

FINAL REPORT

(3)

DEVELOPMENT OF
NON-CHROMATE WATERBORNE WASH PRIMER

Research and Development Report
For Period 8/1/81 - 2/28/83

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PREFACE

The effort documented in this report was conducted by the following Springborn Laboratories personnel:

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The work described herein was conducted under research Contract No. DAAK 70-81-C-0101 and carried out during the period from August, 81 to February, 83.

The author wishes to acknowledge the many helpful contributions of Mr. Stan Koutek and Mr. Stan Dowdy, Material Technology Laboratory, Fort Belvoir.

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SUMMARY

This effort was undertaken to develop lead and chromate-free waterborne corrosion inhibiting wash primers for ferrous and non-ferrous substrate application. This primer would replace military specification DOD-P-15328D (#117 wash primer), a solvent-borne system containing a chromate pigment. A second objective was to decrease solvent air pollution.

Of the numerous potential primers screened, only one was selected for extensive testing. This primer had as its binder resin a carboxylated aliphatic urethane (Witco Chemical Witcobond W-231) with Butrol 22 pigment formulated as a one part system.

Aluminum and steel panels were coated with the Springborn Laboratories (S/L) experimental urethane primer, and also with the #117 wash primer, as a control. Both W-231 urethane and #117 wash primer were dry and overcoatable one hour after spray-up. The coatings were MEK rub-resistant at one hour, but the urethane was not cellosolve rub-resistant. Other sets of panels, primed with the S/L urethane and separately, #117 wash primer, were tie coated approximately one hour after priming with either MIL P-23377 or MIL P-52192 and then top-coated with MIL C-83286.

After aging for at least 7 days, the panels were subjected to extensive testing, i.e. flash rusting, knife adhesion, salt spray, WeatherOmeter, tape adhesion, water immersion, Fuel III immersion and impact. The S/L experimental urethane primer formulation was also subjected to one week at 60°C, and the same sample was then subjected to five freeze/thaw cycles without ill effect.

None of the tests severely affected the panels primed with the S/L urethane or the #117 wash primer, although some tests did cause some of the steel panels to rust slightly along the scribe. With the Witcobond W231, we did not need phosphoric acid in the formulation to achieve good adhesion and salt spray resistance.

The Witcobond urethane formulation was not suitable for coating magnesium. An acrylic amine (Rohm and Haas QR-765M) cured with epoxy was found to be suitable for magnesium coating and was recoatable at one hour. The coating, however, was not MEK rub-resistant.

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SECTION I

INTRODUCTION

This work was undertaken to find a viable substitute for the Number 117 wash primer. The number 117 wash primer has performed well in very difficult environments for a great many years with the possible exception of some filiform corrosion problems. There are two difficulties, however, with the present number 117 formulation. Chromate pigment is the keystone of the formulation's ability to crosslink the butyral component, promote adhesion to the metal substrate, and prevent further corrosion, but chromates are believed to be toxic. If chromate pigments are actually confirmed as toxic, this class of pigments constitute an unsatisfactory hazard to personnel handling the solution or spraying the military equipment.

The second major consideration is the organic solvent content of the (dilute) number 117 formulation. If a waterborne system can be found to replace the number 117 formulation, the potential air pollution resulting from large scale use of solvent-based systems could be eliminated.

The criteria to be fulfilled by the new coatings are:

- . Non-toxic pigments
- . Low solvent content to meet the Los Angeles County Pollution Control Department (LAPCD) Rule 66
- . Dry to the touch in one hour
- . Overcoatable in one hour by a solvent-borne system
- . Good adhesion
- . Solvent rub resistance in one hour (MEK & Cellosolve)
- . Salt spray resistance - 48 hours un-overcoated and 300 hours overcoated with tie coat and topcoat
- . Resistance to 600 hours Weather-Ometer exposure overcoated

SECTION II

LITERATURE AND TELEPHONE SURVEY

1. Direction of Survey Effort

A Literature and Telephone Survey was carried out . The objectives were:

- . To find any existing literature and patents on wash primers
- . To determine if any work on lead and chromate-free water-borne wash primers was currently in progress by coating manufacturers.
- . To determine lead and chromate free corrosion-resistant pigments most widely used in waterborne systems and new developments in this area.
- . To solicit any new ideas industrial contacts might have for lead and chromate-free waterborne wash primers.
- . To solicit samples of waterborne resins, pigments, etc.

For the literature survey, Springborn Laboratories' files, Chemical Abstracts, Lockheed Dialog Computer Banks 2, 3, 4, Chemical Abstracts (6), NTIS and 115 were searched and pertinent citations were requested. The general literature was searched under "Wash Primer", "Corrosion-Resistant Pigments" and " Waterborne Primers".

2. General Conclusions

a. Wash Primer, eq. Formulation 117 Type

Since the Lockheed Dialog is more recent and since most of the wash primer research was carried out many years ago, the Polymer Encyclopedia references and cross references therefrom were particularly valuable.

- . The latest thinking is that 0.5 mil wash primer is more valuable than a 0.2-0.3 mil wash primer⁽¹⁾. Thicker films can delaminate⁽³⁷⁾.
- . Substitution of other ingredients for chromate is complicated by the fact that chromate causes crosslinking of the butyral, promotes adhesion to the metal substrate and releases ions to prevent further corrosion. (37, 60, 71, 76, 79, 94 & 98)

- . Alternate solvent-borne wash primers have been disclosed. (10, 22)
(46, 51, 54, 55, 56, 69, 87 & 99)

b. Waterborne Primers - Especially Wash Primers

- . No one appears to be working on waterborne wash primers (see telephone survey) with the possible exception of the Kronstein publications/ patents (54) (56) based on polyvinyl alcohol (too water sensitive).
- . Numerous binders are recommended. (24, 25, 29, 32, 47, 49, 54, 66 101)
- . Cationic polymer binders should be considered. (14, 47, 61, 101)
- . Numerous anticorrosion pigments have been investigated (2, 3, 5 & 6)
(7, 11, 18, 21, 28, 29, 33, 34, 35, 36, 38, 39, 40, 42, 43, 44 & 45)
(50, 53, 55, 56, 59, 62, 63, 65, 67, 68, 70, 82, 85, 86, 88, 90 & 91)
(93, 95, 97, 100, 102 & 103).
- . Inhibitors such as nitrite are recommended to prevent flash rusting on steel. (9 & 34) Corrosion inhibitors in the coating may be helpful.
- . Permeability to chloride ion is an important consideration. (72)
- . Good cleaning of surface is essential. (17)
- . Surface treatment of the metal before priming may be helpful and should be considered. (16, 18, 64 & 83)

Companies contacted include:

Rohm and Haas, National Starch, Polyvinyl Chemical, Spencer Kellogg, Dow Chemical, DuPont, Celanese, Ciba Geigy, Shell, Morton Chemical, B.F. Goodrich, Monsanto, Union Carbide, Henkel and Witco Chemicals for binder resins. Sherwin Williams, Halox Pigments, Buckman Laboratories, N&L Chemicals Reichard Coulston and BASF for non-toxic corrosion-resistant pigments.

The (numbered) bibliogoraphy and telephone survey are to be found in the appendix.

SECTION III

EXPERIMENTAL

1. Background Summary

Numerous samples of water-based polymers and non-toxic corrosion-resistant pigments were received from commercial manufacturers.

The resins were classified according to polymeric structure and first evaluated for phosphoric acid compatibility. The resins that were found to be compatible with phosphoric acid were then screened further using other criteria. From the results obtained from this screening three binder systems were chosen for initial pigment screening; National Starch's hydroxyl functional (78-3936, and carboxyl functional (78-3953), styrene-acrylic latexes and Dow's XD7080 /epoxy. The non-toxic corrosion-resistant pigments screened were Moly White 212 and MZA, Halox ZA-111 and BW-191 , Walzin SC-1, 317 zinc phosphate, Busan 11-M1 , Butrol 22 , and Sicorin RZ. Pigmented formulations were initially screened for adhesion (crosshatch tape test) and resistance to salt fog (48 hours) . Later criteria used to evaluate formulations were time to overcoat and solvent resistance.

As the project progressed, we were informed that phosphoric acid compatibility was no longer absolutely essential , which made available more resins for screening. MEK and cellosolve rub-resistance at one hour were added to the requirement that the formulation be oversprayable at one hour.

Of all the systems evaluated, the only one that fulfilled almost all the requirements: (overcoatable in one hour, methyl ethyl ketone resistant in one hour, resistant to 48 hours of salt fog and good adhesion to steel and aluminum) was Witco Chemical aliphatic urethane Witcobond W-231. (Introduced into the program at a later date).

2. Final Formulation Testing, Steel and Aluminum

a. Final Spray-up Formulations and Testing

a.1. Urethane Wash Primer

Coating #1 - Formulation #15591, Experimental

<u>Pigment Mix</u>	<u>Parts Based on</u> <u>100 gms Resin Solids</u>	
Witcobond W-231 (Witco Chemical) (30.5% solids)	41.89	} Part A
Byk 301 (Mallinckrodt)	4.44	
Butyrol 22 (Buckman Laboratories)	10.00	
Nytal 300 (R.T. Vanderbilt)	16.00	
TiPure R-960 (E.I. DuPont)	25.00	
<u>Premixed Let Down</u>		
Witcobond W-231	290.33	} Part B
FC-120 (3M Company) (25% Active)	1.67	
Colloids 675 (Colloid)	0.45	
Deionized Water	60.00	

The above formulation was sprayed onto clean steel and aluminum panels at a thickness of 0.4 - 0.7 mils. All panels for spray-up were first cleaned with a 1:1 mixture of toluene and VM&P Naptha, and Scotch Brite, then wiped with cheesecloth soaked in the above solvent mixture. The above urethane experimental primer was allowed to dry approximately one hour before overcoating with one of two MIL epoxy primers.

a.2 Overcoating Number 2
MIL Epoxy P-23377 Tie Coat

This is a two part yellow epoxy system believed to be Epon 828 or similar epoxy with a Versamid curing agent (DeSoto 513J102 and 910J138). The pigment is believed to be strontium chromate with talc, approximately 50 weight percent pigment. Spray-up is 0.8-1.2 mil, 1 coat. Urethane topcoat was sprayed on within 3-4 hours after epoxy spray-up.

a.3 Overcoating Number 3
MIL P-52192 , Tie Coat

This is a two part red epoxy system procured from Fort Belvoir. The mix (4 parts by volume of pigment mix plus 1 part catalyst) was allowed to stand approximately 1/2 hour before spraying. Spray-up is 0.8-1.2 mil, one coat. Urethane topcoat was sprayed on within 3-4 hours after spray-up.

a.4 Overcoating Number 4
MIL C-83286 (White Gloss Urethane), Topcoat

This material was procured from DeSoto, #821 x 400 + 910 x 480. The coating system is believed to consist of a polyester polyol with Desmodur N (hexamethylene diisocyanate trimer) and pigment. The cure is part polyol and part moisture.

The coating was mixed, allowed to stand 1/2 hour or more and sprayed on panels, two 1 mil. coats, 1/2 hour apart.

a.5 Wash Primer, Coating Number 5
Number 117 Wash Primer

This is a two part system obtained from Fort Belvoir. The mix (1 part phosphoric acid mix, 1 part Butanol and 2 parts isopropanol by volume were premixed and added to an equal volume of the pigment mix) is sprayed 0.4-0.6 mil thick, 1 coat. Coating is allowed to dry approximately 1 hour before overcoating with the above described two epoxy tie coats.

a.6 Coating Number 6, MIL Epoxy P-24441

This is a two part system believed to be epoxy Versamid with a red lead pigment. The system was procured from Ameron (Amercoat 83") . The mix (293 gm resin solution plus 38 gms curing solution) was allowed to stand 1/2 hour or more before applying to the backs and edges only of steel panels reserved for prolonged water exposure (salt spray, WeatherOmeter and water immersion).

b. Panel Preparation

b.1 Aluminum

The following sets of 0.020" T₃ Alclad aluminum panels were sprayed with the following coating systems:

<u>Set No.</u>	<u>Primer</u>	<u>Epoxy Tie Coat</u>	<u>Topcoat</u>
1	Coating No. 1 (experimental urethane)	Coating No. 2 (MIL P-23377 yellow epoxy)	Coating No. 4 (MIL C-83286 White gloss urethane)
2	Coating No. 5 (117 Wash Primer)	Coating No. 2	Coating No. 4
3	Coating No. 1	-	-
4	Coating No. 5	-	-

b.2 Steel

The following set of 0.032" Type S ground finish panels (Q Panel) were sprayed up with the following coating systems:

<u>Set No.</u>	<u>Primer</u>	<u>Tie Coat</u>	<u>Topcoat</u>
1	Coating No. 1	Coating No. 2	Coating No. 4
2	Coating No. 1	Coating No. 3 (MIL P-52192 Red Epoxy)	Coating No. 4
3	Coating No. 5	Coating No. 2	Coating No. 4
4	Coating No. 5	Coating No. 3	Coating No. 4
5	Coating No. 1	-	-
6	Coating No. 5	-	-

The backs and edges of the steel panels designated for prolonged water exposure were coated with coating number 6. All panels were removed from the hood immediately after spray-up of each coat and stored flat.

c. Test Procedures

Tests were carried out in triplicate, with two out of the three panels being scribed.

c.1 WeatherOmeter (ASTM E42)

Panels were mounted in an Atlas WeatherOmeter Type XW. This is a carbon arc WeatherOmeter with Corex glass filters. Cycle is 18 minutes deionized water spray followed by 102 minutes of UV exposure (no water). Total exposure for topcoated panels was 600 hours with a spot check at 300 hours. A complete set of topcoated steel and topcoated aluminum panels were exposed to this test.

c.2 Salt Spray (ASTM B-117)

Panels were mounted in an Industrial Salt Spray Type 411-3ABC. Panels were exposed to 5% (NaCl) mist at 95°F for the duration of the test. Total exposure for panels with only wash primer coat was 100 hours with a spot check at 48 hours; and for topcoated panels it was 300 hours with spot check at 48 hours. A set of all spray-up panels was exposed to this test. Final testing was for tape adhesion, scribe undercutting, blistering and corrosion and any other noticeable damage.

c. 3 Chemical Exposure

Panels were totally immersed in the test fluid with narrow spacer strips of porous paper between panels at the ends. Final testing was the examination of panels for wrinkling, blistering, undercutting and other obvious damage. Crosshatch tape adhesion and pencil hardness was carried out where feasible.

Fuel III

Panels were immersed 18 hours at room temperature in Fuel III. The Fuel III was prepared as follows:

70% Isooctane (Aldrich, reagent 2,2,4 - trimethyl pentane)
30% Toluene (Aldrich, reagent)

. Water

Panels were immersed in deionized water for 18 hours then observed for obvious damage. Panels were then allowed to dry for 2 hours before running adhesion and hardness tests.

. Methyl Ethyl Ketone Rub

Panels were checked for methyl ethyl ketone (MEK) resistance by rubbing 10X with a cotton swab saturated with MEK one hour after spraying on the experimental primer.

2 c.4 Drying Time

Panels were checked for handleability (being able to withstand touching without indentation and transportation without any damage) within 1 hour after spray-on of experimental primer.

c.5 Recoatability

Panels sprayed with our experimental primer were overcoated approximately 1 hour after spray-up, then checked for blistering, lifting and delamination.

3 c.6 Knife Adhesion

Panels were checked for knife adhesion after at least seven days drying by checking for flaking and chipping.

4 c.7 Heat Aging

5 A sample of formulation number 15591 (urethane) was aged at 73°F and 50% RH for 24 hours in a sealed container. The viscosity is then taken, using a Brookfield Viscometer, before sample is placed in a 60°C air circulating oven for 7 days. After the 7 days, sample is then aged for 24 hours at 73°F and 50% RH before viscosity was again taken, noting any change in viscosity before and after 60°C aging.

c.8 Freeze Thaw Stability

The 60°C aged sample of number 15591 urethane was then placed in a freezer for 20 hours to be frozen solid. Sample was then thawed at room temperature for 4 hours and examined for any noticeable change in viscosity or appearance. This cycle was repeated 5 times after which viscosity was again taken, noting any change.

c.9 Flash Rusting

Coating was applied to steel and dried for 2 days, after which coating was removed, and surface examined for rusting.

c.10 Gardner Impact

The 0-30 inch Gardner impact apparatus was employed. The 2 pound impacting head has a 1.27 cm/0.5 inch protruding diameter round nose end. Samples to be tested were aged at room temperature. The maximum drop height of 30 inches was employed initially, and decreased if necessary, to find the height just below what is needed to split the coating.

SECTION IV

DISCUSSION OF RESULTS

1. Test Results of Urethane vs Number 117

a. Storage Stability

After seven days aging at 60°C the increase in viscosity of our (one part) urethane formulation (#15591) was negligible (Table I)* which led us to conclude that this type of aging would not affect this formulation. We also had no problems in trying to spray this formulation.

b. Freeze/Thaw

After five freeze/thaw cycles, on the sample that was aged 7 days at 60°C, there was no noticeable change in viscosity, which would let us conclude that freezing would not be a problem.

c. Drying Time, Recoatability and Methyl Ethyl Ketone (MEK) Rub Resistance

The S/L #15591 and #117 wash primers were dry to the touch and could be handled with little or no precaution in less than one hour.

The S/L #15591 and #117 wash primers also experienced no lifting, blistering or delaminations when overcoated with MIL P-52192 and MIL P-23377, (both solvent-borne systems) one hour after spray-up.

The S/L #15591 and #117 wash primers experienced no noticeable damage when rubbed 10 times with a Q-tip saturated with MEK one hour after spray-up.

The S/L #15591 was not resistant to 10 cellosolve rubs at one hour while the #117 wash primer was resistant to cellosolve.

* Page 15

d. Flash Rusting

When coatings from formulation #15591 (S/L urethane) were removed from steel panels, two days after spray-up, there were no visible signs of rusting on the metal surface. Similar results were obtained for #117 wash primer sprayed panels.

e. Knife Adhesion

The coatings were scribed down to the metal, by means of a 0.030 inch thick dull spatula blade. There was no noticable flaking or chipping of the panels coated only with primer, nor the overcoated systems, when examined visually. On the other hand, when the overcoated systems were evaluated under the microscope, a slight amount of chipping of the topcoat from the tie coats were observed. The S/L #15591 and #117 wash primers appeared to be cut through, but otherwise unaffected by the knife cut.

f. Salt Spray

When examined, after 48 hour exposure, none of the primer only panels (steel and aluminum) coated with #117 wash primer or #15591 S/L urethane primer showed any sign of corrosion. After 100 hours exposure, the appearance of both primer coatings was very good, there was no blistering or corrosion. When coatings were removed from around the scribe area, the steel panels coated with #117 wash primer or #15591 S/L urethane were found to have a few rust spots in the scribe, but there was no undercutting or rusting on any other part of steel surface. All aluminum panels did not experience any form of corrosion, not even in the scribe areas. Crosshatch tape test (ASTM D3359) performed on all panels one hour after removal from the salt spray chamber were very good, indicating no loss of adhesion during exposure, (Table II, Page 15),

In the case of the top coated panels, (steel and aluminum) 100 hours examination did not indicate any form of corrosion. After exposure for 300 hours the general appearance and adhesion of all panels was good, with the exception of very few small (1-2mm) blisters on one or two edges of some of the steel panels, prime coated with #15591 S/L urethane (Table III)*. When the coatings were removed around the scribe area of all scribed panels, the general appearance of the metals surface (steel and aluminum) was very good with the exception of an area along the scribe of some of the steel panels. Three of the four scribed steel panels primed with the #117 wash primer, and two of the four primed with #15591 S/L urethane rusted slightly along the scribe. None of the aluminum panels had any form of corrosion before and after removal of coatings in the scribe area, (Table III) .

g. Fuel III Immersion

After 18 hours immersion in Fuel III, none of the overcoated steel or aluminum panels, primed with #117 wash primer or #15591 S/L urethane, wrinkled or blistered. Pencil hardness after immersion was the same as before. Crosshatch tape adhesion test performed one hour after removal indicated no loss in adhesion. When coatings were removed around scribe area, on both the steel and aluminum panels, no form of corrosion or other damage was observed , (Table IV , page 17).

h. Water Immersion

After 18 hours immersion in deionized water, none of the top coated steel or aluminum panels, primed with #117 wash primer or #15591 S/L urethane, wrinkled or blistered. Pencil hardness, performed two hours after removal, did not change from what it was before immersion. Cross-hatch tape test after immersion, indicated no loss of adhesion on both steel and aluminum panels. Steel panels, that were primed with #117 wash primer or #15591 S/L urethane and tie coated with MIL P-52192, had a few rust spots showing through topcoat in the scribe area, but when coatings were removed there was no sign of corrosion on the steel surface, not even in the scribes. None of the other panels that were subjected to this test showed any sign of corrosion , both before or after removal of coatings, (Table V Page 18).

i. Impact Resistance

The Gardner impact results tabulated in Table VI indicate that both the #117 wash primer and the #15591 S/L urethane, on both steel and aluminum, will withstand greater than 30 inch pound force without any noticeable damage. Results did not change when these primers were overcoated.

j. WeatherOmeter

When examined after 300 hours of exposure, none of the panels subjected to this test showed any sign of corrosion.

After exposure to 600 hours, the general appearance and adhesion of all panels (steel and aluminum) was very good, with the exception of one of the three steel panels primed with the #117 wash primer and tie coated with MIL P-23377 yellow epoxy. This lone # 117 panel experienced some loss of adhesion between tie coat and primer by the crosshatch tape test one hour after removal. When the coatings were removed around the scribe area of the scribed panels, (steel and aluminum) there were no signs of corrosion or undercutting on the metal surface, not even along the scribe.

TABLE I

Seven Days Storage Stability 60°C of #15591 S/L Urethane

	<u>73°F Viscosity⁽¹⁾</u>	<u>Apparent Condition</u>	<u>Sprayable</u>
Before Aging	58 cps	OK	Yes, no problem
Aged 1 week 60°C	63 cps	OK	Yes, no problem

(1) Brookfield Viscometer with a #3 spindle, at 100 RPM

TABLE II

100 Hours Salt Spray Exposure of Wash Primer Coated Panels

<u>Metal</u>	<u>Primer</u>	<u>Scribe Area</u>	<u>1 Hr. Crosscut Tape Test⁽¹⁾</u>	<u>Metal Surface⁽²⁾</u>	<u>Comments</u>
Steel	#117 Wash Primer	Few rust spots, no undercutting	5 ⁽³⁾	5 ⁽³⁾	OK, appearance good
Steel	#15591 S/L Ure- thane	Few rust spots, no undercutting	5	5	OK "
Aluminum	#117 Wash primer	OK	5	5	OK "
Aluminum	#15591 S/L Ure- thane	OK	5	5	OK "

(1) ASTM D3359 performed 1 hour after removal from test apparatus

(2) Strip coatings around scribe, check metal surface for corrosion and undercutting.

(3) Rating 5 = excellent

TABLE III
Salt Spray, 300 Hour Exposure, Topcoated (1) Panels

Metal	Coating System (1)		Scribe Area	1 Hr. Crosscut Tape Test (2)	Metal Surface (3)	Comments
	Primer	MIL Tie Coat				
Steel	#117 Wash Primer	P-23377	Rust along parts of scribes in both scribed panels	5	5 (4)	General appearance of all 3 exposed panels was good. Both scribed panels had rust spots along scribe
Steel	#117	P-52192	Rust along parts of scribe in one panel	5	5	Appearance of all three panels was good. One scribed panel had rust along scribe
Steel	#15591 S/L urethane	P-23377	Few rust spots along scribe in one panel	5	5	Appearance of all 3 panels good, but one panel had 2 small blisters on edge & rust along scribe
Steel	#15561	P-52192	Few rust spots along scribe in one panel	5	5	General appearance good. One panel had few rust spots in scribe & small blisters on edges.
Aluminum	#117	P-23377	OK	5-4 (5)	5	General appearance of all 3 is good
Aluminum	#15591	P-23377	OK	5	5	General appearance of all 3 is good

- (1) All coating systems were top coated with MIL C-83286 moisture cure urethane.
(2) Performed 1 hour after removed from test chamber (ASTM D-3359)
(3) Strip coating off, around scribe, check metal surface for corrosion and undercutting.
(4) Rating system: 5-excellent
(5) One panel showed slight loss of adhesion, tie coat vs #117.

TABLE IV

Fuel III - 18 Hours Immersion, RT

Metal	Coating Systems (1)		Scribe Area	Pencil Hardness		1 Hr. Crosscut (4) Tape Test	Metal Surface (5)	Comment
	Primer	MIL Tie Coat		Initial (2)	Final 1 hr. (3)			
Steel	#117 Wash Primer	P-23377	OK	5H-3H ⁽⁶⁾	5H-3H	5	5 ⁽⁷⁾	OK
Steel	#117	P-52192	OK	5H-3H	5H-3H	5	5	OK
Steel	#15591 S/L Urethane	P-23377	OK	5H-3H	5H-3H	5	5	OK
Steel	#15591	P-52192	OK	5H-3H	5H-3H	5	5	OK
Aluminum	#117	P-23377	OK	5H-3H	5H-3H	5	5	OK
Aluminum	#15591	P-23377	OK	5H-3H	5H-3H	5	5	OK

(1) All coating systems were top coated with MIL C-83286.

(2) Before immersion

(3) One hour after removal

(4) ASTM D3359 performed one hour after removal.

(5) Coatings stripped around scribe, checked metal surface for corrosion and undercutting.

(6) 5H Pencil gave permanent indentation in topcoat and 3H pencil did not affect coating.

(7) Rating: 5=excellent

TABLE V

Distilled Water, 18 Hours Immersion, RT

Metal	Coating System (1)		Scribe Area	Pencil Hardness		2 Hr. Crosscut Tape Test (4)	Metal Surface (5)	Comment
	Primer	Tie Coat MIL		Initial (2)	Final 2Hr (3)			
Steel	#117 Wash Primer	P-23377	OK	5H-3H (6)	5H-3H	5	5 (7)	OK
Steel	#117	P-52192	Few rust spots on topcoat	5H-3H	5H-3H	5	5	Few rust spots showing through scribe area but no rusting of metal visible when coating was removed.
Steel	#15591 S/L Urethane	P-23377	OK	5H-3H	5H-3H	5	5	OK
Steel	#15591	P-52192	Few rust spots on topcoat	5H-3H	5H-3H	5	5	Few rust spots showing through scribe area but rusting of metal visible when coating was removed.
Aluminum	#117	P-23377	OK	5H-3H	5H-3H	5	5	OK
Aluminum	#15591	P-23377	OK	5H-3H	5H-3H	5	5	OK

(1) All coating systems were top coated with MIL C-83286.

(2) Before immersion

(3) 2 Hours after removal

(4) ASTM D3359 performed 2 hours after removal.

(5) Strip coatings around scribe, check metal surface for corrosion and undercutting.

(6) 5H Pencil gave permanent indentation in topcoat and 3H pencil did not affect coating.

(7) Rating: 5= excellent

TABLE VI
(1)
Gardner Impact or RT Aged Panels

<u>Metal</u>	<u>Primer</u>	<u>MIL Tie Coat</u>	<u>MIL Topcoat</u>	<u>Result</u>
Steel	#117 Wash Primer	-	-	> 30 inch/lbs
Steel	#117	P-23377	C-83286	> 30 inch/lbs
Steel	#117	P-52192	C-83286	> 30 inch/lbs
Steel	#15591 S/L Urethane	-	-	> 30 inch/lbs
Steel	#15591	P-23377	C-83286	> 30 inch/lbs
Steel	#15591	P-52192	C-83286	> 30 inch/lbs
Aluminum	#117	-	-	> 30 inch/lbs
Aluminum	#117	P-23377	C-83286	> 30 inch/lbs
Aluminum	#15591	-	-	> 30 inch/lbs
Aluminum	#15591	P-23377	C-83286	> 30 inch/lbs

(1) Direct impact

2. Semi-Final Urethane Formulations

a. Witco Chemical Witcobond W-231

Formulation #15586

<u>Pigment Mix</u>	<u>Parts Based on</u> <u>100 gms Resin Solids</u>	
Witcobond W-231 (Witco Chemical)	41.89	} Part A
Bubblebreak 748 (Witco Chemical)	1.33	
Byk 301	4.44	
Butrol 22	10.00	
Nytral 300	16.00	
TiPure R-960	25.00	
<u>Let Down</u>		
Witcobond W-231	290.33	} Part B
FC 120 (3M)	1.67	
Deionized Water	60.00	

Mixing Procedure: Same as 2 (a.1) Final Formulation

This was the formulation that was sent to Fort Belvoir for evaluation. The major problem with this formulation was that we noted some cratering when we overcoated this coating. The source of this problem was traced to the presence of silicone in the coating from the Bubblebreak anti-foam. To alleviate this problem, we first tried reducing the quantity of anti-foam down from 0.3% to 0.12% (formulation #15588) and adding it to the let down instead of the pigment mix, but this did not solve the problem. Next we tried an anti-foam from Colloids Inc. as suggested by Mr. Koutek, Fort Belvoir. The material Colloids submitted was Colloid 675, and it was again added to the let down (Part B) portion of the formulation at a level of 0.12 % of total formulation weight (#15589). This anti-foam did solve the problem and the only other change that was made to enable the final formulation was to decrease its level down to 0.1% on weight of total formulation.

b. Polyvinyl Chemical NeoRez R-960

Formulation #15576

<u>Pigment Mix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
TiPure R-960	25.00	} Part A
Nyral 300	16.00	
Butrol 22	10.00	
Busperse 47 (Buckman Labs)	0.56	
Triton CF-10 (Rohm & Haas)	0.78	
NeoRez R-960 (Polyvinyl Chemical) (33% solid)	15.56	
Foamaster NS-1 (Diamond Shamrock)	1.11	
<u>Let Down</u>		
NeoRez R-960	287.44	} Part B
Dow Corning 14	2.22	
Drew Y381 (Drew Chemicals) (1)	0.89	
Jeffersol EE	5.56	

This formulation was evaluated as a substitute for the Witco Chemical's Witcobond 231, which we were told was similar to Witcobond W231. The formulation, when sprayed onto steel and aluminum panels dried in less than one hour, and could be overcoated in one hour. The 48 hour salt spray exposure and tape adhesion on this coating was also considered good.

The R-960 appears to be an alternate for W231.

3. Semi-Final Epoxy Formulations

a. Rohm & Haas Amine Acrylic QR 765M

Formulations using Rohm & Haas Amine Acrylic QR-765M epoxy curing agent with several different epoxy systems were evaluated. The main purpose for all the evaluation work carried out with these formulations was that the QR-76 with a PH of 10, was the only material we found in our evaluation that did not react with magnesium. All epoxy formulations were allowed to stand at least 1/2 hour after mixing before spraying.

(1) Texaco Chemicals Ethylene Glycol Monoethyl Ether

a.1 Henkel Gen Epoxy 370-H55

The first epoxy that we tried was Henkel Gen Epoxy 370-H55.

Formulation #15577-A

<u>Pigment Mix</u>	<u>Parts Based on 100 gms Rosin Solids</u>	
Gen Epoxy 370-H55 (Henkel) (55% Solids)	118.22	} Part A
Triton N-101 (Rohm & Haas)	1.33	
Atlas G-3300 (ICI Industries)	1.78	
Foamaster NS-1 (Diamond Shamrock)	1.11	
Nytal 300 (RT Vanderbilt)	16.00	
TiPure R-960 (E.I. DuPont)	25.00	
Zinc Phosphate 317 (Richard-Coulston)	15.00	
Natrosol 250 HR (Hercules)	0.33	
Deionized Water	88.89	
<u>Let Down</u>		
QR-765M (Rohm & Haas) (50% Solids)	70.00	} Part B
DMP-30 (Rohm & Haas)	8.11	
Proposal P (Union Carbide)	0.56	
ZZL-0822 (Union Carbide)	3.00	
Dow Corning II	0.78	

This was the first formulation that we developed to give a very good coating on magnesium, plus steel and aluminum. The problem with this formulation was that it was not sufficiently dried in 1 hour to be overcoated or to withstand ten MEK rubs. The formulation had to be dried overnight (16-18 hours) before it could be overcoated.

Another approach that we tried was to increase the pigment loading up from 16 to 30 weight percent (on total formulation) and also double the amount of catalyst (DMP-30) used in the above formulation. This new formulation (#15577-B) still would not dry to touch in one hour, nor would it resist 10 MEK rubs at one hour.

The 15577-B formulation test results are tabulated, Table 1.

a.2 Celanese Epoxy CMD 55-3520

This material is a water dispersion of an epoxy with a high equivalent weight per epoxy (solid epoxy) , which was said to be much faster drying than the Henkel's liquid epoxy. We found it was faster drying but still not sufficiently fast curing.

Formulation #15581-A

<u>Pigment Mix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
CMD 55-3520 (55% Solids)	149.44	} Part A
Foamaster NS-1 (Diamond Shamrock)	0.22	
QR-765M (50%solids) (R&H)	35.67	} Part B
Propasol-P (Union Carbide Propoxy Propanol)	15.00	
DMP-30 (Rohm & Haas)	0.44	
ZZL-0822 (Union Carbide)	1.44	
Foamaster NS-1	0.89	
TiPure R-900(DuPont)	33.33	
Nytal 400 (R.T. Vanderbilt)	16.67	
Zinc Phosphate 317 (Reichard -- Coulston)	15.00	
Triton N101 (Rohm & Haas)	0.78	} Part B
Atlas G-3300 (ICI Industries)	1.00	
Deionized Water	150.00	Let Down

This formulation was dry enough one hour after spray-up to be overcoated, but would not resist 10 MEK rubs. We tried modifying the formulation (#15581-A) by adding 10% (#15581-B) and 5% (#15581-C) of Celanese trimethylol propane triacrylate (TMPTA) to try to decrease the cure time. This did not help much because the modified formulations would not withstand 10 MEK rubs one hour after spraying, and as a matter-of-fact, would not withstand 25 MEK rubs after 7 days drying.

a.3 Shell Epon 828 Epoxy

Because of the problems we were having with the (high MW) Celanese epoxy not curing, even after 7 days drying (not MEK-resistant), we decided to try a new epoxy. The new epoxy examined at the suggestion of Rohm & Haas, was Shell Epon 826.

Formulation #15587

<u>Pigment Mix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
Epon 828 Epoxy (Shell Chemical)	63.11	} Part A
Foamaster NS-1 (Diamond Shamrock)	0.22 Preemulsify	
Cap Cure 65 (Diamond Shamrock epoxy emulsifier)	4.00	
D.I. Water	51.67	
TiPure R-900 (DuPont)	27.78	} Part B
QR-765M	73.78	
Propasol P	15.78	
DMP-30	0.56	
DC-11	0.78	
ZZL-0822	3.11	
Foamaster NS-1	2.22	
TiPure R-900	38.89	
Nytal 300	16.67	
Busan 11-M	10.00	
Triton N101	1.33	
Atlas G-3300	1.89	
<u>Let Down</u>		
Deionized Water	100.00	

This formulation was not tack-free, or resistant to 10 MEK rubs approximately one hour after spraying. However the coating was able to withstand 100 MEK rubs after 7 days drying. At this point it was decided that no further work would be done with the Rohm and Haas QR765M Amine Acrylic Systems, because none of the formulations were resistant to 10 MEK rubs at one hour after spraying up.

b. Dow Chemical Amine Acrylic/Epoxy Systems

This system was developed early in the project and is the system on which we spent the most time and effort to make the system meet the goals of the contract. The reason for this was that it was the system that initially met most of the goals, specifically:

- . Phosphoric acid compatibility
- . Overcoatability in one hour
- . Methyl ethyl ketone resistance upon drying
- . Good adhesion to steel and aluminum
- . Resistance to 48 hours of salt spray

b.1 Initial Effort

Formulation #14542

Pigment Premix

Parts Based on 100 gms
Resin Solids

Dow XD-7080.00 (50% solids)	106.44 gms	} Part A
Moly White 212 (Sherwin Williams)	10.00 gms	
Rutile TiO ₂ (2)	24.00 gms	
Talc - Nyltal 300 (R.T. Vanderbilt)	15.56 gms	
VM & P Naphtha (Reagent)	17.00 gms	
Disperbyk (Millinckrodt)	0.44 gms	
Deionized Water	159.67 gms	

Epoxy Premix

DER 331 Epoxy (Dow Chemical)	39.56 gms	} Part B
DER 732 Epoxy (Dow Chemical)	7.23 gms	
Dowanol DPM (Dow Chemical)	8.44 gms	
Deionized Water	458.22 (1) gms	

Acid Premix

Deionized Water	50.56 gms	} Part C
Phosphoric Acid (85%)	20.00 gms	

Mixing Procedure:

Part I of the starting formulation was mixed together by means of a small Waring blender. Water was added in two parts (first add 14.37% water) because if part A premix is not viscous enough it becomes very difficult to mix in the part B premix. The required amount of part A mixture is then transferred from the Waring blender into a suitable container and the required amount of premixed part B is added. Both parts are then mixed until a uniform mix is obtained. At this time, the remainder of the water is added, mixed in and total mixture allowed to stand approximately half hour to allow for some reaction between epoxy and curing agent. Part C premix is then mixed in.

- (1) Added after part 1 and 2 are mixed.
(2) American Cyanamid Unithane OR 572

This formulation was sprayed into clean 6 x 4 steel and aluminum panels using a Jeffco stainless steel pressure gun. Dry films from spray application were much more uniform than films that were doctored on with a glass rod, which was the application method first tried. The major problem found with this formulation was adhesion of dried film to both metal substrates. Films could be easily removed with both fingernail and 3M scotch tape. Our first direction for solving this problem was to come up with a better solvent system to give us better film fusion to the metal substrate.

b.2 Solvent Study

We modified the above starting formulation (#14542) to see if we could get better film fusion by first adding higher levels of solvents to the formulation; then using different solvents. The highest level of solvent that the system would take was twice as much Dowanol DMP glycol ether, and twice as much VM&P Naphtha (coagulation). We tried increasing the Dowanol DPM level, in the premixed formulation, up to five times the starting level by adding more Dowanol, but at this level the formulation coagulated. We then tried using Texaco Chemicals Jeffersol DB (diethylene glycol monobutyl ether) in place of Dowanol DPM in the original formulation at the same level, and twice as much. The only initial benefit we achieved from the higher level of solvent was a glossy finish, but the film was still fingernail removable after one day drying. Because of the incompatibility between water and VM&P Naphtha, we decided to reduce the Naphtha in formulation #14542 by two thirds. We tried this modification with both the Dowanol DPM and Jeffersol DB in the part B premix. The Jeffersol DB we tried in the quantity the formulation called for and also twice as much. The Dowanol DPM was evaluated at 2X original, and film was again found to be fingernail removable at one day aging. It was also observed, that on standing over the weekend the water in part A pigment premix of the modified (1/2 VM&P Naphtha) formulation separated out of the premix - which was likely due to the presence of the naphtha.

To the above three premixed modified formulations - formulation #14542 with the 1/3 level of naphtha, and (1) twice the part 2 level of Dowanol DPM, (2) Jeffersol DB in place of Dowanol in part 2, epoxy premix, and (3) two times the level of Dowanol in Part B, epoxy premix of formulation #14542. We made two other modifications; first we added 5%, on total weight of formulation, of isopropyl alcohol (all three experiments above), and to another set of samples we added 5% ethylene glycol monoethyl ether (Cello-solve). Modification "2" above gave the best results with addition of both isopropanol and cellosolve. Because of the above mentioned problem with formulations (separation of water from Part A, probably due to naphtha) it was apparent that other modifications would have to be made. Another modification made to the formulation at this time was to replace VM&P Naptha in part A pigment premix with Jeffersol EE Cellosolve (which is much more compatible with water) and to use twice as much solvent in part B, epoxy premix. Solvent being used at this time was Dowanol DPM, Jeffersol DB, and Jeffersol EE. One improvement with the Jeffersol EE modification to part A to the formulation (#14549) was that on standing for five days no noticeable separation was observed.

Films obtained from these naphtha-free formulations, when allowed to stand for one week, were much more resistant to fingernail removal than when tested after one day, and were also resistant to tetrahydrofuran (THF) after five days (adequately crosslinked).

Formulation #14549

<u>Pigment Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
Dow XD7080.00 (50% solids)	106.44 gms	} Part A
Moly White 212	10.00 gms	
Unithane OR 572	24.00 gms	
Nyral 300 - Talc	15.56 gms	
Jeffersol EE	17.00 gms	
Disperbyk	0.44 gms	
Deionized Water	159.7 gms	

Formulation #14549-Continued

<u>Epoxy Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
DER 331 Epoxy	39.56 gms	} Part B
DER 732 Epoxy	7.22 gms	
Solvent (1)	16.89 gms	
Deionized Water (2)	458.22 gms	

<u>Acid Premix</u>		
Phosphoric Acid (85%)	20.00 gms	} Part C
Deionized Water	50.56 gms	

Although formulation #14549 did show marked improvement over formulation #14542 in the area of adhesion it still was not good enough, so further modifications were carried out on it.

b.3 Dow Chemicals Recommended Starting Formulation

One thing we decided to try at this point, before trying any further modifications of our present formulation, was to make up a starting formulation recommended by Dow Chemical to check what the final film was like.

Formulation #14544

<u>Pigment Premix</u>	<u>lbs/100 gallons</u>	
Epoxy Curing Agent XD-7080.00	250	} Part A
Unithane OR 572	292.5	
Moly White 212 ⁽³⁾	7.5	
VM&P Naphtha	40.0	
Grind in a Waring Blendor than add under agitation:		
20% Phosphoric Acid	25.0	
Deionized Water	375.0	

(1) Dowanol DPM Jeffersol DB and EE

(2) Added after Part A and B are mixed (Part A was mixed in a Waring Blendor)

(3) Used in place of the recommended Moly White 101

Formulation #14544-Continued

<u>Epoxy Premix</u>	<u>lbs/100 gallons</u>	
DER 331 Epoxy Resin	93.0	} Part B
DER 732 Epoxy Resin	17.0	
Dowanol DPM Glycol Ether	20.0	

Final film properties were very good 24 hours after application - the coating was resistant to tape and fingernail removal tests and also 48 hours salt spray. The drawback to this formulation, however, was that it was much too thick for spray application, and when we tried letting it down with water we started running into problems. Another situation which we thought was a problem at the time, was the quantity of phosphoric acid in the formulation - which was only about one fourth the amount of acid that was being used in the #117 wash primer (control). When we tried increasing the level of phosphoric acid up to the #117 wash primer level, we found that it could not be done. The most phosphoric acid that we could get in was only about one half of the #117 level. At that time with the great emphasis we were placing on presence of phosphoric acid in our formulation, we decided not to do any more work with this formulation and to go back to our own system.

b.4 Acid Study on Amine Acrylic/Epoxy System

. Phosphoric Acid

Another possibility we considered that could be the cause of our adhesion problem was the presence of free phosphoric acid in our system after the initial reaction with the metal surface. This free acid, we thought, could, and may be would, react with the amine acrylic curing agent (XD-7080.00) thus resulting in a longer cure time, or even the situation where the system is never properly cured.

Following this approach, and the fact that we were told by Fort Belvoir that the presence of phosphoric acid was not that critical, we decided to check what kind of effect different levels of acid would have on our formulation. We also tried substituting phenyl phosphoric acid in place of phosphoric acid to see if it would be any better. Different levels of phosphoric acid tried (using 1.80 gms as the base) were 1/4 and 1/2 of the original. A formulation using no phosphoric acid was contemplated, but we were told by Dow Chemical that the phosphoric acid was needed to displace harmful chloride ions present in the XD7080.00 amine acrylic and also to prevent flash rusting.

The first modification we tried was the one with 1/2 the phosphoric acid level (#14904-A). Next, we tried a formulation with 1/2 acid and twice the Jeffersol DB as in #14549. This new formulation (#14904-B), with the smaller amount of acid and larger amount of solvent, gave better adhesion results than #14904-A. Another problem we observed in using formulation #14904-A and B, was that it was not viscous enough and would run excessively during spraying. Hence, the next modification we tried was to decrease both the water and phosphoric acid level in #14904-B by one half.

. Amine Acrylic/Epoxy

Formulation #14912

<u>Pigment Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
Dow XD7080.00 (50% Solids)	106.44 gms	} Part A
Corrosion Resistant Pigment ⁽¹⁾	10.00 gms	
Unithane OR 572	24.00 gms	
Nytal 300 - Talc	15.56 gms	
Jeffersol EE	17.00 gms	
Disperbyk	0.44 gms	
Deionized Water	139.67 gms	

(1) Sherwin Williams Moly White 212 and Buckman Laboratories
Busan 11-MI

Formulation #14912 -Continued

<u>Epoxy Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
Dow DER 331 Epoxy	39.56 gms	} Part B
Dow DER 732 Epoxy	7.22 gms	
Jeffersol DB (1)	33.78 gms	
 <u>Acid Premix</u>		
Deionized Water (2)	149.33 gms	} Part C
Phosphoric Acid (85%)	5.00 gms	
Deionized Water	50.56 gms	

This formulation gave a much better sprayable system plus better film properties with fingernail and tape adhesion, 48 hours salt spray resistance and general appearance, hence was the best formulation we had at that time.

At this point when we were fairly satisfied with our formulation, we started screening the different non-toxic corrosion-resistant pigments we had available; the results of which will be discussed later.

. Phenyl Phosphoric Acid

Formulation #14910

<u>Pigment Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
Dow XD7080.00	106.44 gms	} Part A
Corrosion Resistant Pigment (3)	10.00 gms	
Unithane OR 572	24.00 gms	
Nytal 300 Talc	15.56 gms	
Jeffersol EE	17.00 gms	
Disperbyk	0.44 gms	
Deionized Water	159.67 gms	

- (1) Texaco Chemicals Diethylene Glycol Monobutyl Ether
(2) Added after Part A and B are mixed
(3) Moly White 212 or Busan 11-M1

Formulation #14910 - Continued

<u>Epoxy Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
Dow DER 331 Epoxy	39.56 gms	} Part B
Dow DER 732 Epoxy	7.22 gms	
Jeffersol DB	33.78 gms	
Deionized Water ⁽¹⁾	458.22 gms	
 <u>Acid Premix</u>		
Phenyl Phosphoric Acid	20.00 gms	} Part C
Deionized Water	50.56 gms	

Phenyl phosphoric acid was evaluated in our amine acrylic/epoxy formulation as a substitute for phosphoric acid. Coatings from these formulations did not show any great improvement over the phosphoric acid formulation. Also other tests carried out to give an idea of the rate of reaction between the two acids with the steel surface clearly showed that the phosphoric acid reacted much faster. Further work with phenyl phosphoric acid was discontinued on the grounds that it did not give any better results than the phosphoric acid, and its slower reaction rate with the metal substrate would increase the chances of its reacting with the amine acrylic curing agent.

b.5 Further Improvements

The next undertaking we embarked upon with our amine acrylic/epoxy formulation was to try and reduce it from a three part system, down to a two part system. This was accomplished by incorporating part A pigment premix with the part C acid premix. Several pigments were also evaluated.

(1) Added after part A and B was mixed

Formulation #14920

<u>Pigment Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>		
Dow XD7080.00	106.44 gms	} Pigment Grind	} Part A
Corrosion Inhibiting Pigments (1)	10.00 gms		
Unithane OR572	24.00 gms		
Nytal 300 Talc	15.56 gms		
Jeffersol EE	17.00 gms		
Disperbyk	0.44 gms		
Deionized Water	159.67 gms		
Phosphoric Acid (7.65%)	55.55 gms		
<u>Epoxy Premix</u>			
Dow DER 331 Epoxy	39.56 gms	} Part B	
Dow DER 732 Epoxy	7.22 gms		
Jeffersol DB	33.78 gms		
<u>Let Down</u>			
Deionized Water	244.44 gms	>Part C	

By this time our pigment screening had been largely completed and the pigments (combinations) being used in this formulation were the ones with which we decided to carry out further screening. (See Section III-8.c) . The Part A premix was made up and stored at RT for 24 hours before mixing with Part B premix, also another batch using the above mentioned pigments was made up for long term aging. Film properties from these formulations were not as good as those obtained from formulation #14912 (three part system). The most noticable problem was the difficulty of mixing part A and B together. This resulted from the fact that on adding the phosphoric acid premix to the pigment grind, we got a very noticable decrease in viscosity, which might have left it not viscous enough for easy mixing with the Part B epoxy premix. First, we tried adding a thickening agent

(1) Sherwin Williams Moly White MZA, Buckman Labs Butrol 22 and 1:1 mixture of Moly White 212 and Busan 11-M1

(Rohm & Haas E845) to the acidified Part A premix, but this did not help very much. Our next approach was to reduce the water used in the part A premix by 63% (formulation #14931). Film properties from these formulations were much better than the ones obtained from formulation #14920.

In the case of the long term RT storage of part A premixes of formulation #14931, the one with Shwewin Williams Moly White MZA gave the best results, i.e. minimal pigment settling out and increase in viscosity.

b.6 Catalyst Study

At this point, a sample of our amine acrylic/epoxy formulation #14944 was sent to Fort Belvoir for evaluation. After evaluating the formulation, their main source of concern was the length of time it took the formulation to become tack-free and resistant to MEK. The first step taken to solve this problem was the addition of known and recommended epoxy curing promoters.

Additives screened

- . Dow Chemical - Bisphenol A
- . Texaco Chemical - Accelerator 399
- . Rohm & Haas - DMP-30
- . Celanese - Trimethylol propane triacrylate (TMPTA)

General Formulation #14945

<u>Pigment Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
Dow XD7080.00	106.44 gms	} Part A
Moly White MZA	10.00 gms	
Nytal 300 - Talc	16.00 gms	
Unithane OR572	25.00 gms	
Jeffersol EE	17.00 gms	
Disperbyk	0.56 gms	
Deionized Water	65.00 gms	
Foamaster NS-1 (Diamond Shamrock)	1.22 gms	
Epoxy Curing Promoter - Phosphoric Acid (10% premix)	40.00 gms	

General Formulation #14945-Continued

<u>Epoxy Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>
Epoxy / Solvent	79.78 gms > Part B
<u>Let Down</u>	
Deionized Water	250.00 gms

In our initial screening we added Bisphenol-A at a level of 2.5% (based on weight of XD7080.00). Accelerator 399 and DMP-30 at a level of 2.0% and a mixture of Bisphenol-A and Accelerator 399 at the above mentioned levels. These four formulations were made up and sprayed onto steel panels, but were all tacky and removable by MEK after one hour drying.

With the results we obtained from the above mentioned screening, and from other results, we decided to try a formulation with 5% Bisphenol-A in the part A premix and to replace the Dow DER 731 epoxy with Celanese Trimethylol Propane Triacrylate (TMPTA) in the part B premix. We also replaced the high boiling Jeffersol DB with a mixture of lower boiling solvents.

Formulation #15555-A

<u>Pigment Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
Dow XD 7080.00	106.44 gms	} Part A
Dow Bisphenol-A	5.33 gms	
Jeffersol EE > Premix	17.00 gms	
Foamaster NS-1	1.22 gms	
Disperbyk	0.56 gms	
Mo'ly White MZA	10.00 gms	
Nytal 300	16.00 gms	
Unithane OR-572	25.00 gms	
Deionized Water	65.00 gms	> Premix
Phosphoric Acid (10%)	40.00 gms	

Formulation #15555-A -Continued

<u>Epoxy Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
Dow DER 331 Epoxy	39.55 gms	} Part B
TMPTA	7.22 gms	
Jeffersol EE	1.55 gms	
Dowanol DPM	0.55 gms	
<u>Let Down</u>		
Deionized Water	250.00 gms.	

This formulation gave a coating that was tack-free in about two hours, but with these modifications we started getting problems with the part A premix, experiencing noticable increase in viscosity on standing and poor adhesion on some of our sprayed-up panels. The adhesion problem was solved by employing a more rigorous cleaning method - using Scotch Brite pad and mixture of VM&P and toluene then wiping with the same solvent mixture and cheesecloth.

After a few more modifications, we devised formulation #15565 which we sent to Fort Belvoir for evaluation.

Formulation # 15565

		Parts Based On 100 gms Resin Solids		
<u>Pigment Premix</u>				
Dow XD7080.00 (49% Solid)		107.67		
Dow Bisphenol A	} Premix	4.00		
Jeffersol EE		17.00		
Foamaster NS-1 (1)		1.22	} Grind at High Speed	
(Diamond Shamrock)				
Millinckrodt Disperbyk (2)		0.56		
Moly White MZA		10.00		
(Sherwin Williams)				
Nytal 300		16.00		
Rutile TiO ₂ (American Cyanamid)		25.00		
				} Part A Grind
D. I. Water	} Premix	65.00		
Phosphoric Acid (10%)		40.00	} Add at Lower Speed	
Dow DER331 Epoxy		40.00		
Trimethylol Propane Triacrylate		7.33	} Part B	
(Celanese)				
Jeffersol EE		16.67		
Dowanol DPM (3)		5.56		
D. I. Water		150.00	} Let Down	

-
- (1) Antifoam Agent
 - (2) Anionic Wetting and Suspending Agent
 - (3) Dow Chemical Dipropylene Glycol Methyl Ether

In storage, the part A premix of formulation #15565 eventually increased in viscosity to the point where it would not flow out of container, so the formulation was not evaluated by Fort Belvoir. At this point, because of the problems with the increase in viscosity, the fact that it could not be used on magnesium, and the length of time for it to develop MEK resistance, we decided to discontinue work with the XD-7080.00 system.

b.7 Dow XD 7080.01

During the time when we were trying to come up with a one hour tack-free formulation, we received what was recommended to be a more reactive form of the amine acrylic curing agent (XD-7080.01). The difference in identification of this product to the one we were using was the last two digits. Formulations tried were similar to those tried with the XD-7080.00, but none were significantly better and the gelling problem was always worse in the case of XD-7080.01.

The latest development with these amine acrylic curing agents is that Dow Chemical is planning to discontinue selling them, at least in a "primer" form. This is due to the fact that they contain ethylene glycol monoethyl ether which they consider to be harmful in spraying applications.

c. Celanese Acrylic/Epoxy Formulations

This was a system we decided to evaluate because of its fast drying (tack-free) time as recommended, this system did produce coatings that were dry to the touch in less than one hour.

Formulation #14934

	Parts Based on 100 gms Resin Solids	
<u>Pigment Premix</u>		
Celanese CMD 979 Acrylic (70% solid)	111.78 gms	} Part A
Moly-White MZA	10.00 gms	
Nytal 300	15.56 gms	
Rutile TiO ₂	24.00 gms	
Barium sulphate	12.00 gms	
Drew L-475 ⁽¹⁾	1.44 gms	
TMA (19.35% in water) ⁽²⁾	24.00 gms	
Deionized Water	111.11 gms	
Disperbyk	0.44 gms	
<u>Epoxy Premix</u>		
Epi-Rez 510 Epoxy	15.22 gms	} Part B
Epi-Rez 5018 Epoxy	6.56 gms	
E845 ⁽³⁾	27.78 gms	
<u>Let Down</u>		
Deionized Water	166.67	

Mixing Procedure:

Materials in part A were weighed out into a 50 cubic centimeter plastic beaker, mixed together with a spatula, then transferred to a small Waring Blendor for final mixing. The premix part A is then added to the required weight of a part B premix and this is mixed until a uniform mixture is obtained. Formulation is then let down with water and allowed to stand for approximately 1/2 hour before spraying onto steel and aluminum panels. Coatings were very grainy in appearance, but were dried enough to be overcoated in approximately one hour without any noticable problems.

-
- (1) Drew Chemical Defoamer
 - (2) Air Products Trimethylamine
 - (3) Rohm and Haas Experimental Thickener

The pigmented part A premix and the final formulation were checked with a Hegman apparatus and by doctor coating on a glass slide and in both cases no grains were observed.

Apart from the grains, other film properties - drying time, adhesion, overcoatability and salt spray resistance were very good. On discussing the grain problem with a technical representative from Celanese, we were told that we would be better off using the less viscous version of this product (CMD 9790 - 42% solids) which would be easier to work with. This new product was also supplied pre-neutralized with the amine. After a couple of modifications we came up with the following formulation which we sent to Fort Belvoir for Evaluation.

Celanese Acrylic/Epoxy

Formulation #15566

<u>Pigment Premix</u>	Parts Based on 100 gms Resin Solids	
CMD 9790 (42% solids) (Celanese)	185.22 gms	} Part A
Busperse 47 (Buckman Labs)	0.56 gms	
Drew L475 (Drew)	1.44 gms	
Triton X100 (Rohm & Haas)	1.67 gms	
Butrol 22 (Buckman Laboratories)	10.00 gms	
Nytal 300 (R.T. Vanderbilt)	16.00 gms	
Unithane OR-572 (American Cyanamid)	25.00 gms	
Barium Sulfate	11.00 gms	
Deionized Water	13.33 gms	} Part B
<u>Epoxy Premix</u>		
EpiRez 510 Epoxy (Celanese)	22.44 gms	
Jeffersol EE (Texaco)	7.33 gms	
<u>Let Down</u>		
Deionized Water	130.00 gms	

The main drawback with these Celanese systems was that even after seven days drying the coatings never became sufficiently resistant to MEK (rub test), and this was the bases on which it was rejected by Fort Belvoir.

d. Morton Mor-Flo Acrylic/Mor-Cure Epoxy

This was another epoxy system that we looked at when we were trying to come up with an alternate epoxy system for the Dow XD-7080 system.

Formulation #14923

<u>Pigment Premix</u>	<u>Parts Based on 100 gms Resin Solid</u>	
Mor Flo 40 ⁽¹⁾ (40% solids)	181.33 gms	} Part A
Jeffersol EE	17.00 gms	
Basan 11-M1	10.00 gms	
Nyral 300	15.56 gms	
Rutile TiO ₂	24.00 gms	
Mallinckrodt Disperbyk	0.44 gms	
Deionized Water	152.67 gms	
<u>Epoxy Premix</u>		
Mor-Cure 75 Epoxy (75% active)	36.56 gms	} Part B
Jeffersol DB	33.78 gms	
<u>Let Down</u>		
Deionized Water	178.00	

The above formulation was mixed and allowed to stand approximately 1/2 hour before spraying onto steel and aluminum panels. Appearance of film on both the sprayed-up steel and aluminum panels was very good. Coatings were allowed to dry approximately one hour then overcoated with MIL P-52192 red epoxy primer. This epoxy primer/tie coat formulation dissolved the Mor-Flo/Mor-Cure film after being in contact with it for a short time. Coating only became overcoatable with this epoxy primer after drying overnight.

On speaking with a technical representative from Morton Chemicals we were told that this system could not be formulated to give a coating that could be overcoatable or MEK resistant in one hour. With that information and the results we were observing, we decided to terminate all work on this system.

(1) Believed to be an acrylic amine

e. W. R. Grace Urethane/Epoxy System

This was a system that was evaluated because of its compatibility with phosphoric acid.

<u>Formulation #14930</u>	
<u>Pigment Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>
WB4000 ⁽¹⁾ (35% solid)	66.00 gms
Moly-White MZA	10.00 gms
Rutile TiO ₂	24.00 gms
Nytal 300 Talc	15.56 gms
Jeffersol EE	17.00 gms
Deionized Water	86.67 gms
E845 (20% solid)	27.78 gms
Mallinckrodt Disperbyk	0.44 gms
Phosphoric Acid (7.65%)	55.56 gms
<u>Epoxy Premix</u>	
Dow DER 331 Epoxy	28.78 gms
Dow DER 732 Epoxy	5.22 gms
Jeffersol DB	24.67 gms

} Part A

} Part B

Above formulation with and without the phosphoric acid did not give a continuous film on metal. Also, the coatings when tested after seven days drying were still soft and fingernail removable. With these initial results, we decided not to do any further work with this system.

(1) Waterborne Urethane Amine Prepolymer, W. R. Grace "Hypol"

f. Other Epoxy Systems

Another epoxy system looked at briefly was Ciba Geigy Araldite GY9513 liquid epoxy/XU207 hardener. We had a great deal of trouble getting this system to mix well, so we stopped working on it.

Another system, also looked at, was Henkel Gen Epoxy 370-H55 aqueous epoxy emulsion/Gen Amid 5701-H65 aqueous amidoamine. This system did produce a good looking coating, but the coating took much too long to become tack-free and MEK-resistant.

g. Discussion/Summary of Results From Epoxy Systems

The epoxy systems cured with Rohm and Haas amine acrylic QR-765M were the only systems that gave very good coatings on magnesium. Adhesion on steel, aluminum and magnesium was also good on all these substrates. The problems with these QR-765M systems were in the area of one hour MEK-resistance, overcoatability in one hour and tack-free time which was greater than one hour for all the systems with the exception of the one using the high molecular weight Celanese epoxy CMD 55-3520. The system using the Celanese epoxy was overcoatable and tack-free in one hour, but was not MEK-resistant, even after seven days drying.

The Dow amine acrylic (XD-7080)/epoxy system also gave films that had good adhesion to steel and aluminum, were resistant to 48 hours salt spray, and were overcoatable in one hour. The main problem with this system was the time it took to become tack-free and MEK-resistant. Efforts taken to reduce tack-free time down to one hour resulted in other problems such as an unstable part A premix. Added to the above mentioned problems was that this epoxy system would not be able to coat magnesium. Finally we were told by Dow Chemicals that they were going to discontinue sale of their XD7080 amine acrylic, because it contained solvents they considered to be harmful in spraying application.

Coatings formulated with Celanese acrylic (CMD 979 & 9790)/ Epi-
Rez Epoxy systems gave films with very good properties, but again the
problem was the length of time the coating took to become MEK-resistant.

The Morton Mor-Flo Acrylic/Mor Cure epoxy and Henkel Gen Amid 5701-
H65/Gen epoxy 370-H55 systems gave coatings that were not overcoatable
in one hour and the W. R. Grace Urethane (Hypol WB4000)/ epoxy system was
not MEK-resistant even after seven days drying.

The epoxy formulation test results are summarized, Table 1, (pg. 69).

4. Acrylic Formulations

a. Polyvinyl Chemical NeoCryl A622 Acrylic Emulsion

This was the acrylic system that gave the best results in most of
the areas tested, such as:

- . fast drying time to the touch,
- . overcoatable in less than one hour,
- . good adhesion (tape-test) to steel and aluminum,
- . good salt spray resistance .

Formulation #14937-A

<u>Pigment Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
NeoCryl A622	184.33 gms	} >Part A
Tamol SF-1 ⁽¹⁾ Rohm & Haas	6.00 gms	
Triton CF-10 Rohm & Haas	2.00 gms	
Foamaster NDW - Diamond Shamrock	1.22 gms	
Nytal 300	16.00 gms	
Unithane OR-572	24.00 gms	
Halox SW-111 (Halox Pigments)	10.00 gms	
<u>Let Down</u>		
NeoCryl A622	81.33 gms	} Part B
Deionized Water	166.67 gms	
E-845 (20% solid) Rohm & Haas	25.00 gms	

(1) Rohm & Haas pigment dispersant

Formulation #14937-A Continued

<u>Premix Added to Above</u>		<u>Parts Based on 100 gms Resin Solids</u>
Epotuf 38-690 ⁽¹⁾	21.44 gms	} Part C
NH ₄ OH (conc.)	2.67 gms	

The above formulation was also repeated (#14937-B) with Richard Coulston 317 zinc phosphate in place of the Halox SW-111. Both formulations were the first (acrylic) to show very good resistance to salt spray exposure as was claimed by its manufacturer. The drawback to this system is that it never becomes MEK rub-resistant, although it can be overcoated with solvent-borne primers in less than one hour. This MEK rub resistance was a problem which we were not going to be able to overcome, so we did not do anymore work with this system.

Test results on formulation #14937 are also summarized, Table 2.

b. Polyvinyl Chemical NeoCryl A623 Acrylic Copolymer

This was recommended by Polyvinyl as an (acrylic) latex that would be able to resist MEK rubs.

<u>Formulation #15583</u>	
<u>Pigment Premix</u>	<u>Parts Based on 100 gms Resins Solids</u>
Halox SW III (Halox Pigments)	15.00
Nyral 400 (RT Vanderbilt)	16.67
TiPure R-960 (DuPont)	33.33
Tamol 165 (Rohm & Haas)	7.22
Triton CF-10 (Rohm & Haas)	0.89
Foamaster NDW (Diamond Shamrock)	0.22
D.I. Water	44.44

(1) Reichold Chemicals epoxy ester resin solution

Formulation #15583- Continued

<u>Let Down</u>	<u>Parts Based on 100 gms Resins Solids</u>	
NeoCryl A623 (35% Solids)	285.67	} Part B
Foamaster NDW	1.11	
DC-14 (Dow Corning)	0.56	
Jeffersol EB ⁽¹⁾ (Texaco Chemical)	7.89	
Jeffersol DE ⁽²⁾ (Texaco Chemical)	2.22	
Ammonium Hydroxide (Conc)	1.22	
Deionized Water	55.56	

This formulation when sprayed on steel and aluminum panels was dry to the touch in less than one hour so that it could be overcoated with a solvent-borne primer (MIL P-52192). As recommended, the coating after one hour drying was resistant to greater than 50 MEK rubs and 50 cellosolve rubs. The drawback to this coating was that its' adhesion (tape test) to aluminum was poor and was marginal in adhesion to steel. We tried modifying this formulation (#15585) by adding 10% Polyvinyl Chemical NeoCryl A622, but this did not improve the adhesion.

c. National Starch Styrene Acrylic Latexes

c.1 #78-3936 Hydroxyl Functional Styrene Acrylic

c.2 #78-3953 Carboxylic Functional Styrene Acrylic

These were the acrylic latexes that we first evaluated very early in the program because they were compatible with phosphoric acid.

The first formulations to give a reasonably good sprayed-up coating was:

- (1) Ethylene glycol monobutyl ether
- (2) Diethylene glycol monoethyl ether

Formulation #14543

<u>Pigment Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
Acrylic Latex ⁽¹⁾ (50% solids)	200.00 gms	} Part A
Moly White 212	10.00 gms	
Unithane OR-572	24.00 gms	
Nytal 300 Talc	15.56 gms	
Jeffersol DB	8.89 gms	
Deionized Water	571.11 gms	
 <u>Acid Premix</u>		
Phosphoric Acid (7.65%)	222.22 gms	> Part B

Although this was the best sprayed-up formulation at the time, we were still having running and adhesion problems with it. Formulation was also repeated (#14901) with the carboxylic functional latex (78-3953) with the same results.

The adhesion problems were due to not enough solvent in the formulation and the running problem was caused by the fact that the formulation was not viscous enough. So the first modification we made to the above formulation was to increase the solvent and add thickener to it. Thickeners evaluated were Hercules Klucel H and Natrosol 250 MHR at a level of 0.25% of total formulation and Rohm & Haas experimental thickener E-845 at a level of 0.45%.

Thickeners were first evaluated in both latexes (#78-3936 hydroxylic and #78-3953 carboxylic functional) individually, and the results obtained from the formulations with both latexes containing Klucel H and E-845 was encouraging enough for us to try them again at higher levels and in combination. The best results were obtained from the formulations with both thickeners.

(1) Hydroxyl functional acrylic (#78-3936)

At this point, we were satisfied enough with the formulation to start evaluating most of the non-toxic corrosion-resistant pigments we had in house.

General Formulation #14913

<u>Pigment Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
Acrylic Latex (#78-3936 or 78-3953)	200.00 gms	} Part A
Corrosion-Resistant Pigment ⁽¹⁾	10.00 gms	
Unithane OR-572	24.00	
Natal 300 Talc	15.56 gms	
Jeffersol DB	17.78 gms	
Deionized Water	571.11 gms	
Klucel H	2.67 gms	
E-845 (20% solids)	37.56 gms	
Disperbyk	0.44 gms	

Acid Premix

Phosphoric Acid (7.65%)	222.22 gms	> Part B
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(The pigment results are discussed in Section 8c).

The above formulation was also made up with no phosphoric acid and no corrosion-resistant pigment. All the formulations were made up and sprayed onto clean steel and aluminum panels and allowed to dry one hour before overcoating with one of the following primers/tie coats: MIL P-7962C (yellow cellulose nitrate), MIL P-52192 (red epoxy), TTP-664 and Fort Belvoir experimental latex 34-20-100. None of the above mentioned primers affected our wash primer coatings, which were then allowed to dry at least one week before testing for adhesion and salt spray resistance. Before panels were exposed in the salt spray chamber, their backs and edges were coated with Ameron Amercoat 83 epoxy primer.

(1) Moly White 212, Busan 11-M1, Halox BW 191 & ZX 111 and NalZin SC-1

Formulations with both latexes and no phosphoric acid flash rusted slightly and their adhesion, especially on aluminum, was not as good as the systems with phosphoric acid before and after salt spray. None of the formulations from both latexes gave particularly encouraging salt spray exposure results in areas where they were not overcoated. They all blistered, rusted and lost adhesion. In the areas where they were overcoated, their resistance to salt spray exposure was much better and only when overcoated with MIL P-7962C did they seem to loose adhesion.

Another problem with these formulations was that they were not cross-linked (soluble in THF) . Next, we tried adding crosslinking agents to the formulations to see if we could make them MEK-resistant and to improve their salt spray resistance. The first crosslinking agent tried was a DuPont Titanate (Tyzor AA), which was evaluated at a level of 5 parts per 100 parts acrylic solids. This was added in the form of a solution (containing 10% Tyzor, 20% glacial acetic acid and 70% deionized water). After a few modifications we ended up with the following formulation:

Formulation #14912-C

<u>Pigment Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
Latex (78-3936) (50% solids)	200.00 gms	} Part A
Moly White 212	10.00 gms	
Unithane OR 572	24.00 gms	
Nytal Talc 300	15.56 gms	
Jefferson DB	17.78 gms	
Deionized Water	526.11 gms	
E-845 (thickener) (20% solids)	37.56 gms	
Tyzor AA (10% solution)	50.00 gms	
Disperbyk	0.44 gms	
<u>Acid Premix</u>		
Phosphoric Acid (1.91%)	222.22 gms	> Part B

The phosphoric acid level had to be lowered to 1/4 the usual level with Tyzor (coagulation at higher levels). Also, initial work with the Tyzor AA gave better results with the #78-3936 latex. After one week aging, the coating was resistant to tetrahydrofuran (THF), which indicated adequate crosslinking, but the salt spray resistance still was not good enough, and the Tyzor formulation, with both latexes, coagulated on standing.

The second titanate we tried was Kenrich Petro Chemicals KR-238D, at a level of 0.5% on total formulation. This was evaluated in both latexes, but the coatings never became THF-resistant, and the formulations also coagulated on standing.

With the problems we were having with the titanate formulations, we decided to try some different kind of crosslinker such as phenolics, but all of the phenolics tried caused the formulations to coagulate.

The last thing we tried, as a crosslinker for the latex, was the addition of a self-crosslinking latex from National Starch (#2813). This was evaluated as a 2:1 mixture with the hydroxylated styrene acrylic latex (78-3936).

Formulation #14925

<u>Pigment Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
Latex (78-3936) (50% solids)	133.33 gms	} Part A
Latex (2813) (45% solids)	73.33 gms	
Moly White MZA	10.00 gms	
Unithane OR-572	24.00 gms	
Nytal 300	15.57 gms	
Jeffersol DB	17.78 gms	
Deionized Water	277.78 gms	
E-845 Rohm & Haas (20% solids)	27.78 gms	
Foamaster NS-1	1.11 gms	
Disperbyk	0.44 gms	
<u>Acid Premix</u>		
Phosphoric Acid (7.65%)	222.22 gms	> Part B

The film obtained from the above formulation never became MEK rub-resistant, and salt spray results, also were not very good. By this time we were getting much better salt spray results from other acrylic systems, thus we decided to discontinue work on this sytem.

d. Rohm & Haas Rhoplex MV-23 Acrylic Emulsion

This acrylic emulsion was recommended to provide excellent resistance to salt fog, flash rusting, early rusting and high humidity without the use of high levels of corrosion-inhibiting pigments.

Formulation #14932

Parts Based on 100 gms
Resins Solids

Pigment Premix

Moly White MZA	10.00 gms	} Part A
Rutile TiO ₂	24.00 gms	
Nytal 300	15.56 gms	
Disperbyk	0.44 gms	
Deionized Water	16.67 gms	
Jeffersol DE	21.00 gms	
QR-681 M ⁽¹⁾ (35%)	9.33 gms	
Triton CF-10	1.11 gms	
Drew L-405	0.10 gms	

Let Down

Deionized Water	277.78 gms	} Part B
Rhoplex MV-23 (43% solid)	209.33 gms	
Texanol ⁽²⁾	2.22 gms	
Sodium Nitrite (13.8% in H ₂ O)	3.00 gms	
Drew L-475	1.22 gms	
E-845 (20% solid)	27.78 gms	
Aroplaz 1272 ⁽³⁾	9.10 gms	
Cobalt Naphthenate (6%)	0.04 gms	
Manganese Naphthenate (6%)	0.04 gms	} Premix
Zirconium Octoate (6%)	0.54 gms	

(1) Rohm & Haas experimental dispersant
(2) Eastman Chemicals ester alcohol

(3) Spencer Kellogg long-oil
linseed alkyd

Formulation #14932 experienced severe blistering after 48 hours salt spray exposure, and adhesion after salt spray exposure on both steel and aluminum was not good.

e. B.F. Goodrich Geon 450 x 20 Vinyl Chloride/Acrylic Latex

This was a system that was evaluated because it was compatible with phosphoric acid.

Formulation #14935

Parts Based on 100 gms
Resin Solids

Pigment Premix

Deionized Water	55.56 gms	} Part A
Ethylene Glycol	15.44 gms	
Tamol 850 (Rohm & Haas)	6.22 gms	
Moly White MCA	10.00 gms	
Nytal 300	15.56 gms	
TiO ₂	24.00 gms	
Triton x 100 (Rohm & Haas)	4.33 gms	
Drew L-405	0.10 gms	
E-845 (Rohm & Haas)	27.78 gms	
Disperbyk	0.44 gms	

Let Down

Geon 450 x 20 (54% solids)	185.22 gms	} Part B
Drew L-405	0.10 gms	
D.I. Water (1)	222.22 gms	

Phosphoric Acid (7.65%)	56.56 gms	> Part C
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Formulation #14935 was evaluated with and without the phosphoric acid, but in both cases the coatings offered little or no corrosion protection to the steel panels during the 48 hours salt spray exposure.

(1) Deionized water

f. B.F. Goodrich Carboset #514-H Carboxylated Acrylic Latex

In our attempt to devise a formulation that would be MEK-resistant we decided to evaluate this system because we knew that it could be crosslinked with zinc.

Formulation #15572

<u>Ingredient</u>		<u>Parts Based on 100 gms Resin Solids</u>
Carboset 514-H (40% solids)	} Premix	250.00 gms
D.I. Water		305.56 gms
Conc. Ammonium Hydroxide (28%)		5.56 gms
Zinc Oxide (7% solution) (1)		33.33 gms
Butrol 22	} Pigment Premix	10.00 gms
Nyral 300		16.00 gms
Titanium Dioxide		25.00 gms
D.I. Water		33.33 gms
Jeffersol EE (Texaco Chemical)		16.67 gms
Busperse 47		0.56 gms
Foamaster NS-1		1.11 gms

(1) 7% Zinc Solution:

Deionized Water	68.60	%
Ammonium Carbonate	16.00	
Ammonium Hydroxide (Conc. 28%)	8.40	
Zinc Oxide (NJ Zinc Kadox 15)	7.00	

Mixing Procedure:

The ammonium carbonate was dissolved in the water. Next the zinc oxide (Kadox 15) was added to the mixture and mixed well. The mixing was continued while the ammonium hydroxide is added until the solution becomes clear.

Unlike all the other acrylic binders evaluated, the Carboset 514-H produced a coating that was not dry in one hour after spray-up. Coating took about three hours to become dry to the touch, and after drying overnight (20 hours) it still could be removed with 10-15 MEK rubs. Coating did become MEK-resistant after drying for some time, however.

g. Discussion/Summary of Results From Acrylic Latex Systems

All the latex systems evaluated were dried hard enough within one hour to be handled and overcoated with the exception of B.F. Goodrich Carboset 514-H. The major problems with the acrylics evaluated were lack of resistance to MEK and/or THF rubs (with the exception of Polyvinyl Chemical NeoCryl A-623) and their resistance to salt spray exposure (with the exception of Polyvinyl Chemical NeoCryl A622).

The Polyvinyl Chemical NeoCryl A622 was the best acrylic latex evaluated. It produced a coating with the following advantages:

- . Fast drying time to the touch
- . Overcoatable in one hour by solvent-borne primers
- . Good adhesion to steel and aluminum (tape test)
- . Good resistance to 48 hours salt spray exposure
- . Good resistance to 18 hours water immersion at room temperature.

The problem with this binder is that it produces coatings that never become MEK-resistant.

The NeoCryl A623, although MEK-resistant one hour after spray-up, never develops good adhesion even when mixed with 10% NeoCryl A622 adhesion promotor.

The two styrene acrylic latexes from National Starch, #78-3936 and #78-3953, did not produce coatings that were resistant to 48 hours salt spray exposure or MEK rubs. All efforts to try to incorporate crosslinking agents into formulations with these binders did not produce useful results.

The Rohm & Haas Rhoplex MV-23 produced a coating at 0.5 mil thickness that blistered excessively during salt spray exposure. Its adhesion to steel and aluminum was also inadequate, both before and after salt spray exposure.

B.F. Goodrich Geon 450 x 20 produced coatings that offered little or no protection against salt spray exposure. Carbo-set 514H, when formulated with zinc as a crosslinking agent was too slow in drying.

5. Evaluating Coatings on Magnesium

The final coating system we selected should have, as one of its criteria, the ability to coat magnesium.

Formulations initially evaluated on this substrate were:

- . Dow, Amine- Acrylic/Epoxy #15565
- . Celanese, Acrylic/Epoxy #15566
- . Witco Aliphatic, Urethane #15570
- . Polyvinyl Chemical, Aliphatic Urethane #15576
- . Rohm and Haas, Amine Acrylic/Henkel Gen Epoxy #15577
- . Polyvinyl Chemical NeoCryl A623, #15583.

Of all the above mentioned formulations, the only one that gave a good coating on magnesium was #15577. All the other systems evaluated reacted so much with the magnesium, giving off hydrogen gas, that some ended up with films containing trapped bubbles or numerous holes. One of the main reasons for these results is the fact that magnesium is very sensitive to acidic and weakly alkaline water solutions. Magnesium was even found to react with deionized water if the surface is properly cleaned (removal of the oxide). Magnesium susceptibility to acidic and weakly alkaline conditions was substantiated by the fact that the only coating system that did not react with it was the one containing Rohm & Haas Amine Acrylic QR-765M (which has a pH of 10).

This amine acrylic was found to give good coatings on magnesium regardless of the epoxy. We could not come up with a formulation using this system that would become MEK rub-resistant in one hour, however.

Because of the success we were having in all other areas with the Witco Chemical Aliphatic Urethane Witcobond W-231 (anionic) we decided to see if we could get it to give good coatings on magnesium. Also, at the recommendation of the technical representative of Witco, we decided to evaluate Witcobond W-216 (cationic urethane) which they used on magnesium. Because of the success we were having with the Rohm & Haas QR-765-M pH10 system and the constant suggestion in the literature to the fact that magnesium is not sensitive to strongly alkaline conditions, i.e. pH above 10.6, we decided to raise the pH of the W-231 up to 10.6 with ammonia.

This adjustment did not stop the W-231 from reacting with the magnesium. The cationic urethane (W-216), both as received and with its pH raised, reacted with the magnesium.

Next we tried to devise a corrosion-inhibiting additive that would protect the magnesium from attack by our waterborne coating systems. Experiments were carried out with known corrosion inhibitors, in both the above mentioned urethanes and also water (because it was a major ingredient in all our formulations and it was also found to react with magnesium). Unfortunately, none of the additives tried really worked, (for results, see Tables 3, 4, 5, & 6). Even the additives that looked encouraging in the water experiments, did poorly when tried with the Witcobond W-231. We also tried a few mixtures of sodium silicate with other corrosion inhibitors in the Witcobond W-231. The mixtures that reacted only slightly with magnesium (high additive content) had no adhesion to the magnesium, and as one decreased the amount of additive, the extent of hydrogen generation increased.

The last thing we tried was to attempt to passivate the magnesium surface by first degreasing it, then applying a heavy coat of the following mixture for 10 minutes before rinsing off:

	<u>Parts</u>
Quram 220 (Emery Ammonium Silicate)	1
Poly-step B-22 ⁽¹⁾ (Stepan) 27% Active	3
Diammonium Phosphate (Reagent)	3
Deionized Water	93

The idea behind this action was that if the magnesium was passivated sufficiently, then it would not be as sensitive to the coating being applied over it. This also did not work, the magnesium panels when coated with a Witcobond W-231 formulation (#15586), still bubbled and the dried coating was peeled off readily.

6. Springborn Laboratories Cationic Latex

This work was undertaken with the objective of preparing a cross-linkable cationic unsaturated⁽²⁾ acrylic latex. Cationic latex should adhere well to metal and provide increased corrosion resistance. The residual cyclopentenyl unsaturation is, according to Alcolac, polymerizable with a Cobalt drying catalyst after the film is cast, but not readily polymerizable during the latex polymerization process. Rapid crosslinking after drying should render the acrylic fairly MEK rub-resistant.

Formulation #15578

		<u>Mixture Number</u>
Methylmethacrylate monomer (Rohm & Haas)	269.82 gms	} (2)
Butylacrylate (Rohm & Haas)	130.59 gms	
Dicyclopentenyl Methacrylate (Alcolac)	31.87 gms	
Siponic F-400 (Alcolac Detergent)	22.75 gms	
D.I. Water	167.90 gms	
Phosphoric Acid (85%) (to adjust emulsion to pH3)		

(1) Ammonium alkyl ether sulfate

(2) Cyclopentenyl groups

Formulation #15578-ContinuedMixture
Number

Potassium Persulfate	1.10 gms	} (1)
D.I. Water	168.35 "	
Sodium Erythorbate (0.32% in water) (Pfizer)	7.19 "	(3)
Sodium Erythorbate (0.32% in water) (Pfizer)	37.45	(4)

Polymerization was carried out in a 1-liter resin kettle fitted with half-moon agitator, a graduated dropping funnel with agitator, thermometer, condenser, nitrogen inlet (running through the condenser into the kettle) , and constant temperature water bath. Mixture #1 (potassium persulfate and water) was charged to the kettle. Nitrogen was then passed through system to displace all the air . This purging of the system with nitrogen was maintained throughout the polymerization. Mixture #2, with the exception of the phosphoric acid was mixed well to emulsify the mixture. After a good emulsion was obtained, the pH was adjusted to three with phosphoric acid (added dropwise until the desired pH was obtained). The emulsion was then added to the graduated dropping funnel and the initial volume recorded. Kettle contents were then heated to 50°C, before mixture #3 was added. After the addition of mixture #3 to kettle, the temperature of the kettle contents was raised to 60°C before we started adding the emulsion (#2), dropwise, at a rate that would allow it to be all in after 4 hours. Mixture #4 was added at a rate of 2.50 cc each 1/4 hour. After all the materials were all in (approximately 4 hrs.) the product was allowed to remain in the heated bath for an additional 3/4 hour. Then it was cooled and filtered. When we air-dried this material and tried dissolving it in both cold and boiling solvents (MEK & DMSO), we were unable to do so. (Similar results were obtained by adding the latex to solvent). This led us to believe that product was crosslinked during polymerization.

This problem can probably be overcome, but may be a project in itself.

7. Initial Development Work

a. Initial Binder Screening

Initial binder screening was carried out to determine compatibility with phosphoric acid. This was carried out by adding a diluted solution of phosphoric (14.17% phosphoric acid in water) to a 13.04% dispersion or solution of binder in water.

General Formulation #14502

<u>Polymer Premix</u>	<u>Parts Based on 100 gms Resin Solids</u>	
Polymer	100.00 gms	Part A
Deionized Water	666.67 gms	
<u>Acid Premix</u>		
Phosphoric Acid (85%)	20.00 gms	Part B
Deionized Water	100.00 gms	

Latexes were diluted to the required solids level shown above, as part A. Carboxylated drying oils were dissolved in water with amine or ammonia according to the manufacturer's instructions.

Compatibility was determined by whether or not the polymer premix coagulated when the phosphoric acid premix was added to it, (Table 7).

All the solutions and latexes that did not coagulate on addition of the diluted acid, were cast (doctored-on) on glass slides and Q-Panel steel, then checked for adhesion, (tape test and fingernail), appearance (clarity, flash rusting, general rusting) and thickness, (Table 8).

The panels that had good coatings from acid-compatible systems were placed in a one gallon jar with deionized water, pH adjusted to 6 with sodium hydroxide. These films were checked at 4 and 24 hours for adhesion (tape test) and appearance (rusting), (Tables 9 & 10).

The water immersion test was also carried out on the #117 wash primer.

Formulations, from acid-compatible systems, that caused the steel panel to flash rust or gave white chalky films were further evaluated after the addition of a potential flash rust inhibitor. National Starch's Hydroxyl functional (#78-3936) and Carboxyl functional (#78-3953) styrene acrylic latexes were used as screening resins, (Table 11) and inhibitors, that gave good results with these two latexes, were then tried on all other resins that were experiencing these problems, (Table 12). Quantity of inhibitor used was 0.3% on resin solids.

Sodium nitrite (NaNO_2), a widely used flash rusting inhibitor, did not seem to work in our two control latexes (#78-3936 and #78-3953). We thought the phosphoric acid in these systems was at fault, so we tried adding the NaNO_2 to just the resin and water, to check our assumption. As a control, we also cast films of just the resins and water, (Table 13).

Because of the excessive water sensitivity, we noted from the water immersion test with polyvinyl alcohol (DuPont-Elvanol 90-50 G, Tables-9 & 10), we tried adding different zirconium salts to a 10% solution of this polymer to try and promote crosslinking. We expected greater crosslinking of the PVA resin would alleviate the excessive swelling problem we had in the water immersion test. Zirconium salts used were Magnesium Elektron zirconium acetate, ammonium zirconium carbonate and zirconium oxynitrate.

None of these worked well. On adding the phosphoric acid solution to the polymer zirconium premix, only the formulations with the acetate did not coagulate, and this formulation, when cast on steel, flash rusted in addition to not giving any better water immersion results.

The results obtained from our initial binder screening, and the belief at the time that phosphoric acid compatibility was very important, led us to decide on concentrating our initial efforts on the Dow amine acrylic (#XD7080.00)/epoxy (#DER 331 + 732) and the two National Starch styrene acrylic latexes (#78-3936 & #78-3953).

We discovered later on in the project that phosphoric acid content was not a necessity which opened the door to our screening many more binder systems.

b. Butyral Control

A masterbatch of Monsanto Butvar B-90 solution was made up to use as a control with the pigments that were going to be screened.

	<u>Parts Per 100</u>	<u>Gms</u>
Butvar B-90	10.22	51.00
Butyl Alcohol	22.76	113.60
Isopropyl Alcohol	64.30	321.00
D.I. Water	2.72	13.60

Formulation of phosphoric acid solution:

	<u>Parts Per 100</u>	<u>Gms</u>
Phosphoric Acid (85%)	18.38	25.40
D.I. Water	16.50	22.60
Isopropyl Alcohol	65.12	90.00

Formulation of pigmented Butvar solution:

	<u>Gms</u>
Butvar Solution	41.5
Pigment	1.07 cc ⁽¹⁾
Nytal 300 (Industrial Talc)	0.64

(1) Weight varies with pigment.

These pigmented Butvar solutions were ball milled for approximately two days in a 230 cc ball mill which was cleaned out before each use with a diluted charge of the ingredients along with the above ceramic balls, and milled overnight. The cleaning contents would then be discarded and the mill and balls washed with isopropyl alcohol, dried and above formulation charged to it with balls and milled.

Films of the butyral control containing Sherwin Williams Moly White 212 pigment mixed with a solution of phosphoric acid, water, and isopropyl alcohol were cast on small steel panels (1-1/2" x 2") to check on appearance and adhesion to metal and also to check water immersion effects.

Films produced from formulations with acid solution containing water were all cracked up; therefore the formulation had to be revised. An acid solution with all isopropyl alcohol and no water was evaluated. This formulation produced much better films but, after immersion of 2-3 hour air-dried film in deionized water, blisters immediately appeared and, after about ten minutes the film was lifting off. The experiment was repeated, this time allowing the film to dry for 5 days. The result was similar except that it took a little longer for failure to occur. Apparently, chromate is needed with a butyral system

Because of the above mentioned problems, and the fact that we had the #117 wash primer as a control, no further work was carried out with this system.

c. Corrosion-Inhibiting Pigment Screening

A number of non-toxic corrosion-inhibiting pigments, (Table 14), that were recommended for waterborne systems, were screened initially with the two National Starch styrene acrylic latexes (#78-3936 & #78-3953) and the Dow amine acrylic/epoxy systems. The first method for screening was compatibility with waterborne binders followed by their performance in the salt spray.

These pigments were initially screened at a level of 26.22 cc per 100 gms of binder solids. Because of the problems we were encountering with the Dow amine acrylic/epoxy system, and this high level of corrosion inhibiting pigments, plus information from pigment manufacturers, we decided to reduce the screening level down to 10 grams per 100 gms binder solids. At this level, all the pigments screened were compatible with the

two National Starch acrylic latexes, but we were still having coagulation problems with Nalzin SC-1, 317/Sicorin RZ mixture (the Sicorin RZ was screened at a 1:9 level with 317 zinc phosphate).

All the compatible systems were exposed in the salt spray for 48 hours, but there were no noticeable differences in corrosion protection between pigments. All National Starch acrylic latex systems rusted extensively during the 48 hours salt spray exposure, while none of the epoxy systems rusted. These results seem to be more a function of the binders than the pigments. Because of the above mentioned results, and information obtained from Sherwin Williams, (who stated that Moly White MZA was formulated to provide increased adhesion of water based systems to ferrous metal substrates and more acid resistance than any of their waterborne pigments) we decided to use it (Moly White MZA) in all of our formulations containing acid. This decision was also supported by the fact that we were told by a representative from Buckman Laboratories that their meta-borate pigments function much better in systems with basic pH.

In formulations that contained no phosphoric acid, we would first try to use the recommended pigment or Buckman Laboratories Butrol 22, which, we were told, had out performed strontium chromate in salt spray exposures.

SECTION V

VOLATILE ORGANIC COMPOUNDS

The volatile organic compound in the formulation was contributed by two sources, the binder (12.3% Methyl Pyrrolidinone) and the Fluoro Chemical surfactant (37.5% Butyl Cellosolve).

The calculated values of volatile organic compounds (VOC) in urethane formulation #15591 are:

- (a) 101.23 cc VOC/liter of coating
- (b) 311.03 cc VOC/liter of coating minus water
- (c) 2.36 lb VOC/gallon coating minus water

All these values fall well within the requirement of the contract and Los Angeles County Pollution Control Department - Rule 66.

SECTION VI

GENERAL CONCLUSIONS

- . Witco Chemical aliphatic waterborne urethane, Witcobond W231, showed a great deal of promise for the application at hand. It produces a coating that is in compliance with all the requirements of the contract, with the exception of being Cellosolve rub resistant and being able to coat magnesium.
- . Only the Rohm and Haas amine acrylic (QR765M)/epoxy systems were suitable for coating magnesium. A formulation using the above mentioned amine acrylic with a high molecular weight epoxy dispersion from Celanese was developed to give a coating which was dry to the touch and recoatable in one hour. Unfortunately this coating was not MEK rub-resistant in 1 hour.
- . With Witcobond W231 we were able to obtain very good corrosion resistance without the phosphoric acid normally used in wash primers or metal pretreating systems.

SECTION VII

SUGGESTED FURTHER WORK

1. Present Urethane Formulation

- . It may be necessary to do some work with thickeners to prevent running during spray-up of large vertical substrates. This was not a problem up to now, possibly because we were only spraying-up small panels.
- . We are getting some grains in our coating, the amount of which varies from batch to batch. This led us to conclude that this is a result of our mixing procedure, using a Cowles type mixer. Other types of mixing procedures, such as ball milling, should be investigated.
- . One criteria, which was brought to our attention very late in the project(and which our coating did not meet) is resistance to Cellosolve rubs. This problem could be overcome by using a more solvent-resistant urethane to be available soon from Polyvinyl Chemicals and Witco Chemicals. Preliminary work done with the new Polyvinyl product (12A100-C) showed excellent solvent resistance but with adhesion and water immersion problems. These problems could likely be overcome with further work.

2. Acrylics

The Polyvinyl Chemical NeoCryl A623, did show good promise, especially in the area of solvent resistance. Its major drawback was adhesion, and we think with additional work we could improve its adhesion to an acceptable level.

3. Magnesium

The only systems that gave good coatings on magnesium were the epoxy systems that were cured with the Rohm and Haas amine acrylic QR-765M. Further work should be carried out to develop a faster curing epoxy that will be cured sufficiently to resist 10 MEK rubs one hour after spray-up.

4. Cleaning

A clean surface is very important if waterbornes are to be employed. We are using a solvent wipe procedure but a water cleaner should be developed, e.g. a mixture of water, alkali, detergent and some solvent.

TABLE 1
Evaluation of Final Epoxy Formulations on Steel and

Aluminum

Formulation #	Polymer System	Tack Free Time	Overcoat-ability in 1 hr.	MEK rub resistance in 1 hr.	Salt Spray Resistance		
					Adhesion (Tape Test)	Corrosion ⁽⁴⁾	
					Steel	Aluminum	
15577-B	Rohm & Haas QR765M/ Henkel Gen Epoxy 370-H55	>1 hr	No	No	Good ⁽²⁾ (1)	Good ⁽⁵⁾ / -	- (1)
15581-A	QR765M/Celanese CMD 55-3520	1 hr	Yes	No	Good / -	Good / -	-
15587	QR765M/Shell Epon 828	>1 hr	No	No	Good / -	Good / -	-
15565	Dow XD7080.00/DER331	1 hr	Yes	No	Good/Good	Good/Good	No
15566	Celanese CMD 9790/Epi- Rez 510	<1 hr	Yes	No	Good/Good	Good/Good	No
14923	Morton MorFlo/MorCure	>1 hr	No	No	Good/Good	Good/Good	Yes ⁽³⁾
14930	W.R. Grace Eypol WB4000/Dow DER 331 & 732	>1 hr	No	No	-	-	-

- (1) Test was not performed
(2) Rating before slash is for test performed before salt spray exposure, and that after slash is for after salt spray exposure.
(2) Blistered and rusted under blisters
(4) Corrosion of steel panel (48 hrs.; did not affect uncoated aluminum)
(5) Also gave good coatings on magnesium

TABLE 2
Evaluation of Final Acrylic Formulations on Steel and

Aluminum

Formulation No.	Polymer System	Tack Free Time	Overcoat-ability in 1 hr.	MEK rub resistance in 1 hr.	Salt Spray Resistance		
					Adhesion (Tape Test)	Corrosion(5)	
					Steel	Aluminum	
14937	Polyvinyl Chemical Neo-Cryl A622	1 hr	Yes	No	Good/Good (1)	Good/Good	No
15585	Polyvinyl Chemical NeoCryl A623 + A622	1 hr	Yes	Yes	Poor/- (2)	Poor/-	(2)
14925	National Starch 78-3936 + National Starch 2813	1 hr	Yes	No	Good/Good	Good/Good	Yes (3)
14913	National Starch 78-3953	1 hr	Yes	No	Good/-	Good/-	Yes
14932	Rohm & Haas Rhoplex MW23	1 hr	Yes	No	Good, Poor	Poor/Poor	Yes
14935	B.F. Goodrich Geon 450 x 20	1 hr	Yes	No	Good/ (4)	Good/Good (6)	Yes (4)
15572	B.F. Goodrich Carboset 514H	3 hr	No	No	-	-	-

(1) Rating before slash represents performance before salt spray exposure and that after slash is for after salt spray.

(2) Test was not performed

(3) Coating and steel surface turned brown , but metal was not rusted.

(4) Area totally rusted

(5) Steel panels (48 hrs did not affect uncoated aluminum)

(6) Formulation with phosphoric acid. Formulation without acid gave poor results.

TABLE 3

Evaluation of Corrosion Inhibitors
in
Deionized Water on Magnesium Panels

<u>Additive</u>	<u>Source</u>	<u>Results/Comments</u>
Molybdenum Trioxide	Reagent	Reacted (bubbles)
Nonic #218	Alcolac Thiodetergent	Reacted/slight
Nonic #260	Alcolac Thiodetergent	Reacted/slight
Sodium Nitrite (13.8% Sol. in H ₂ O)	Reagent	Reacted/slight
Sodium Silicate	Reagent	Reacted/slow reaction
Sarkosyl-S (1)	Ciba Geigy	Reacted
Ammonium Thioglycolate	Evans Chemicals	Reacted
Mercaptopropionic Acid	Evans Chemicals	Reacted
Dithiodiglycolic Acid	Evans Chemicals	Reacted
Phosphotungstic Acid	Sylvania Chemicals	Reacted/ turns panel surface blue
Z6062	Dow Corning Aminosilane	Reacted
KR 2380 Titanate	Kenrich Petrochemical	Reacted
Sodium Molybdate	Climax Molybdenum	Reacted
Ammonium Paramolybdate	Sylvania Chemicals	Reacted/turns panel surface brown
Ammonium Carbonate	Reagent	Reacted
Sodium Silicate	Reagent	Reacted/slow reaction
Diammonium Phosphate	Hampden Color & Chemical	Reacted
Dimethyldithio oxamide	Mallinckrodt Chemical	Reacted
Oxypruf E (Amine)	Olin Chemical , corrosion inhibitor	Reacted
Oxypruf 6 (Amine)	Olin Chem., corrosion inhibitor	Reacted
2-Ethylhexanol	Reagent	Reacted
Sodium Benzoate	Pfizer Chemical	Reacted
Sodium pyrophosphate	Reagent	Reacted
Acetophenone	Reagent	Reacted

(1) Amino Acid detergent

TABLE 4

Evaluation of Corrosion Inhibitor in
Ammonia Water on Magnesium Panels

<u>Additive</u>	<u>Source</u>	<u>Results</u>
Boric Acid	Reagent	Reacted (bubbles)
Citric Acid	Reagent	Reacted
Glycolic Acid	Eastman Chemical	Reacted
Levulinic Acid	Crown Zellerbach	Reacted
Nonyl Boric Acid	Callery Chemical	Reacted

TABLE 5

Evaluation of Corrosion Inhibitors
in Witco Chemical Witcobond W-231 on Magnesium Panels

<u>Additive</u>	<u>Result</u>
Sodium Silicate	Reacted with panel (bubbles)
Ammonium Silicate	Reacted with panel
Nonic #218	Reacted with panel
Nonic #260	Reacted with panel
Sodium Nitrite (13.8% sol. in H ₂ O)	Reacted with panel

TABLE 6

Evaluation of Corrosion Inhibitive Pigments in
Witco Chemical Witcobond W-216 on Magnesium Panels

<u>Pigment</u>	<u>Source</u>	<u>Results</u>
Busan 11-M1	Buckman Laboratories	Reacted with panels (bubbles)
Butrol 22	Buckman Laboratories	Reacted with panels
Moly White 101	Sherwin Williams	Reacted with panels
Moly White 212	Sherwin Williams	Reacted with panels
Moly White 414	Sherwin Williams	Reacted with panels
Moly White MZA	Sherwin Williams	Reacted with panels
Moly White ZNP	Sherwin Williams	Reacted with panels
Halox SW111	Halox Pigments	Reacted with panels
Halox ZX111	Halox Pigments	Reacted with panels
Halox BW 191	Halox Pigments	Reacted with panels
Nalzin SC-1	N&L Chemical	Reacted with panels
317	Reichard Coulston	Reacted with panels

TABLE 7
Effect of Acid on Latex or Solution

Polymer	Manufacturer	Polymer Nature	Result
Epotuf 38-690	Paichhold Chemicals, Inc.	Epoxy Drying Oil	Coagulated Totally
Neocryl A621	Polyvinyl Chemicals	Acrylic ⁽¹⁾	Coagulated
NeoRez R940	Polyvinyl Chemicals	Urethane ⁽¹⁾	Coagulated Totally
Kelsol 3906	Spencer Kellogg	Alkyd Drying Oil ⁽¹⁾	Coagulated Totally
Spensol F-71	Spencer Kellogg	Urethane Drying Oil ⁽²⁾	Coagulated Totally
Butyral FP	Monsanto	Plasticized Butyral Emulsion	Coagulated Totally
Butvar B-90	Monsanto	Butyral (Solution) ⁽⁵⁾	Good
MV-23	Rohm & Haas	Acrylic	Coagulated Slightly
MV-9	Rohm & Haas	Acrylic	Coagulated Totally
XD-7080 + } (3) (Epon 826) }	Dow Shell	Amine Acrylic + Epoxy (2 part system)	Good
DuPont - 115 Latex	DuPont	Neoprene Latex ⁽¹⁾	Good
Milloxane 5HS	Millmasters Onyx	Urethane Latex	Good
Ucar Latex 4341	Union Carbide	Styrene Acrylic Latex	Good
Ucar Vehicle 4358	Union Carbide	Acrylic Latex	Coagulated Totally
2813 Latex	National Starch	Crosslinkable vinyl Acrylic Latex	Good
Gen Epoxy 370H55 ⁽²⁾	Henkel	Epoxy Emulsion	Good
Amine Acrylic QR-765H }	Rohm & Haas	Amine Acrylic	
Methocel F-50	Dow	Hydroxypropylmethyl Cellulose	Good
Elvanol 90-50	DuPont	Polyvinyl Alcohol	Good
78-3936	National Starch	Styrene Acrylic ⁽¹⁾	Good
78-3953	National Starch	Styrene Acrylic ⁽⁴⁾	Good
HA-16	Rohm & Haas	Self Crosslinking Acrylic	Good
Gen Epoxy 370H55 & Gen Amid 5701-H65	Henkel	Epoxy Emulsion Amidoamine Solution	Good
MorFlo-40 Mor Cure -75 }	Morton Chemical	Amine Acrylic Epoxy	Good
XD-7080.00 DER 331 +732 }	Dow Chemical	Amine Acrylic Epoxy	Good

- (1) Carboxylated
(2) Some settling-out in less than 1 hour
(3) Noticable settling-out overnight
(4) Hydroxylated
(5) Solution in alcohol

TABLE 8.
Film Evaluation of Acid Tolerant Waterbornes With Phosphoric Acid Added

Polymer	App. on Glass	Steel					Adhesion (Tape Test)	Comment
		Thickness	Clarity	Flash Rusting	Gray Phosphate Uniformity			
Rohm & Haas MV23	Hazy	0.53-0.57mil	Yes	No	Mottled	O.K.	White foam spot, some hair-like ridges	
DuPont 115 Neoprene	Hazy	0.67-0.97mil	Yes	No	Fairly Good	O.K.	foam-like blisters in thick areas	
Union Carbide Ucar 4341	Clear	0.35-0.42mil	White (1)	Yes (3)	--	O.K. (5)		
National Starch-2813	Clear	0.35-0.85mil	Yes	Yes (2,3)	Good in non- rusted areas	O.K.		
Millmaster- Milloxane 5Hs	Hazy	0.25-0.45mil	White (1)	Yes (3)	--	O.K. (5)		
Dow-XD7080 + Shell-829 (3)	Clear	0.7-0.98mil	Hazy	No	Fairly Good	O.K.	Blisters due to thickness of film	
R&H- QR-765M + Henkel-Gen Epoxy	Clear	0.25-0.58mil	Yes	No	Fairly Good	O.K. (4)	Soft film	
Dow Methocel F-50	Clear	--	No	Yes (2)	Fail			
DuPont-Elvanol 90-50	Clear	--	Hazy	Some		O.K.	Forms greenish gray film on metal surface	
Monsanto- Butvar B-90 (Solutions)	Clear	--	Yes	No	Fairly Good	O.K.		
Formulation No. 117-Wash Primer	--	0.45-0.55mil	-	No	Good	O.K.		
National Starch 78-3936	Sl. Hazy	0.1-0.12	Rusty	Yes	-	O.K.		
National Starch 78-3953	Clear	0.2-0.23	White & Rusty	Yes	Good	O.K.		
Henkel Gen. Epoxy 370H55 Gen. Amid 5701H65	Yellow- ish	0.8 - 1.0	Yellow- ish	No	Good	O.K.	Film was soft and tacky after 24 hours	
Morton Chemical Mor-Flo-40 Mor-Cure-75	Sl. Hazy	0.5-0.65	Fairly Clear	No	-	Failed	Formulation did not wet steel good, beaded up	
Rohm & Haas HA-16	Clear	0.7 (Rusty) 1.0 (White)	White & Rusty	Yes	Good	O.K.		

(1) Chalky
(2) Rusted on outer areas
(3) Rusted in thinner areas

(4) Fingernail removable
(5) Outer layer of chalk comes off

TABLE 9

4 Hour Water Submersion Test

Resin	Appearance	Adhesion - Tape	Comment
Monsanto-Butvar B-90 Solution	No Rust	Lost 40-50% of Film	
Henkel-Gen-Epoxy & R&H QR765M	No Rust	0-10% Film Loss	
DuPont -115 Neoprene	No Rust	20-30% Film Loss	
Rohm & Haas MV-23	No Rust	20-30% Film Loss	
Dow-XD7080+ Shell 828	No Rust	Trace Film Loss	
National Starch 2813	-	10-20% Film Loss	Started out with about 30-40% of rust.
DuPont-Evanol 90-50	No Rust	10-20% Film Loss	Film got very soft in water
Dow-Methocel F-50	-	-	Film dissolved off panel
Formulation No. 117 Wash Primer	No Rust	O.K.	

TABLE 10
24 Hour Water Submersion
Test

Resin	Appearance		Adhesion-Tape	Comment
	No Rust			
Butvar B-90	No Rust		15-25% Film Loss	Less film came off than at 4 hrs.
Gen Epoxy + QR-765M	No Rust		20-30% Film Loss	
XD7080+828	No Rust		5-15% Film Loss	Some blistering due to thickness of film
MV-23	No Rust		80-90% Film loss	
115 Neoprene	No Rust		80-90% Film Loss	Blisters due to thickness of film
2813	Rust		20-30% Film Loss	Panel totally rusted
Elvanol 90-50	No Rust		20-30% Film Loss	Some blistering. After removal-turned brownish on standing.
Wash Primer 117	No Rust		OK	

TABLE 11
Effect of Rust Inhibitor on Rust Film

Inhibitor	Added to	Latex - National Starch 78-3936						Latex - National Starch 78-3953					
		Thickness (mils.)	Clear %	Chalky %	Flash Rust %	Tape (3) Adh.		Thickness (mils.)	Translucent %	Chalky %	Flash Rust %	Tape (3) Adh.	
Diethylaminomethanethiol ·HCl, Evans	Acid	0.30-0.35	95	0	5	0		0.50-0.55	95	5	0	0	
Thiourea	Latex	0.35-0.42	75	0	25	0		0.25-0.35	45	40	15	0	
Sarcosyl-1, Ciba Geigy	Latex	0.50-0.32	40	30	30	25		0.65-0.80	0	50	50	15	
Ammonium Thiocyanate	Latex	0.40-0.60	40	0	60	40		0.55-0.60	20	40	40	5	
Salicylic Acid	Latex	0.30-0.31	15	0	85	80		0.55-0.60	0	20	80	75	
Surfynol 104, Air Products	Latex	0.50-0.55	10	0	90	90		0.55-0.60	30	40	30	90	
Methyl Pentynol, Air Products	Latex	0.42-0.55	10	20	70	80		0.45-0.46	0	70	30	5	
Ethyltriphenyl- phosphonium Iodine	Acid	0.55-0.60	0	40	60	20		0.99-1.0	35	50	15	15 (1)	
2,2',2"-Nitrilotri- ethanol	Acid	0.61-0.70	0	0	100	15 (2)		1.2-1.3	20	40	40	5 (1)	
Isocetyl Acid Phosphate	Acid	0.55-0.60	0	40	60	5 (1)		1.0-1.1	10	80	10	5 (1)	
2-Ethyl 4-methylimid- azole	Acid	0.55-0.60	0	0	100	80		0.40-0.60	0	90	10	5 (1)	
Hyamine 1622	Acid	0.55-0.65	0	50	50	25		0.75-0.80	0	90	10	0	
Benzotriazole	Acid	0.65-0.71	0	10	90	80		0.30-0.55	0	95	5	5 (1)	
Sodium Nitrite	Latex-Acid Mixture	1.0-1.2	85 (4)	0	15	0		0.75-1.0	0	70	30	0	
No Inhibitor (control)	-	0.1-0.12	0	75	25	0 (5)		0.20-0.23	5	0	95	0	

- (1) Mostly chalky areas
(2) Rust area
(3) % removed, crosshatched
(4) Greenish grey film
(5) Upper layer of chalk removed

TABLE 12
Flash Rust Inhibitor Evaluation With Urethane And Acrylic Latexes
(3)

Inhibitor	Polymer-Union Carbide-Ucar Latex 4341						Polymer-Millmaster Onyx-Milloxane 5HS						Polymer-Rohm & Haas-HAL6					
	Thickness (mil)	% Clear	% Chalky	% Flash Rust	% (1) Tape Adh.	Thickness (mil)	% Clear	% Chalky	% Flash Rust	% (1) Tape Adh.	Thickness (mil)	% Clear	% Chalky	% Flash Rust	% (1) Tape Adh.			
Diethylsalmo-ethanethiol HCl.	0.42-0.50	30	50	20	0	0.70-0.90	30	70	0	0	0.32-0.33	80	0	20	0			
Thiourea	0.35-0.37	0	70	30	0	0.55-0.60	30	70	0	0	0.50-0.6	95	0	5	0			
No Inhibitor (control)	0.35-0.42	10	50	40	0	0.25-0.45	5	50	45	0	0.7-1.0	0	25	75	0			

(1) % removed, crosshatched

(2) Yellow

(3) Contains phosphoric acid

TABLE 13

Comparison Between Sodium Nitrite⁽¹⁾ and
Latexes as Received Diluted With Water 50%, Cast on Steel

Polymer	NaNO ₂					As Received			
	Thickness	Clear %	Flash Rust	Tape Adh. ⁽⁸⁾	Thickness	Clear %	Flash Rust	Tape Adh.	
National Starch 78-3936	0.40-0.85	100	0	0	0.5-1.0	(4)	0	0	
National Starch 78-3953	_(2)	0 ⁽⁷⁾	0	_(2)	0	0 ⁽⁷⁾	0 ⁽²⁾	_(2)	
Rohm & Haas HA16	0.35-1.5 ⁽⁵⁾	100	0	0	1.2-1.3	100 ⁽⁴⁾	0	0	
Union Carbide Ucar 4341	0.15-0.2	100	0	0	0.45-0.60	100	0	0	
Millmaster Oryx Milloxane 5HS	1.7	100 ⁽³⁾	0	0	0.25-0.6	30	70 ⁽⁶⁾	0	

- (1) 0.03 gm of a 13.8% solution of NaNO₂ was added per gram of solid resin content
 (2) Dry film broke up and lifted off steel
 (3) Solution turn from white to yellow on addition of NaNO₂ which resulted in yellow film
 (4) Film was yellowish in thick areas
 (5) Film was wrinkled in thick areas
 (6) Rusted in thin areas
 (7) Translucent
 (8) % removed, crosshatched

TABLE 14

List of Non-Toxic Corrosion-Inhibiting Pigments
Recommended For Waterborne System

<u>Pigments</u>	<u>Manufacturer</u>	<u>Chemical Composition</u>
Moly White 212	Sherwin Williams	Basic calcium zinc molybdate
Moly White MZA	Sherwin Williams	Basic calcium zinc molybdate-phosphate
Busan 11-M1	Buckman Laboratories	Modified barium metaborate monohydrate
Butrol 22	Buckman Laboratories	Mixture of Busan 11-M1 and unknown pigment
Halox BW-191	Halox Pigments	Calcium-barium phospho silicate
Halox ZX111	Halox Pigments	Zinc phospho silicate
Halox SWIII	Halox Pigments	Calcium strontium phospho silicate
317	Reichard-Coulston	Zinc Phosphate
Nalzin SC-1	N.L.Chemicals	Zinc Oxide Complex
Sicorin RZ	BASF Wyandote Corp.	Metal salt of organic nitro compound

A P P E N D I X

Literature Search and Telephone Interviews

1. Literature Search
2. Telephone Interviews

LITERATURE SEARCH AND TELEPHONE INTERVIEWS

1. Literature Search

- (1). Adler, R.S.: Naval Air Engineering Center, Philadelphia, PA.

Aeronautical Materials Lab. (245820)

Report No. NAEC-AML-2343; PAN 12-12 January 21, 1966

"An Evaluation of the Effect of the Thickness of Wash Primer".

Adhesion characteristics of the specifications MIL-C-22750A (WEP) epoxy-polyamide and the MIL-C-19537 (Aer) acrylic-nitro-cellulose systems using thick and thin coatings of MIL-C-8514 (Aer) wash primer are compared over various metal surfaces. The adhesion of both finish systems utilizing the heavier .6 plus or minus .1 mils wash primer is significantly better in dry adhesion tests and as good, or better, in wet adhesion tests than the .2 - .3 mils wash primed systems. Corrosion resistance of 2024 bare aluminum alloy panels with no chemical treatment, and coated with the aforementioned systems is better when thick .6 plus or minus .1 mil MIL-C-8514 (Aer) wash primer is applied as compared to the thin .2 - .3 mil wash primer. Recommendation is made to use the thicker coat of wash primer and to incorporate the necessary changes in the applicable process specifications. (Author)

- (2). Adrian, G.: et al, Farbe + Lack, 87 No. 10, 833-837 (October, 1981)
(in German)

"New Phosphate-Based Anti-Corrosion Pigments."

New active anti-corrosion pigments are described and their protective action in coatings compared with zinc chromate and phosphate. The following test parameters were varied: binding agent, pigment and filler compositions, coating thickness and duration of load. The anti-corrosion properties were evaluated by accelerated weathering in the salt spray test to DIN 50021 and in the Kesternich-Test to DIN 50018.

- (3). Anisfeld, J.: Farbe + Lack. 81. No. 11 1024-1027 (Nov. 1975)

"Modern Anti-Rust Primer "(In German)

Anticorrosive coating materials are important in efforts of the coatings industry to improve the longevity of products made of steel. Active anti-rust protection depends mainly on the primer vehicle and pigments contained therein. A review of the related technological developments is given, and advantages and disadvantages of the various rust-protection primers are discussed.

- (4). Anon : Brit. Pat. 1,271,629 (to Continental Oil Co., Paint Manuf., 42, No. 10, 50 (Oct. 1972)' Anticorrosion Primer "

Imperfect surfaces are primed before painting with a thixotropic mixture of solvent, oil soluble dispersing agent, alkaline earth metal carbonate and a low crystallinity polyolefin .

- (5). Anon : Indus. Finish. & S.C., 27, No. 326, 28-29 (September 1975)

"Corrosion Resistant Non-Toxic Coatings "

New moly-white pigments are a significant advance in paint manufacturing technology, since they make it possible for the paint industry to formulate high-quality exterior and interior protective coatings that offer users excellent corrosion-inhibition performance plus non-toxicity.

- (6). Anon: "Metal Chromate Rust Inhibitor Replacement"

In an article of unknown origin, a metal chromate rust inhibitor replacement is described. Broadly, the total replacement of metal chromates in corrosion preventive maintenance paints is stated to be possible by using silica coated with 1% pyrophosphato-titanate.

- (7). Anon.; Pigment and Resin Technology, August, 1979, p 20.
"Tin Compounds in Rust Inhibiting Primers"

The 1978 Annual Report of the International Tin Research Council (published last month) gives details of a study that has been carried out on the inhibition of rusting of steel by incorporating inorganic tin compounds into primer paints, which is necessarily a long-term project.

Results accumulated over a number of years with chlorinated rubber paint systems and more recently with an alkyd system, demonstrate that the hydroxystannates and stannates of calcium, strontium and zinc show a rust inhibiting action comparable to, or in some cases better than, zinc phosphate, which is a commercially used material.

During 1978, accelerated testing and limited outdoor testing of tin compounds in an alkyd binder have been continued, states the report, in order to establish optimum paint formulations for each of the compounds studied. The data have been used to construct a further programme of testing which will include a full range of outdoor exposure tests.

Of equal importance to International Tin Research's own tests, large quantities of the tin compounds have been made at the Institute and supplied to paint manufacturers and users for their own evaluation studies. [See also (100)].

- (8). Anon : #7604977 "Vinyl Coatings Protect World's Tallest Structure".
Mod. Paint Coatings 1976, Vol 66 No. 1, 38
Doc Type: Journal Article
Journal Announcement: 7608

Conditions which the 1,815 ft. high radio tower in Toronto will have to withstand are briefly described. The paint system applied to the topmost steel transmission mast comprises a vinyl butyral wash primer, a zinc chromate pigmented hydroxylated vinyl resin anticorrosive primer and a vinyl chloride/vinyl acetate copolymer topcoat.

Section Heading Codes: 53 (Weathering, corrosion, etc.)

- (9). Antonucci. American Paint and Coatings Journal, Technical Report,
June 22, 1981 48,50

Discussion of flash rusting of metals under water-borne paints.
At a meeting of the Houston Society for Coatings Technology flash rusting was observed to be an oxygen-deficient reaction in which the ferrous ions can react with the latex polymer solids. Flash rust inhibitors (proprietary) added to the latex prior to pigmentation were stated to be extremely effective in preventing the condition.

- (10). Arakawa Rinsan Chemical Industry Co. : "Corrosion Preventive Wash Primer".

Patent No. : Jap. 78/046,851,4 pp: Jap. Pat. Rept. 1979.
Vol. 78 No. 51, Gp G, 2.

Doc Type: Patent

Journal Announcement: 7908

The compsn. contains an epoxy/polyamide resin with chelating properties . . . obtained by treating a mixture of epoxy and polyamide resins with gallic acid; a phosphoric acid; and solvent.

Section Heading Codes: 54. (Patents for Weathering, Corrosion, etc.)

- (11). Banke, Modern Paint and Coatings, February 1980, 43-47
"Non-toxic Molybdate Pigments Provide Corrosion Inhibition"
(of the work of Sullivan and Vurasovich, ibid March 1981 41-43)

Basically a study of the utility of pigments based on molybdate ions as replacements for pigments containing lead and/or chromium ions. One such material (Sherwin-Williams Moly-White 212) is a basic calcium-zinc molybdate, designed for water dispersible and latex systems of traditionally low bivalent ion stability. The mode of corrosion protection of iron surfaces by the molybdate pigment is covered. When the corroding surface is covered with a protective film of ferric molybdate, corrosion ceases. The molybdate pigments discussed are non-toxic.

- (12). Barton, H.D. : Mats. Protn., 12, No. 6, 16-19 (June 1973)

"Phenolics and Furans in Chemical Process Equipment "

Phenolic and furan resins are thermoset materials. They are putty-like in the uncured state but become strong and inflexible when cured. Asbestos has been the primary filler for the corrosion resistant materials. Other fillers, including carbon, graphite, glass, synthetic fibers, and powders have also been used. These resins are not a panacea to all corrosion problems, but they are useful in many applications in the chemical processing industry.

- (13). Berger, D. M.: Metal Finish., 73, No. 6, 25-27 (June 1975)

"Organic Coating Programs as a Means for Controlling Corrosion"

The use of organic coatings to control corrosion is one of several methods to achieve an objective. The objective is "to maintain or operate an investment at the lowest possible cost consistent with legal and social guidelines." The author gives methods to determine in advance if the painting costs are in line with the value of the investment.

- (14). Brewer: Source Unknown

"Corrosion Resistance of Paint Films From Anodic and Cathodic Resins."

Assuming that an actively rusting area is an anodic site, then the surrounding area is relatively cathodic and should attract film formers which contain residual cathodic groups to adhere more firmly. Thus, it is postulated that cathodic polymers will provide inherently higher corrosion protection compared with anodic resins.

Various test and field results are presented, lending support to the above theory.

- (15). Brewer, G. E.F.: Metal Finish., 72, No. 8, 49-50 (August 1974)
"Actively Corrosion Resistant Coatings"

The past decade witnessed the world-wide acceptance of "electrodeposition" as a paint application process, because of the increased corrosion resistance obtained. Yet electroprimed test panels, when compared with panels painted with solvent-borne, neutral, and epoxy spray primer do not show better corrosion resistance. Thus it appears that the superior corrosion resistance of electrocoated merchandise is due to the uniform paint film thickness in recessed areas, rather than improved film properties. Indeed, most electrocoated test panels show a considerable tendency to lift away from the scribe marks, or other lesions in the film during a salt spray test, and are prone to exhibit filiform corrosion. Both of these defects constitute a lifting away of the paint film from the substrate. A study of the underlying theory is warranted.

- (16). Bronder, W.: #7903790 "Hydroxylation of Metal Surfaces Prior to Coating".

Ind. - Lack. - Betrieb 1978, Vol 46 No. 8, 278-81

Doc Type: Journal Article

Journal Announcement: 7906

A new pretreatment process for iron, copper and aluminum is anti-corrosive in character, promotes the adhesion and permits a reduction in the film thickness of subsequent paint systems. The oxygen permeability of copper at higher temperatures is also decreased. It is furthermore environmentally acceptable, requiring no special effluent treatment. It may replace the more expensive and laborious process of wash primer, two-component primers, pickling and brushing traditionally used on aluminum. (in German)

Section Heading Codes: 49. (Pretreatment and Application).

- (17). Buser, K. R.: Journal of Coatings Technology Vol. 54, No. 589
"Methods for Measuring the Surface Quality of Steel Substrate and
Zinc Phosphate Conversion Coatings".

Wetting tension of cold rolled steel correlates with corrosion resistance of painted products. This correlation provides a simple, useful guide to the corrosion resistance potential of steel substrates has been monitored and the effect of surface contaminants, cleaning methods, and aging effects on overall corrosion performance of painted products has been determined.

Results show that steel wetting tension should be high: > 80 dynes/cm. Surface contamination leads to poor performance. Extremely good cleaning (better than is normally done commercially) is necessary to ensure good zinc phosphate quality and subsequent good salt spray resistance when painted. Wet abrasion makes bad steel into good steel. Wetting tension decreases rapidly on aging and the steel must be phosphated immediately for good corrosion protection.

A facile, nondestructive, dry, colorimetric method for estimating the quality of zinc phosphate coatings is also described. It should be adaptable as a line quality control test.

- (18). Castelluci: Adhesives Age, Nov. 1978 p 70; "Rustproofing with Vitamin C".

Members of the American Chemical Society attending a recent meeting in Miami Beach, Fla., heard a rather startling claim: Ascorbic acid - vitamin C to most people - has been used successfully as a corrosion inhibitor on ferrous objects. According to Nicholas Castelluci of PPG Industries, Pittsburgh, Pa., the procedure is quite simple.

"Articles as degreased and dipped into a 10% solution of ascorbic acid containing 1% molybdenum powder at 40°C," Catellucci said. "The dipping time is dependent on the mass of the object . . ."

- (19). Ciba - Geigy: Pigment and Resin Technology, May 1977 (10,11)

Describes development of a new water-thinnable epoxy compound (XD823) useful with certain Ciba-Geigy hardeners (XD797 and XD798) to yield air drying enamel compositions.

- (20). Corrosion Inhibitors : Chemical Processing Mid-Nov. 1978, 105

To anonymous articles discuss corrosion/scale inhibitors. In one article, corrosion inhibitors for open recirculating cooling systems were discussed. One award-winning system consisted of products formulated with organo-phosphorous compounds combined with low level molybdenum compounds.

In the other article effective corrosion control was claimed through the use of blends of biodegradable organic and non-polluting inorganic compounds.

- (21). Cupr and Pleva: [Maschinenmarkt, 84,64 (1978) p 1253]

Metallic pigments with anticorrosive properties have been reviewed. Pigments based on zinc, cadmium, lead, manganese and aluminum are described. The protective mechanisms of these are also discussed.

- (22). Dai Nippon Toryo: Ger 27-16588

The formulation utilizes solvent based butyral wash primers without chromate. Butyral or a 50/50 phenolic/butyral is used as the resin. The key element is the use of a borate pigment in all cases, combined with either molybdate or polyphosphate pigment. Aluminum flake is optional. Examples are given which are resistant to 100 hours salt spray.

Examples of borate are: Barium metaborate ($\text{Ba B}_2\text{O}_4 \cdot \text{H}_2\text{O}$)

Zinc borate ($2 \text{ ZnO} \cdot 3 \text{ B}_2\text{O}_3 \cdot 3.5 \text{ H}_2\text{O}$)

Magnesium metaborate ($\text{Mg}_2\text{B}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$)

Examples of molybdate are: Zinc molybdate

Calcium molybdate

Examples of polyphosphate are: Aluminum polyphosphate

Zinc polyphosphate

(23). DuPont (and Monsanto) Tech. Brochure, Polyvinylalcohol.

Methods for crosslinking polyhydroxy compounds:

Aldehydes, aldehyde resins

Borax (pH 7?)

Metals -

$\text{Zn}(\text{NO}_3)_4$, Fe^{+++} , UNO_3 , MoO_3 , NaMolybdate

$\text{Cr}(\text{NO}_3)_3$, Na_2CrO_3 , "Quilon" chrome complex

Copper ammonium hydroxide, "Tyzor" titanates,

tetravalent titanates, potassium titanium oxalate

(pH sensitive)

(24). Edser, M.H.: Pigment and Resin Tech., 1, No. 3, 5-13 (Mar. 1972)

"Emulsion Based Anti-Corrosive Primers for Metals"

This article discusses the many advantages of a styrene-acrylic composition for an emulsion-based aqueous anti-corrosive primer. The merits of basic zinc potassium chromate and zinc orthophosphate in the styrene-acrylic system are also presented.

- (25). Ellinger, M.L.: Paint Manuf., 45, No. 1, 16-17, 20 (January/February 1975) "Anticorrosive and Marine Paints"

The author reviews the latest developments in various types of anti-corrosive coatings for various substrates and environmental conditions. Raw materials for anticorrosive systems are discussed as well as important film characteristics. Electrodeposition as a means of applying anticorrosive coatings is reviewed. The special considerations of marine paint is also discussed.

- (26). Ellinger, M.L.: Paint Manuf., 44, No. 9, 20-22, 27 (October 1974) "Anticorrosion and Marine Paints"

The length of guarantee periods for anticorrosion systems has been much debated. The problem is highly complex, having legal aspects. To find out whether the many years of guarantee, sometimes requested to equal the expected useful life of the protective system, a really necessary study of case histories was carried out. On the basis of this extensive study, a guarantee-period of two years has been suggested, because in almost each case failure due to faulty materials or inefficient application occurred well before this time.

- (27). Ellinger, M.L.: Paint Manuf., 45, No. 5, 17-18, 23 (June 1975) "Anti-Corrosion and Marine Paints"

The author discusses some of the new developments in anti-corrosion and marine paints such as: surface preparation, pigment selection, coating system, testing and anti-fouling properties.

- (28). El-Saawy, Abov - Khali and Ghanon : Pigment and Resin Technology, March, 1979 5-9, "Anti-Corrosion Behavior of Some Laboratory Prepared Barium Meta Borate Based Paints."

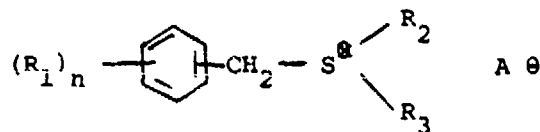
No water-borne systems were studied. The lab-prepared borate materials were about the same in performance as commercially made materials. Good corrosion protection, regardless of binder type, was observed.

- (29). French Patent 2,382,512

Uses phosphates or borophosphates of iron, zinc or manganese as prime pigment, hydroxyl-aldehyde or amine-containing bodies (as reducing agents?), and vinyl, vinyl-acrylic or styrene-acrylic as resin bodies, any or all of which may be in emulsion or aqueous dispersion provided they do not coagulate under strongly acidic conditions.

- (30). Frenier, W. W. and Settineri, W. J. (Assigned to Dow Chemical Co., Midland, Michigan) USP 4,101,438 (7/18/78) (See also USP 3,996,147 to Settineri) "Sulfonium Compounds as Corrosion Inhibitors in Aqueous Acidic Cleaning Solutions (20 claims)"

An aqueous acidic cleaning solution of at least one organic acid having dissolved or dispersed therein a sulfonium salt corresponding to the formula .



- (31). Feliu, S; Morcillo, M: "Study of Variables in the Dual System: Anti-corrosive Paint and Cathodic Protection".

Proteccion 1979, Vol 10 No. 1-2, 7-13

Doc Type: Journal Article

Journal Announcement: 7910

The effect of film thickness and applied voltage on the corrosion protection given by the system of cathodic protection with epoxy/tar, chlorinated rubber or aluminum/vinyl paint used over a wash primer was studied. Tests were carried out on fully coated panels and panels with a small unpainted zone. At potentials below -1.0 V, protection increased with film thickness from 150-250 microns. At a more negative potential of -1.5 V, defects occurred, even at the highest paint thickness, in and around the unpainted zone. (In Spanish)

Section Heading Codes: 53 (Weathering, corrosion, etc.)

- (32). Ghanem, N.A. and Abu-Khalil, M.A.: Farbe+ Lack, 79, No. 11, 1041-1049 (November 1973) (In German)

Three sets of paints were prepared and tested. The first set depended on basic lead pigments and red iron oxide in a neutral binder. The absence of any acidic binder in this set may have been responsible for the observed low efficiency of this set. In the second set, an acidic binder replaced part of the neutral binder, but the same pigments were used. The paints began to show better protecting properties. In the third set with basic lead carbonate or basic lead sulphate, the content of iron oxide was reduced to 5% of the dry film, the pigment/binder ratio was lowered to 0.70 and china clay was introduced. Improved corrosion protection resulted. Thus an acidic binder component and proper formulation are essential in anodic passivation paints. Conclusions on the efficiency of the paints in protection were based on electrode potential, electrical resistance and water uptake measurements, together with examination of the steel substrate.

- (33). Graham, T.: Paint Manufact. & Resin News. 51, No. 4, 14, 26
"Alternative to Red Lead Primers" (July/August 1981)

An eight year research and development program to find a safe alternative to the highly toxic red lead primer has resulted in a new product being introduced by Crown Protective Coatings. It is being marketed under the name of Crown Ferrox Steelguard and is a high solids zinc phosphate primer which, the company claims will mean healthier working conditions for professional painters and will result in better application and finished results.

- (34). Groucke, Journal of Coatings Technology 49, 632 (Sept. 1977) 69-74
"Formulation of Early Rust Resistant Acrylic Latex Maintenance Paints"

Acrylic latex maintenance paints properly formulated and applied have demonstrated long term corrosion protection. Recently, failures have been observed on these same paints within the first few days of application. It occurs under a narrow set of practical conditions: (1) thin latex films (approx. 1.5 dry mils primer); (2) cool substrate 50°F (10°C); and (3) exposure of the coating to high moisture conditions after the tack-free stages, but before complete film formation has occurred. A laboratory test has been developed to simulate these conditions and formulating steps (use of Busan 11-M1 combined with a soluble nitrite salt) have successfully eliminated this effect.

- (35). Haagenson and Ross, Pigment and Resin Technology, July 1979 5-21
"Modified barium metaborate: A non-lead, non-chromate corrosion inhibitor for alkyd paints".

The authors state that barium metaborate appears to be an excellent corrosion inhibitor in both latex and organic solvent (oleoresinous) binder systems but data are only shown for the oleoresinous type. There is a short description of work comparing strontium chromate with BMB in a water-dispersed binder system (Aroclon 585) in which the authors give test fence data showing BMB to yield better results.

- (36). Hamner . Corrosion (NACE Publication) For the year 1973 190-195
"Inhibitors in Organic Coatings".

Chemisorption and physical absorption are the two bonding modes between inhibitive substances and substrates. Both anodic and cathodic inhibitors are used in coatings. Lists of inhibitors and the effects of some of them in epoxy primers on aluminum are presented. The author summarizes as follows:

" Many additives, including the so-called pigments used in modern protective coatings have been found to confer useful properties to coatings. In some cases the additives are specific with respect to environments and applications in which they are used. In contrast to what often has been the case, modern coatings investigations involve the application of inhibitor theory and the use of sophisticated equipment.

Many inhibitive materials are listed together with references to additional information. Results of some recent laboratory investigations into the reactions of inhibitors at the coatings-environment interface are described and some comparisons of performance are made between formulations that include inhibitors and those that do not."

- (37) . Hare . Federation Series on Coatings Technology, Unit 26
"Corrosion and the Preparation of Metallic Surfaces for Painting".

The author writes on wash primer on pages 47-53. Important comments on their chemistry by this author:

" The WP-1 Wash Primer should be applied to clean metal in a very thin film (0.3-0.5 mils); thicker films may delaminate. In the presence of metal the reactions occurring in the film are thought to proceed as follows; the phosphoric acid converts the zinc tetroxychromate to chromic acid, zinc phosphate, and other chromates of lower basicity. The primary alcohol is then oxidized by the chromic acid to its respective aldehyde and, in the presence of more phosphoric acid, chromic phosphate is formed. Still, more phosphoric acid attacks the metallic substrate, depositing a film of the pertinent phosphate. At the same time, the chromium phosphate forms a chelated matrix with the polyvinyl butyral resin creating a complex film that is bonded to the deposited phosphate coating by primary and/or secondary valency bonds. Free chromates and phosphates remaining in the film serve as a source of inhibitive ions in the same manner as do the inhibitive pigments of an organic metal primer."

- (38). Hare, C.H.: Mod. P. & C., 65, No. 7, 31-39 (July 1975)

"Zinc Oxide vs Chromates in Metal Primers"

Zinc Oxide has been found to be effective as an extender in anti-corrosive primers based on simple chromates, with reactions between these pigments shown to produce basic zinc chromates. These reactions occur within the film in the presence of diffusing moisture and are thought to be related to improved performance.

- (39). Hare, C. H.: PVP, 64, No. 7, 19-25 (July 1974)

"Corrosion Inhibitive Pigments in Shop Primers: A comparative Study"

Inhibitive pigments have been studied at low loadings for corrosion and blister resistance properties in shop primers under varying environmental conditions. The effectiveness of chromate-based primers is shown, particularly an organic chromate and a mixture of strontium chromate and zinc oxide.

- (40). Hasmanis: Metal Finishing 74, 11 (1976) 55

The author studied adhesion of coatings applied on chromium surfaces by spraying. Adhesion loss in salt spray exposure is caused by cathodic alkali displacement. Corrosion inhibitive pigments improve performance in this test by slowing the overall corrosion rate.

- (41). Hermelin, R.: Paint Manuf., 44, No. 5, 10, 12, 15 (May 1974)

"Incorporation of Basic Lead Silico-Chromate into Paint Formulations"

More than 20 years after its birth, basic lead silico-chromate continues to enjoy popularity for anti-corrosive paints. This article has attempted to show its versatility and the various possibilities of formulation with these pigments.

- (42). Higgins, J.F. : (Assigned to DuPont, Wilmington, Del) USP 4,046,589 (9/6/77) calcium-silico-zirconate Primer Pigment (2 claims)

A method of imparting corrosion-inhibition to a primer by formulating into the primer from 0.1% to 65% by weight of calcium-silico-zirconate of the formula $x\text{CaO} \cdot \text{SiO}_2 \cdot \text{ZrO}_2$ wherein x is from 2.75 to 3, based on the weight of the primer.

- (43). Hodgson, K.V.: Indus. Finish. & S.C., 26, No. 286, 16-18,22 (Apr. 1972) "Blast Primers for the Marine Industry"

As technical manager for a large group including paint manufacturing firms and painting contractors, the author is able to evaluate paint from the viewpoints of both supplier and user. Among topics he discusses are primer requirements in the liquid state (he cites 17), principal primer media-epoxy, PVB, zinc silicates, and principal pigmentations, aluminum metallic, iron oxide/chromate, zinc rich, and reduced zinc.

- (44). Hollander, O; Geiger, G.E. and Ehrhardt, W.C.(Betz Labs Inc.) Papers in Corrosion/82 Program, NACE Meeting March 22-26, 1982. "A Review of Non-Chromate Inhibitors: Mechanisms and Experimental Methods"

Overview of mechanisms by which non-chromate inhibitors work is presented, followed by survey of modern experimental techniques used in mechanistic studies. Specific inhibitor systems are discussed, with emphasis on those having greatest practical importance in protection of ferrous metallurgy.

- (45). Horiguchi, S.; Nakamura, M.; and Yoshifumi, S. (Assigned to Daimicheika Color and Chemicals Mfg. Co., Ltd. Tokyo, Japan) . USP 4,066,462 (1/3/78) Anti-Corrosive Organic Pigment (15 claims)

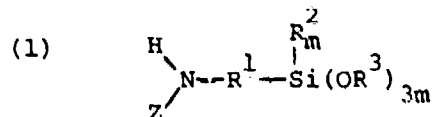
An anti-corrosive organic pigment prepared by a process, comprising:

mixing 1 part by wt of a lignin compound with from 0.5 to 5 parts by wt. of at least one nitrogen containing compound selected from the group consisting of urea, biuret, guanidine, biguanide, dicyandiamide, melamine, ammeline, ammelide, melame, ammonium carbamate, cyanates, isocyanates, methylenediurea, ammonia, ammonium carbonate, and ammonium formate; condensing said compounds by heating the mixture to the molten state, and preparing said pigment by pulverizing, grinding or dispersing said condensed product.

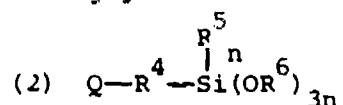
- (46). Hoshino, M.: et al (Assigned to Dia Nippon Tokyo Co. Ltd. Osaka, Japan) USP 4,098,749 (7/4/78) "Anticorrosion Primer Coating Composition" (10 claims)

An anticorrosion primer coating composition comprising ;

- (I) 100 parts by weight of a polyvinyl butyral resin,
- (II) 1 to 25 parts by weight of at least one organo functional silane selected from the group consisting of aminoalkoxysilane compounds represented by the following general formula:



wherein R^1 stands for a divalent hydrocarbon group having 1 to 4 carbon atoms, R^2 and R^3 represent a monovalent hydrocarbon group having 1 to 4 carbon atoms, Z stands for a hydrogen atom or an aminoalkyl group, and m is 1 or 0, and alkylalkoxysilane compounds represented by the following general formula:



wherein R^4 stands for a divalent hydrocarbon group having 1 to 4 carbon atoms, R^5 and R^6 represent a monovalent hydrocarbon group having 1 to 4 atoms, Q stands for a methacryloxy, acryloxy, glycidoxy or epoxycyclohexyl group, and n is 1 or 0.

- (III) 20 to 350 parts by weight of at least one member selected from the group consisting of inorganic borate compounds and polyphosphate compounds and ,

- (IV) 5 to 50 parts by weight of phosphoric acid.

- (47). Inhibition of Corrosion: Source and author unknown. In discussion of filiform and other forms of corrosion, the author states:

"Residual ionization in polymeric films seems to affect corrosion resistance and should, therefore, be utilized to increase corrosion protection in various cases.

The use of cationic and anionic polymers is not confined to electro-deposition, they may be formulated to lend themselves to spray, dip, roll, and other applications, thus offering a variety of opportunities.

Bimetallic joints, or dissimilar metals in vicinity of each other are frequently encountered. In these situations an increased corrosion protection should be achieved through coating the relatively base metal with a coat of anionic polymers, while protecting the relatively noble metal with a cationic material."

Interesting results could be obtained by use of polymers which are carrying both anionic and cationic groups.

- (48). Jocca 1979, vol. 62 No. 12, 475-85

Doc Type: Journal Article

Journal Announcement: 8007

Trials of anti corrosive paints, intended for ships' bottoms were carried out on experimental rafts in preference to accelerated corrosion and weathering tests, which were judged inadequate. Vinyl resins provided paints with good anticorrosive properties during an immersion of 22 months. Chlorinated rubber added to oleoresinous varnishes improved the resistance to sea water, while plasticized high-build chlorinated rubber paints exhibited superior performance. Use of a vinyl wash primer improved the anticorrosive properties of the paint systems. Mixtures of basic lead sulphate/non-leaving aluminum and two basic zinc chromates showed inhibitive properties superior to red lead or basic lead silico-chromate; coating thickness (above 300 microns) was more important, than the type of pigment in improving the protective properties of paints.

Section Heading Codes: 53 (Weathering, corrosion, etc.)

- (49). Kasprzak,: American Paint and Coating Journal, June 2, 1980 53-62
"Urethanes in water".

The article is not particularly pointed to corrosion-resistance nor even to use as a primer vehicle. Two resin types, both supplied in water-borne condition, are discussed. One is an oil-modified, thermosetting polymer and the other is an anionic colloidal thermoplastic polymer (Spensols L-51, L-53 and L-55). In formulated white lacquer, coating properties compare most favorably to organic-solvent soluble coatings.

- (50). Kerfoot, D.G.E.: (Assigned to Noranda Minca Ltd., Toronto, Canada)
USP 4,132,667 (1/2/79) "Corrosion Inhibiting Molybdate Pigment and Preparation thereof", (23 claims).

A corrosion inhibiting pigment comprising a zinc molybdate compound selected from the group consisting of sodium zinc molybdate, potassium zinc molybdate, ammonium zinc molybdate and mixtures thereof, in combination with a suitable carrier, the proportion of the zinc molybdate compound being such that the Mo content in the pigment is between about 1 and 30% by weight.

- (51). Koutek, S.F.: Army coating and chemical Laboratories, Aberdeen Proving Ground, MD ; Final Report: CCL-228 Project DA-2CD 22401A329. April, (1967) "Polyamide Diphenolic Acid Wash Primer:

A solid polyamide resin containing diphenolic acid was formulated into one and two package wash primers and evaluated against the control pretreatment primer, MIL-C-15328, for salt spray and water immersion resistance on steel, aluminum and magnesium substrates. Differences in performance between MIL-C-15328 and the two package diphenolic acid wash primer were negligible; however, the one package wash primers were inferior to the two package ones, particularly in water immersion. (Author)

- (52) . Kresse; Pigment and Resin Technology, July, 1978 18-20

"Influence of Inert Pigments on the Anti-Corrosive Properties of Paint Films: Part I"

The author examines pigment properties that are responsible for the anti-corrosive action of inert pigments. In this study, measurements of water permeation and water vapor diffusion; water permeation and degree of corrosion; and water permeation with water accumulation at the pigment/binder interface were made on paints of varying pigment/volume concentration (PVC). The particle diameter of a pigment plays an important part as far as the behavior of the pigment in primers is concerned. Thus, distance between particle centers influences the formation of capillaries throughout the paint film. Long oil Linseed oil alkyds were the binders employed - - no water-borne systems were discussed.

- (53). Kresse: Pigment and Resins Technology, Sept. 1979 15-20

"Influence of Inert Pigments on the Anti-Corrosive Properties of Paint Films: Part II"

The author covers the influence of water permeation without water accumulation at the pigment/binder interface; the influence of pigment aggregates, particle shape, pigment packing, flocculation and photoactivity. The binder - -long oil alkyd resin. No water-borne system. As conclusions for both parts I and II, the author states:

"Inert pigments, i.e. pigments which do not form metal soaps of passivation ions, are not so passive in primers as had been supposed until now. Their particle size, the presence of aggregates and aggregates and agglomerates, their wettability by the binder and, consequently, their tendency to accumulate water at the pigment/binder interface if the film is subjected to water.

Their tendency to flocculation and their photoactivity have an important influence on their behaviour. It cannot be excluded that there are even more relevant factors which so far have not been revealed. Besides the influence of the pigment, also the binder and the substrate have a part in the mechanism of corrosion. But if the function of an inert pigment is concerned, the tests should be designed in such a way that all the other factors can be neglected. The described investigations are intended to contribute to the elaboration of optimum formulations for primers and, in addition, to the development of inert pigments with better anti-corrosive properties."

- (54). Kronstein, M.: ACS Div. Org. Coatings Plastic Chem. Preprints 26
(2) 1966 "Phosphate Coatings on Steel as Chemical Complex Formations".

Utilizes polyvinyl alcohol, hydroxypropylmethyl cellulose or hydroxyethyl cellulose as the polymer; molybdenum, vanadium or tungsten oxide as the metal; and sodium phosphate-phosphoric acid (pH 4). This is sprayed on hot and followed by a chromic acid/phosphoric acid rinse.

- (55). Kronstein, M.: USP 3,272,663 (1/13/66)

Kronstein claims zinc molybdate as substitute for chromate salt in polyvinyl butyral wash primer. (Example 1) claims replacement of zinc molybdate by any other sparingly water-soluble polyvalent metal molybdate (examples - - barium, calcium or nickel molybdates). (Example 2) claims use of molybdic anhydride in place of zinc molybdate with polyvinyl butyral resin and phosphoric acid. No comparisons in performance of these compositions versus "regular" zinc tetroxochromate wash primer (WP-1).

- (56). Kronstein, M.: USP 3,528,860 9/15/70

A film forming wash primer composition containing (1) finely divided discrete particles of molybdenum trioxide or polyvalent metal molybdate, (2) an aqueous dispersion of a stable water-dispersible film-forming resin capable of undergoing cross-linking and, (3) a water soluble acidic phosphate-ion-providing compound: which forms a corrosion resistant coating on clean metal over which a finish coating may be applied.

- (57). Lobine, P. Wells, T. et al.: (Petrolite Corp.) Papers in Corrosion/82 Program, NACE Meeting March 22-26, 1982 "An Evaluation of Non-chromate Cooling Water Treatment Programs".

Nonchromate treatment programs normally provide less protection against pitting corrosion and deposition than zinc chromate cooling water treatment programs. Potentiodynamic polarization techniques were used to obtain pitting rates on both mild steel and admiralty test electrodes.

Corrosion screening test results, and experimental cooling tower results will be shown. Phosphate esters, phosphonates, silicates, molybdate, organo sulfur derivatives, and selected chelants have been evaluated.

- (58). Lafferman, F.L.: Modern Paint and Coatings, December 1981, 48-52
"An Interview With the Army's Coatings R&D Chief"

Basically an interview in which Lafferman comments on the coatings industry, the regulatory climate and the Army's special problems.

- (59). Lapasin, R.: et al. -- J. Oil Col. Chem. Assoc., 58, No. 8, 286-297 (August 1975) "Rust-Inhibiting Chlorinated Rubber Paints Based on Active Pigments, Which Are Claimed to be Non-Toxic and Non-Polluting"

The possibility is investigated of formulating rust-inhibiting chlorinated rubber paints, with low or zero toxicity and polluting action, by the use of new active pigments. Zinc phosphate, chromium phosphate, zinc and calcium molybdates and various organic pigments are taken into consideration. The evaluation of those formulations studied has been carried out by means of mechanical, chemical and cathodic tests. The results are compared with those for rust-inhibiting chlorinated rubber paints pigmented with red lead, zinc and strontium chromates, whose characteristics are well known.

- (60). Larson, V.L. "Metal Conditioners" Official Digest 837-846 September (1950) . Discusses early development of wash primer WP-1 , also known as MIL-P-15328(ships). Details some of the problems, particularly the decrease in adhesion noted approximately 8 hours after the phosphoric acid solution has been mixed with the pigmented base solution, also mentions and discusses briefly wash primer formulated with chromicphosphate in place of basic zinc chromate. The author concludes that the metal conditioners or wash primer principle assures a better foundation for paint systems while preventing under film corrosion.

- (61). Leidheiser H. : Jour. of Coatings Tech. 53 672 Pg 77 1981

"Some Substrate and Environmental Influences on the Cathodic Delamination of Organic Coatings".

The cathodic delamination of a polybutadiene coating appeared to be proportional to the number of coulombs passing through the interface. No delamination occurred without dissolved oxygen. (Oxygen was found to be poorly soluble in NH_4Cl solutions).

- (62). Leidheiser H.: Journal of Coatings Technology Vol. 53, No. 678 (July 1981) 29-39 "Mechanism of Corrosion Inhibition with Special Attention to Inhibitors in Organic Coatings".

Proposed mechanisms by which inorganic and organic substances provide corrosion inhibition are reviewed. Basic corrosion theories are discussed as is the mechanism of operation of inhibitors. Effects of oxidizing inhibitors are well-covered. Requirements for an inhibitor to be used in organic coatings are stated.

- (63). Leidheiser, H.: Natl. Assoc. of Corrosion Engineers 36 7 pg. 339 July (1980). "A review of Proposed Mechanisms for Corrosion Inhibition and Passivation by Metallic Cations".

Article discusses 11 mechanisms whereby metal ions can inhibit corrosion. Of particular interest, aluminum corrosion has been inhibited by Sn, Be, and Bi ions; iron corrosion has been inhibited by Sn, Pb, and As.

- (64). LeRoy, R.L.: Materials Performance (NACE), Vol. 19, No. 8, pg 54 (August 1980)

An organic chelating agent has been developed which imparts remarkable white rust resistance to galvanized products. This is the trithioglycolate ester of 1,2,6-trihydroxyhexane (TTH). Unlike the widely used inorganic chromate treatments, the organic protective coating resulting from TTH application is readily compatible with common paint formulations.

- (65). Marr: Canadian Paint and Finishing, March (1978) pg. 20

The author reviews the properties of various anticorrosive pigments and groups them according to reactive pigments, water-soluble pigments, and "other" pigments. In the latter category are zinc phospho oxide and micaceous iron oxide. Reactive pigments include red lead, zinc oxide, zinc orthophosphate, and calcium plumbate. The water-soluble group includes zinc yellow, zinc tetraoxy chromate, strontium chromate, basic lead silico chromate, barium metaborate and zinc molybdate.

The author points out that understandings are necessary and careful choices are important in order to achieve the optimum corrosion inhibiting that a pigment-binder combination can offer.

- (66). Mercurio and Flynn: Journal of Coatings Technology 51, 654 (July, 1979) 45-51 "Latex-Based All-Surface Primers".

Corrosion problems discussed from the binder rather than the pigment standpoint. New acrylic latex vehicles in conjunction with a new pigment dispersant (Exp. No. QR681), a new latex thickener (QR708), and optimized formulations offer promise of providing greatly improved water-based primers that the authors state may even surpass the performance of the best alkyls. Prime pigments used were 90% rutile TiO_2 and 10% zinc oxide.

- (67). Meyer, G : Farbe + Lack, 79, No. 4, 293-300 (April 1973) (In German) "Protective Action of Lead-free Iron Primer Strongly Dependent From the Cathodic Potential"

Under a protective coating an inhibiting layer is formed from pigment anions directly on the iron substrate. The e.m.f. for the primary reaction depends from a potential difference between anode and coating, that of a secondary reaction from a potential difference between cathode and coating (which compares with the primary inhibiting layer). Only after the anodes are covered, a pole changing of the original cathodes may occur if the cathode potential results in an effective potential difference. The low potential of phosphate layers requires the necessary pole changing the conversion of the cathodic hydrogen peroxide to soluble anions. The pole changing theory is explained with examples.

- (68). Meyer, Gottlieb: Farbe & Lack (in German), 78, No. 3, 227-230 (Mar. 1972) " Important Electrochemical and Complex Chemical Reactions in Pigmented Corrosion-Inhibiting Coatings on Iron"

Based on literature information and the author's own test results the anodic inhibitor complex formation is described. The little-known electrochemical reactions in cathodic areas which are of decisive importance for the inhibiting effects are discussed. A change of poles and the resulting formation of an inorganic inhibitor complex also at the originally cathodic centers are only possible if the hydrogen peroxide formed at the cathode with oxygen in solution is destroyed by the inhibitor system.

- (69). Mitsubishi Heavy Industry Co.: #7804160 "Two-pack Type Primer"
Patent No.: Jap. 78/000,410, 3pp: Jap. Pat. Rept. 1978, Vol 78 No. 2 Gp G,4.

Doc Type: Patent

Journal Announcement: 7806

A two-pack wash primer contains (1) a mixture of polyvinyl butyral, phenolic resin, chromate, iron powder and alcohol, and (2) a mixture of oxalic acid, citric acid, malonic acid or sulfamic acid, tannic acid, water and alcohol.

Section Heading Codes: 54 (Patents for weathering, corrosion, etc.)

- (70). Morawek, R.: MOD. P & C, 6, 43-45 (June 1975)
"Metal Salt Dispersions for Rust Preventives"

Metal salt dispersions have been found to impart unusually low moisture vapor transmission properties and other desirable characteristics and are now undergoing evaluations by formulators and manufacturers of corrosion preventive coatings.

- (71). Müller, G. et al "Wash-Primer" Angew Chem 68 #23 746 (1956)

The authors characterized the zinc chromate pigment. The effect of water content, and the effect of phosphoric acid content.

- (72). Murray, J. D.: J. Oil Col. Chem. Assoc., 56, No. 11, 507-514
(November 1973) " Chloride Ion Transport in Epoxy Polyamide Films and the Substrate Effect"

In the field of corrosion prevention by surface coatings, one outstanding problem that has remained unanswered concerns the effect of the substrate on a film's permeability properties. The behavior of free and attached films of epoxy polyamide lacquer have been observed under identical conditions by means of desorption and sorption techniques. The data has been interpreted in terms of the diffusion and partition coefficients for chloride ion in the polymer system.

- (73). Nazarova, E.V.; Lamaka, T.A.; Andreeva, V.V.; Moiseeva, I.P.
#7804951 "Use of Thixotropic Primer EF-094 for Painting Waterlines of ships"
Lakokras, Mat. 1977, No. 6, 60: Continent, Paint Resin News
1978, Vol 16 No. 3, 47
Doc Type: Journal Article
Journal Announcement: 7807

It has been demonstrated that the title epoxy ester primer has better adhesion to the metal surface of a ship's hull at the waterline than the polyvinyl butyral wash primer at present in use, and that a single coat will give adequate corrosion protection for a considerable time. Annual savings in material and labor costs are noted. (In Russian)

Section Heading Codes: 63. (Paints, etc., for other specific uses).

- (74). Fila, S: J. Oil Co. Chem. Assoc., 16, No. 5, 195-209 (May 1973)
"Factors Involved in the Formulation of Anti-Corrosive High Build Vinyl Coatings"

A new approach to the formulation of high build anti-corrosive vinyl coating systems is described. The use of vinyl chloride-vinyl acetate copolymers prepared in solution makes possible the formulation of coatings with substantially increased non-volatile content and suitable for application at high film thickness by airless spray equipment. Formulation parameters are reviewed and suggestions for formulae and manufacturing procedures for such a system are described.

- (75). Riggs, O : National Assoc. of Corrosion Engineers; Corrosion Inhibitors; Editor, Nathan; (1973) pg. 7. "Theoretical Aspects of Corrosion Inhibitors and Inhibition".

Also discusses organic inhibitors suitable for retarding anionic and cathodic corrosion.

- (76). Roberti, A : #7601698 "Development of Paint Systems Resistant to Filiform Corrosion for Aircraft".

Ind.-Lack.- Betrieb 1975, Vol 43 No. 8, 285-7

Doc Type: Journal Article

Journal Announcement : 7603

The system considered best comprises a special wash primer, polyurethane primer and polyurethane finish. (In German)

Section Heading Codes: 53. (Weathering, Corrosion, etc.)

- (77). Rocklin, A.L. : ACS ORPL Division Preprints Vol. 45 August
"Water/Cosolvent Blend Evaporation During Sprayout at Different Humidities."

Water reducible coatings are very sensitive to evaporation conditions during application and drying. As the solvent evaporates, changes in water/cosolvent balance can have large effects on rheology with important consequences for film quality and acceptability. For example, loss of a small amount of cosolvent can bring about a sudden viscosity change which may lead to sag or poor leveling. These effects can be minimized by careful selection of cosolvents, but the problem is complicated because the changing water/cosolvent balance during evaporation can be strongly affected by relative humidity. A blend which maintains a satisfactory water/cosolvent balance at a low humidity can rapidly lose most of its valuable cosolvent if the humidity rises. This is an expensive vulnerability. To cope with it requires as much information as possible about evaporation behavior under application conditions. Since spraying is a preferred application method, we studied solvent evaporation during sprayout at various humidities, using both a water reducible paint and a corresponding model system consisting of a neat water-solvent blend having the same composition as the blend used in the paint. This paper reports the results of that study and shows that some trends can be predicted with a previously developed computer program for calculating evaporation of water/solvent blends at any given humidity.

- (78). Roebuck; Corrosion (NACE) 1973 245-249
"Inhibition of Corrosion From Caustic Attack"

The extent of corrosion by alkaline solution; inhibition of copper corrosion; mechanism of inhibition of copper corrosion; inhibition of aluminum corrosion; and alkalies as inhibitors are discussed. The author's summary is as follows:

"Fundamental causes of caustic attack on materials are fairly well understood. There is less agreement on the fundamental causes for the

effectiveness of inhibitors, but this has not prevented the discovery of effective inhibition schemes that are commonly applied in alkaline environments.

Research into the causes of reactions in the alkaline range in aqueous and other environments is widespread and has produced information on useful inhibitors. Many of these inhibitors are being tested in laboratories and applied in the field to add to the store of information about effective inhibitors for alkaline environments. Trial and error methods have identified some materials useful as inhibitors in alkaline solutions and established the parameters needed to make their performance effective."

- (79). Rosenbloom, H. : Ind. and Eng. Chem. 45 No. 11 2561 (1953) "Chemistry of Wash Primers".

The phosphoric acid apparently attacks the zinc chromate pigments forming a solubilized Cr^{+++} phosphate. The chrome apparently complexes with the butyral hydroxyls as the pH rises, causing insolubility of the butyral. Intermediate valence chromium (Cr^{+5} Cr^{+4}) is apparently instrumental in complex formation - chromic $^{+++}$ sulfate does not insolublize the butyral in alcoholic phosphoric acid. (The chrome complexes postulated are similar to our April 23 '81 proposal discussions, pg. 2-36, 2-37).

The hexavalent chromium in the zinc chromate is reduced to lower valences by reaction with the alcohol solvent (presumably oxidized to acid). The reduction of hexavalent chromium can be prevented by utilizing low water content or tertiary alcohols - but the final coating is then useless.

Phosphoric acid did not react with the butyral in the absence of chromium. If the weight ratio of $\text{H}_3\text{PO}_4/\text{CrO}_3$ falls below 1.5 the solution can gel. A higher ratio reduces the viscosity of the solution. The maximum adhesion to metals occurred at 30 $\text{H}_3\text{PO}_4/100$ resin.

Soaking the primed metal in water at various pH levels caused loss of adhesion in 4 hours at pH6, but 260 hr. resistance at pH 2.7-3 was found.

The zinc chromate WP-1 solution passivated steel in 2 minutes, while a $\text{CrO}_3\text{-H}_3\text{PO}_4$ wash primer required 40 minutes.

- (80). Rycerska-Lazacka, H; Szaniewski, S; Polapowicz-Lewandowski-A,A

#800236Q "Painting of Hot-Dip Galvanized Steel,II",

Ochrona Przed Koroz, 1979, Vol 22 No. 9, 237-9

Doc Type: Journal Article

Journal Announcement: 8004

Hot-dip galvanized steel plates with surfaces prepared in 16 ways have been painted with two paint systems and subjected to natural and artificial weathering. Use of a wash primer followed by an alkyd paint gave the best results, whatever the conditioning of the zinc surface. (In Polish)

Section Heading Codes: 49 (Pretreatment and application)

- (81). F. Sarx (Herbig - Haarhaus A- G., Cologne - Bickendorf, Ger.)

Werkstoffe : U. Korrosion 6, 331-4 (1955) "Wash Primer as a Preconditioner of Metals and as a Universal Primer Coating".

Evaluated zinc chromate - butyral wash primer.

- (82). Schatz, H.: Fabre+Lack, 79, No. 7, 645-652 (July 1973)

"Storage Stability and Anti-Corrosive Properties of Red Lead Paints"

Red lead is a generally known anti-corrosive pigment. Its protective qualities are to be ascribed to lead orthoplumbate (Pb_3O_4). Additionally red lead contains various amounts of free lead monoxide (PbO). In systematical tests the effect of the degree of oxidation of red lead on the storage stability of red lead paints and on the anti-corrosive properties of coatings obtained with them were determined.

(83). Seavll, J: Oil Color Chemist Assoc. (1978) 61, 439-462

"Anticorrosive Properties of Mimosa (Wattle) Tannin "

The author's summary is as follows:

"A wash primer treatment for steel, suitable for use on new structural work or for maintenance work, has been tested over a period of four years under widely differing site conditions.

The treatment is based on Mimosa tannin (*Acacia Mearnsii*) acidified with phosphoric acid. By the formation of iron tannate, this greatly enhances the durability of an air-drying paint system, especially when the site conditions make the complete removal of all rust costly or impracticable and when painting is delayed for periods of from one to eight weeks after surface preparation. Similarly, if the painting has to be done during a period of high relative humidity, a preliminary application of the Mimosa-based wash primer has invariably shown a considerable advantage in delaying the onset of blistering and thus increasing the durability of the paint system as a whole.

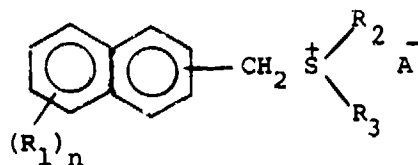
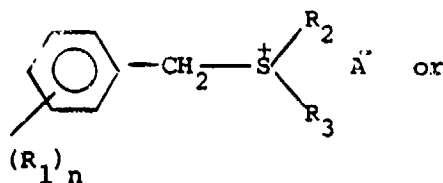
The formation and the protective role of iron tannate has been studied in a concurrent investigation by Ross and Francis and, as a result of their conclusions, it has been possible to qualify more precisely the advantages, which field trials have shown, from the use of Mimosa-based wash primer.

Apparently for iron surface only and needs light rust to function, the paper offers a good discussion of corrosion theory. It investigates a) wash primer aging before regular primer is applied; b) differing primers over the wash primer; c) high RH application and d) wash primer aging over non-rusted surface versus freshly formed rust.

(84). Settineri, W.J.; Frenier, W.W.; and Oswald, J.H.: (assigned to Dow Chemical Co., Midland, Michigan) USP 3,996,147 (12/7/76)

"Novel Sulfonium Corrosion Inhibitors in Aqueous Acid Solutions"
(16 claims)

The corrosion of metal surfaces in contact with aqueous acid cleaning solutions is inhibited by sulfonium salt corresponding to the formula:



These sulfonium salts are effective corrosion inhibitors even in the presence of ferric ions.

- (85). Shirsalkar, Mulay and Sivasamban : Metal Finishing, July 1981 57-60
"New Anticorrosive Pigments From Iron Oxide".

Laboratory trials have shown that iron oxide modified with oxides of barium calcium and lead possess good anticorrosive properties and they offer promise as anticorrosive pigments.

- (86). Smith: Pigment and Resin Technology, 8, 10 (1979) pg. 17

Aluminum flake pigments are reviewed. The author discusses leafing behavior, vapor permeability, and optical properties such as tinting, strength, hiding power, gloss lightfastness and saturation.

- (87) Specifications Board, Supplies & Services Canada
#7804432 "Standard for Coating, Vinyl, Pretreatment for Metals
(Vinyl wash Primer).

CGSB 1-GP-121M, 1977: BSI Worldwide List Stand, 1978, Mar. 36

Doc Type: Standards

Journal Announcement: 7806

Fast-drying primers for use on metal are specified. Two types are covered, one being applied by spray and the other, for touch-up work, being packaged in an aerosol dispenser.

Section Heading Codes: 88 (Standards and Specifications)

- (88). Sullivan and VuKasovich: Modern Paint and Coatings, March 1981,
41-43 "Molybdate - Pigmented Latex Protects Against Corrosion".

Authors state that the corrosion-inhibiting pigment is a basic calcium zinc molybdate (Sherwin-Williams Moly-White 212), low in water solubility (0.002 g MoO_4 per 100 ml) and is designed for use in water-dispersed or latex systems. It has been shown to give long-term outdoor corrosion protection and is not a toxic substance according to Federal regulations.

- (89). Svoboda et al: Farbe and Lack, 86 9 (1980) pg. 780

The corrosion-inhibiting properties of pigments and coatings have been reviewed broadly.

The authors were particularly interested in examining the aqueous extracts of corrosion-inhibiting pigments and of coating films containing these pigments. The basic inhibiting properties of such extracts were then ranked for the various extracts. The authors found the extract from ferric oxide to be non-corrosion-inhibiting. Lead containing pigments and calcium orthoplumbate pigments were quite inhibitive.

- (90). Szklarska-Smialowska; Brit. Corros. J, 4 Sept. (1969)
"Cathodic Inhibition of the Corrosion of Mild Steel in Phosphate,
Tungstate, Arsenate and Silicate Solutions Containing Calcium Ions."

Calcium phosphate and tungstate inhibited corrosion better than the
arsenate and silicate salts in dilute aerated solutions. The cal-
cium appears to deposit on cathodic sites and diminishes the access
of oxygen to cathodic sites.

- (91). Tachibana: Journal of the Japan Society of Colour Material, 52, 5
(1979) pg. 268

Recent developments in non-toxic anucorrosive pigments have
been reviewed.

- (92). Touhsaent, R.: Corrosion 28 12 Dec Pg. 435 (1972)
"A Capacitance - Resistance Study of Polybutadiene Coatings on
Steel".

The capacitance and resistance of polybutadiene coatings were de-
pendant on the amount of water in coating capillaries.

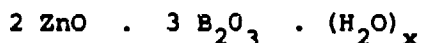
- (93). Traister, A. and Troop, G. : (Assigned to PPG Industries, Inc.
Pittsburg, PA) USP 4,049,596 (9/2/77) "Corrosion Resistant
Aqueous and Solvent-based Primer Compositions Containing Synergistic
Blends of Zinc Borate and Barium Metaborate Pigments". (10 claims)

A corrosion resistant primer composition comprising;

a. a film forming resin vehicle blend consisting essentially of:

1. from about 60 % to about 80% by weight solids of an acrylic
polymer latex and from about 20 % to about 40% by weight
of solids of an alkyd resin, styrene-allyl alcohol ester
adduct or a polymerized dehydrated castor oil; or
2. from about 85 % to about 95% by weight solids of an epoxy
ester resin and from about 5 to about 15% by weight solids
of a chlorinated paraffin; and

b. a pigment blend consisting of from 10 to 95% by weight of zinc borate and from 5 to 90% by weight of barium metaborate, wherein said zinc borate has the formula:



wherein x is from 3.3 to 3.7 and wherein the ratio of said pigment blend to said resin vehicle solids is from about 40:100 to about 90:100.

- (94). Ullman R: ACS Organic Coatings and Plastics Chemistry, Preprints 18, 2, Pg 279 (1958) "On the Action of Polyvinyl Butyral Acid Wash Primers". (Exploratory Work on the Chemical Reaction of Wash Primers).

The chromium "complexes" with the butyral resin. The chromium is difficult to remove but can be removed with oxalic acid at 85°C, 4 hours, leaving a partly soluble white resin. When the hydroxyls were blocked with acetate the chromium was removed readily by oxalic acid and the polymer residue was entirely soluble.

The addition of phosphoric acid (no chromium present) caused approximately 20% aldehyde to be liberated within 20 minutes.

The wash primer highly diluted shows a reduced viscosity vs concentration curve similar to a moderately strong polyelectrolyte. Since the mol ratio of CrO_3 ; H_3PO_4 ; PVB is 0.5: 1:10, there is excess capacity to pick up additional foreign multivalent ions moving along the surface. There are not however, enough mobile ions to allow for a strong osmotic swelling on water exposure. The film has a high resistance to current flow perpendicular to the surface.

The author's conclusions regarding the finding of a substitute wash primer follow:

"Find a corrosion product which adheres strongly to the surface; find chemical groups which will complex strongly with the corrosion product (and/or adsorb strongly to other large segments of the surface); attach these groups to a flexible oxidation resistant self-plasticized polymer of medium molecular weight; see that the polymer is self-cross-linking on drying, aging, or contact with air and is able to retain a few percent of water; deposit the resin in a thin layer from a fairly good solvent at or above room temperature; prevent very fast drying or allow exchange of the last few percent of solvent by moisture. "

- (95). Van Oeteren: Fette, Seifen, Anstrichmittel, 81, 2 (1979) pg. 91

The author stresses the role of structure, particle size, and ratio of pigment to binder as these affect anticorrosive properties.

- (96). Vukasovich, M.S. and Sullivan, F.J.: Papers in Corrosion /82 Advance Program, NACE Meeting March 22-26, 1982 Pg 49-265

Investigation of corrosivity of experimental automotive engine coolants was conducted using as laboratory procedures: ASTM D 1384-70 (1975), Corrosion Test for Engine Coolants in Glassware; a modified Ford Laboratory Test Methods BL3-2, Cavitation Erosion-Corrosion Characteristics of Engine Coolants on Aluminum Coolant Pumps; and a Non-Pressurized Aluminum Cylinder Head Heat-Transfer Corrosion Test. Emphasis was given to the contributing role of sodium molybdate on corrosion inhibition while in the presence of common coolant inhibitors.

- (97). Vukasovich, M.S. and Sullivan, F.J. : (Assigned to Amax, Inc., New York, N.Y.) USP 4,017,315 (4/12/77) " Molybdate-Phosphate Corrosion Inhibiting Pigment" (11 claims)

A corrosion inhibiting pigment comprising discrete particles of an average particle size up to about 25 microns comprising a mixture of a metal molybdate compound selected from the group consisting of zinc

molybdate, calcium molybdate, strontium molybdate, barium molybdate and mixtures thereof and a metal phosphate compound selected from the group consisting of zinc phosphate, calcium phosphate, magnesium phosphate and mixtures thereof, said metal molybdate compound being present on a pigment volume concentration basis of from about 2 parts up to about 3 parts per part of said metal phosphate compound.

(98). Weigel, K.: "Experience with Polyvinylbutyral Wash Primers", Farbe and Lack 68 January #5 309 (1962), Literature summary circa 1962

(99). Whiting: USP 2,525,107 (1950) Discloses a one part wash primer with polyvinyl butyral, zinc tetroxychromate and phosphoric acid.

(100). Williamson, T.A.: Poly., Paint and Col. J., No. 4056, 630, 635 (September 30, 1981) "New Rust-Inhibiting Pigments for Steel Primer Paints".

The International Tin Research Institute Greenford, Middlesex, has undertaken an extensive research program in this field in the course of which a large number of tin chemicals have been screened as rust-inhibiting pigments. Although the project is not yet complete - over 240 test panels are now being exposed to the vicissitudes of mild urban/industrial atmosphere on the roof of the Institute building - there are indications that a particular group of chemicals, the stannates of calcium, strontium and zinc may have commercial value as inhibitive pigments. [See also (7)]

(101). Young: Journal of Coating Technology 49, 632 (Sept., 1977) 76-81 "Novel Ambient-Cured, Water-Borne, Acrylic-Epoxy Coatings"

New materials for water-borne coatings, combining the weathering advantages of acrylics with the cured properties of epoxies are described. The novelty of these systems is provided by an amine-functional acrylic polymer used as the curing agent. Formulating techniques are presented as is documentation of corrosion resistance, chemical resistance and weathering qualities.

(102). Eschwey et al: USP 4,329,381

This invention relates to corrosion protective coatings for metal surfaces, particularly, for iron which coatings contain, in addition to the other customary components, zinc and/or lead salts of nitrogen-containing heterocyclic organic compounds as corrosion inhibitors.

The chelating group is $\text{N} = \underset{\text{OH}}{\text{C}}$ or $\text{N} = \underset{\text{SH}}{\text{C}}$

(This is believed to be the "Sicorin" patent).

(103). Tin and It's Uses - ISSN 0040-7941 No. 129 (1981) P 9

Work with stannates and hydroxy stannates of calcium, strontium and zinc as pigments in primers for protecting steel structures is under study. Principal binders used have been chlorinated rubber and alkyds. Preliminary results show that such compounds are at least comparable with zinc phosphate inhibited primers.

2. Telephone Interviews

. Ameron Prot. Coating: Corporate Research

A. E. Seneker

They had developed a material for aluminum on aircraft which used zinc phosphate as the active pigment - - this was for aircraft only and he did not think that the precise formulation would have worked on steel. However, Ameron sold their interest in aircraft finishes, so they are not currently doing any type of development on wash primers.

. Cook Paint and Varnish Co., Kansas City, MO

Mr. Woods

Per Mr. woods, they make a wash primer, butyral type, zinc chromate pigmented, their code number 900Y2. This is for the standard uses (on aluminum, galvanized and steel) and is applied as a very thin film. Data sheet is available if desired. They are not doing any work on any other wash primer development.

. Desoto Chemical Coatings-Des Plaines, Ill.

Marketing Director's Office (G. Furey)

They have not made wash primer for many years and are not now doing any development on such a product with or without non-toxic pigments.

. E. I. DuPont, Wilmington, Del.

Product Reference Dept.

They do not make a true wash primer with "non-toxic" pigmentation but they have a two-package epoxy primer which is chromate and red-lead free. This product is 825-Y-9031 and it is about 50% solids by volume and sells (mixed 1:1) at \$20-\$22/gallon. Representative in this area is Tofshesko Coatings in Boston. They are not aware of any work at DuPont on any other type primer to remove "toxic pigments" therefrom.

• Farboil Paint Co., Baltimore, MD

Joe Bendix & Mike Anderson

They make a conventional wash primer (WP-1 type) for specification uses. It is the conventional two package type and the active pigment is zinc chromate. They are not doing any research in this area.

• Glidden Division, SCM Corporation, Westlake OH

They made a wash primer but it was discontinued several years ago. Although they have not been applied to wash primer, studies on pigmentation in other type primers have shown that certain zinc complexes (chromate-free) and molybdates could be used with reasonably good, but not up to the efficiency of chromate performance in corrosion control.

• Lilly Industrial Coatings, Indianapolis, Ind.

Bill Richardson

They make a standard two-package wash primer, product number is primer #418, to be used with reducer #1548 (which contains the acid) at a one to one ratio by volume. Minimum order is 200 gallons. They are doing no development work in wash primers.

• NL Industries, Hightstown, NJ

M. Grabowski

They make NALZIN SC-1 which is a zinc complex of phospho-oxide. This is used by their customers in anti-corrosion coatings - both primer and topcoat. In solvent systems it is most commonly used with medium to long oil alkyds, epoxy esters and other ester-type binders. It is also used in waterborne (latex) maintenance coatings with, most commonly, acrylic latex. They will send data on SC-1 and other Nalzin materials.

National Association of Corrosion Engineers (NACE)

Mr. Hamner

NACE has a good abstracts list on primers with low toxic pigments, but they do not have much on pigments specific to use in wash primers or wash primer per se. They do have a lot on zinc-silicate coatings. NACE Journal of Corrosion Abstracts is available at the University of Connecticut.

They are working on "Conf. on Corrosion Control by Organic Coatings" by Leidheiser. This should be published by January 1982. He suggested contacting Richard W. Drisco, Port Hueneme, California.

National Bureau of Standards (NBS)

Ms. Mary McKnight

NBS is doing nothing under its own auspices on wash primer but she knew of some work at the Naval Air Development Center in Warminster, PA. (Dr. Vinod Agarwala) which was discussed at a conference in Warminster on May 14, 1981 - suggested this be checked with Agarwala directly. Other suggestions; 1) raw material people, e.g. Rohm & Haas, BASF, DuPont, Carbide, 2) Dr. Appleman at DOT, 3) NPCA and NPSCT, SSPC (we already checked these).

She would like a copy of our report in the area of modified wash primer for steel and aluminum. It is suggested that we mention this to our project monitor and ask that this be considered when the report is issued.

(National Bureau of Standards, Attn: Ms. Mary McKnight)

. National Federation of Societies for Coatings Technology (NFSCT)

Tom Kocsis, Technical Editor

He could not give a company or organization who, to his personal knowledge, were actively engaged in current or past work on wash primer development. He said that the New England Society was doing or had done work on corrosion-inhibiting primers but he did not know if this included wash primer (Note: will contact New England Society Technical Committee chairman, Brad Brakke). He suggested contracting Dr. Tom Miranda, at Whirlpool in Benton Harbor, Michigan, who is the Technical Publication Chairman.

. National Paint & Coatings Association (NPCA)

R. Brown, J. Zacharias, Ms . Kardowski

Brown and Zacharias both said no work specific to wash primer development (H_2O -borne, chromate and lead-free) had ever been done or was projected under their auspices. Further, neither had any ideas from their own personal experience which they thought might be helpful. Both were familiar however, with the general nature and end use areas for WP-1 and variations of this chromate-type of primer. Referred to Donna Kardowski, Librarian, who edits their "Abstract Review" to which Springborn Laboratories (S.L.) subscribes. There is no specific category in their index for "wash primer". She thought we would have to look under "primers" and select articles which would pertain. She offered to abstract the "primer" category from 1975 back to 1970 (we can do 1981 back to 1975 ourselves) and send us the index page numbers for each year on the subject of primers.

O'Brien Corp., Southwest Division (Napko), Houston TX

They make only the standard zinc-chromate type of wash primer. This is a two-package material, product number 332600, sold as a unit to be mixed by the user one to one by volume. Its major use is on clean steel but can also be used on galvanized, brass, aluminum and light metals, e.g. magnesium. They know nothing about any development work on non-toxic pigmentations in such products anywhere in the O'Brien organization, including the Baltimore research group.

Organic Coatings and Plastics Div. of ACS (ORPL Div)

(G.G. Schurr, Treasurer)

Gar Schurr is an officer of the ORPL Division. He is also Senior Research Scientist at Sherwin-Williams, Research & Development in Chicago. The division conducted a Symposium about 15-20 years ago on primers - - he was sure there were a couple of papers on wash primers, but he was also sure that they all embodied zinc chromate or lead chromate as the inhibiting pigment. To the best of his knowledge, the division has not published in its preprints anything on wash primer in which non-toxic pigments are involved.

Paint Research Institute (PRI)

Dr. R. R. Myers at Kent State University

The Institute has not yet reported on any work in the area of chromate-free wash primer. However, Dr. Myers said that work in this area is under present consideration for the immediate future and he is sure a PRI grant will be made, most probably to Dr. Leidheiser at Lehigh who, he feels is well qualified in this area. (Dr. Myers, at Kent State University is Director of PRI).

. PPG Industries, Pittsburg, PA

Mr. Keeling 's Office

They make a wash primer but it is a standard chromate type. Persons who answered did not know of any development effort to reformulate to use only non-toxic pigments.

. Port Hueneme , California Naval Center

R. Drisko

They are doing nothing directly on wash primer or substitute materials therein. He suggested SSPC as a source for test data (We have already contacted Dr. Bruno at SSPC who was not able to contribute anything specific on the subject). Drisko suggested talking to E. Matsui in his department for anything on substitute materials. He seemed to think that the Air Force had done some work in the area of wash primer but he could not recall what it embodied.

. Port Hueneme, California Naval Center

E. Matsui

His work is all on substitute materials. For zinc chromate, he said zinc molybdate and barium metaborate had some present utility in metal primers as substitute materials, but he himself did not know of any work in this area of development by the Navy Department . He did not know of any West Coast coatings company who would be doing any research on wash primers.

Seaguard Corporation, Portsmouth, VA.

Fred Kinsler

They make only the standard wash primer pigmented with zinc chromate as the active pigment. He knew of no one in the United States who made a wash primer without using chromate or molybdate pigments - - the latter not being nearly as effective as the chromate. He said that in Europe and the British Isles they made an iron oxide pigmented primer with a phenolic-vinyl binder which was claimed to be as effective as chromate-pigmented types but no one in the United States has yet offered such a material.

Steel Structures Painting Council (SSPC)

Dr. Bruno

He said he was aware that effort to produce a "non-toxic" wash-primer was in the works in some quarters but nothing had been submitted to them for evaluation which had the normal wash primer performance without the normal "toxic" composition, e.g. without chromate or lead. Other acids than phosphoric (e.g. polyfunctional organic acids such as citric) might activate the anticorrosive aspects on steel with "non-toxic" passivating pigmentations. Dr. Bruno said he felt that our project of a substitute wash primer with no chromate or lead therein and with minimal organic solvent content was a difficult, but not an unsolvable one; however, he had one suggestion for us and stated that SSPC neither sponsored nor did any research themselves in this area.

Wisconsin Protective Coatings, Green Bay, Wisc.

They make a number of epoxy and vinyl primers for steel and other metals but all of these contain inhibitive pigmentations, such as chromates or lead salts. They do not now, nor have they ever sold a true wash primer and they felt that if they did, and if it were not pigmented with chromate or other inhibitive pigment, it would not be a corrosion-deterrent material. They felt that one might as well use a topcoat formulation as a primer as to prime with non-inhibitive primer pigmentation; (Note: WPC opinion only).