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Technical Note N-767

PROTECTIVE COATINGS IN SHALLOW AND DEEP OCEAN ENVIRONMENTS

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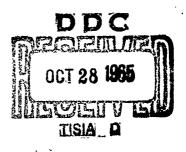
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C. V. Brouillette, R. W. Drisko, Ph. D., and R. L. Alumbaugh

20 August 1965

U. S. NAVAL CIVIL ENGINEERING LABORATORY Port Hueneme, California



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PROTECTIVE COATINGS IN SHALLOW AND DEEP OCEAN ENVIRONMENTS

Y-F015-01-05-002a Y-F020-03-04-001

Type B

by

C. V. Brouillette, R. W. Drisko, Ph. D., and R. L. Alumbaugh

ABSTRACT

A number of organic coating systems, topcoated zinc inorganic systems, and splash zone compounds were exposed on steel specimens in shallow and deep ocean environments. Performance was generally better at shallow depths. Notable exceptions were soft asphaltic and coal tar coating systems that are susceptible to barnacle damage in surface waters. Organic coating systems of 13-mil or greater dry film thickness performed markedly better than those of less thickness. Post-cured zinc inorganic systems tended to perform better than those self-cured. and the second second and the same of the second second second second second second second second second second

INTRODUCTION

Field activities of the Navy's Bureau of Yards and Docks have frequently encountered difficulty in protecting from corrosion steel structures exposed to a submerged marine environment. Until comparatively recently, almost all attempts at corrosion control were directed to structures at very shallow depths. Increasing interest is now being paid to protection in deep ocean environments.

Where a source of electrical power is readily available, cathodic protection is frequently placed on submerged steel structures. Protective coatings are generally used in conjunction with cathodic protection to minimize current requirements and are almost always used on steel structures in tidal areas where cathodic protection is ineffective and at geographical locations where electrical power is unavailable.

The U. S. Naval Civil Engineering Laboratory has conducted several studies^{1,2} into protective coatings for steel located in a submerged marine environment. One such study utilized coated steel piling and angle iron driven into surf and harbor areas, another utilized coated steel panels ten feet long, four inches wide, and one-eighth inch thick suspended from piers at two locations, and a third utilized mooring buoys serving the fleet at San Diego Bay. The data to be presented on the performance of protective coatings at shallow depths were taken from these studies.

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Coated steel specimens exposed at greater depths were 12 inches long, six inches wide, and one-eighth inch thick. These were placed in racks and secured to a submersible test unit (STU)³ exposed at various bottom depths off the coast of Southern California.

Exposed specimens in all environments had been coated under the direction of application specialists. Sandblasted steel surfaces were coated in accordance with the best recommended practices at a temperature greater than 60°F and a relative humidity less than 85%. Surfaces were primed immediately after sandblasting to white metal, and additional coats were applied after undercoats had completely dried. Total dry film thickness was determined by magnetic gage.

All test specimens were carefully installed to avoid coating damage and permit meaningful conclusions to be made. This paper will compare the performance of a number of protective coatings in shallow and deep ocean environments.

ORGANIC COATING SYSTEMS

Ten coating systems, nine completely organic and one containing a zinc inorganic silicate, were exposed in one deep ocean exposure program. These systems were exposed on pairs of panels, one scribed and the other unscribed. Test panels were first exposed for four months at 5,600 feet. When found to suffer no deterioration in this environment, they were exposed at a depth of 6,800 feet for an additional thirteen months. The performance of these systems at 6,800 feet and in a shallow ocean environment will be discussed individually.

<u>Mica-filled asphalt emulsion</u> - This system consists of one coat of pretreatment primer MIL-P-15328B, two coats of phenolic primer MIL-P-12742A, and three coats of mica-filled asphalt emulsion giving a total dry film thickness of 20-21 mils. The coating system gave good protection to steel at shallow depths in spite of the susceptibility of the soft asphaltic topcoats to abrasion damage and penetration by barnacles. The underlying zinc chromate-pigmented primer provided good protection where much of the asphaltic topcoat had been lost by barnacle attack.

This system performed well at 6,800 feet. The only deterioration was a very slight rusting and tuberculation at the scribe. It should be noted that there was practically no fouling on any of the panels at great depth, the only occasional organisms present being identified as small hydroids and perifera (sponges).

<u>Coal Tar</u> - This system consists of three coats of cold-applied coal tar coating MIL-C-18480A to a total dry film thickness of approximately 40 mils. The soft coating was very susceptible to abrasion damage and penetration by barnacles at shallow depths in the same manner as the asphaltic topcoat of the previous system.

At 6,800 feet there was no coating damage and only slight rusting at the scribe.

<u>Coal Tar Epoxy</u> - This system consists of two coats of catalyzed coal tar epoxy primer and one aluminum-filled catalyzed coal tar epoxy topcoat giving a total dry film thickness of 15 mils. This system had provided excellent protection for steel specimens at shallow depths up to three years.

At 6,800 feet this system performed well with only slight rusting and tuberculation at the scribe.

<u>Epoxy</u> - This system consists of one coat of catalyzed epoxy primer and three catalyzed epoxy topcoats giving a total dry film thickness of 10 mils. It has given very good protection to steel specimens for three years at shallow depths.

At 6,800 feet the unscribed panel showed no deterioration, but the scribed panel had medium blistering, and tuberculation at the scribe.

<u>Epoxy-Phenolic</u> - This system consists of one coat of catalyzed epoxy primer and two catalyzed epoxy-phenolic topcoats giving a total dry film thickness of 15 mils. It has given excellent protection to steel specimens for two years at shallow depths.

At 6,800 feet the unscribed panel showed no deterioration, and the scribed panel had only two blisters at the scribe.

<u>Phenolic Mastic</u> - This system consists of one coat of catalyzed mica-filled phenolic primer and one catalyzed phenolic topcoat giving a total dry film thickness of 18-20 mils. This hard, smooth coating system has provided very good protection for steel panels at shallow depths but has suffered moderate amounts of abrasion damage on test mooring buoys.

At 6,800 feet there was no coating damage and c ly slight rusting at the scribe.

Saran - This system consists of alternate coats of vinylidene chloride resin lacquer MIL-L-18389, Types I and II (white and orange) giving a total dry film thickness of 6-8 mils. It has given excellent protection to steel panels for four years at shallow depths. Slight pinpoint rusting and blistering was noticed after four years exposure.

At 6,800 feet the unscribed panel showed no deterioration, but the scribed panel had medium blistering near the scribe and rusting and tuber-culation in the scribe (Figure 1).

<u>Vinyl</u> - This system consists of one coat of pretreatment primer MIL-P-15328B, five coats of vinyl primer MIL-P-15929A, and two coats of either vinyl-alkyd enamel, MIL-P-15936B (gray) or vinyl-alkyd enamel MIL-P-16738B (white), giving a total dry film thickness of 10-12 mils. It has provided very good protection for steel specimens at shallow depths for two years. It has also performed well on Coast Guard navigational buoys and navy vessels for two or more years.

At 6,800 feet the unscribed panel showed no deterioration, but the scribed panel had considerable blistering and lifting of coating at the scribe (Figure 2).

The framework of a STU unit exposed at 5,300 feet for three years was coated with the vinyl system. This coating showed no deterioration (Figure 3) other than a slight pin-point rusting and very slight blistering.

Urethane - This system consists of one coat of catalyzed urethane primer and three catalyzed urethane topcoats giving a total dry film thickness of 10-11 mils. In some cases, it has performed satisfactorily for two years before light blistering occurred and in other cases moderate blistering was noted after one year.

At 6,800 feet both panels had extensive blistering and pin-point rusting (Figure 4).

Zinc Inorganic Silicate - Vinyl Mastic - This system consists of one coat of post-cured inorganic zinc silicate, one coat of vinyl-phenolic primer, and two vinyl mastic topcoats giving a total dry film thickness of 13-14 mils. It had extensive blistering and loss of the organic coatings on panels at shallow depth and on a mooring buoy, but the underlying zinc inorganic silicate has provided excellent protection from corrosion for two years.

At 6,800 feet both panels showed no coating deterioration, and there was only light rusting at the scribe.

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Panels coated with the above ten coating systems were exposed in a 5% salt spray cabinet for 3181 hours. The test results are listed in Table I. There was no apparent correlation between performance under salt spray and under field exposure conditions.

The pressure at 6,800 below the ocean surface exerted considerable pressure on the coated panels. The scribed panels had much more coating deterioration than the unscribed panels. All scribed panels with coating thicknesses greater than 12 mils had little, if any, deterioration, and those with coating thicknesses less than 13 mils had significant amounts of deterioration. Thus, one requirement for good performance of an organic coating at great ocean depth may be a minimum dry film thickness of 13 mils. Any coated structure to be placed at depth must be able to perform well when bare steel is exposed by abrasion or impact damage.

The soft asphalt and coal tar coatings performed better in a deep than in a shallow ocean environment because of susceptibility to barnacle damage in surface waters. In general, however, the organic coating systems performed better in a shallow than in a deep ocean environment.

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ZINC INORGANIC SYSTEMS

Three proprietary post-cured and six proprietary self-cured zinc inorganic coatings were applied to steel panels, and overcoated with the proprietary coatings recommended by the supplier. In addition, one of each type was overcoated with the vinyl system described in the previous section of this paper. Sets of these coated panels were exposed in a salt spray cabinet for 3,181 hours, at shallow depth, on the ocean floor at 2,340 feet for six months, and on the ocean floor at 6,800 feet for thirteen months. All specimens had either no or only slight rusting after exposure. The blistering of the overcoating, along with a description of each coating system, is given in Table II. The condition of some of the blistered panels exposed at 6,800 feet is shown in Figures 5-10.

As with the organic coated panels, the scribed panels with inorganic zinc coatings had more blistering at 6,800 feet than the unscribed panels. Those coating systems that performed well at shallow or deep environments performed well when exposed to salt spray. It should be noted that Systems using zinc inorganic coatings B and R performed well in salt spray testing but did not perform well in deep exposure. Performance was generally better in a shallow than in a deep ocean environment.

The post-cured coating systems generally had less blistering at all exposures than the self-cured systems. Since the observed blistering was probably accelerated by the presence of soluble zinc salts on the overcoated surface, it appears that the thorough hand scrubbing and washing of the post-cured zinc inorganic coatings (probably much better than would be received in field applications) removed most of these salts. The post-cured zinc inorganic coatings were found after exposure to be generally harder than those self-cured. The system with product Q performed well in spite of its relative thin film thickness. The other systems were of approximately the same dry film thickness, and thickness could not be related to performance.

SPLASH ZONE COMPOUNDS

Four two-component splash zone compounds (underwater-curing epoxy coatings) were applied to four panels coated with some of the previously described organic coating systems. Two 22-inch square areas were sandblasted to white metal on one side of each of the coated panels. A $3\frac{1}{2}$ inch square of splash zone compound was placed by hand over each sandblasted area so that there was a $\frac{1}{2}$ -inch overlap over each side. The test pattern is shown in Table III where Epoxy A has an asbestos filler added to the catalyst. Epoxy B was prepared directly from the Shell formulation, Epoxy C has a very fluid catalyst, and Epoxy D has copper oxide added to the epoxy resin to retard marine fouling. After thirteen months exposure at 6,800 feet, all epoxy patches were adhering tightly to the panels with the exception of Epoxy D that had a slight lifting at the edges that permitted rusting of the underlying steel (Figure 11). Epoxy D was rather easily chiseled from the test panels, and there was rusting of the underlying steel (Figure 12). Epoxies A and B were chiseled from the panels with considerable difficulty, and it was virtually impossible to remove the Epoxy C patches in one piece. The surface under these three epoxies were free of corrosion. All four splash zone compounds tested have performed well in patching damage coatings on mooring buoys.

ACKNOWLEDGEMENT

Mr. A. F. Curry of the U. S. Naval Civil Engineering Laboratory was most helpful in the monitoring of coating applications, placement of coated specimens, and rating of coating conditions.

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1, R. W. Drisko. A study of coatings in a marine environment. Offical Digest Journal of Paint and Engineering Technology, <u>36</u>, 767-778 (1964) July.

2. R. L. Alumbaugh. Field test data on coatings for steel piling in sea water. Materials Protection, <u>3</u>, 34-35 (1964) July.

3. K. O. Gray. Materials testing in the deep ocean. Materials Protection, 3, 46-53 (1964) July.

4. ASTM Designation: D-714-56, Standard Method for Evaluating Degree of Blistering of Paints. 1964 Book of ASTM Standards, Part 21, 138-147. American Society for Testing and Materials. Philadelphia, Pennsylvania, 1963.

7

Coating	Blistering Ratings,* Size/Frequency								
System	216 hrs 456 hrs 1,117 h		1,117 hrs	3,181 hrs					
Mica-filled asphalt emulsion	6/F	4/M	2/M	2/MD					
Coal tar	10/N	10/N	10/N	10/N					
Coal tar epoxy	10/N	2/F	2/F	2/MD					
Ероху	6/F	4/M	2/M	2/MD					
Epoxy-phenolic	10/N	2/M	2/M	2/M					
Phenolic mastic	10/N	10/N	10/N	10/N					
Saran	6/M	2/MD	2/MD	2/D					
Viny1	10/N	2/MD	2/MD	2/D					
Urethane	10/N	2/MD	2/MD	2/D					
Zn Silicate-Vinyl Mastic	10/N	10/N	10/N	10/N					

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Table I. Size and Frequency of Organic Coating Blisters After Salt Spray Exposure

* The rating method was ASTM Designation D-714-56. The size ranges from no blistering (10) to large blisters (2). The frequency of blistering was none (N), few (F), medium (M), medium dense (MD), or dense (D).

Size and Frequency of Blisters on Zinc Inorganic Panels Table II.

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Coating System		System		1		Blistering Ratings	ltings ^b		
nıck- ness		Thick-		Th Salt	spray		At Shallow	At 2.340	At 6.800
	Description of Overcoating	(mils)	216 hrs	456 hrs	1,117 hrs	3,181 hrs	Depth		Feet
2½ 3 c	3 coats epoxy	12½	10/N	4/F	2/F	2/MD	4/F	N/01	N/01
2½ 3	3 coats vinyl	10½	10/N	10/N	10/N	N/01	4/F	2/MD	2/MD
2½ 1	<pre>1 tie coat+3 Al-filled hydrocarbon coats</pre>	11ځ	N/01	N/01	10/N	N/01	N/01	N/01	4/D ^C
2 } Mi	Mil. Spec. vinyl system of previous section	12	10/N	N/01	10/N	N/01	N/01	N/01	2/D ^C
2½ 1	l coat coal tar epoxy	125	6/F	2/M	2/MD	2/MD	N/01	4/F	4/F
e.	coats epoxy	13	N/01	4/F	2/F	2/MD	2/F	2/F	2/M
en	coats epoxy	14½	10/N	10/N	10/N	10/N	10/N	6/F	2/M ^C
3½ 1	anti-corrosive coat + 1 coat epoxy	15	N/01	N/01	N/01	2/F	2/F	N/01	8/F ^d
<u></u>	inorganic coats	5≵	N/01	N/01	10/N	10/N	8	N/01	10/N
3 7	<pre>1 tie coat + 3 Al-filled hydrocarbon coats</pre>	12	N/01	N/01	10/N	N/01	4/F	2/D	2/MD ^c
2 } X	Mil. Spec. vinyl system of previous section	14	2/Fc	2/F	i I	8	2/F	2/D	4/D

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Zinc coatings A-C were post-cured and M-R self-cured. See Table I for method of rating.

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The topcoats of both panels had loss of adhesion.

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Panel Coating	Splash Zone Compound Used
Mica-filled asphalt emulsion	А, В
Ероху	B, C
Urethane	C, D
Coal tar epoxy	A, D,

Table III. Pattern of Splash Zone Compound Testing

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APPENDIX

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SOURCES OF PROPRIETARY MATERIALS

ORGANIC COATING SYSTEMS

Mica-filled Asphalt Emulsion

Mica-filled asphalt emulsion:

Coal Tar Epoxy

Coal tar epoxy primer:

Coal tar epoxy topcoat:

Epoxy

Epoxy primer:

Epoxy topcoat:

Epoxy-Phenolic

Epoxy primer:

Epoxy-phenolic topcoat:

Phenolic Mastic

Mica-filled phenolic primer:

Laykold Fibrecoat American Bitumuls and Asphalt Co. 320 Market Street San Francisco.20, California

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Carbomastic No. 3 Carboline Company 32 Hanley Industrial Court St. Louis 17, Missouri

Carbomastic No. 5 Carboline Company

Devran 202 Devoe and Raynolds Company, Inc. 2625 Durahart Street Riverside, California

De ran 203 voe and Raynolds Company, Inc.

Plasite No. 7103 Wisconsin Protective Coatings Corp. 614 Elizabeth Street P. O. Box 243 Green Bay, Wisconsin

Plasite No. 7122-H Wisconsin Protective Coatings Corp.

Phenoline 300 Orange Primer Carboline Company (address above) Phenolic topcoat:

Urethane

Urethane primer:

Urethane topcoat:

Zinc Inorganic Silicate-Vinyl Mastic

Zinc inorganic silicate:

Phenoline 300 White Topcoat and a Carboline Company

Laminar No. 4-G-14 Magna Coatings and Chemical Corp. 1785 North Eastern Avenue Los Angeles, California

Laminar X-500, 11X2 Magna Coatings and Chemical Corp.

Dimetcote No. 3 with D-3 Curing Solution Amercoat Corporation 201 North Berry Brea, California

Amercoat 86, Primer Amercoat Corporation

Vinyl mastic topcoat:

Viny1-phenolic primer:

ZINC INORGANIC SYSTEMS

System with A

A:

Epoxy overcoats:

System with B

B:

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Vinyl overcoats:

Catha-Coat 300 Devoe and Raynolds Company, Inc. (address above)

Amercoat 87, Vinyl Mastic White

Amercoat Corporation

Devran 201, 204, and 209 Devoe and Raynolds Company, Inc.

Rust-Ban 190 Humble Oil and Refining Company P. O. Box 2180 Houston, Texas 77001

Humble Nos. 520, 9512, and 516 Humble Oil and Refining Company

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System with C

C:

Tie coat:

Hydrocarbon topcoat:

System with M

М:

Coal tar epoxy topcoat:

System with N:

N:

Epoxy overcoats:

System with O

0:

Epoxy overcoats:

System with P

P:

Anti-Corrosive primer:

Dimetcote No. 3 with D-3 Curing Solution Amercoat Corporation (address above)

Amercoat No. 86 Tie Coat Amercoat Corporation

Amercoat 29AC Amercoat Corporation

Carbo-Zinc-11 Carboline Company (address above)

Carbomastic No. 12 Carboline Company

Rust-Ban 191 Humble Oil and Refining Company (address above)

Humble Nos. 9664 (2 coats) and 671 Humble Oil and Refining Company

Catha-Coat 302A Devoe and Raynolds Company, Inc. (address above)

Devran 201, 204, and 209 Devoe and Raynolds Company, Inc. Copon Self-cure Z (SCZ) Reliance Universal Inc. P. O. Box 1113 Houston, Texas 77001

Copon PBC 510 Reliance Universal Inc. Epoxy topcoat:

System with Q

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Q:

Inorganic topcoat:

System with R

R:

Tie coat:

Hydrocarbon topcoat:

Epoxy A:

Epoxy B:

Epoxy C:

Epoxy D:

Copon Chemicure 75 Reliance Universal Inc.

Zinc-ite B Plas:Chem Corporation 6177 Maple Avenue St. Louis 30, Missouri

Ceramite Plas-Chem Corporation

Dimetcote No. 4 Amercoat Corporation (address above)

Amercoat No. 86 Tie Coat Amercoat Corporation

Amercoat 29AC Amercoat Corporation

SPLASH ZONE COMPOUNDS

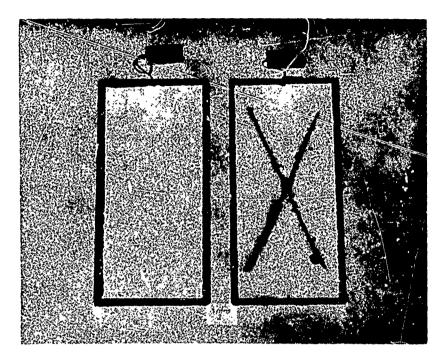
Splash Zone Compound Andrew Brown Company 5431 District Boulevard P. O. Box 22066 Los Angeles 22, California

Aqua-Coat 600 Carl H. Biggs Company, Inc. 1547 14th Street Santa Monica, California

Splash Zone Compound Cook Paint and Varnish Company 2519 Crockett Street Houston, Texas いいうちょう いいがいちいしょう ないないいいいい

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Sea Go-In Poxy Putty Permalite Plastics Corporation 608 Terminal Way Costa Mesa, California



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Figure 1. Saran-coated panels after 13 months at 6,800 feet.

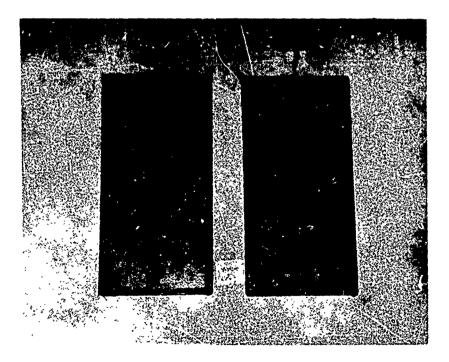


Figure 2. Vinyl-coated panels after 13 months at 6,800 feet.

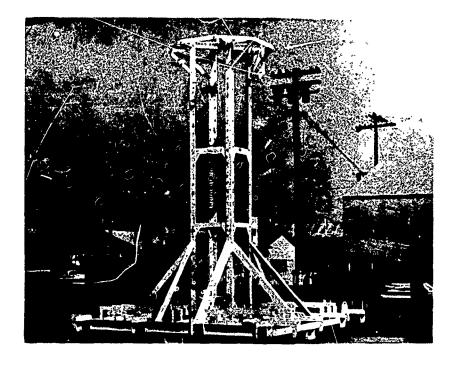


Figure 3. Vinyl-coated STU framework after 3 years at 5,300 feet.



Figure 4. Urethane-coated panels after 13 months at 6,800 feet.

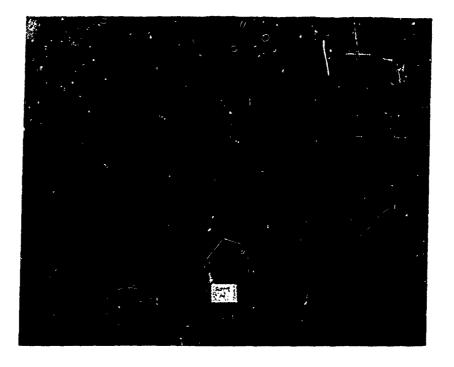


Figure 5. System with zinc inorganic coating B after 13 months at 6,800 feet.



Figure 6. System with zinc inorganic coating C and hydrocarbon topcoats after 13 months at 6,800 feet.

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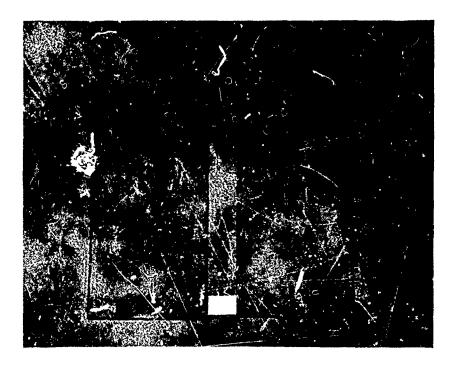


Figure 7. System with zinc inorganic coating C and vinyl overcoating after 13 months at 6,800 feet.

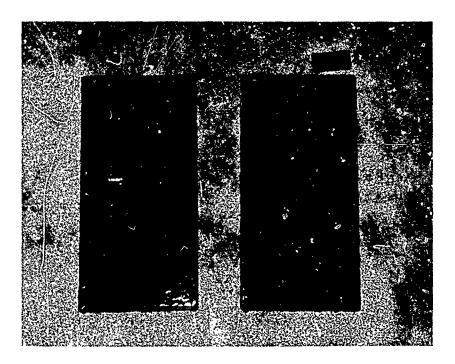


Figure 8. System with zinc inorganic coating P after 13 months at 6,800 feet. Note how easily the blistered topcoating was peeled back.

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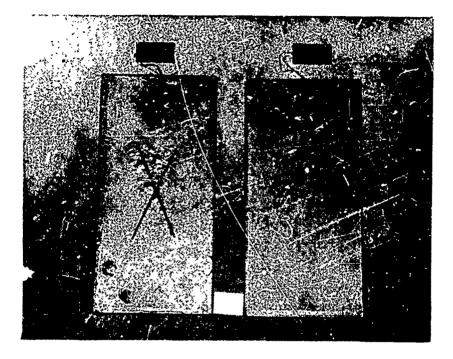


Figure 9. System with zinc inorganic coating R and hydrocarbon topcoats after 13 months at 6,800 feet.

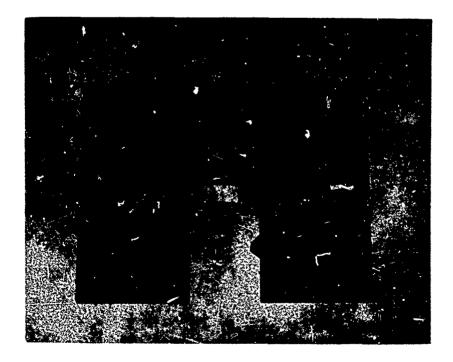
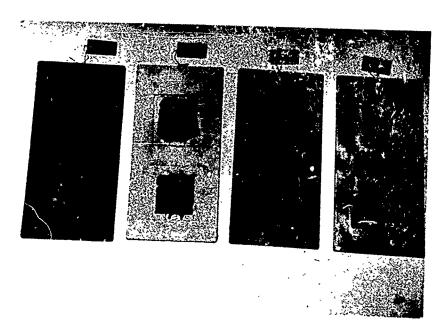


Figure 10. System with zinc inorganic coating R and vinyl overcoating after 13 months at 6,800 feet. Note how easily the blistered overcoating was peeled back.

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Figure 11. Splash zone compounds on coated panels after 13 months at 6,800 feet. From left to right and top to bottom, asphalt emulsion-coated panel with Splash Zone Compounds B and A, epoxy-coated panel with Splash Zone Compounds B and C, urethanecoated panel with Splash Zone Compounds C and D, and coal tar epoxy-coated panel with Splash Zone Compounds A and D.



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Figure 12. Same panels as on previous slide after splash zone compounds were removed.

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