samples to be dry-to-touch quicker than the standard MIL-T-81772 Type I. the samples were dry to touch approximately 8 minutes quicker. Thinner C was dry-to-touch in the same time as MIL- T-81772 Type I.

The dried samples were then tested for flexibility and adhesion. With both the primer and the topcoats, there were no changes in these physical properties. All of the samples thinned with the experimental thinners performed at the same level as the standard MIL-T-81772.

For the primer samples, corrosion resistance was tested. In B-117 salt fog testing, the samples were tested for 1008 hours and in GMW 14872 cyclic corrosion testing the samples were tested for 40 cycles. Table 6 shows the results for the B-117 testing. The samples with the experimental thinners performed on par with the samples with MIL-T-81172 Type II. The exact same thing can be said for the results of the GMW 14872 testing shown in Table 7. The experimental thinners had no significant effect on the performance of the primer in these tests.

TABLE 6
AVERAGE SCRIBE CREEP, PRIMER SAMPLES B-117

Products	ASTM D 1654 Ratings		
	336 Hour	672 Hour	1008 Hour
81772	7	7	6.33
A	7	6.67	6.33
B	7	7	6
C	6.67	6.33	6

TABLE 7
AVERAGE SCRIBE CREEP, PRIMER SAMPLES GMW 14872

Products	ASTM D 1654 Ratings	
	20 Cycle	40 Cycle
81772 Type II	6.67	5.67
A	6.33	5.67
B	7	6
C	6.67	5.67

For the topcoats, accelerated weathering was completed. The samples were exposed in the same fashion as expressed in MIL-DTL-53039D paragraph 4.6.25[9]. Thinner B performed on par with MIL-T-81772 Type I. Thinners A and C did not perform as well as MIL-T-81772 Type I. While the results would still pass according to MIL-DTL-53039D, there was a performance loss due to the use of thinners A and C.

TABLE 8
AVERAGE DELTA E, ACCELERATED WEATHERING

Products	Delta E
81772 Type I	0.895
A	1.330
B	0.905
C	1.437

DISCUSSION/PATH FORWARD

Experimental thinner B performed as well as the current MIL-T-81772 thinner in all of the testing. Experimental thinners A and C both performed below par with accelerated weathering. Also, experimental thinner C was not able to effectively clean the topcoat for the gun. For these reasons, Thinner B was selected to move forward.

The failures of thinners A and C have not yet been fully determined. The common link between the two samples is the use of methyl acetate. Methyl acetate commonly has a water content that can cause issues with moisture cure polyurethanes. Because of the accelerated dry times with these thinners in the topcoats, the samples did not cure in the way that they should have.

Another concern with experimental thinner A is the use of parachlorobenzotrifluoride. There are facilities that would not be able to use a thinner containing this solvent. Facilities with certain air treatment systems will not be able to use this due to the damage the byproducts of parachlorobenzotrifluoride will cause to the treatment system.

Moving forward, experimental thinner B is being tested with MIL-PRF-23377, “Primer Coatings: Epoxy, High-Solids and Coating”, and MIL-PRF-85285, “Polyurethane, Aircraft and Support Equipment”. If testing produces favorable results, a specification will be produced offering a HAPs free thinner for Army use.

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