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VOC Compliant Wash Primer (U)

by
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ARL-MR-190

September 1994

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE <p style="text-align: center;">September 1994</p>	3. REPORT TYPE AND DATES COVERED <p style="text-align: center;">Progress October 93 to September 94</p>	
4. TITLE AND SUBTITLE <p style="text-align: center;">VOC Compliant Wash Primer (U)</p>		6. FUNDING NUMBERS	
6. AUTHOR(S) <p style="text-align: center;">Kestutis G. Chesonis and Christopher E. Miller</p>		8. PERFORMING ORGANIZATION REPORT NUMBER <p style="text-align: center;">ARL-MR-190</p>	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <p style="text-align: center;">U.S. Army Research Laboratory Materials Directorate Polymers and Mechanics Division, AMSRL-MA-E Fort Belvoir, Virginia 22060-5606</p>		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		11. SUPPLEMENTARY NOTES <p style="text-align: center;">POC: Kestutis G. Chesonis, AV 654-2798 or Comm. (703) 704-2798</p>	
12a. DISTRIBUTION AVAILABILITY STATEMENT <p style="text-align: center;">Approved for public release; distribution unlimited.</p>		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) <p>DOD-P-15328 Wash Primer is a unique coating that passivates metal surfaces against corrosion and enhances adhesion of primers/topcoats. However, the chromate and high solvent content subject it to strict EPA regulations. This report evaluated a waterborne substitute with the desired properties. Laboratory evaluations revealed a film softening effect when topcoated with solvent type epoxy primers due to trapped solvents in the wash primer.</p>			
14. SUBJECT TERMS <p style="text-align: center;">Wash primer waterborne coatings metal passivating</p>			15. NUMBER OF PAGES <p style="text-align: center;">12</p>
17. SECURITY CLASSIFICATION OF REPORT <p style="text-align: center;">Unclassified</p>			16. PRICE CODE
18. SECURITY CLASSIFICATION OF THIS PAGE <p style="text-align: center;">Unclassified</p>	19. SECURITY CLASSIFICATION OF ABSTRACT <p style="text-align: center;">Unclassified</p>	20. LIMITATION OF ABSTRACT <p style="text-align: center;">UL</p>	

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1. Introduction

1.1 Background Information

The wash primer that became DOD-P-15328 was developed during WWII under US Government contract by the Bakelite Co. due to an urgent need for a substitute metal pretreatment in ship construction. The two component system consisted of a zinc chromate rust inhibiting pigment in a flexible, adhering polymer solution activated by phosphoric acid just before use. Since then, the wash primer has performed admirably to passivate the metal surface against corrosion and to act as a tiecoat to enhance the adhesion of subsequent primers/topcoats. In the struggle against corrosion of tactical vehicles, the US Army requires that ferrous metal surfaces be treated with a zinc phosphate immersion system or a wash primer prior to coating with an epoxy primer and a urethane camouflage topcoat.

Due to recent EPA regulations, the use of the wash primer by Army Depots that refurbish older equipment has come under close scrutiny. The hexavalent zinc chromate makes the application process subject to toxic waste regulations and the high solvent content, low solids percent results in high Volatile Organic Compound (VOC) content.

1.2 Objectives

Commercial vendors have tried to come up with replacements for the wash primer by formulating changes only in the pigmentation and also by going to waterborne systems with non-toxic corrosion inhibiting pigments. So far, no one has been able to completely formulate an equivalent replacement. Our objective for FY94 was to formulate a substitute with good adhesion to metal surfaces and with good intercoat adhesion to the epoxy primer.

2. Experimental

2.1 Reactions of the Wash Primer

The current wash primer, when activated with the phosphoric acid, performs the following three functions:

- a. As a dilute alcoholic solution of phosphoric acid able to phosphate the metal surface.
- b. As a solution of chromium ions able to passivate the metal surface.
- c. As a resin solution able to seal the metal surface from corrosive attack.

The zinc chromate is basic in nature and reacts readily with phosphoric acid to form, in the presence of an organic polymer solution, a mixture of chromium in cationic and anionic forms.

Chromium is available for passivating the phosphate surface with the formation of a wide scope of chelates and complexes. The most likely complex in this reaction is that of chromium with the acetal groups of the polymer in the formation of a three dimensional organic-metallic polymer¹ (see Figure 1). Thus, the three processes of phosphating, passivating and polymers sealing explain the excellent results achieved by wash primers on ferrous and non-ferrous metal surfaces.²

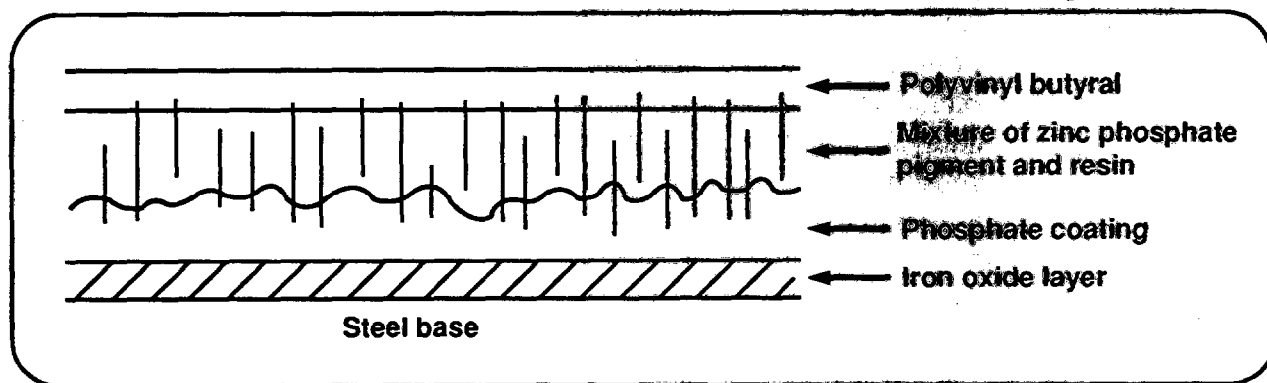


Figure 1. Stylized diagram of the wash primer film with vertical lines representing the chromium-phosphorous polymer complex

1. Kruger, J., Bloom, M. C., *Industrial and Engineering Chemistry*, 1956, 48, 1356-60.
2. Chandler, R. H., *Paint Technology*, Vol. 20, No. 7.

2.2 Waterborne Polymers

There are many and varied waterborne polymers systems available and they cover the spectrum from low cost interior house emulsions to two component epoxy and urethane systems. However, they all function in the pH range of 5 to 10, from slightly acidic to mostly alkaline. A thorough search of waterborne polymers that can function with high levels of phosphoric acid resulted in only one candidate (a proprietary epoxy-urethane emulsion) that required the addition of phosphoric acid to be done in a diluted form.

2.3 Non-toxic Corrosion Inhibiting Pigments

Inquiries were directed to all known vendors of corrosion inhibiting pigments for suitable non-toxic replacements for zinc chromate in a water based acidified polymer systems. Twenty-six samples (see Table I) were received and screened for compatibility with phosphoric acid. The field was narrowed down to five eventually and the initial studies were made with three: Halox SZP-391, Heucophos-ZPO and K White-84S.

Table I

PIGMENT/ADDITIVE		
Akkaterge TIV	Halox SZP391	Lubrizol 2063
Ancor CR538	Heucophos ABO	Molywhite MZAP
Ancor CR539	Heucophos ZPO	Molywhite X92
Borogard ZB Fine	Irgacorr 153	Molywhite 212
Busan 11-M1	Ken React NZ38	Nacorr 1352
Cotrol AMB	Ken React QB-012	Nacorr 1651
Cotrol 18-8	Ken React QB-512	Surfynol 104E
Cotrol 316	K-White 84S	Surfynol 502
Halox CW491	Lubrizol 219	

2.4 Corrosion Test Methods

The old standard way of testing coatings for corrosion resistance is the 5% salt spray, ASTM B117. However, it is not a cyclic test and results have been questioned in the technical literature. For comparison, scribed panels were exposed for 100 hours to 4 hour cycles of UV at 70°C and 100% RH at 50°C according to ASTM G53 and to 336 hours of salt spray.

The UV-condensate cyclic testing of corrosion in the scribed area was more uniform than the salt spray and was used for subsequent testing. Panels used were cold rolled steel 4" x 12", solvent cleaned before use.

2.5 Testing

The first test series compared the three pigments using the manufacturers suggested loadings in the waterborne polymer. After the addition of diluted phosphoric acid, drawdowns were made on the steel panels, air dried for 24 hours and flow coated with MIL-P-53022 epoxy primer. The panels then were air dried for a minimum of 4 days and exposed with the control DOD-P-15328 to 100 hours of UV-condensate. Results in comparison to the control were very promising and the second series samples were prepared to evaluate different concentrations of acid and pigments for the three chosen pigments. After 9-13 days of UV-condensate exposure, the three pigments with various amounts of phosphoric acid gave equal or better results when compared to the control for corrosion creepage at the scribe. Further testing was run to evaluate the effect of excess phosphoric acid and no detrimental effects were found. All the panels were evaluated for wet adhesion by means of the cross hatch test, ASTM D3359. All systems showed very good adhesion comparable to the control.

After these initial screening tests, a series of 4" x 12" panels were sprayed with two of the optimized formulas and the control DOD-P-15328, air dried for 24 hours and topcoated with MIL-P-53022. The purpose was to reevaluate the coating systems on larger panels at different film thicknesses. This series uncovered a problem not evident when the screening tests were done by drawdowns and flowouts. When the epoxy topcoated panels were checked the next day, a typical appearing dry surface film was evident. However, fingernail pressure easily ruptured the film to expose a soft, flexible layer beneath the top. Analysis and consultation with polymer suppliers indicated that the waterborne polymer of the wash primer absorbed the solvents of the epoxy topcoat and retained them while the topcoat cured. It required more than 7 days for the film to eventually air dry to a hard coating due to the slow diffusion of solvent through the cured epoxy coating.

When these panels were scribed and exposed to UV-condensate and salt spray, they were comparable to the control.

3. Discussions and Conclusions

During the many test series run with the acid tolerant waterborne (WB) polymer, it was evident that it was a strong contender to replace the solvent type wash primer. However, the film was not resistant to the solvents of the topcoat and the air dry times became unacceptably long. The acid tolerant WB polymer has an epoxy-urethane structure that could be crosslinked to a higher degree as a two component system. With a higher degree of crosslinking, the system would be more resistant to solvent absorption and would give acceptable dry times. For FY95, improving the WB system through crosslinking will allow the continuation of research and development of an acceptable replacement for the wash primer.

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