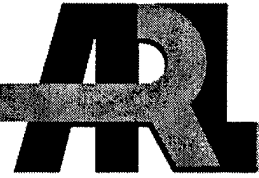


ARMY RESEARCH LABORATORY



# Formulating Multifunctional Protective Ammunition Coatings

by Kestutis G. Chesonis and Pauline M. Smith

ARL-TR-2795

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# **Army Research Laboratory**

Aberdeen Proving Ground, MD 21005-5069

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**ARL-TR-2795**

**August 2002**

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## **Formulating Multifunctional Protective Ammunition Coatings**

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## **Abstract**

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The U.S. Army Research Laboratory (ARL) Coatings Team and the U.S. Army Armament Research, Development, and Engineering Center (ARDEC) Munitions Metal Parts Team have established a major collaborative effort to eliminate various obsolescent coatings and consolidate them into a universal coating system. The exterior ammunition coatings provide ready identification and corrosion protection for long-term storage stability. The fast-drying exterior coatings used on large-caliber projectiles are susceptible to contamination and staining by explosives. Staining of the topcoat can occur during the loading process when explosives are poured into the steel projectiles after fabrication and painting.

The ARL Coatings Team, in conjunction with ARDEC, has developed a modification to the ammunition coating specifications by combining the properties of the primer and topcoat into one coating. The new coating is ammunition-explosive compatible, highly resistant to corrosion, fast drying, low in cost, and can be used as a single coat for the medium- and large-caliber ammunition systems. A research and development effort is ongoing to substantially increase the chemical resistance of the coating. These coatings will comply with environmental regulations including The National Emissions Standard for Hazardous Air Pollutants, which eliminates the use of hazardous air pollutant solvents.

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## 1. Background

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The traditional protective coatings for mortar and artillery projectiles are based on quick drying enamels. The main requirements are thin, fast drying, corrosion-resistant, durability, ease of application and low cost. The coatings that have been used for ammunition were developed over time from diverse origins, both from military and federal specifications.

Coatings on these various ammunition components typically contained substances that were either toxic or hazardous, with high levels of volatile organic compounds (VOCs), hazardous air pollutant (HAP) solvents, hexavalent chromium, and other heavy metals. The need to reduce or eliminate these hazardous substances is dictated by environmental regulations and changes in the coating process, federal and state regulations mandating lower levels which control the types of solvents and methods for disposing of these organic coatings. This regulatory and performance-driven process led to a major consolidation effort by the U.S. Army Research Laboratory (ARL) and the U.S. Army Armament Research, Development, and Engineering Center (ARDEC) to eliminate coatings with hazardous materials and high levels of polluting solvents.

In 1972, the military specification MIL-L-11195D [1] was issued for use as a nitrocellulose (NC) lacquer topcoat in many colors for automotive and ammunition use. It had very good adhesion to bare metal due to the mandated use of semi-oxidizing castor oil with NC. This specification also mandated and permitted the use of lead chromate in various colors. For improved corrosion resistance, MIL-L-11195D is used with an analogous red oxide primer, MIL-P-11414D [2], formulated with zinc chromate.

In 1993, the primer and topcoat were completely revised from NC to oil-based, oxidizing alkyd as military specifications MIL-E-11195E [1] and MIL-P-11414E [3]. These specifications had no lead or chromate and met federal regulation limits of 420 g/L of VOC. Since then, these fast-drying enamels are being used on containerized mortars. MIL-E-11195 has a few limitations and cannot be used by itself on some projectiles because of inadequate corrosion resistance. Some coatings require both a topcoat and a primer while certain systems require only a topcoat because of close dimensional tolerances.

ARL, in conjunction with ARDEC, has recently qualified and implemented HAPs-free, VOC-compliant, fast-dry MIL-P-11414E and MIL-E-11195E into large-caliber ammunition production.

In order to address the aforementioned coatings issues, this effort has been executed to improve and modify these ammunition specifications by combining the properties of the primer and topcoat into one coating. Some projectiles require single-coat systems to combine functions of primer and topcoat and yet remain fully functional. Generally, single coats are used on products that need only basic corrosion protection. In all cases, this fast-drying coating should meet all the current specification requirements but with enhanced durability and performance. Additionally, this coating should provide protection and less susceptibility to explosive staining and contamination. The use of environmentally friendly corrosion-inhibiting pigments in the topcoat specification was evaluated in addition to the resistance properties to solvents and propellants.

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## **2. General Characteristics**

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The ammunition coating system is in one word “multifunctional,” with a multitude of requirements to fulfill. The coating system must be durable for long-term storage stability and corrosion resistance. The laboratory criterion for corrosion resistance is a minimum of 120 hr in a salt spray environment [4] on 0.8 to 1.2 mils thickness of paint. Another crucial requirement is fast dry at ambient temperatures and specifically “dry hard” in 12 min after application.

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## **3. Experimental Challenge**

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The topcoat is occasionally stained when it comes in contact with explosives during the explosive-loading process into the steel projectiles after fabrication and painting. Trinitrotoluene (TNT), symmetrical 2,4,6-TNT, and Composition B are the explosives most generally employed in loading mortars and projectiles. Composition B is a mixture of 60% TNT and 40% wax. TNT is a pale yellow crystal of specific gravity 1.6 with a melting point of 82 °C or 180 °F. This low melting point allows it to be melted and poured into artillery shells and other explosive devices. In the absence of a detonator, it is a stable material and does not attack metals nor does it absorb moisture. It dissolves in benzene and acetone but is practically insoluble in water.

A driving force of this formulation is the development of a stain-resistant coating to TNT and to Composition B. During experimentation, the most effective solvent for explosive residual stain removal was acetone, or a mixture of acetone diluted with a weaker solvent. Any reformulated topcoat should have moderate resistance to limited application of acetone to the film and also to explosive staining.

Environmental regulations require the VOC to be less than 3.5 lb/gal (3.3 lb/gal for Scranton Army Ammunition Plant T) and the total HAPs less than 1% of the formulation. Some ammunition items require that the coating has to be chemical agent decontaminable. After neutralizing chemical agents and removal of the paint with the decontamination solution, the ammunition should pass the chemical agent resistance testing.

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## **4. Laboratory Formulations**

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The basic composition of the formulation is listed as found in Figure 1:

		CHEMICAL COMPOSITION			
<b>PIGMENT</b>		%	8.73	YELLOW OXIDE	
		%	2.03	TITANIUM DIOXIDE	
		%	61.96	SILICA ILL MINERALS IMSIL A15	
		%	11.61	SAPP anti-corrosive	
		%	1.01	LAMPBLACK acidic	
		%	4.31	DIATAMACEOUS CELITE 499	
		%	0.35	R-9998 PFIZER RED OXIDE	
<b>VEHICLE COMPONENTS</b>		%	65.34	McWHORTER HS CHAIN STOP TOFA ALKYD	
		%	23.97	UREA-FORMALDEHYDE RESIN	
<b>ADDITIVES</b>		%	3.73	IRGACOR 153 (anti-corrosive agent)	
		%	0.93	ZIRCONIUM 24%	
		%	1.54	DISPERBYK 163 (Dispersing agent)	
		%	0.93	DOW CORNING 11 (anti-mar agent)	
		%	0.21	10% CALCIUM	
		%	0.10	12% COBALT	
		%	3.28	PARA TOLUENE SULFONIC ACID	
<b>SOLVENT BREAKDOWN</b> VOC-#/GAL= 3.08 VOC-GM/L= 369.7 SOLVENT CPS = 1.055					
			<b>WEIGHT</b>	<b>WT %</b>	<b>VOL %</b>
32-708	BUTYLAC		101.14	28.64	28.90
32-305	N-BUTANOL		102.08	28.91	31.86
S-1004	PM-ACETATE		65.53	18.56	17.12
S-ETOH	ETHANOL		71.40	20.22	17.96
32-324	ISOPROPANOL		12.96	3.67	4.16
<b>TOTAL SOLVENT WT. =</b>			<b>353.11</b>		

Figure 1. Basic composition of formulation.

## 5. Resin Modifications

The properties of particular topcoats are controlled by the resins used as the principal binder. Various blends of alkyd and amino resin were evaluated for dry time and stain resistance. Alkyd resins comprise a group of synthetic polymeric materials generally defined as reaction products of polyols, polybasic acids, or anhydrides. Alkyds tend to be lower in cost than other polymers and offer easy and foolproof applications. The systems are generally economical and provide moderate performance and chemical resistance.

Amino resins are the main cross-linking agents for coatings. The amino resins of greatest commercial importance are the condensation polymers formed by the reaction of urea or melamine with formaldehyde.

Melamine-formaldehyde types are dominant for thermosetting coatings and have gained popularity because of their ability to improve properties of baked alkyd coatings. In general, the urea-formaldehyde (UF) resins are more economical and the most reactive. With a sufficient acid catalyst, coatings formulated with UF can cure at ambient or slightly elevated temperatures. Some of their properties include excellent durability, hardness, flexibility, and alkali resistance. The chemistry of amino resins is complex because of the large number of variables and the fact that amino compounds are known to exist in tautomeric forms. Amino resins are almost never used by themselves in coatings; they are used to cross-link resins having hydroxyl, carboxylic acid, and/or amide groups. For ambient cure, they demand the use of a strong, ionizing acid such as sulfonic acids.

Various polymeric resin modifications for chemical resistance were evaluated with different polymer systems along with various manufacturers and technologies including acrylic resins, styrene modified acrylics, hydrocarbon resins, high solids acrylic copolymer alkyds, and some styrene modified alkyd copolymers. The system that provided the best results was the high solids chain-stopped tall oil fatty acid (TOFA) alkyd, exhibiting acceptable dry times, gloss, and hardness. Formaldehyde amino resin was used to enhance cross-linking density and chemical resistance. Room temperature curing was achieved by using para-toluene sulfonic acid (pTSA) at various levels.

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## **6. Pigmentation**

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Pigments are the finely divided insoluble solids that are dispersed in the vehicle and remain suspended in the binder during film formation. They are used in the coatings industry for several reasons, including color, hiding, application, and economics. Specific functional pigments are used to control gloss and surface roughness. Inert inorganics are used for prime pigments, and siliceous extenders are the primary flattening agents.

For improved corrosion resistance, numerous anticorrosive pigments were evaluated including some basic and neutral pH anticorrosive pigments. Some showed reactivity with the sulfonic acid, adversely affected the drying properties, and therefore were eliminated.

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## **7. Additives**

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Additives are materials that are included in small quantities to modify some property of the coating. By nature, drying oils are slow drying and need metal salt driers to catalyze the drying rate. The most widely used catalysts are a combination of oil insoluble metal salts. The amounts used are system specific and are kept to a minimum. The type of fatty acid, drying oils, and oil length all govern the rate of cure. These alkyd coatings can be made more resistant to impacts by incorporating a few percent of slip agents, usually very small particle polyolefins.

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## **8. Solvent Modification**

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Coatings contain volatile materials that evaporate during application and film formation. The selection of these volatile components is very critical and has effects on solubility, viscosity, toxicity, air pollution, film properties, corrosion, and durability. Our major objective is to reduce the amounts of solvents used and to specify compliant types, thus eliminating VOCs and HAPs.

## 9. Experimental

### 9.1 Stain Removal

Besides meeting HAPs regulations, another thrust of the formulation is the development of a stain-resistant coating to TNT and Composition B. During experimentation, the most effective solvent for explosive residual stain removal was acetone, or a mixture of acetone diluted with a weaker solvent. However, a side effect of using acetone for stain removal was coating removal of the standard alkyd enamel system. Diluting the acetone with isopropyl alcohol (IPA) or hexane to lower acetone concentrations resulted in a reduction of coating removal, but sacrificed the ability of the solvent to remove the stain.

Primarily, the aim in modification of these specifications is to give them stain resistance to TNT and Composition B, as well as to acetone. The improvement to acetone resistance will reduce the coating removal when wiped with the solvent.

Table 1 summarizes the results of the stain removal experiment and the development of proper solvent proportions for stain removal without damaging the coating.

Table 1. Stain removal experiment.

Removal Test No.	Panel Etching No. Paint	Solvent	Result
1	#15/MIL-E-11195E (Brown stain migrated to film.)	H <sub>2</sub> O	No effect.
	#15/MIL-E-11195E	Ethanol	No effect.
	#15/MIL-E-11195E	Hexane	No effect.
	#15/MIL-E-11195E	NMP	Dissolved Composition B but discolored the coating to a grayish purple color.
	#15/MIL-E-11195E	Toluene	Removed stain, no color change of coating.
	#15/MIL-E-11195E	Acetone	Dissolved Composition B, no color change, removed stain.
	#15/MIL-E-11195E	MIBK	Dissolved Composition B.
2	#18/MIL-P-53022B <sup>a</sup> Material stained (migrated into coating)	Acetone	No effect.
	#18/MIL-P-53022B	NMP	No effect (slight lightening).
	#18/MIL-P-53022B	Toluene	No effect.
	#18/MIL-P-53022B	H <sub>2</sub> O	No effect.
3	#2/MIL-E-11195E	N/A	Weakly removed stain and coating.
	#2/MIL-E-11195E	N/A	N/A
	#2/MIL-E-11195E	Acetone (100%)	Effectively removed stain, but also removed coating.
4	#8/MIL-E-52798 <sup>b</sup>	Acetone (100%)	Removed stain and some coating.
	#8/MIL-E-52798	Acetone/H <sub>2</sub> O (1:1)	No effect.
	#8/MIL-E-52798	IPA	Whitens area.

Table 1. Stain removal experiment (continued).

Removal Test No.	Panel Etching No. Paint	Solvent	Result
5	#20/MIL-E-52891B <sup>c</sup>	Acetone/IPA (1:1)	Weakly removed the stain and some coating.
	#20/MIL-E-52891B	Acetone (100%)	Removed the stain and some coating.
6	#13/"Ammo CARC"	Acetone (100%)	Moderately removed surface stain.
	#13/"Ammo CARC"	NMP	No effect.
7	#19/MIL-C-46168 <sup>d</sup>	Acetone (100%)	Removed the stain, but left a glossy area/highlights.
8	#12/MIL-C-53039A	Acetone (100%)	Removed the stain, but left a glossy area/highlights.
9	#1/TT-E-516 <sup>e</sup>	Acetone (100%)	Removed the stain and coating.
	#1/TT-E-516	MIBK	Removed the stain and some coating.
10	#5/Satin Black	Acetone (100%)	Removed the stain, no coating removed, coating only slightly discolored.
11	#12/MIL-C-53039A	Acetone/IPA (3:1)	Removed the stain, but left a glossy area/highlights.
12	#13/"Ammo CARC"	Acetone/IPA (3:1)	Did not remove the stain.
13	#20/MIL-E-52891B	Acetone/IPA (3:1)	Removed the stain and a little bit of coating.
	#20/MIL-E-52891B	Acetone/IPA (2:1)	More dilute acetone removed less coating.
14	#17/MIL-P-22332B <sup>f</sup>	Acetone/IPA (1:1)	No effect.
	#17/MIL-P-22332B	Acetone/IPA (2:1)	Removed some of the stain and coating.
	#17/MIL-P-22332B	Acetone (100%)	Removed the stain and coating.
15	#6/MIL-P-11414	Hexane/acetone (1:1)	Removed the stain and coating.
16	#7/MIL-P-11414E	Hexane	Removed very little of the stain.
	#7/MIL-P-11414E	Hexane/acetone (1:1)	Removed coating.
17	#4/MIL-E-11195	Hexane/acetone (2:1)	Removed coating.
18	#10/TT-P-1757A	Acetone (100%)	Removed coating down to the panel with very little effort.
19	#11/120 mm Topcoat (Crystalline stain below the surface.)	Acetone (100%)	No effect.

<sup>a</sup> U.S. Department of Defense. "Primer, Epoxy Coating, Corrosion Inhibiting, Lead and Chromate Free." MIL-P-53022B, Washington, DC.

<sup>b</sup> U.S. Department of Defense. "Enamel, Alkyd, Camouflage (Future Procurement MIL-C-46168)." MIL-E-52798, Washington, DC.

<sup>c</sup> U.S. Department of Defense. "Enamel, Lusterless, Zinc Phosphate, Styrenated Alkyd Type." MIL-E-52891B, Washington, DC.

<sup>d</sup> U.S. Department of Defense. "Coating, Aliphatic Polyurethane, Chemical Agent Resistant." MIL-C-46168, Washington, DC.

<sup>e</sup> U.S. Department of Defense. "Enamel, Lusterless, Quick-Drying Styrenated Alkyd Type (No S/S Document)." TT-E-516, Washington, DC.

<sup>f</sup> U.S. Department of Defense. "Paint, Priming, Exterior and Interior (For Ammunition)." MIL-P-22332B, Washington, DC.

Notes: CARC = chemical agent resistant coating.

IPA = isopropyl alcohol.

The following illustrations and tables summarize the results for the panels stained with TNT after melt pour, explosive removal, and steam cleaning.

The amount of staining and blooming was measured on a scale of 1–4, with 1 being the best result (i.e., least staining and/or blooming) and 4 being the worst. In evaluating each panel, comments were made to better assess the results of the experiment. Table 1 summarizes the results and evaluation of the vendor panels after solvent cleaning.

## 9.2 TNT Cleaning

Figure 2 is an illustration of the panels before staining with explosives. The panels were masked with aluminum foil and duct tape to keep one half of the coated panel clean from explosive staining.

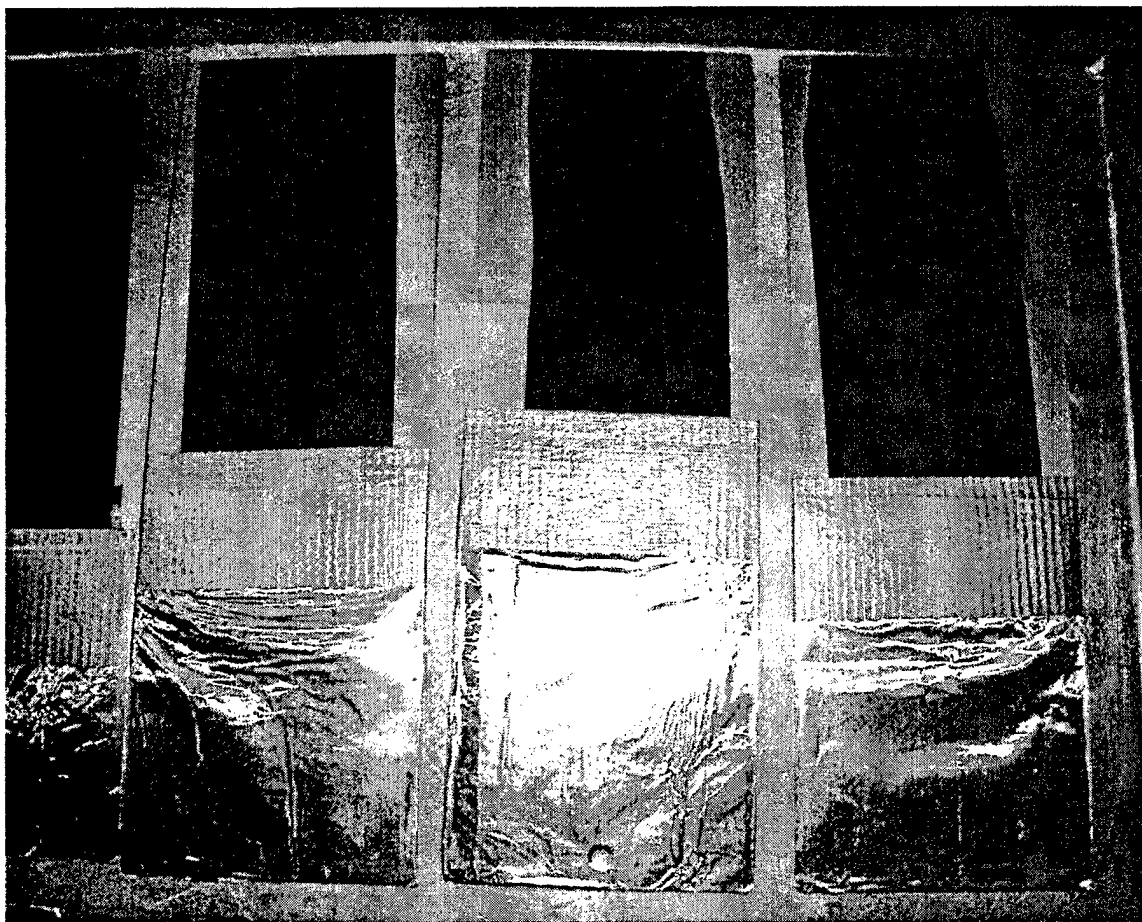


Figure 2. Masked panels before staining.

Figure 3 illustrates a panel after the explosive was melted, poured, and kept in an oven for the required time. All of the panels stained with TNT were placed in an oven at 220 °F for 4 1/2 hr. Afterwards, the residual TNT was scraped off the panels, and the panels were steam cleaned.

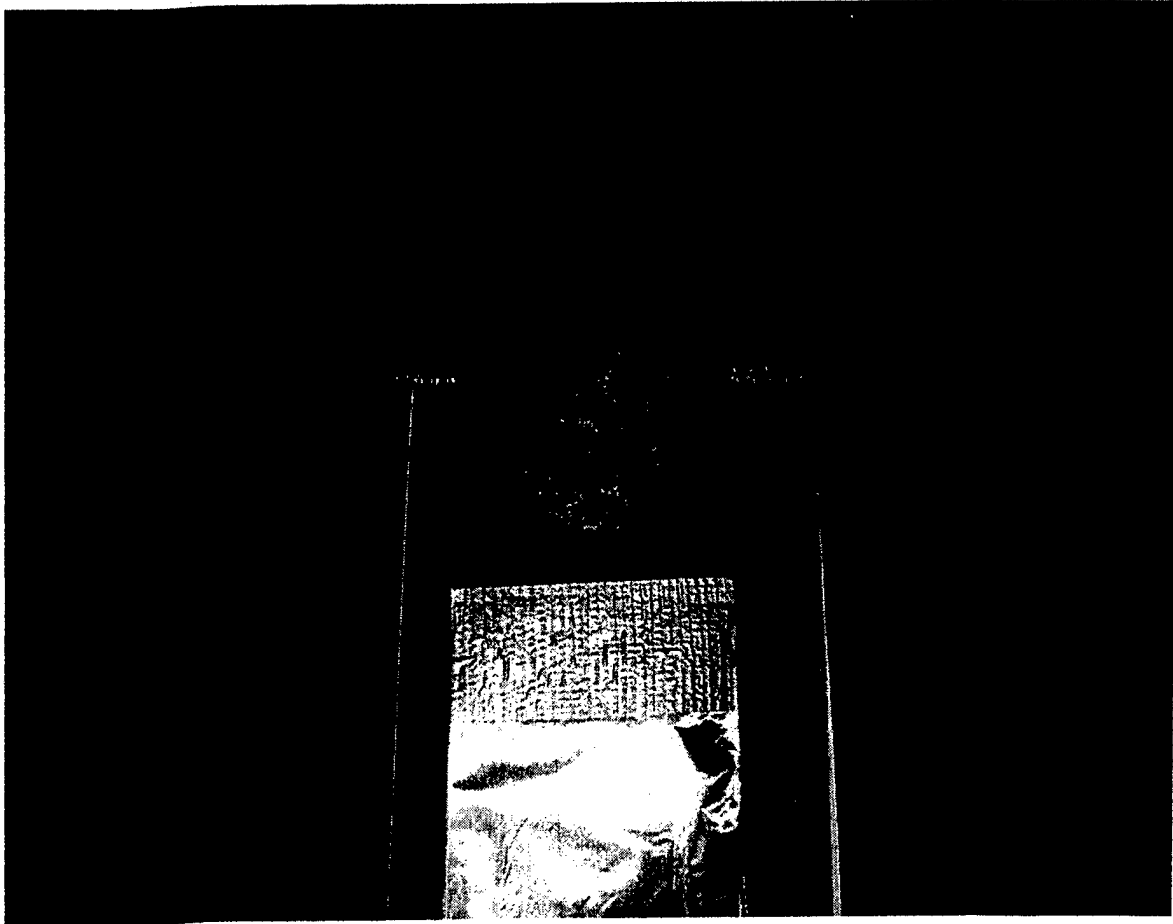


Figure 3. Masked panel during exposure to TNT.

The following tables summarize the results for the panels stained with TNT after melt pour, explosive removal, and steam cleaning. The amount of staining and blooming was measured on a scale of 1-4, with 1 being the best result (i.e., least staining and/or blooming) and 4 being the worst. In evaluating each panel, comments were made to better assess the results of the experiment. Table 2 summarizes the results and evaluation of panels after steam cleaning.

Table 2. Vendor sample results for TNT staining.

Panel	Ranking	Comments
1	3	Stain
4	3	Stain and blooming
6	3	Stain and blooming
9	3	Stain
12	2 1/2	Stain
14	2	Minor stain and minor blooming
16	4	Severe stain
19	4	Severe stain
22	3	Stain
26-a	2 1/2	Stain
27	2	Minor stain and minor blooming
28	2	Minor stain and minor blooming

ARL prepared the panels and the results show that PS 41-1, PS 43-1, and PS 44-1 were the panels that performed the best. Two panels from each group were stained and steam cleaned in concurrence with the batch of panels from the vendor sample. Table 3 summarizes the results and evaluation of the ARL panels after steam cleaning.

Table 3. ARL panel results for TNT staining.

Panel	Ranking	Comments
99E12a	3	Wrinkled paint
99E12b	3	Wrinkled paint
52891a	2 1/2	Stain/minor blooming
52891b	2 1/2	Stain/minor blooming
PS 39-1a	3	Stain/minor blooming/some wrinkling
PS 39-1b	3	Stain/minor blooming/some wrinkling
PS 39-2a	2 1/2	Minor wrinkling/stain
PS 39-2b	2 1/2	Minor wrinkling/stain
PS 39-3a	2 1/2	Stain/more blooming than others
PS 39-3b	2 1/2	Stain/more blooming than others
PS 40-1a	3	Stain/some blooming
PS 40-1b	3	Stain/some blooming
PS 41-1a	1	No blooming/no stain
PS 41-1b	2	No stain
PS 42-1a	3	Stain/blooming/wrinkling
PS 42-1b	3	Stain/blooming/wrinkling
PS 43-1a	2 1/2	Stain/blooming
PS 43-1b	2 1/2	Stain/blooming
PS 44-1a	2	Stain/minor blooming
PS 44-1b	2	Stain/minor blooming

Figure 4 illustrates the difference between two panels after TNT staining and before steam cleaning. The panel on the right (PS 41-1a) showed no evidence of TNT staining, while the panel on the left (PS 42-1b) had staining and residual TNT adhering to the surface.

The panels that showed the best performance were the panels prepared with PS 41-1, PS 43-1, and PS 44-1. The best performer from that group was PS 41-1, which had the best resistance to TNT and the least blooming.

### 9.3 Composition B Cleaning

The panels stained with Composition B were placed in an oven at 220 °F for 10 min. The oven was then turned off, and the panels were kept in the oven and cooled for an additional 90 min. Afterward, the panels were cleaned of any residual Composition B and selected panels were cleaned with acetone.

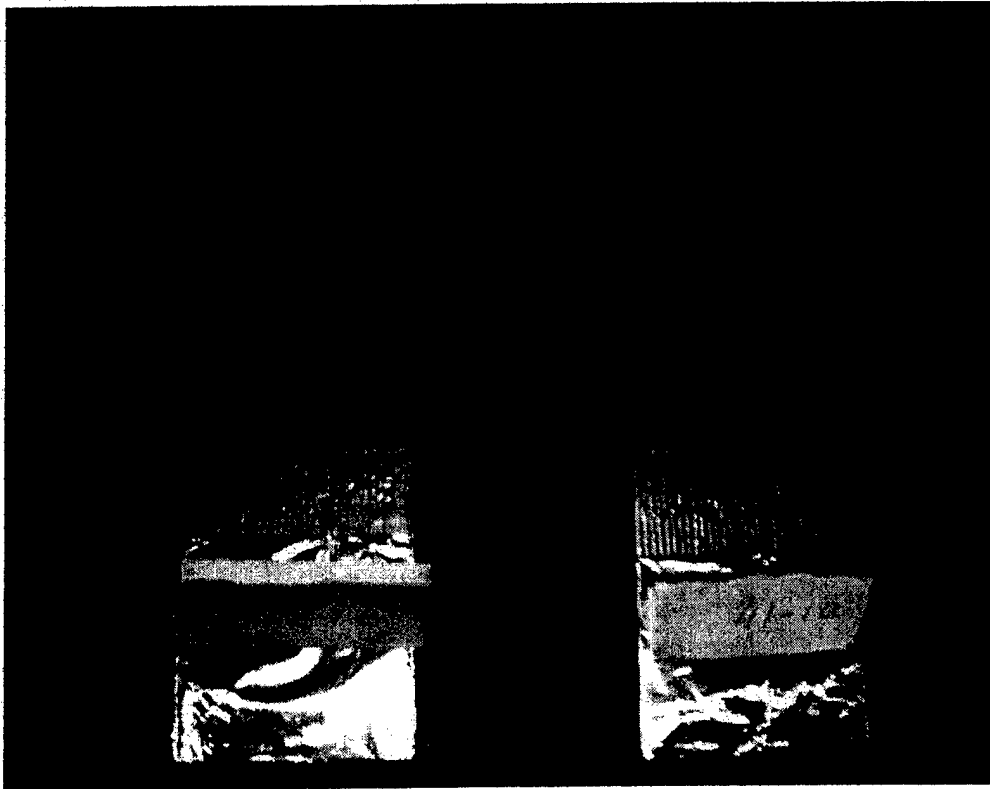


Figure 4. Performance comparison of two ARL panels.

The following tables summarize the results for the panels stained with Composition B after melt pour and explosive removal before acetone cleaning. Two panels from each group prepared by ARL were stained, and one panel from each group prepared by Vendor sample was stained. The amount of staining was measured on a scale of 1–5, with 5 being the best result (i.e., least staining) and 1 being the worst. The vendor sample results are summarized in Table 4, and the ARL results are summarized in Table 5.

Table 4. Vendor results for Composition B.

Panels	Ranking
2	2
5	3
7	2 1/2
10	2 1/2
13	2
15	2 1/2
17	2
20	1
23	1
25	2
30	3
31	3

Table 5. ARL results for Composition B.

Panels	Ranking
99E12C and D	1
52891C and D	1
PS 39-1C and D	1
PS 39-2C and D	3
PS 39-3C and D	2 1/2
PS 40-1C and D	1
PS 41-1C and D	2
PS 42-1C and D	1
PS 43-1C and D	3
PS 44-1C and D	4

Figure 5 compares the results after Composition B staining and before acetone cleaning. Figure 6 illustrates the panels with the best performance before acetone cleaning.

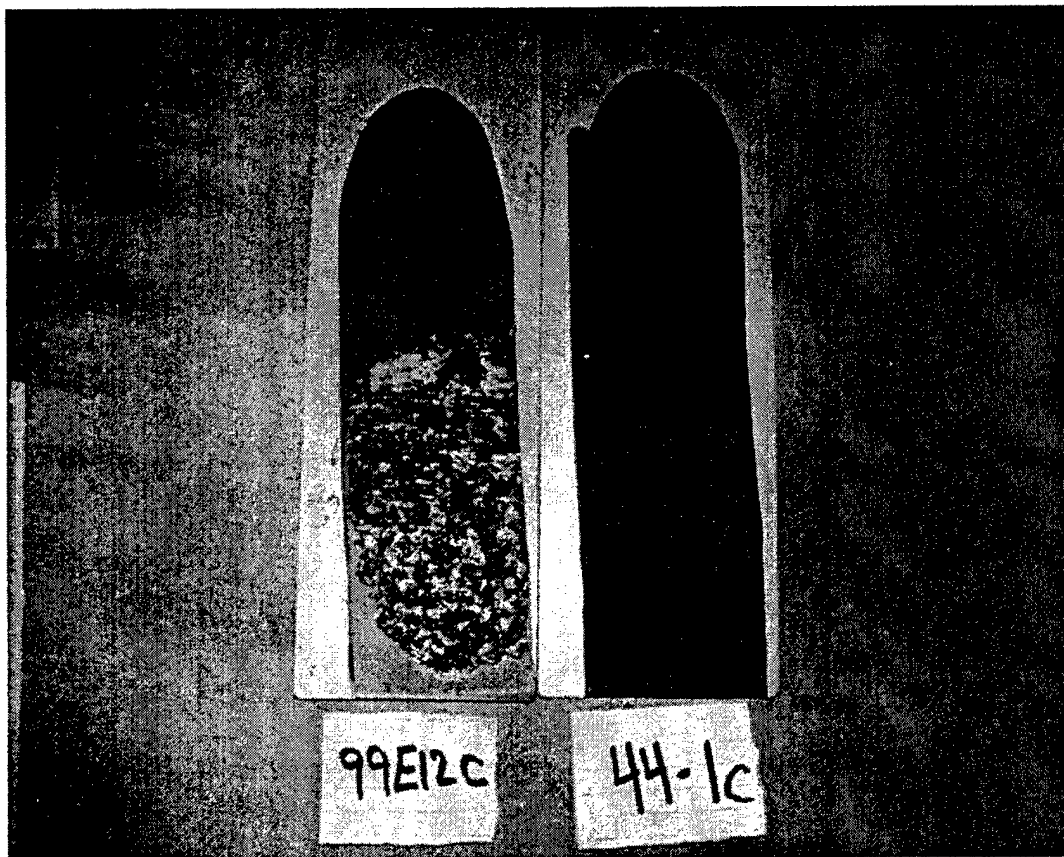


Figure 5. Composition B staining.

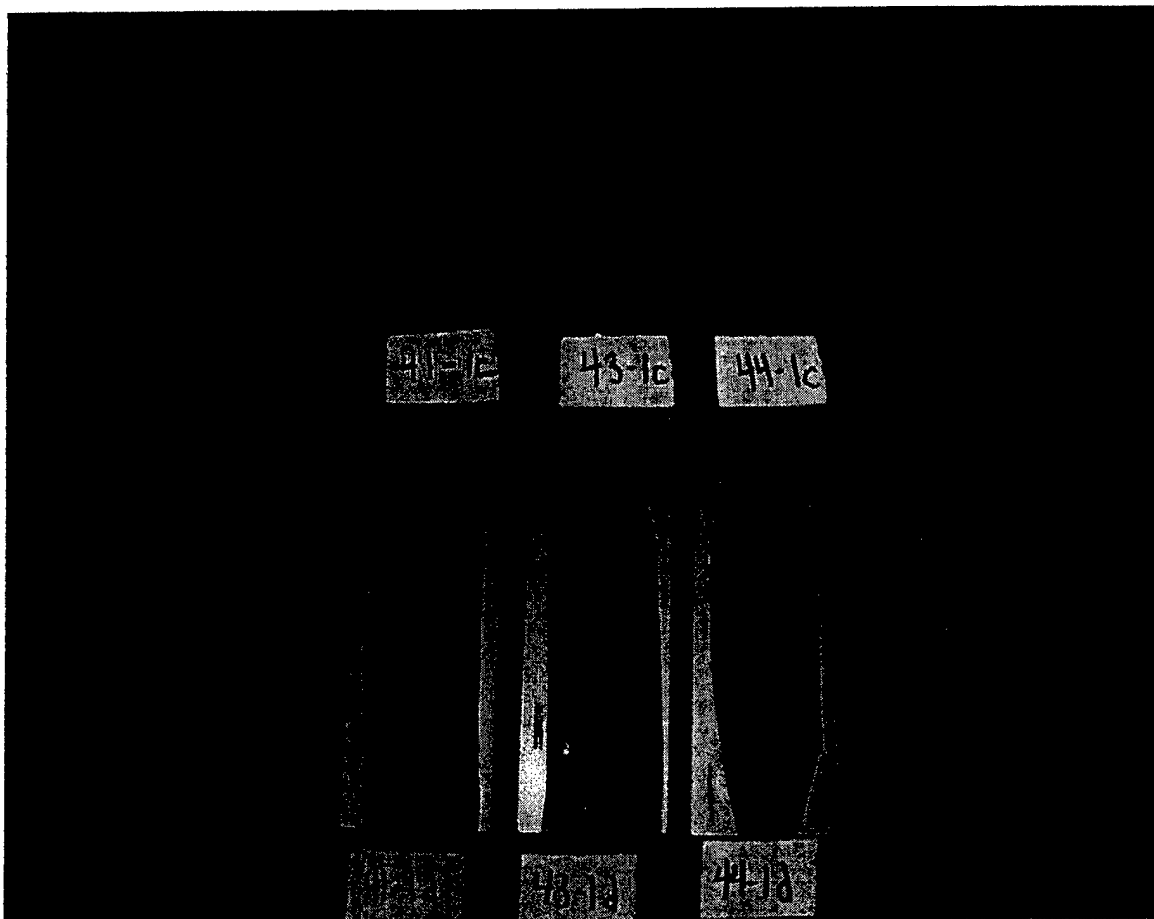


Figure 6. Panels steam cleaned.

Figure 7 shows two panels cleaned with acetone. Above each panel is the cheesecloth used to clean the panel. The cheesecloth was wetted with acetone, and the panels were rubbed with pressure four times in the same direction. The same procedure was used to clean the panels illustrated in Figure 8. The panels that showed the best acetone resistance were panel 10 from vendor sample and panel PS 41-1c. However, panel 10 exhibited a stain after acetone cleaning, and panel PS 41-1c did not exhibit any stain after acetone cleaning.

The panels that showed the best resistance to acetone and Composition B staining were panels PS 41-1, PS 43-1, and PS 44-1. The panels with the best performance were the panels from group PS 41-1.

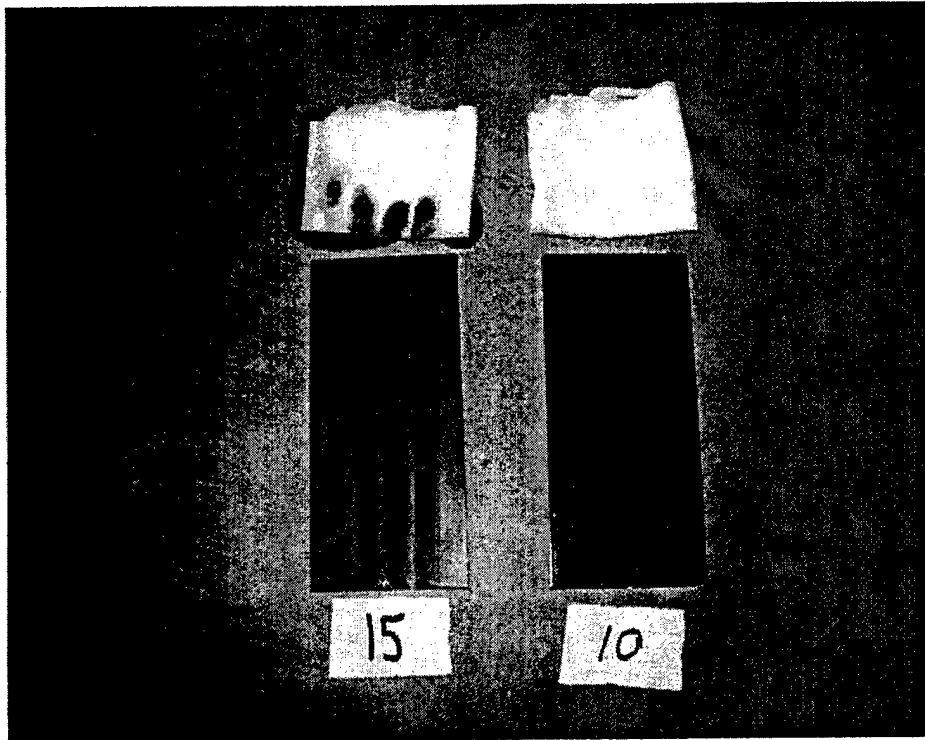


Figure 7. Panels cleaned with acetone.

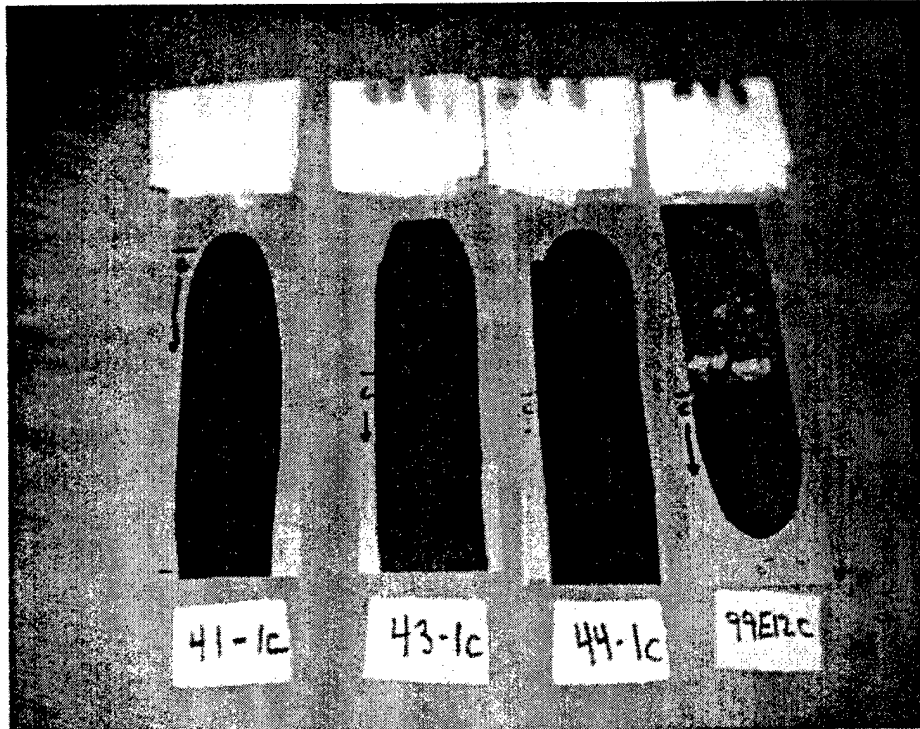


Figure 8. Panels cleaned with acetone.

## 10. Experimental Results

Table 6. Acetone wipe test.

Sample	Alkyd Resin/Formaldehyde/ Acid Catalyst	Rating <sup>a</sup>
PS 41-1	5720/933/5%	4
PS 41-1	5720/933/5%	5
PS 41-1C	5720/797/5%	2
PS 41-1B	5720/100%	4
PS 41-1A	5720/933/0%	1
MIL-E-52891	Control	3
MIL-E-52891	Control	3

<sup>a</sup>Rating of 5 is best and 1 is worst.

Table 7. Acetone cleaning results.

Panel	Resin	933	PISA	Before Acetone	After Acetone
43-1	MIL-E-52891	N/A	N/A	Blooming	Paint removed/clean, no visible stain
41-1	5720	Yes	Yes	Little blooming	Little paint removed/clean, no visible stain
41-1	5720	Yes	Yes	Little blooming	Little paint removed/clean, no visible stain
41-1C	5720	No	Yes	Blooming	Paint removed/clean, visible stain
41-1B	5720	No	No	Blooming	Less paint removed/clean, no visible stain
41-1A	5720	Yes	No	Blooming	Substantial paint removed (down to bare metal)/clean, no visible stain
52891	MIL-E-52891	N/A	N/A	Blooming	Paint removed/clean, no visible stain (few spots)

On the systems that showed a blooming problem, it seems that steam or hot water physically removes all of the explosives from the film surface and at the same time insolubilizes and/or precipitates out a portion of the propellant and/or its minor constituents that have penetrated deepest into the film. The most penetrating are the ones with the lowest molecular weight. And possibly they may be solubilized at steam temperature and become insoluble at room temperature. It is a standard test for the solvency power of some of the solvents used in coatings such as ketones and esters where a small percentage (1 part NC to 8 parts solvent) solution of NC is added to a solvent, for instance, toluene until the NC precipitates out of solution. A good strong solvent like methyl ethyl ketone (MEK) will require increased toluene to precipitate out while a good weaker solvent like ethyl acetate will precipitate out with less amounts.

### 10.1 Adhesion Testing ASTM D 3359 Method B Adhesion [5]

Table 8 lists the panels used in adhesion testing and the results. The ASTM Cross-Cut Adhesion testing was performed with 2-mm line spacing, appropriate for dry film thickness between 2 and 5 mil (1 mil = 0.001 in).

Table 8. Adhesion testing.

Substrate	Control (Styrenated Alkyd)		Control (Styrenated Alkyd)		Olive Drab		Olive Drab	
	Panel	Result	Panel	Result	Panel	Result	Panel	Result
Bondrite B37 P60	9	5B (pass)	10	5B (pass)			2	5B (pass)
Bondrite B37 P60 + 53022 (2.8 VOC)	1	5B (pass)	13	5B (pass)	7	4B (pass)	5	5B (pass)
Cold roll steel S412	15	5B (pass)	12	5B (pass)	14	5B (pass)	8	4B (pass)
Cold roll steel S412 + 53022 (2.8 VOC)	11	4B (pass)	6	4B (pass)	4	4B (pass)	3	4B (pass)

Notes: 5B rating means no removal.  
 4B rating means <5% removal.  
 3B rating means 5–15% removal.  
 2B rating means 15–35% removal.  
 1B rating means 35–65% removal.

### 10.2 Wet Adhesion Testing

Coated samples were partially immersed in water for 24 hr and subjected to cross-cut adhesion testing within 5–10 min. Samples were also evaluated for changes in color, blistering, softening and loss of adhesion, upon removal and also after a 24-hr recovery period.

Table 9 lists the panels used in adhesion testing and their results. The cross-cut adhesion was performed with 2-mm line spacing, appropriate for a dry film thickness between 2 and 5 mil (1 mil = 0.001 in).

Table 9. Wet adhesion testing.

Substrate	Control (Styrenated Alkyd)		Control (Styrenated Alkyd)		Olive Drab		Olive Drab	
	Panel	Result	Panel	Result	Panel	Result	Panel	Result
Bondrite B37 P60	9	5B (blister)	10	1B (100% blister)			2	5B (pass)
Bondrite B37 P60 + 53022 (2.8 VOC)	1	3B (blister)	13	4B (100% blister)	7	5B (color soft)	5	4B (soft)
Cold roll steel S412	15	5B (pass)	12	5B (pass)	14	5B (color stain)	8	5B (pass)
Cold roll steel S412 + 53022 (2.8 VOC)	11	1B	6	4B (pass)	4	1B (color change)	3	2B

Notes: 5B rating means no removal.  
 4B rating means <5% removal.  
 3B rating means 5–15% removal.  
 2B rating means 15–35% removal.  
 1B rating means 35–65% removal.

### 10.3 General Motors (GM) Standard Test 9540P [6]

A cyclic corrosion test chamber was used to evaluate the MIL-E-11195 [1] coated test panels. The panels were placed into the chamber and tested using GM Standard Test 9540P [6], Method B10, which provides a more realistic accelerated environmental test than conventional salt spray. The test consists of the repetition of 18 separate stages including salt (1.25% by mass: 0.9% NaCl, 0.1% CaCl<sub>2</sub>, 0.25% NaHCO<sub>3</sub>) water mist, humidity, drying, ambient, and heated drying. The environmental conditions and duration of each stage for one complete 9540P cycle are given in Table 10. The above process repeated 80 times to a scribed panel is claimed by industry to be equivalent to 10 years of field exposure in South Florida. For this test, the groups of scribed coupons were exposed until failure or termination. The panels were observed after testing for 22 cycles. As with B117 salt fog, the extent of damage was assessed using ASTM D 1654 [7].

Table 10. GM 9540P cyclic corrosion test details.

Interval	Description	Interval Time (min)	Temperature (±3 °C)
1	Ramp to salt mist	15	25
2	Salt mist cycle	1	25
3	Dry cycle	15	30
4	Ramp to salt mist	70	25
5	Salt mist cycle	1	25
6	Dry cycle	15	30
7	Ramp to salt mist	70	25
8	Salt mist cycle	1	25
9	Dry cycle	15	30
10	Ramp to salt mist	70	25
11	Salt mist cycle	1	25
12	Dry cycle	15	30
13	Ramp to humidity	15	49
14	Humidity cycle	480	49
15	Ramp to dry	15	60
16	Dry cycle	480	60
17	Ramp to ambient	15	25
18	Ambient cycle	480	25

### 10.4 Salt Fog Testing in Accordance With ASTM B117 [4]

Salt fog testing in accordance with ASTM B117 [4] was used to screen the coated panels. The solution used was the standard 5% NaCl. The panels were all inspected prior to testing, upon significant changes, and at failure. The coated panels (three each) for each coating were exposed for 120 hr of salt fog. These panels were "X" scribed using standard carbide-tipped hardened steel scribe. Final detailed ratings for the 120-hr duration were assessed using ASTM D 1654, which quantitatively indicates the damage caused by pitting or delaminating outwards from the scribe. Panels were air dried for 7 days, and a subset was also baked at 105 °C for 30 min.

Table 11. ASTM B117 [4] results.

Data on Test Series #24, KC-76 -1	
(#1 to #3) Modified 5720 Tall Oil Alkyd	a) 19-1002 amino resin b) With and without anticorrosive @ 2× c) 3% pTSA 1040
(#4 to #6) Modified 5720 Tall Oil Alkyd	a) UF resin b) With and without anticorrosive @ 2× c) 3% pTSA
(#7 to #9) Modified 5720 Tall Oil Alkyd	a) UF resin b) With and without #1552 @ 2× c) 3% pTSA
(#10) Controls – Olive Drabs – MIL-E-52891 [8]	N/A
(#11) Controls – Olive Drabs – MIL-E-11195 [1]	N/A
(#12) Qualified Products List (QPL) sample (99E13)	N/A

## 11. Results

### 11.1 Acetone Resistance

Ratings (5 = best, 1= worst)

On these coatings, with a decrease to 3% catalyst level, we found a borderline resistance for acetone. The air-dried films showed no improvement over the controls (1 to 2 out of 5). The baked films showed very good resistance to acetone with the use of the catalyst, pTSA (5 out of 5) slightly better than the acid phosphate (4 out of 5). The two controls had showed slight improvements (3 out of 5) after baked. Force drying for 30 min at 60 °C did not improve acetone resistance in these systems.

### 11.2 Corrosion Resistance 120 hr in ASTM B117 [4]

For control MIL-E-11195 [1], after exposure both the air-dried and the baked samples were acceptable. For control MIL-E-52891 [8], the air-dried samples showed a moderate amount of small-scattered blisters. Baked samples were satisfactory. The experimental samples KC- 76 (#1 to #12) showed no blisters but displayed surface rust on all panels with KC-76, (#3) with the least and KC-76 (#5, #12) with the most. Baking provided only a marginal improvement.

### 11.3 GM 9540 [6]

After 14 cycles in GM 9540, the system supports ASTM B117 [4] results. The standard MIL-E-52891 passed, but the systems with the acid catalyst had severe blistering and surface rust. As a result, a series (KC #25) was prepared with increased (4%) acids catalyst and maximized anticorrosive additives.

#### 11.4 Corrosion Resistance 144 hr in ASTM B117 [4]

Several attempts were made to improve salt spray results of the acetone and corrosion resistant topcoat, which will be revised as MIL-E-11195, TYP 111, using MIL-E-52891 as the control and the base MIL-E-11195 formula, and 8 variations to improve corrosion resistance. Formulations were analyzed using different anticorrosive pigments (Sicorin RZ, SAPP) and additives (Nacorr 1552 and Ciba 153).

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### 12. Observations

Using as criteria acetone resistance and corrosion resistance, there is no one formula where both properties can be maximized.

The basic formulation, with corrosion-inhibiting phosphate pigments SAPP and the anticorrosion liquid Nacorr 1552, has excellent resistance to acetone, significantly better than MIL-E-52891. However, it fails the salt spray B117 at 120 hr. There is a possibility that it may have good corrosion resistance in the real world but verifying that would require running cyclic weathering and humidity cabinet exposures.

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### 13. Summary

The anticorrosive additives Sicorin RZ and Ciba 153 promote corrosion resistance in the salt spray environment but also reduce the acetone resistance.

There were several attempts to further improve salt spray results on the TYP III formulation, Sample C. Panels were prepared and primed. Topcoats were applied after intervals of 5 min, 15 min, 30 min, 60 min air drying, and after a force dry of 30 min at 105 °C. In addition to using MAK as the reducer for the catalyst, a change to a faster solvent was used in this formula. An epoxy primer was also tested and was compared to the existing primer with the same time intervals. A decrease in the catalyst level to 4% was also applied. A list of the samples tested are in Table 12.

Table 12. Samples tested in B117.

Sample Identification	Formulation
Sample B	MIL-E-52891 [8] olive drab
Sample C	Acetone resistant MIL-E-11195 [1] olive drab TYP III
Sample D	Acetone resistant MIL-E-11195 TYP III/ MIL-P-11414E [3] red oxide primer
Sample E	Corrosion resistant MIL-E-11195 on no fire/olive drab TYP II

After 120 hr in the salt chamber, sample C, acetone-resistant coating without the primer failed severely with blisters and discoloration; the remaining panels showed very little degradation.

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## **14. Conclusion**

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We have completed in-house formulation for a corrosion-resistant coating and incorporated it into MIL-E-11195 [1] as TYP II. A 50% improvement in salt spray resistance is evidence of enhanced durability, and production line results indicate less handling damage.

The product is currently used on the 155-mm and 120-mm projectiles. The QPL includes the approval of the colors olive drab, green, white, black, and blue.

Work is being continued to revise chemical resistance coating MIL-E-11195 as TYP III, to permit better corrosion resistance, maintain acetone resistance with the use of neutral and acidic anticorrosive pigments, and also to evaluate the compatibility of these anticorrosive pigments.

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