

Submarine Topside Coatings for Application in Cold, Damp Weather

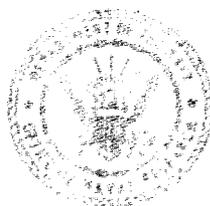
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ABSTRACT

It is often necessary to paint ships in adverse weather. Such is the case with our FBM submarine fleet in Holy Loch, Scotland, where temperatures frequently are near freezing and the relative humidity near 100 percent. This has created a severe maintenance problem insofar as topside painting is concerned.

To develop a coating for this purpose, special equipment was devised and constructed in the laboratory to simulate both the weather conditions under which the coatings must be applied and the environment they must endure. Although all experimental one-package coatings using water-displacing solvents lacked adequate adhesion and durability, two multi-package systems proved successful. These systems were the epoxy-polyamide and the moisture-cured urethane. Although both of these systems showed good durability in service, the urethane system was chosen for further development, since it would cure to a serviceable coating far more rapidly under these severe weather conditions. As a result of this research, three paints were developed using the same vehicle and pigment ratios - an anticorrosive primer, a flat black topcoat, and a white tint-base to mix with the flat black for making various specified grays. Formulations and suggested specifications for these paints have been developed.

PROBLEM STATUS

This is a final report on this phase of the problem; work on the problem is continuing.

AUTHORIZATION

NRL Problem C03-20
Project SR 007-08-05-1201

Manuscript submitted June 2, 1965.

SUBMARINE TOPSIDE COATINGS FOR APPLICATION IN COLD, DAMP WEATHER

INTRODUCTION

Present day national defense requires many U.S. Navy ships to operate in remote seas and from bases in the proximity of their operations. Frequently these locations have weather conditions which are not conducive to repair and maintenance. One such base is Holy Loch, Scotland. Here, throughout much of the year, temperatures remain near freezing; and the presence of fog, rain, wind, and very high relative humidity have resulted in extensive failure of the presently specified vinyl and vinyl-alkyd topside paints. The objective of this research was to develop a coating that can be applied under these conditions to the topsides of submarines without elaborate preparations. The paint should solidify rapidly to a durable, tenacious, and protective film. Although this coating is not intended to replace presently specified paints, which can be applied at other locations, in fair weather, it must exhibit equivalent properties of hull preservation for 6 months or more. Included in this development program were the design and construction of laboratory equipment for application and durability tests of both experimental and proprietary paints.

EXPERIMENTAL PROCEDURE

Test Equipment

In order to apply and observe experimental coatings under adverse weather conditions, an environmental chamber was made from a laboratory hood as shown in Fig. 1. Test panels were painted on the 2 x 4 ft, 1/8-in.-thick copper tray which is placed on a frame stand allowing it to slope 6 in. from rear to front and 2 in. from left to right. This slope somewhat simulates that of a submarine hull and allows run-off of water from condensation and fog. Soldered to the bottom of the tray and covered with insulation are fourteen runs of 1/4-in. copper tubing. These lines are connected to a 3/4-ton refrigeration unit which is operated by a differential temperature control. The gas bulb for this control is inserted in a brass block located on the tray. During the operation cycle, the block varies from 32° to 36° F, and the test panel surfaces range about 2° higher. Fog is created with an air brush which is connected to tap water and compressed air lines. The air in the hood varies between 90 and 95% relative humidity. Figure 2 is a close-up view of the temperature control block and coated and uncoated test panels on the cold, damp tray.

Figure 3 is a schematic of a cross section of a test panel. The experimental coating was applied to the ground side of a 6 x 12 in. cold-rolled steel panel which was partially lap coated with the normally specified ship topside paints. In this manner the experimental coating was tested for adhesion to, and protection of steel, as well as adhesion to the existing paint which it must lap. The opposite side of the panel, which served as a control surface, was coated with the specified one coat (0.3 to 0.5 mils) of Formula 117 (MIL-P-15328B), primer pretreatment (a pigmented polyvinyl-butyril, phosphoric acid mixture); four coats (6 mils) of Formula 119 (MIL-P-15929B) or 120 (MIL-P-15930B), primer, vinyl-red lead or zinc chromate type; and three to four coats (4 mils) of Formula 122-3 (MIL-E-15933B), enamel, outside, dull black, vinyl-alkyd. Total minimum film thickness could be 10.5 mils.

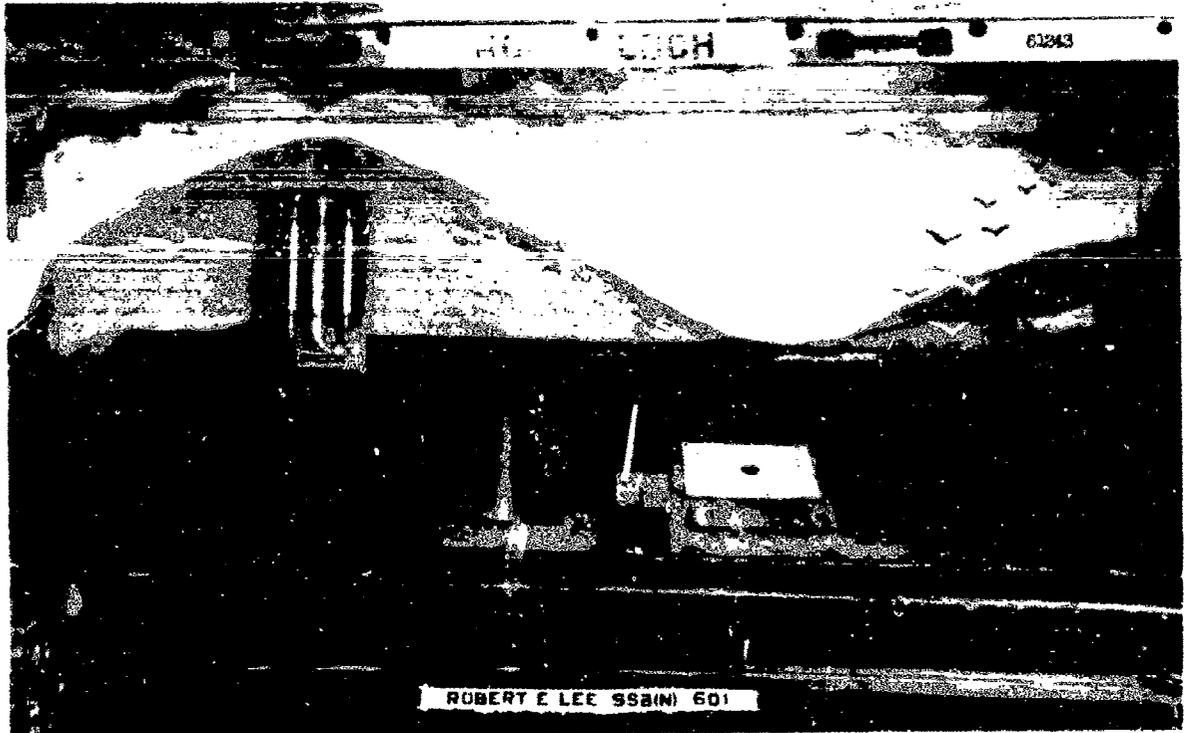


Fig. 1 - Environmental chamber for applying experimental coatings, showing painted and unpainted (center two) test panels on a cold, damp surface

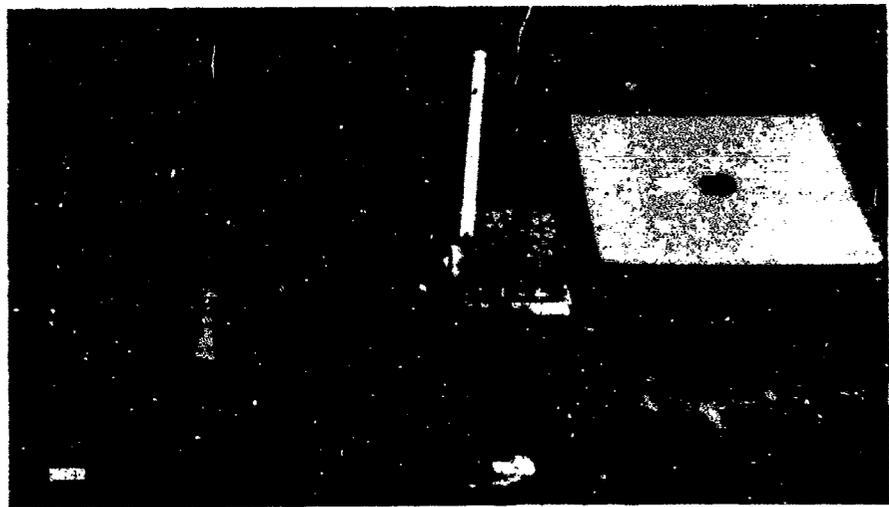


Fig. 2 - Close-up view of unpainted test panel (left), a spin test panel (right), and temperature control block for the platen

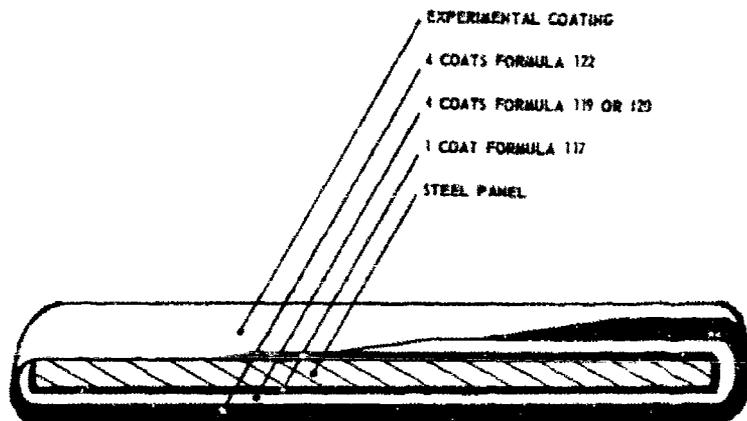


Fig. 3 - Schematic cross section of a test panel

Experimental coatings were applied by brush, starting at the top and working down the panel to force the water to run off. It appeared to be of little benefit to spray the panel first with a water-displacing liquid, since condensation and fog wet the panel constantly. The coated panels were allowed to remain on the tray for three days, where they were observed for hardening rate, adhesion of the film, and other physical properties. At the end of this period, the panels were placed in the test apparatus, where weekly observations for film failure were made.

Coated panels were subjected to immersion tests in circulating tap water and in cold, synthetic sea water. In the latter test both the standard panel and a 6-in.-square, center-drilled panel were used. These panels were mounted on shafts as shown in Fig. 4 and rotated in a sea-water bath maintained at 32° to 35°F with equipment shown in Figs. 5 and 6. The large panels were rotated at 57 rpm, imparting a curvilinear velocity of 2 knots to the panels. The small panels were rotated at 1000 rpm, resulting in velocities of from 5 to 30 knots on the surface of the panels at distances of 1 to 6 in. from the shaft.

Coatings

Since much experience has been gained at this Laboratory in depositing rust-preventative compounds on wet surfaces, using water-displacing fluids (1,2), it was believed that a paint might be formulated from certain vehicles and volatile water-displacing fluids which would be applicable under the stated conditions. Indeed, Formula 117, which contains butanol, has been applied successfully to damp surfaces with satisfactory results.

Table 1 lists some solvents with high equilibrium spreading pressures. Most of these solvents were used to formulate coatings from many polymeric resins. In general, the resins with low polarity such as polyvinyl chloride-acetates and styrene-butadiene lacked proper adhesion to bare steel when applied under the experimental conditions. Highly polar resins such as the polyvinyl formals and butyrals exhibited good adhesion but poor water resistance after long exposure. Many combinations were made from polyvinyl butyral and other resins such as phenolics, ureas, silicones, and acrylics. Curing agents such as phosphoric acid and silicone intermediates were also used with these combinations. Although several of these one-package formulations at first appeared promising, none was found to possess long-time durability.

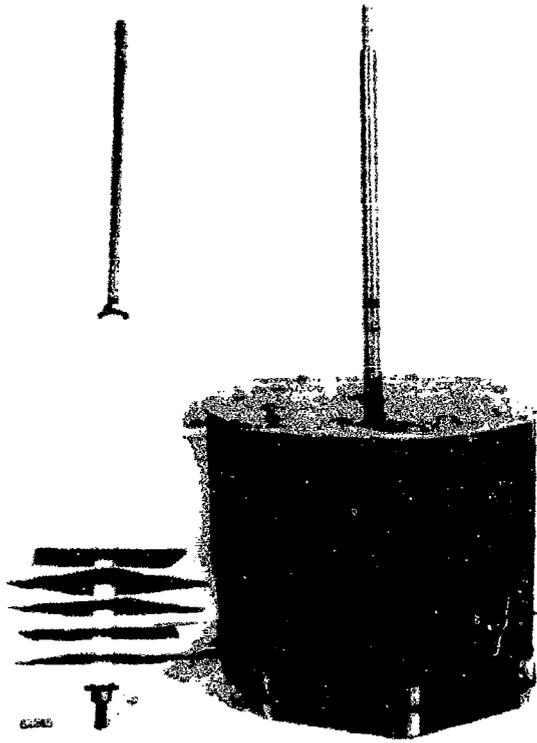


Fig. 4 - Mounted test panels for rotation in sea-water bath

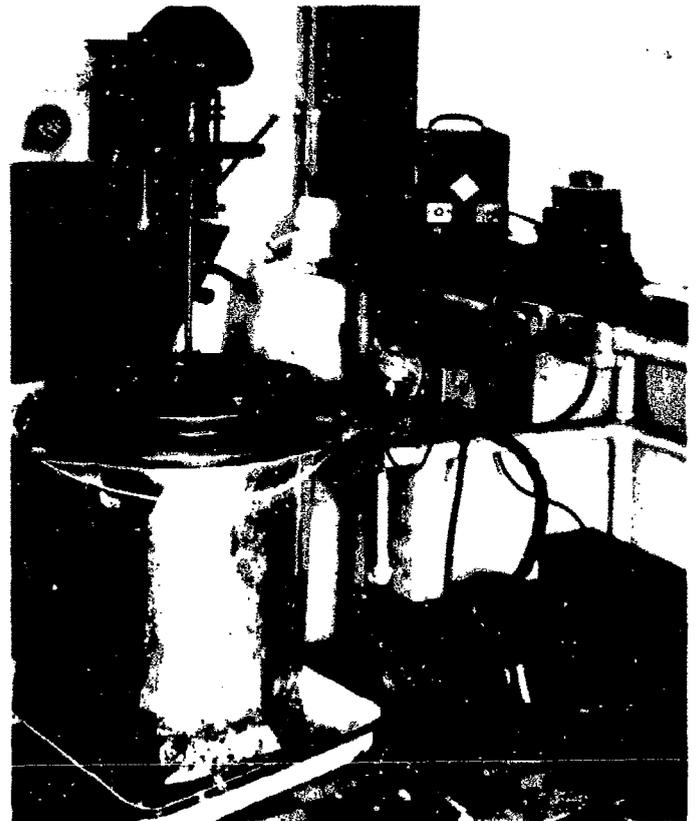


Fig. 5 - Sea-water bath showing drill-press drive and refrigeration compressor



Fig. 6 - Inside view of sea-water bath showing rotating shaft and cooling coil

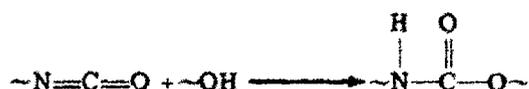
Table 1
Selected Solvents with High Equilibrium
Spreading Pressures, F_0

Solvent	F_0 (dynes/cm at 25 °C)	Approx. V. P. (mm at 20 °C)
sec-Butyl alcohol	50.4	12
Isobutyl alcohol	49.3	8
Butyl alcohol	48.5	4
Methyl ethyl ketone	46.2	70
tert-Amyl alcohol	43.6	12
Butyl lactate	43.5	<1
Cellosolve acetate	43.2	2
Ethyl acetate	41.9	74
Methyl cellosolve	41.2	9
Cellosolve	40.2	4
Dimethyl carbonate	40.1	-

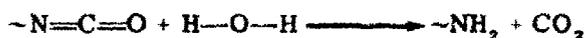
Since several two- and three-package proprietary coatings were found to have better qualities for this application, research was directed to multi-package coatings. Although multi-package coatings have disadvantages of limited application periods or "pot life" and afford maximum chance of improper handling in the hands of inexperienced painters, they are some of the most durable coatings known. Certain epoxy resins, pigments, solvents, and polyamide resins (condensation products of polyamines and dibasic acids) have been blended to form paints which make tough, durable, and tenacious films even on damp surfaces (3). Water on the surface is probably partially displaced and emulsified by the polyamide-solvent combination and brushing. The cure of these systems, however, is very temperature dependent, and at near-freezing temperatures it may take days or even

weeks before the coating will attain its optimum properties. The slow cure of epoxy-polyamide resins at low temperatures was their primary disadvantage. Although many attempts were made to increase the rate of cure at low temperatures, they were only partially successful.

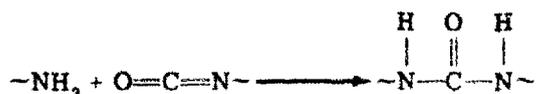
Research was directed to urethane coatings of the moisture-cured type when it was discovered that these coatings could be made to dry in minutes and harden in several hours even at freezing temperatures. Urethane coatings are derived from polyisocyanates and compounds containing hydroxyl groups. The reaction forms the repeating urethane linkage:



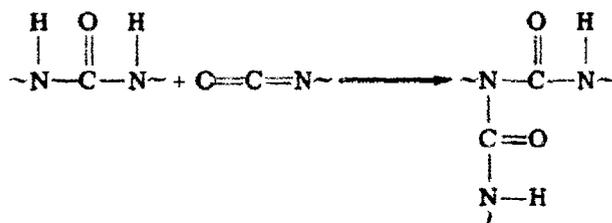
If atmospheric moisture is present, the following reaction also will take place:



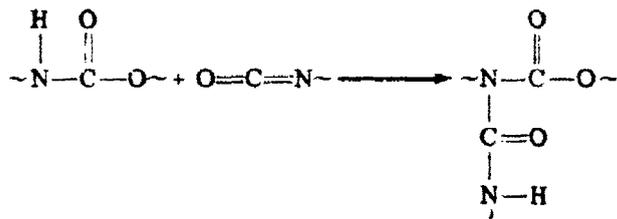
The amine group thus formed reacts very rapidly with another isocyanate group to form a urea linkage:



This urea linkage can further react with another isocyanate group to form a biuret structure:



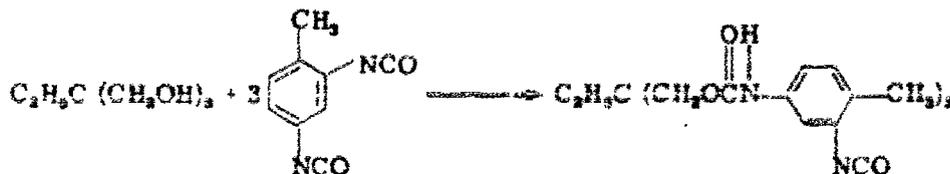
The isocyanate group may also react with a urethane linkage to form an allophanate:



These last two reactions are very slow and probably are of no consequence in film formation at near-freezing temperatures.

Since low-molecular-weight polyisocyanates such as toluene diisocyanate are volatile, toxic, and irritating to the respiratory system, they are reacted with polyols to form adducts having low vapor pressures. These high-molecular-weight adducts are used as solutions and may be handled in relative safety. In addition, these adducts have a lower reactivity rate than toluene diisocyanate and therefore give a longer pot life to the coating.

The following adduct, available from two commercial sources, was used in our formulations. It is made by reacting trimethylolpropane with toluene diisocyanate:

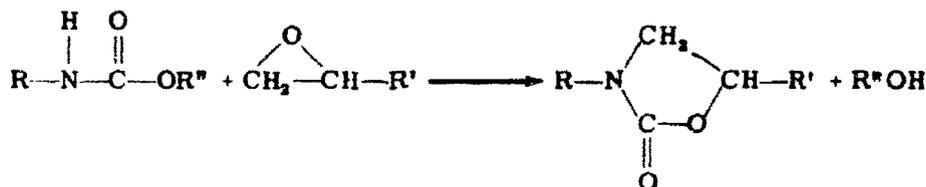


The 75% solids solution of this adduct (as supplied commercially) will have an isocyanate content of 11.5 to 13.5% and a very low free diisocyanate content.

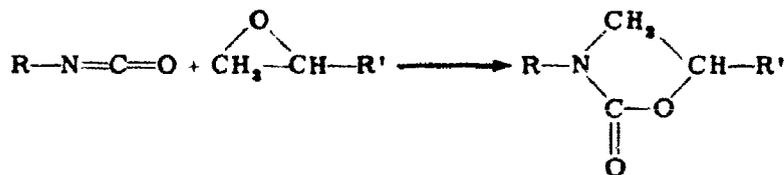
Many polyols and polyol combinations were used with this adduct in varying proportions to develop the most satisfactory vehicle for a paint for cold, damp surfaces. The properties of these paint vehicles are dependent on the molecular weight, structure, and functionality of the polyol(s) and the molar ratio of polyisocyanate to polyol. It was found that a 1 to 1.5 by volume ratio of an epoxy resin to modified, urethane-grade, ethylene glycol monoricinoleate in combination with the above adduct in an isocyanate-hydroxyl ratio (NCO/OH) of 0.9 gave the most satisfactory paint vehicle. The glycol is a mono-ester of castor oil acids and ethylene glycol, and the epoxy resin is a condensation product of Bisphenol-A and epichlorhydrin, having a molecular weight of 1300 to 1520.

DISCUSSION

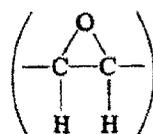
Since each NCO group of the isocyanate adduct will react with one OH group of the polyol(s), it is necessary to know the hydroxyl equivalent of the polyol(s) to determine the amount of adduct required for a stoichiometric reaction. The analytical procedure for determining the hydroxyl equivalent of the polyol is either by carbanilation (4) or esterification (5) of the hydroxyl groups. If the hydroxyl equivalent of an epoxy resin is determined by an esterification reaction, the epoxy groups, as well as the hydroxyl groups, enter the reaction. Each epoxy group will react with two equivalents of acid, making it equivalent to two hydroxyl groups. In the case of the carbanilation reaction, it was not known if the epoxy groups would react with isocyanate groups. In addition, it was thought that the epoxy groups might react with the urethane reaction product or the amines and urea reaction products formed in the presence of water. According to Iwakura and Izawa (6), glycidyl ethers will react with urethanes and ureas to form 2-oxazolidones:



The authors further state that there is no evidence that the following reaction between glycidyl ethers and isocyanates will take place:



This was more or less confirmed when a solution of a diglycidyl ether of Bisphenol A (no OH present) and polyisocyanate adduct did not change viscosity over a month of observation. However, when a trace of a tertiary amine was added, the solution became solid in about 1 hour. After the solvent was allowed to evaporate from this solid, a rock-hard resin of unknown composition remained. If a few drops of water are added instead of amine a soft, milky solid forms over a much longer period. The progress of this reaction may be followed by infrared spectroscopy by observing films cast from the solution as the viscosity increases. Although the isocyanate (—N=C=O) band at 4.42μ became less intense with a corresponding increase in the intensity of the secondary amine ($>\text{N—H}$) band at 3.04μ , there was no apparent change in the epoxide



band at 10.9μ . Finally a gravimetric determination of the hydroxyl equivalent was made by a modified procedure of that used by Malm et al. (7) to determine the free hydroxyl in cellulose esters. The results of this determination by carbanilation indicated that the phenyl isocyanate would react with only the hydroxyl groups on the epoxy resin in the presence of a base. In the presence of small amounts of water the hydroxyl equivalent seemed indeterminate because of side reactions. Any amines and ureas formed from the reaction of isocyanate and water would probably react with more isocyanate to form ureas and biurets rather than with the epoxy group, since the former reaction has a higher rate. It is apparent that the reaction between a polyisocyanate and a mixture of a diol and an epoxy resin in the presence of moisture is a complex reaction, and the stoichiometry of this reaction can be calculated based only on the percent NCO and the percent OH of the reactants.

FIELD TESTING

After completion of laboratory testing, final evaluation of all marine paints must be made on ships in service. Coatings which had passed all laboratory tests were an NRL-developed flat black urethane topcoat, a flat gray epoxy-polyamide topcoat developed by the Mare Island Naval Shipyard, and several proprietary paints. A few gallons of each were shipped to Holy Loch to be applied on the topsides of FBM submarines. NRL personnel supervised application of these paints and observed their condition after one patrol. Observations and reports of paint condition after two or more patrols have been made by ships' crews.

Observations

All repair work as well as supply handling and other operations are accomplished on the FBM submarines during their between-patrols upkeep period in Holy Loch. Topside surface preparation and painting are done by each ship's crew. Surface preparation is accomplished with wire brushes (manual and pneumatic) and chippers, and varies from poor to fair. Paint is applied with brushes in close and irregular areas and with rollers on flat areas. The rollers have 5-ft handles, and two are taped together to reach the top of the sail. Spray guns are used only to paint the inside of the sail, since the average daily winds at Holy Loch are in excess of 20 knots. Priming and painting are usually done over a small area, weather permitting, because of the large amount of traffic on the deck. Even so, some paint will receive traffic before it is completely dry. In addition to the high winds, the average number of days of rain per month over the past three years is sixteen. The relative humidity is nearly always above 70%, resulting in an invisible film

of moisture on all surfaces irrespective of rainfall. This condition results in poor adhesion of the vinyl paints even though it may appear adequate initially. During patrol the vinyl paint will often peel in sheets, while the nonskid coating, applied on certain deck areas, usually fails in chips about 2 to 6 in. in diameter. Figure 7 illustrates a typical portion of paint failure. The present condition of the topside paint on an FBM submarine is the cumulative result of the quality of the builder's initial application, the length of service, the ability and the conscientiousness of the ship's crew in making paint repairs, and the weather conditions during both initial and upkeep painting. From observations made in Holy Loch, it is obvious that not only are the presently specified vinyl-alkyd topside paints unsatisfactory for application under the existing weather conditions, but also the surface preparation and painting techniques are inadequate. It was the object of this research project to develop a coating system which could be applied under adverse weather conditions with assurance that it would remain serviceable for at least 6 months. In order to accomplish this objective, loose and poorly adhering paint must be removed prior to painting or the topcoat will be removed along with the loose underlayers during submerged operations. A coating is only as durable as its foundation, and serviceability will be satisfactory only when proper preparatory measures are applied.



Fig. 7 - Close-up view of typical failure of topside paints on the deck of a FBM submarine [Photograph, courtesy of the USS HUNLEY (AS-31)] (Ed. Note: Permission is granted to use this official photograph in AS31/3150 ltr Ser 3618 of 3 May 1965, route sheet No. 158540.)

Tests and Results

Service tests showed that both the moisture-cured urethane and epoxy-polyamide systems applied to submarine topsides under the severe weather conditions at Holy Loch remain in good condition after 6 months' service, if the undercoats have good adhesion. The disadvantage of the epoxy-polyamide coating as compared to the moisture-cured urethane coating was the rate of cure. When applied under cold, damp conditions the urethane coating was dry to touch in 30 minutes and hard enough for minor traffic in less than 8 hours, while the epoxy-polyamide coatings required several days to reach equivalent hardness. It is anticipated that the urethane coating may have further use on surface craft operating in the Holy Loch climate.

PAINT FORMULATION

Service tests have not been completed on a total urethane coating system (i.e., both primer and topcoat) because the need for a urethane primer was not seen before the visit to Holy Loch to initiate service tests of the topcoat. Although the original project authorization was for development of a flat black topcoat to replace the Formula 122-3 vinyl-alkyd paint, it became apparent that a new primer was needed to replace the often misused pre-treatment primer (Formula 117) and vinyl primers (Formulas 119 and 120), which also lack adequate adhesion when applied under adverse weather conditions. In addition, the Holy Loch visit showed that a flat white paint was needed which could be tinted to various depths of gray by addition of the flat black topcoat. Gray paint is used in certain areas of submarine topsides, as well as on the topsides of surface craft. Since the surface craft operating at Holy Loch are experiencing paint failure similar to that of the submarines, any paints suitable for submarine topsides may have additional use for topside maintenance of these craft.

On return to the Laboratory, a complete urethane coating system was developed and tested. It has endured two months of high-speed rotation in cold sea water. (See Figs. 5 and 6).

Table 2 gives the formulas for the primer, flat black, and flat white paints by volume and the material specifications and paint requirements. Sample calculations leading to the paint formulation in Table A1 are given in the Appendix. These paints are supplied as a two-package system, with 1/2 gallon of pigmented vehicle in a 1-gallon can (Part A) and 1 quart of polyfunctional isocyanate in a "piggyback" or screw-top can (Part B). When Part B is added to Part A the mixture occupies only three quarters of the container, thereby facilitating stirring or shaking. After mixing thoroughly, the paint is allowed to stand at least 1 hour before using. Once mixed, the entire batch should be used within 8 hours if any moisture is introduced by exposure to the atmosphere or from brushes and rollers. Since these paints react with moisture, their pot life can be maximized by pouring only the amount needed into another container for brush or roller application. In this way, the paint may be used up to 30 hours after mixing the two components. Gray colors are made by stirring the mixed (Part A plus Part B) flat black paint into the mixed flat white paint. A Navy No. 7 gray requires one volume of black and three of white, and a Navy No. 27 gray requires one volume of black to twenty-six of white (1 pt. to 3-1/4 gal). An exact color match may require some slight adjustments in these volumes.

RECOMMENDATIONS

It is recommended that for test and evaluation purposes several hundred gallons of these paints be procured for between-patrols topside painting of FBM submarines and surface craft operating in the Holy Loch climate. However, a note of caution is in order: the formulas herein specified are designed specifically for use in cold, damp climates such as

Table 2
Paint, Exterior, Cold-Damp Weather, Moisture-Cured Urethane Type

The following formulas have their ingredients specified in volumes based on 100 gallons of solids. In all three paints the pigment volume is 40 gallons and the resin solids volume is 60 gallons. The two polyhydroxy resins shall be in a volume ratio of 1.0 to 1.5 (epoxy resin to ethylene glycol monoricinoleate, respectively). The polyfunctional isocyanate and polyhydroxy resins shall have an isocyanate to hydroxyl stoichiometric ratio of 0.9. Friction-top, 1-gallon cans shall be used to package 1/2 gallon of Part A. Part B shall be packaged in a full quart (0.25 gal) "piggyback" or screw-top can.

Part	Ingredient	Specification	Amount (gal) Used In		
			Primer	Flat Black	Flat White
A	Basic lead silico chromate*	As in TT-P-615b	26	-	-
	Black iron oxide	TT-P-390	2	6.7	-
	Carbon black †	TT-P-343, Type II, Cl. B	-	6.7	-
	Titanium dioxide	TT-T-425, Type III	-	-	5.7
	Zinc oxide	MIL-Z-15486A	-	-	11.4
	Copper-phthalocyanine-blue	TT-P-355, Type II	-	1.6	-
	Magnesium silicate	MIL-M-15173	6	15	22.9
	Silica diatomaceous	MIL-S-15191A	-	10	-
	Mica	MIL-M-15176A	6	-	-
Total volume of pigment in Part A			40.0	40.0	40.0
	Epoxy resin ‡		Volume of monoricinoleate is 1.5 times the volume of epoxy resin		
	Ethylene glycol monoricinoleate §				
B	Polyfunctional isocyanate solution ¶				
	Total resin solids		60 gal, proportional to give a NCO/OH ratio of 0.9		
A and B	Solvent**		As necessary to meet volume and viscosity requirements		
	Requirements		Primer	Flat Black	Flat White
	Isocyanate to hydroxyl (NCO/OH) ratio		0.90 ± 0.03	0.90 ± 0.03	0.90 ± 0.03
	Pigment volume (%)		40	40	40
	Viscosity, at 35° F, KU (Krebs Units)		72-80	72-80	72-80
	Set to touch (maximum) in minutes at 35° F and 75% R. H.		40	40	40
	Dry hard (maximum) in hours at 35° F and 75% R. H.		8	8	8
	Full cure (maximum) in hours at 35° F and 75% R. H.		24	24	24
	Gloss, 60°		10 (max)	5 (max)	10 (max)
	Grind (minimum)		5	5	5
	Pounds per gallon		12.8-13.4	11.0-11.4	12.7-13.3
	Nonvolatiles, percent by weight		68.5-72.5	56.5-60.5	67-71
	Pot life mixed (minimum) in hours sealed at 35° F		30	30	30

*ASTM specification, D1648-59T (National Lead Co., Oncor M50 or equivalent).

†Gas furnace black; oil absorption 65-75, pH 9.4-9.6 (Sterling S or equivalent).

‡Condensation product of Bisphenol A and epichlorohydrin; molecular weight, 1300-1520; epoxide equivalent, 875-1025; hydroxyl equivalent, 175-180; softening point, 95-105°C, pounds per gallon, 9.6-10.0; refractive index 1.59-1.60; % chlorine <0.5; Sodium, ppm <10.

§Modified, urethane grade, ethylene glycol monoricinoleate, mono-ester of castor oil acids and ethylene glycol; OH number, 245-285; acid value, 3 max; water, %, 0.1 max; Sapon. value, 160-175; Iodine value, 75-83; refractive index at 25°C, 1.4730-1.4745; Viscosity, stokes @25°C 3.3-4.3; color, Gardner, 3 max

¶Solution of 25% dry ethyl acetate and 75% adduct of toluene diisocyanate and trimethanol propane; NCO %, 11.5-13.5; weight per gallon, pounds 9.8-10.6; free toluene diisocyanate, trace.

**1:1:1 by volume Ethyl acetate:Toluene:2-Nitropropane, 7.74 lb/gal (0.1293 gal/lb), ingredients 99.5% pure, 0.25% water and/or free alcohol (max).

that prevailing in Holy Loch and may not be suitable for use in warmer climates because of the highly volatile solvents which they contain. Similar formulations might be prepared for use in warmer climates if less volatile solvents were used.

In addition, it is apparent that suggestions are warranted in the matter of upkeep painting at Holy Loch. Painting should be done by a crew assigned to the tender who are schooled in surface preparation, paint application, and paint technology. They should be equipped with the most up-to-date paint removal equipment and paint applicators, as well as specially designed working platforms, rigs, and wind screens to accomplish their task expeditiously, properly, and safely. If a painting crew is not practical, at least the equipment and one coatings expert should be available from the tender to aid and advise first lieutenants and/or the leading deckhands of the submarines.

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APPENDIX

SAMPLE CALCULATIONS LEADING TO A PAINT FORMULATION

To calculate the amount of isocyanate to react with the epoxy resin and ricinoleate the equivalent weight of each reactant must be known. The equivalent weight of polyisocyanates is usually expressed as % NCO and will be given by the manufacturer. For the ricinoleate it will be the sum of the OH value and acid value given on the shipping container. In the case of the epoxy resin, it can be calculated from the epoxide and hydroxyl equivalents given by the manufacturer. The sample calculations will be based on the following properties:

Polyisocyanate solution (P49-75S)	11.8% NCO
Ricinoleate (Polycin 53)	$\left\{ \begin{array}{l} 273 \text{ OH value} \\ 3 \text{ acid number} \\ 273 + 3 = 276 \text{ OH number (value)} \end{array} \right.$
Epoxy resin (Epon 1004)	$\left\{ \begin{array}{l} 945 \text{ epoxide equivalent} \\ 175 \text{ hydroxyl equivalent} \end{array} \right.$

The hydroxyl equivalent of the epoxy resin is determined by esterification, a reaction which also consumes the epoxide group when it is present. However, epoxide groups do not react with isocyanate groups, and an $\text{OH}_{(\text{NCO})}$ -equivalent weight for isocyanate must be found. This is illustrated below for the ingredients above having composition constants as shown. (The following three publications are cited as the basis for these calculations: (1) "Urethane Coatings," second ed., Mobay Chemical Co., Pittsburgh 34, Pa.; (2) "Urethane Coatings Chemicals," Union Carbide Corp., Chemicals Division, 270 Park Avenue, New York, N. Y.; and (3) "Epon Resin Esters for Surface Coatings," Shell Chemical Co., Plastics and Resins Division, 110 West 51st Street, New York 20, N. Y.)

Each epoxide group is equivalent to two hydroxyls (OH) as determined by esterification. In one epoxy-equivalent weight (945) of Epon 1004, there are a total of $945/175$ hydroxyls (= 5.4), of which 2 are "epoxy-hydroxyls" as determined from esterification, but which are incapable of isocyanate reaction. Therefore, $5.4 - 2$ or 3.4 is the number of "OH-hydroxyls" capable of reacting with isocyanate (NCO). The $\text{OH}_{(\text{NCO})}$ -equivalent weight of Epon 1004 is then

$$\frac{945}{3.4} = 278$$

and the OH number =

$$\frac{56,100}{\text{OH}_{(\text{NCO})}\text{equivalent}} = \frac{56,100}{278} = 202.$$

[56,100 is the molecular weight of KOH expressed as milligrams]

The weight of polyisocyanate per "W" parts of polyhydroxy compound is equal to

$$\frac{(W) (\text{NCO/OH ratio desired}) (\text{OH number}) (7.5)}{(100) (\% \text{ NCO})}$$

[7.5 = constant derived from "Summary of Calculations," Ref. 1 above]

Since the volume ratio of the epoxy resin to ricinoleate is 1 to 1.5, a ratio of 10 to 15 gal is used for calculation purposes:

$$10 \text{ gal epoxy resin} \times 9.60 \text{ lb/gal} = 96 \text{ lb}$$

$$15 \text{ gal ricinoleate} \times 8.03 \text{ lb/gal} = 121 \text{ lb.}$$

Weight of polyisocyanate solution needed for 10 gal epoxy resin:

$$\frac{96 \times 0.9 \times 202 \times 7.5}{100 \times 11.8} = 111 \text{ lb.}$$

Weight of polyisocyanate solution needed for 15 gal ricinoleate:

$$\frac{121 \times 0.9 \times 276 \times 7.5}{100 \times 11.8} = 191 \text{ lb.}$$

Total polyisocyanate solution needed = 302 lb.

$$302 \text{ lb solution} \times 0.75 (75\% \text{ solids}) = 226.5 \text{ lb solids, and}$$

$$\frac{226.5}{10.50 \text{ lb/gal}} = 21.6 \text{ gal of solids.}$$

Total volume of resin solids = 10 + 15 + 21.6 = 46.6 gal.

A 40% PVC paint contains 60 gal resin solids per 100 gal of paint solids; therefore each volume must be multiplied by 60/46.6 or 1.2875.

	<u>Volume</u>	<u>Weight</u>
Epoxy resin:	$10 \times 1.2875 = 12.88 \times 9.60 \text{ lb/gal} =$	124 lb
Ricinoleate:	$15 \times 1.2875 = 19.31 \times 8.03 \text{ lb/gal} =$	155 lb
Isocyanate:	$21.6 \times 1.2875 = 27.81 \times 10.5 \text{ lb/gal} = 292/0.75 = 389 \text{ lb of } 75\% \text{ solution}$	
Total resin solids:	$= 60.00$	

Final volumes and weights of the pigments and vehicles are adjusted in this ratio after solvent is added to Part A, to obtain a proper grinding viscosity, and to Part B to obtain a proper brushing viscosity, and so that the volume of Part B equals one half the volume of Part A.

A sample formulation from the above calculations using proprietary materials is given in Table A1.

Table A1
Sample Formulation for Paint, Exterior, Cold-Damp Weather, Moisture-Cured Urethane Type

Part	Ingredients	Primer		Flat Black		Flat White	
		Pounds	Gallons	Pounds	Gallons	Pounds	Gallons
A	National Lead Co.	448	13.15	-	-	-	-
	C.K. Williams & Co.	42	1.01	126	3.05	-	-
	Godfrey L. Cabot, Inc.	-	-	46	3.05	-	-
	E. I. DuPont de Nemours & Co.	-	-	-	-	97	2.77
	New Jersey Zinc Co.	-	-	-	-	259	5.54
	E. I. DuPont de Nemours & Co.	-	-	9	0.73	-	-
	R. T. Vanderbilt Co., Inc.	72	3.04	163	6.85	264	11.10
	Johns-Manville Sales Corp.	-	-	88	4.57	-	-
	English Mica Co.	71	3.03	-	-	-	-
	Shell Chemical Co.	62	6.46	56	5.82	59	6.19
	Baker Castor Oil Co.	78	9.68	70	8.75	75	9.29
		(1:1:1) Solvent*	235	30.30	262	33.85	246
			66.67		66.67		66.67
B	Spencer Kellogg Div. of Textron Inc.	200	20.50	181	18.58	192	19.68
		99	12.83	114	14.75	106	13.65
	(1:1:1) Solvent*	1307	33.33	1115	33.33	1298	33.33

*1:1:1 by volume Ethyl acetate; Toluene; 2-Nitropropane, 7.74 lb/gal (0.1293 gal/lb), ingredients 99.5% pure, 0.25% water and/or free alcohol (max).

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13. ABSTRACT It is often necessary to paint ships in adverse weather. Such is the case with our FBM submarine fleet in Holy Loch, Scotland, where temperatures frequently are near freezing and the relative humidity near 100 percent. This has created a severe maintenance problem insofar as topside painting is concerned. To develop a coating for this purpose, special equipment was devised and constructed in the laboratory to simulate both the weather conditions under which the coatings must be applied and the environment they must endure. Although all experimental one-package coatings using water-displacing solvents lacked adequate adhesion and durability, two multi-package systems proved successful. These systems were the epoxy-polyamide and the moisture-cured urethane. Although both of these systems showed good durability in service, the urethane system was chosen for further development, since it would cure to a serviceable coating far more rapidly under these severe weather conditions. As a result of this research, three paints were developed using the same vehicle and pigment ratios - an anticorrosive primer, a flat black topcoat, and a white tint-base to mix with the flat black for making various specified grays. Formulations and suggested specifications for these paints have been developed.			

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
FBM submarines Submarine topside paints Multi-package paints Cold, damp climate Paint performance Epoxy-polyamide paints Urethane paints Holy Loch, Scotland						

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