An Investigation of Primers for Marine Atmospheric Environments

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Introduction

The superiority of red lead paints as rust-inhibitive primers for steel structures has been recognized for many decades. Many reports (1) have been published enumerating the advantages of red-lead-in-oil paints. For general maintenance and repainting where thorough surface preparation is not feasible, these paints still offer the most dependable protection. However, since the problems of corrosion protection and paint formulation are extremely complex and no single paint or type of paint will give the best protection under all conditions, red lead base mixed pigment primers containing synthetic vehicles have been developed to supplement the universally accepted red-lead-in-oil paints. These primers were developed to meet a demand for shorter drying schedules and for special service conditions.

In its search for improved red lead base primer paints for different types of atmospheric and marine exposure, the Red Lead Technical Committee of the Lead Industries Association has carried out several projects embracing various types of synthetic vehicles with a variety of red lead base pigmentations. The primary objective of the particular project discussed here was the attainment of improved primer paints for use in marine atmospheric environments. A series of modern red lead base primer paints is presented. Typical practical applications for these primers would be on all parts of ships above the water line, docks and dock buildings, cranes, buoys, bridges located along the coast or over tide waters, and machinery in marine installations.

Another project on red lead base primers for tide range and total immersion exposure was discussed in a previous paper (2).

Objectives

In planning and carrying out this investigation the following problems were given particular consideration:

a. Determination of the best modifying pigments for use with red lead in synthetic vehicle type paints. Included among these pigments were iron oxide, zinc oxide and zinc yellow (zinc chromate), and micaceous and other inert pigments.
b. The effect on protective performance of variations in vehicle constituency. Included among the vehicles were phenolic, coumarone-indene modified phenolics, and alkyds.
c. The effect of variations in pigment-volume ratios on protective paint performance.

Scope of Project

This paper is based on exposure results obtained on twenty-one test pigmentations, nine test vehicles, and two zinc yellow specification primers. Sixty-seven primers including controls were exposed. The pigment and

* Presented before the [illegible] Paint and Varnish Production Clubs: Houston and Dallas, September [illegible] and Baltimore January [illegible].
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TABLE I - [illegible]

COMPOSITION	[illegible]																				
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]				[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Red Lead (97% Grade)	[illegible]	[illegible]	90	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	70	72	70	72	[illegible]	[illegible]	[illegible]
Lead Chromate, Basic		20																			
Litharge				14																	
Lead Sulphate, Basic												20									
Zinc Oxide	10	10			15	15	10	10	10	20			10	10		10		10		20	10
Zinc Yellow (In. Chrom)	10				[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		10	[illegible]		10	20		[illegible]		10
Iron Oxide, Siliceous	7				7		7	7	7	7	7		[illegible]								
Diatomaceous Silica	8	5	10																		[illegible]
Magnesium Silicate	[illegible]	[illegible]					15														[illegible]
Mica, Graphitic				20	15	[illegible]				15	15	[illegible]			20	15	[illegible]	20	[illegible]	[illegible]	
Mica (325 Mesh)								[illegible]						[illegible]							
Mica, Micronized									15												

TABLE II - [illegible]

VEHICLE NUMBER	COMPOSITION
[illegible]	60% 4 gallon tertiary butyl phenolic-coumarone linseed oil varnish, coumarone resin m.p. @ 127-137°C. 40% linseed oil modified glyceryl phthalate alkyd (32% phthalic anhydride)
[illegible]	60% 4 gallon tertiary butyl phenolic - coumarone linseed oil varnish, coumarone resin m.p. @ [illegible]°C. 40% linseed oil modified glyceryl phthalate alkyd (32% phthalic anhydride)
[illegible]	60% 4 gallon tertiary butyl phenolic-coumarone dehydrated castor oil varnish, coumarone resin m.p. @ 127-137°C. 40% linseed oil modified glyceryl phthalate alkyd (32% phthalic anhydride)
[illegible]	60% 4 gallon tertiary butyl phenolic-coumarone dehydrated castor oil varnish, coumarone resin m.p. @ [illegible]° C. 40% linseed oil modified glyceryl phthalate alkyd (32% phthalic anhydride)
[illegible]	60% 4 gallon tertiary butyl phenolic-coumarone tung oil varnish, coumarone resin m.p. @ [illegible]°C. 40% linseed oil modified glyceryl phthalate alkyd (32% phthalic anhydride)
[illegible]	60% 4 gallon tertiary butyl phenolic-coumarone tung oil varnish, coumarone resin m.p. @ [illegible]° C. 40% linseed oil modified glyceryl phthalate alkyd (32% phthalic anhydride)
[illegible]	60% [illegible] gallon tertiary butyl phenolic varnish with equal parts by weight of linseed and dehydrated castor oils. 40% linseed oil modified glyceryl phthalate alkyd (32% phthalic anhydride)
[illegible]	A dehydrated castor oil modified glyceryl phthalate alkyd (32% phthalic anhydride)
[illegible]	A phenolic modified linseed-glyceryl phthalate alkyd ([illegible] phthalic anhydride, [illegible] phenolic resin)

vehicle compositions are included in *Tables I* and *IA*. Detailed formulations of those primers proved especially outstanding are also included in this report. They are recorded in *Table IV*.

The systems comprised two coats of anti-corrosive primer with Maritime Specification low visibility gray (52-MC-6) as the finish coat.

Description of Test

The paints were all applied by brushing to 6 by 12-inch twelve gage low carbon steel panels. These panels were free from rust and were thoroughly washed with mineral spirits prior to painting. Mill scale was allowed to remain on the panels and was smooth and intact. Each coat was applied to a dry film thickness of approximately 1.5 mils. This was done by applying calculated weights of each of the paints to the panel surfaces. Both the exposed surfaces and the backs of the panels were painted. A period of twenty-four hours was allowed between successive coats and before exposure after the finish coat. This was considered ample since all of these primers were fast drying types, reaching the tack free stage in approximately four hours.

The panels were exposed in a vertical position facing south at approximately thirty inches above the high tide level at the Marine Basin at Sayville, Long Island. The panels were fastened to wooden beams by ⅜ inch steel bolts through bolt holes drilled at the two upper corners. The panels were insulated from the bolt heads and shanks with plastic washers and sleeves.

The panels were inspected periodically for corrosion (edge and general), blistering, and peeling. The systems were rated from zero to ten in each category, the number 10 designating no observable failure and 0 designating failure of the paint or zero protection for the steel. In the case of corrosion, a panel with a rating of 5 would mean that approximately fifty per cent of the surface was rusted.

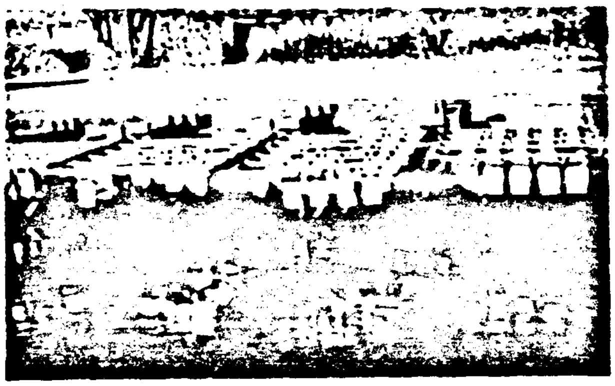

Figure 1. A View of the Marine Basin at Sayville Showing How the Panels Are Suspended a Short Distance Above High Tide Level.

The test specimens were exposed on October 13, 1944.

Description of Exposure Site

The Marine Basin is located at Sayville, Long Island, which is about fifty miles east of New York City on the south shore of Long Island, in a rural area. A view of the Marine Basin is shown in *Figure 1*.

The close proximity of the panels to the water at this location assures an atmosphere high in salinity at all seasons and a great deal of salt spray in stormy weather and throughout the winter months; a condition commonly encountered on the topsides of ships, dock structures, bridges near or over tidewaters, and marine equipment in general.

TABLE [illegible]

PERFORMANCE RATINGS OF CONTROLS AND OUTSTANDING PRIMERS

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	PERFORMANCE RATINGS
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table III

(Location, Sayville, L. I.; Type of Exposure, Atmos. Marine; Date Exposed, 10/26/44; Exposure Period, 41 months.)

Panel No.	LIA Paint No.	Pigmentation No.	Vehicle No.	PV	Performance Rating 41 Months: Blistering	Corrosion: Edge	Corrosion: Gen.	Peeling
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table III (cont.)

Panel No.	LIA Paint No.	Pigmentation No.	Vehicle No.	PV	Blistering	Corrosion Edge	Corrosion Gen.	Peeling
[illegible]	134	43	27	33	9	6	8	9
[illegible]	135	45	19	33	8	7	7	8
[illegible]	136	45	27	33	8	6	7	8
[illegible]	137	46	19	33		1	5	
[illegible]	138	46	27	33	9	7	9	9
[illegible]	179	29	19	33		4	5	
[illegible]	180	30	19	33	8	7	8	8
[illegible]	181	31	19	33		3	5	
[illegible]	182	35	19	33	8	2	6	8
[illegible]	183	36	19	33	10	8	10	10
		Navy Primer 52-P-18						
[illegible]				40	-	3	6	-
		Maritime Commission Primer 52-MC-20						
[illegible]				40	8	4	8	8

TABLE IV

COMPOSITION OF BEST L.I.A. PAINTS AND CONTROL PAINTS

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	—
[illegible]	—	[illegible]	—	—	—	—	—	—	—
[illegible]	[illegible]	—	—	[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]
[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]
[illegible]	—	—	—	[illegible]	[illegible]	—	—	—	—
[illegible]	—	—	—	—	—	—	—	[illegible]	[illegible]
[illegible]	—	—	—	—	—	—	—	[illegible]	—
[illegible]	—	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	—	—
[illegible]	[illegible]	—	—	—	—	—	—	—	—
[illegible]	—	—	—	[illegible]	—	—	—	[illegible]	[illegible]
[illegible]	—	—	—	[illegible]	—	—	—	—	—
[illegible]	—	—	—	—	—	—	—	—	[illegible]
L.I.A. [illegible]	[illegible]	—	—	[illegible]	—	—	—	—	—
L.I.A. [illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	—
[illegible]	—	—	—	—	—	—	—	[illegible]	—
[illegible]	—	—	—	—	—	—	—	[illegible]	—
[illegible]	—	—	—	—	—	—	—	—	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	—	—	—	—	—	—	—	[illegible]	—
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
[illegible]	—	—	—	—	—	—	—	[illegible]	[illegible]
% pigment by weight	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
% vehicle by weight	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Pigment volume	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

Presentation of Performance Data

The numbers, composition, and complete exposure records of the test paints showing very little or no failure are included in *Table II* with comparable data on the standard or control paints. The formulation details on these paints can be found in *Table IV*.

Table III contains the performance ratings after 41 months for all of the test panels.

Conclusions

The following conclusions were reached after careful consideration of the data in *Table II*, containing the complete inspection results on the ten best primers in the project, and *Table III*, containing the 41 months inspection results on all of the paints.

1. The use of limited amounts of zinc yellow (zinc chromate) as modifier of red lead base primers is advantageous. From these tests approximately 15 per cent of zinc yellow by volume (approximately 10 per cent by weight) in the total pigment would seem to be the optimum. The red lead paints modified with zinc yellow were superior, as a group, to the control paints in which the corrosion inhibitive pigment consisted entirely of zinc yellow.

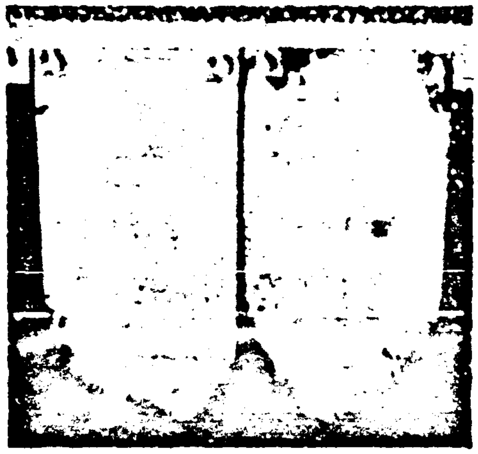

Figure 2. These Panels Illustrate the Disadvantage of Too High a Ratio of Zinc Yellow to Red Lead in Mixed Pigment Red Lead Base Primer Paints for Marine Atmosphere. Panel Nos. 487 and 488 were coated with a primer paint, containing Pigmentation 45, consisting of 19% red lead, 30% zinc yellow, and 21% mica in two vehicles. Both of these specimens show considerable blistering and severe edge corrosion. The suffix letter A stenciled on the panels is not referred to in either the tables or text since it merely designates an atmospheric project.

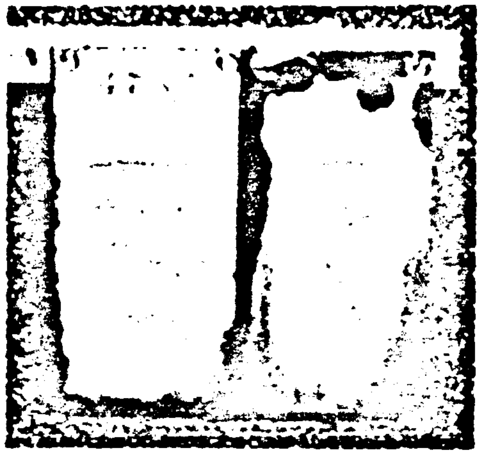

Figure 3. These Two Panels Illustrate the Deleterious Effect of High Concentrations of Zinc Oxide in Short Oil Phenolic Vehicles on the Protective Performance of Red Lead Base Paints Exposed to a Marine Atmosphere. (The primer paint on Panel No. 473 was pigmented with 55% red lead, 20% zinc oxide, 7% iron oxide, and 18% graphitic mica. The pigmentation in the primer on Panel No. 489 consisted of 55% red lead, 20% zinc oxide and 25% graphitic mica. Both primer paints were formulated with Vehicle 19.)

Panel Nos. 487 and 488 in *Figure 2* show that greater volumes of zinc yellow tend to give earlier failure. Both of these panels were coated with a primer paint containing Pigmentation 45 consisting of 55 per cent red lead, 20 per cent zinc yellow, and 25 per cent mica. The primer on panel No. 487 contains this pigmentation in vehicle 19, a six gallon phenolic varnish-alkyd resin combination. The primer on panel No. 488 was formulated with vehicle 27, a dehydrated castor oil modified glyceryl phthalate alkyd.

2. High concentrations of zinc oxide should be used with discretion since such use of this pigment, especially in a short oil vehicle, showed poor performance. See panel Nos. 473 and 489, in *Figure 3*. When these concentrations were used in long oil vehicle primers, this adverse effect was experienced, but not as consistently. (See panel No. 490 in *Figure 6*.)
   The results also indicate that the use of zinc oxide is detrimental where the red lead content is in the order of 70 per cent particularly in short oil vehicles (see panel Nos. 481 and 485 in Figure 4).

3. Iron oxide did not improve the protective performance of these primer paints. It did, of course, contribute to good hiding power.

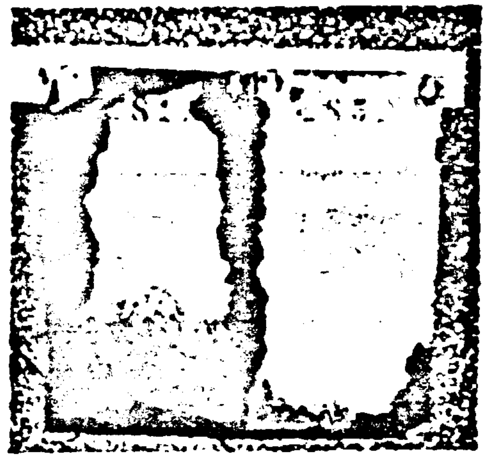

Figure 4. Illustration of the Adverse Effect of Zinc Oxide in Red Lead Primer Paints Containing 70 per cent Red Lead.

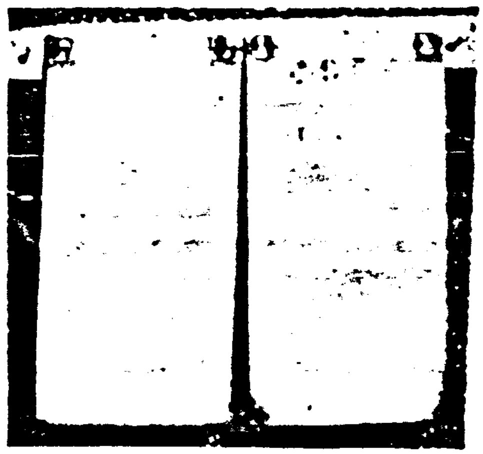

Figure 5. Panel Nos. [illegible] and [illegible] Showed the Best Performance After 41 Months Exposure at 30 Inches Above High Tide Level.

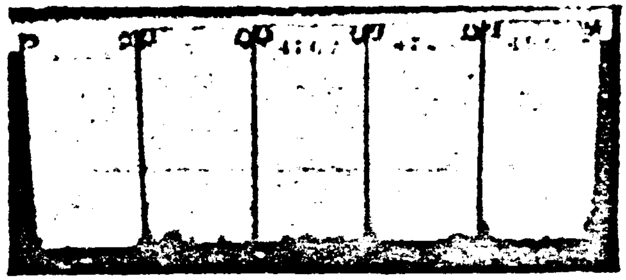

Figure 6. These Panels Contain Five Lead Base Primer Paints Showing Outstanding Performance After 41 Months Exposure to the Rigorous Marine Atmosphere.

4. The use of micaceous pigments as modifiers of red lead base primers has been shown to be effective in improving their performance. Six of the seven best performing red lead paints contained mica. *Table II* and *Figures 5* and 6 illustrate this point very clearly.

Figure 7. This Photograph Shows the Condition After 41 Months of the Panels Painted with the Two Government Specification Zinc Chromate Base Primers. Panel Nos. 501, on the left, and 503 contain Navy Department 52-P-18 and U. S. Maritime Commission 52-MC-29 zinc chromate base primer paints, respectively.

5. Aside from their characteristic suspending properties and other properties specific to each, the other inert pigments used did not contribute significally to primer paint performance.
6. Where litharge was used in one instance as a modifier of red lead, along with a micaceous pigment, excellent performance results were obtained without other modifying pigments. However, the use of litharge in the proportion employed in this test paint would make it necessary to furnish it separately for admixture into the paint just prior to use.
7. A dehydrated castor oil alkyd was consistently outstanding in performance. Six of the seven best paints contained this vehicle. This is also substantiated by work previously reported by the Red Lead Technical Committee on a group of tide range panels (*2*).
8. Another vehicle resulting in good performance was an alkyd modified short linseed oil phenolic-coumarone varnish. This vehicle showed superiority to the castor oil alkyd in just one of the outstanding paint compositions.
9. Modification of the alkyd-short oil phenolic-coumarone varnish (vehicle 19) did not result in improved primer performance.
10. Variations in vehicle and pigment composition seemed to mask the effect of pigment volume variations. A further study of the problem is indicated.
11. The failure of the control paints was characterized by the early appearance of blistering and by more severe ultimate edge corrosion failure as shown in *Figure 7*. Many of the red lead base paints tested gave better protective performance than the two zinc chromate paints formulated in accordance with government specifications.
12. Although paints 116 and 183 on panel Nos. 468 and 495 received top rating among the seven outstanding red lead base primers, the attention of the paint formulator and specifier is called to the limitations of these particular pigment and vehicle combinations.

    To assure container stability of paint No. 116, the litharge portion must be introduced into the balance of the paint just prior to its application. This introduces a practical limitation which may preclude its general use.

    Of the paints formulated with vehicle 19, No. 183 is the only one classed among the best. This vehicle does not permit as wide a latitude in pigmentations as might be desired.
13. A review of the seven best performing paints, giving due consideration to consistency of performance of the vehicles, leads us to conclude that paint Nos. 132, 34c, 118, 120, and 138 all offer the paint manufacturer and user, red lead base primers of the highest quality for the protection of iron and steel structures exposed in marine atmospheric environments.

Summary

After approximately three and one-half years test exposure to a rigorous marine atmosphere, a group of several red lead mixed pigment primers have been proved outstanding. This work has added to our knowledge of both extender pigments and synthetic vehicles for red lead paints. In addition to furnishing formulators, manufacturers, and specifiers with

several fast drying synthetic primer paints tested under conditions simulating actual field exposure, it is our hope that this work will also supply the experienced paint formulator with additional data that might prove valuable in designing anti-corrosive paints for various applications not covered in this paper.

In choosing protective primers for specific applications, good performance in the type of atmosphere encountered is imperative, but other requirements, both of a technical and economic nature, must be considered. In this paper we have endeavored to demonstrate the many possibilities and advantages of red lead pigmentations in synthetic vehicle paints. The paint formulator and specifier must exercise individual judgment in choosing the primer composition for his specific applications.

Even though this series of paints has been on test for a sufficient period of time to permit the culling out of the mediocre and poor paints, much still remains to be learned by continuing periodic inspections of the paints showing little or no failure. We plan to do this and to publish subsequent papers on this and other series when sufficient additional data are available.

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