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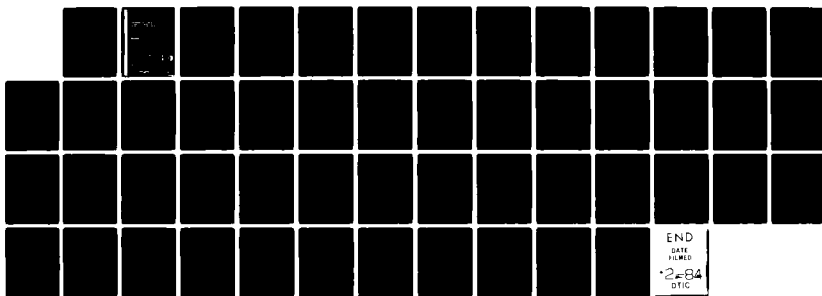
DEVELOPMENT OF A CORROSION CONTROL NONEMISSIVE PAINT
FOR THE PROTECTION OF BILGE SPACES(U) BATTELLE COLUMBUS
LABS OH D E WIRTH ET AL. 27 SEP 82 N00167-81-C-0248

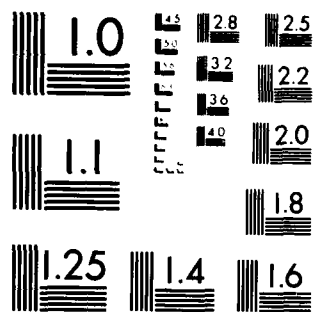
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Contract N00167-81-C-0248

**DEVELOPMENT OF A CORROSION
CONTROL, NONEMISSIVE PAINT FOR
THE PROTECTION OF BILGE SPACES**

By
D. E. Wirth, R. L. Bell, J. P. Pfau,
and R. J. Dick

 **Battelle**
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

27 September, 1982

FINAL REPORT FOR PERIOD 28 SEPTEMBER 1981—27 SEPTEMBER 1982

DAVID W. TAYLOR NAVAL SHIP RESEARCH
AND DEVELOPMENT CENTER
CODE 2841
ANNAPOLIS, MARYLAND 21402

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curing agent	attritor grinding																
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>A research program has been conducted to develop a corrosion control nonemissive paint for the protection of bilges. This report covers Year Two of a multiyear development program.</p> <p>Laboratory studies have been concerned with developing bilge paints based on water-dilutable resins (polyvinylidene chloride, neoprene, acrylic, and polyurethane latices), 100% solids epoxy resins, and cementitious resins. Several (continued)</p>																	

preliminary formulations based on epoxy and cementitious resins have been identified as bilge paint candidates.

The effects of poor surface preparation as encountered on a submarine under way, particularly on paint adhesion, have also been studied. It appears that epoxy-resin based paints may be sufficiently forgiving to accept these limitations without compromising performance. Long-term paint adhesion has yet to be determined.

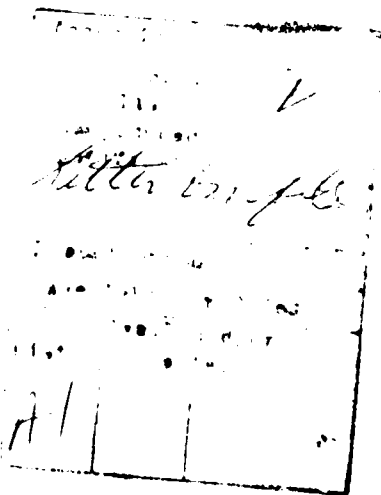


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SUMMARY

A multiyear research program is being conducted to develop a nonemissive, corrosion resistant paint that can be applied to bilge spaces of a submarine while on patrol. This report summarizes both the work done during the second year of the program (Contract No. N00167-81-C-0248) and the last quarter of the first year (Contract No. N00167-81-C-0047). The two contracts ran concurrently for a three-month period.

The research program conducted during this period has been successful in identifying preliminary formulations for a nonemissive general purpose bilge paint. Laboratory effort has been concerned principally with formulation studies based on latex polymers, epoxy resins, and cementitious paints. Formulations from the epoxy resin and cementitious resin study groups are recommended as candidates for optimization in the follow-on third-year program (page 33). Surface preparation has also been addressed during this program year. Each of these activities is summarized below.

Development of Nonemissive, Water-Dilutable, 100% Solids Epoxy, and Cementitious Bilge Paints

Water-Dilutable Resin-Based Paints

Many water-dilutable resins are available that are nonemissive and during application and cure and are easy to apply to various surfaces. Some of these are also fire retardant. Four classes of such resins were identified as viable candidates for bilge paints:

- (1) Polyvinylidene chloride latex resins
- (2) Neoprene latex resins
- (3) Acrylic latex resins
- (4) Polyurethane latex resins.

In addition to the above criteria, these generic resin classes were selected because of outstanding chemical resistance. Selected resins were prepared into bilge paints and were pigmented to obtain a color match for Formula 156 (solvent-based epoxy paint). The following results were obtained.

Polyvinylidene Chloride Latex. Three paints were prepared using AMSCO's P777 resin (See Table 1). These paints dried quickly (1/2 to 2 hours) when applied to steel panels. They also had excellent flexibility and hardness. This resin is fire retardant and thus would contribute another positive property to the bilge paint program. These paints were scheduled for further evaluation.

Neoprene Latex. Two paints were prepared from Du Pont's Neoprene Latex 100 (Table 1), primarily because Neoprene resin is noted for its outstanding chemical resistance. Film properties of these paints were very good and the neoprene paints were to be used in further studies.

Acrylic Latex. Three paints were prepared from Neocryl resins A621, A622, and A623 (Polyvinyl Chemical Industries) (See Table 2), because acrylic resins also are known to have very good chemical resistance. These paints dried quickly (1/2 to 1 hour), had good film hardness and good adhesion to steel substrates. Since these properties were considered marginal for a bilge application, no further work was done using these resins.

Polyurethane Latex. Two paints were made from Neorez R966 and R967 (Polyvinyl Industries) (See Table 2), primarily because polyurethane resins are noted for their excellent adhesion and flexibility to various substrates. These paints possessed excellent flexibility on steel panels but adhesion was not outstanding. Consequently they were not considered for further studies.

100% Solids Epoxy Resin Based Paints

Although water-dilutable resins can be formulated into paints that have excellent physical and chemical resistance properties, it was decided at a meeting with NSRDC personnel (February 2, 1982) that the time and effort needed to develop an outstanding bilge paint would be more productive if directed toward the development of epoxy resin paints and possibly cementitious paints.

For this reason, no further work was done using the water-dilutable resins discussed above.

Low Viscosity Epoxy-Resin Paints. Epoxy resins were considered to be prime candidates for preparing outstanding bilge paints. Early in this program, a survey was made to determine what low viscosity resins were available. Low viscosity is necessary to obtain adequate brushing properties for pigmented paints. Table 3 lists the 27 low viscosity epoxy resins that were obtained for evaluation. A survey was also taken of low viscosity epoxy-resin curing agents that had low emissions and low toxicity. Tables 4 through 6 list paints prepared from various epoxy resins along with their final properties. Many of these paints have outstanding flexibility and adhesion to steel substrates.

The low viscosity epoxy resins and curing agents appear to be outstanding candidates for use in preparing superior bilge paints.

Curing Agent Modification. Epoxy-resin curing agents were modified to insure that they did not contribute to emissivity during cure. Genamid 250 curing agent (Henkel) was reacted with two different alpha-olefin epoxides (Table 7). Ten percent alpha-olefin epoxide was added to the Genamid 250 to tie up any low molecular weight species present in the curing agent. These modified curing agents were combined with an epoxy resin (D.E.R. 324, Dow) and evaluated for curing time against those with unmodified curing agents. As can be seen in Tables 7 and 8, very little difference in drying time was noted between the control coating and the coatings with modified curing agents. These results indicate that the curing agent is still reactive. A sample of these modified curing agents along with epoxy resin D.E.R. 324 was sent to NSRDC for emission testing. Preliminary results indicate no outgassing from these samples.

Cementitious Resin-Based Paints

These paints are designed to be used in harsh environments which demand good chemical resistance. These paints are prepared by mixing pigments and latex polymers together and then adding Portland cement to the pigmented resin just before use. Two paints have been evaluated, one was prepared in the labo-

ratory and one was a proprietary mix obtained from Bywater Coatings (See Table 10). The rheology of both of these coatings prohibits uniform brushing. Spraying is the only technique identified for applying this type of paint. These studies have not been successful in obtaining adequate adhesion of these cementitious paints to steel substrates. If acceptable adhesion cannot be attained with cementitious paints, they will be removed from further consideration in follow-on studies.

Effect of Surface Preparation on Various Physical Properties of Bilge Paints

A brief study was undertaken to determine whether experiment bilge paints developed in the laboratory would adhere to oily surfaces and surfaces cleaned with a detergent. As shown in Table 11, the epoxy-resin paints had excellent adhesion even to oiled steel surfaces and oiled primed steel surfaces. It can be inferred from this that adequate corrosion protection can probably be obtained from bilge paints applied over marginally prepared surfaces. Further work will be done during next year's program to determine if adhesion over oiled surfaces is maintained for long periods of time.

Miscellaneous Studies

Other Methods Used to Reduce Emissions. During Battelle's initial evaluations, it was noted that the reaction of ketimine and/or oxizolidene resins with epoxy resins might produce attractive candidates for one-package bilge paints. These two resins react with epoxy resins only after they have first reacted with moisture in the air or on a substrate. For nonemissivity, ketimine and/or oxizolidene resins were needed that had been prepared with low vapor pressure ketones or aldehydes. However, only resins prepared with high vapor pressure ketones and aldehydes have been identified thusfar.

Water Resistance of Selected Bilge Paints. Unpigmented epoxy coatings have excellent water resistance without any deleterious effects on adhesion or flexibility (Table 12). By contrast, the pigmented epoxy and cementitious paints are not nearly as resistant to water as are the clear epoxies. Thus, more pigmentation work is necessary to qualify both the pigmented epoxies and the cementitious paints as outstanding bilge paints.

INTRODUCTION

The United States Navy has established a military requirement for paints which can be applied by submarine personnel while on patrol. Currently, the painting of submarine interiors is restricted to five days prior to submergence if a coating containing an organic volatile is used. The desired product must be a nonemissive (does not give off toxic or noxious substance during application or cure), general purpose paint which will serve as a protective coating for the submarine's bilge surfaces. The material selection and usages are rigidly governed by submarine codes; for example, the list of materials contained in current atmosphere contaminant restrictions.

The U.S. Navy nonemissive paint program is divided into three areas: (1) non-intumescent paints; (2) intumescent paints; and (3) bilge paints. The non-intumescent and intumescent paints required for the U.S. Navy paint program are covered as Type I and II, respectively, in the military specification "Coating Compounds, Fire Protective" DOD-C-24596. Non-intumescent paint development (Type I) was initiated by Battelle (Contract No. N00167-78-C-0083) in September, 1978. The development of an intumescent nonemissive paint (Type II) was initiated by Battelle (Contract No. N00167-79-C-0183) in October, 1979. Both programs are continuing at Battelle.

This report is concerned with the third component of the U.S. Navy nonemissive paint program, the development of nonemissive, protective paints for bilges (Year Two only). A three to four year program is anticipated which would follow the general format established for the non-intumescent and intumescent paint programs now in progress. The major difference in format lies in first and second year funding; the two programs now in progress were started and continued at annual funding levels permitting full-year efforts, whereas the bilge paint program (Year One and Year Two studies) was restricted to a much more modest program but sufficient to characterize the bilge environment and initiate the paint development phase.

The developed coating is intended for maintenance painting of presently painted steel surfaces, or steel surface from which the present paints have been removed, or never previously painted. The paint must be such that it can be used by submarine personnel while the vessel is on submerged patrol. Volatiles utilized in paints to be developed must meet submarine atmosphere

contaminant restrictions. Atmosphere constituents limits and material restrictions established for submarines are listed in Naval Ship R & D Center Contract Nos. N00167-78-C-0083 and N00167-79-C-0183. For materials not on these lists, Battelle will generally adhere to OSHA and/or American Conference of Governmental Industrial Hygienists guidelines or threshold limit values for chemical substances and physical agents.

Although fire resistance is not a program requirement, the advantages of having all fleet paints being fire retardant are obvious. Because of Battelle's prior and ongoing work with nonemissive paints, it may be possible to add this extra benefit without cost to the proposed program.

The scope of the second year program described in this report is limited to feasibility studies of the paint development phase.

Several documents are considered by Battelle researchers to be of critical importance to the research and are listed below to indicate their visibility in the program:

- (1) Program Plan for the Development of Fire Resistant Materials
- (2) Navy Decision Coordinating Paper Submarine Interior Paints
- (3) Operational Requirement, Submarine Paints, OR-SLH1
- (4) Military Specification; "Coating Compounds, Fire Protective" DOD-C-24596 (not a program requirement but considered by BCL to be a significant benefit if possible)
- (5) Naval Ship R & D Center Contracts N00167-78-C-0083 and N00167-79-C-0183, dealing with specific instructions for submarine atmosphere constituents limits and materials restrictions
- (6) Advanced Change Notice (ACN) No. 2-78 Painting entitled "Deep Diving General Overhaul Specifications" NAVSEA 924T/JPG 9020 Serial 553-924 of 5/8/78

- (7) Chapter 9190 of the Ships Technical Manual, NAVSHIPS 0901-190-0002, January, 1970
- (8) Federal Standard 141B, Paint, Varnish, Lacquer, and Related Materials, Methods of Inspection, Sampling, and Testing
- (9) Fed Std 595 Colors
- (10) "Development of a Nonemissive General Purpose Paint for Submarine Interior Application", Battelle Report No. N00167-78-C-0083, August 31, 1979
- (11) Final Summary Report of Year Two Studies, Battelle Report No. N00167-79-C-0222 - non-intumescent paint program, September 16, 1980
- (12) Summary Report of Year One Studies by Battelle under Contract No. N00167-C-0183 (prepared in September, 1980) - intumescent paint program
- (13) Defense Standardization Manual 4120, 3-N, Standardization Policies, Procedures, and Instructions
- (14) Military Specification, Paint, Polyamide Epoxy MIL-P-24441.

EXPERIMENTAL WORK

Laboratory studies to develop a qualified bilge paint were initiated in the first quarter of Year Two. At that time the Year Two program ran concurrently with the Year One program (Contract No. N00167-81-C-0047) for three months (October through December, 1981). Thus, for "completeness of record" the work accomplished during that period is contained in the final reports for both Year One and Year Two.

The research program to develop a nonemissive, corrosion control bilge paint has been organized into the following activities:

1. Preparation and Evaluation of Water-Dilutable Bilge Paints

- o Studies based on polyvinylidene chloride latex
- o Studies based on neoprene latex
- o Studies based on acrylic latex
- o Studies based on polyurethane latex
- o Discussion of latex resins used to make bilge paints.

2. Preparation and Evaluation of Epoxy- Based 100% Solids Bilge Paints

- o Studies based on low viscosity epoxy resins coupled with amido-amine hardeners
- o Studies based on low viscosity epoxy resins coupled with various resin hardeners
- o Studies based on low viscosity epoxy resins coupled with low emissivity curing agents
- o Studies based on low viscosity epoxy resins coupled with modified curing agents
- o Studies based on low viscosity epoxy resins and curing agents utilizing zinc pigments
- o Studies based on proprietary water-based epoxy paints.

3. Preparation and Evaluation of Cementitious Paints

- o Cementitious paints prepared in the laboratory and proprietary cementitious paints.

4. Effects of Surface Preparation on Various Physical Properties of Bilge Paints

5. Miscellaneous Studies

- o Other methods used to reduce emissions
- o Water resistance of selected bilge paints.

Each of these activities is discussed below. The methods used to prepare paints can be found in Appendix A. A Raw Materials Index is presented in Appendix B.

Preparation and Evaluation of Water-Dilutable Bilge Paints

Water-dilutable bilge paints are attractive candidates for many reasons. Among those are:

- (1) low emissions
- (2) one package
- (3) fast dry
- (4) easy clean-up
- (5) some are fire retardant.

From Battelle's ongoing projects with the general purpose and intumescent paint studies it appeared that some of the water-dilutable resins investigated on these programs might prove to be valuable candidates for superior bilge paints.

Studies Based on Polyvinylidene Chloride Latex

Considerable work has been done utilizing this latex on the two programs mentioned above. This resin has many advantages, such as; excellent adhesion and flexibility, fast dry time, and it is fire retardant. Therefore, bilge paints were prepared utilizing this resin. Results are shown in Table 1. Formulas 20A and 20B have excellent adhesion and flexibility as well as a fast drying time. Formula 21C does not have excellent adhesion and would be eliminated from this study. These paints have only a slight odor and it is believed that they would be classified as nonemissive. Formulas 20A and 20B would be candidates for further development.

TABLE 1. EVALUATION OF NONEMISSIVE PAINTS
PREPARED FROM VARIOUS RESINS

Ingredients	BCL Formula No. (a) (Ingredients, Parts by Weight) (b)				
	20A	20B	21A	21B	21C
TiO ₂ R960 (pigment)	23.7	30.0	30.0	30.0	45.0
Iron Oxide Y0-3587 (pigment)	15.0	15.0	15.0	15.0	22.5
Iron Oxide R0-6097 (pigment)	90.0	90.0	90.0	90.0	135.0
Deionized Water	135.0	135.0	135.0	100.0	150.0
Surfactol ^R 365 (dispersant)	3.8	3.8		1.9	1.9
Colloid 691 (defoamer)	.9	.9	.9	.9	.9
AMSCO P777 (resin)	100.0	100.0			150.0
Texanol (coalescing aid)	10.0	10.0	10.0	10.0	15.0
Propylene Glycol (stabilizer)	10.0	10.0	10.0	10.0	15.0
Tamol 850 (30%)(dispersant)			12.5	6.3	6.3
Neoprene Latex 101 (resin)			100.0	100.0	
Aluminum Trihydrate SB-632 (pigment)	6.3				
Odor	Very Mild	Very Mild	Very Mild	Very Mild	Very Mild
Pot Life (Hours)	-----NOT APPLICABLE-----				
Dry to Touch (Hours)	1/2	1/2	1/2	1/2	1/2
Dry Hard (Hours)	~2	~2	~2	~2	~2
Adhesion(c)	ex. (d)	ex.	ex.	good	good
Flexibility(c)	ex.	ex.	ex.	ex.	ex.
Overall Rating	ex.	ex.	ex.	good	good

(a) Original data are recorded in Battelle Laboratory Record Book No. 37062.

(b) See Appendix B for identification.

(c) Over standard Q panel.

(d) ex = Excellent.

Studies Based on Neoprene Latex

Neoprene resins are noted for their excellent chemical and water resistance and paints made from Neoprene Latex should perform equally as well if formulated properly. Formulas for Paints made from Neoprene Latex 101 (Du Pont) are shown in Table 1. Formulas 21A and 21B had very little odor, fast dry, and excellent flexibility. Formula 21A also had excellent adhesion whereas 21B had only "good" adhesion and was not to be considered for further evaluation. Formula 21A was a candidate for further development.

Studies Based on Acrylic Latex

Acrylic resins are noted for their excellent durability, both indoors and outdoors, and some have excellent chemical resistance. The latexes are usually higher molecular weight materials and would tend to have improved chemical resistance over their lower molecular weight, solvent thinned counterparts. Formula 23A, 23B, and 23C (Table 2) are paints made from low odor acrylic latex (Neocryl A621, A622, and A623). Formulas 23A and 23B had excellent flexibility while 23C was rated only good. Unfortunately, the adhesion of these three paints was only rated good, so no further studies were performed with these acrylic latexes.

Studies Based on Polyurethane Latex

Polyurethane resins comprise the most versatile class of resins available today. Usually, the adhesion of these resins is outstanding and the flexibility can be varied from a very tough inflexible polymer to one that is tough and rubbery. Polyurethane latexes are usually less emissive than their solvent based counterparts, but emissivity could still be a problem with the latexes. Formulations prepared from latexes of two polyurethane resins are shown in Table 2. Formulas 23D and 23E had excellent flexibility on steel panels but the adhesion was very disappointing over steel (rated "good"). These polyurethane latexes were excluded from any further development work.

TABLE 2. FORMULATIONS FOR EXPERIMENTAL BILGE PAINTS

Ingredients	BCL Formula Number ^(a) (Ingredients, Parts by Weight) ^(b)				
	23A	23B	23C	23D	23E
TiO ₂ R960	45.0	45.0	45.0	45.0	45.0
Y03587 Iron Oxide	22.5	22.5	22.5	22.5	22.5
R06097 Iron Oxide	135.0	135.0	135.0	135.0	135.0
Distilled Water	150.0	150.0	150.0	150.0	150.0
Tamol 850	6.3	6.3	6.3	6.3	6.3
Colloid 691	0.9	0.9	0.9	0.9	0.9
Texanol	15.0	15.0	15.0	15.0	15.0
Propylene glycol	15.0	15.0	15.0	15.0	15.0
Surfactol 365	1.85	1.85	1.85	1.85	1.85
NeoCryl A621	150.0				
NeoCryl A622		150.0			
NeoCryl A623			150.0		
NeoRez R966				150.0	
NeoRez R967					150.0
Adhesion ^(c) :	good	good	good	good	good
Flexibility ^(c) :	ex. ^(d)	ex.	good	ex.	ex.

(a) Original data are recorded in Battelle Laboratory Record Book No. 37062.

(b) See Appendix B for identification.

(c) Over standard Q panel.

(d) ex = Excellent.

Discussion of Latex Resins Used to Make Bilge Paints

During the program review meeting in February, 1982 (NSRDC and Battelle personnel), the type of resins to be used to prepare bilge paints was discussed in detail. In the interest of efficiency and economy, it was decided that latexes would be eliminated from consideration in the bilge program. Although some latexes have outstanding chemical resistance and physical properties it was thought that the bilge environment is so severe that water-based paints could not provide the long-term protection needed to protect the bilge spaces. Therefore, as a result of the February 2 meeting, no further work is proposed for the bilge program using latex resins. It was decided to place major emphasis on paints formulated from 100% solids epoxy resins, and from cementitious paints.

Preparation and Evaluation of Epoxy-Based 100% Solids Bilge paints

Epoxy-based paints should provide the superior protection needed to develop a satisfactory bilge paint if (a) emissivity can be reduced by removing low molecular weight species from the curing agents, and (2) the viscosity of the paint can be adjusted to permit brushing and promote good flow out and penetration into the substrate surfaces. Experimental work done to date utilizing epoxy resins and hardeners in bilge paints shows considerable promise.

Studies Based on Low Viscosity Epoxy Resins Coupled With Amido-Amine Hardeners

A number of low viscosity epoxy resins were identified as shown in Table 3. Material Safety Data Sheets (MSDS) were obtained for these resins and the most promising, in respect to low emissivity and toxicity, were obtained for evaluation. Curing agents were also considered for emissivity through the use of MSDS and only those with low emissions were obtained. The amido-amine curing agents appeared to be among the most promising. Table 4 lists data from initial evaluations performed on amido-amine curing agents reacted with a low viscosity epoxy resin. These paints were pigmented to match the Fed. Std. 595A

TABLE 3. LOW VISCOSITY EPOXY RESINS

Epoxy Resin Identification	Viscosity in cps	Epoxide Equivalent
Celanese-Epi Rez 505	200-400	550-650
" " 5071	500-900	180-195
" " 5077	500-700	182-192
Ciba-Araldite CY-179	350-450	131-143
" CY-184	700-1100	159-182
" 506	500-700	175-185
" 507	500-700	185-192
" 509	500-700	189-200
" 9513	500-700	196-213
" 0510	550-850	95-107
DOW-D.E.R. 324	500-700	195-213
" 732	50-100	305-335
" 736	30-60	175-205
Reichhold-Epotuf 37-127	500-1000	195-205
" 37-128	500-1000	190-210
" 37-130	500-700	175-195
" 37-137	500-700	185-200
Shell-Epon 815	500-700	175-195
" 813	500-700	180-195
" 871	400-900	390-470
" 8132	500-700	195-215
Union-Carbide-ERL 4206	13	70-74
" 4221	350-450	131-143
" 4299	550-750	190-210
Vanderbilt-Vanoxy 113	500-700	180-195
" 1132	500-700	195-215
" 171	400-900	390-470

TABLE 4. EVALUATION OF NONEMISSIVE PAINTS
PREPARED FROM EPOXY RESINS

Ingredients	BCL Formula No. (a) (Ingredients, Parts by Weight) (b)				
	14B	15A	17A	18B	19B
Iron Oxide R0-6097 (pigment)	.4	4.5	4.5	3.0	3.0
Iron Oxide Y0-3587 (pigment)				.5	.5
Aluminum Trihydrate 632-ST (pigment)				.2	
D.E.R. 324 (epoxy resin)	10.0	10.0	10.0	10.0	10.0
TiO ₂ R960 (pigment)	6.3	6.3	6.3	.8	.8
Genamid 250 (hardener)	4.0		5.0	5.0	
Genamid 747 (hardener)		5.0			5.0
Odor	Mild	Very Mild	Very Mild	Mild	Very Mild
Pot Life (Hours)	>24	4	3	<3	3.4
Dry to Touch (Hours)	--	>9	>9	>5	>9
Dry Hard (Hours)	--	~30	--	--	~30
Adhesion (c)	--	good	ex. (d)	ex.	ex.
Flexibility (c)	--	good	ex.	ex.	ex.
Overall Rating	poor	fair	good	ex.	ex.

(a) Original data are recorded in Battelle Laboratory Record Book No. 37062.

(b) See Appendix B for identification.

(c) Over standard Q panel.

(d) ex = Excellent.

color standard No. 20109. These paints had an unacceptably long drying time. However, upon drying, their film properties were excellent (especially flexibility and adhesion). For this reason, they were carried forward and modified slightly so that acceptable drying times were obtained.

Studies Based on Low Viscosity Epoxy Resins
Coupled With Various Resin Hardeners

Other curing agents (other than amido-amine) for epoxy resins were evaluated. The formulas for preparing paints utilizing these materials are shown in Tables 5 and 6. Epoxy resin D.E.R. 736 (Dow) in combination with various curing agents in Formulas 10A, 10B, and 10C dried too slowly to be of significant interest. Formula 10C had excellent adhesion and flexibility but a poor overall rating because of slow drying. Epoxy resin D.E.R. 736 was utilized again in Formula 13A and "good" drying times were obtained but the film properties were only good. No further work was done with resin D.E.R. 736. Formulas 11A and 12A utilized epoxy resin Epi-Rez 505 (Celanese) and curing agents Epi-Cure 826 and 855 (Celanese). The drying times of the paints were extremely long and the cured film properties were unsatisfactory. Formulas 11B, 12B, and 13B were made with epoxy resin 50727 (Celanese) and hardeners 826 and 855. Films of Formula 12B were very poor because of their long drying time. Formula 11B had a fast dry time and excellent physical properties, but the pot life of the mixed components was very short. Formula 13B was unattractive because of a slow drying time and poor adhesion after drying. Formula 11C was a combination of epoxy resin 5027 (Celanese) and curing agent 826. The physical properties of this paint were excellent but the drying time was unsatisfactory. Formulas 14A and 17B contained epoxy resin 324 (Dow) and curing agent 826 in two ratios. Formula 14A had a long drying time and was unacceptable. Formula 17B had excellent physical properties after the coating dried but the drying time was excessive. Formula 11B from Table 5 had the best overall properties and with some modification to improve the pot life, it may prove to be an excellent bilge coating. Table 6 lists more developmental formulas utilizing various epoxy resins and hardeners. Formulas 29A, 29B, and 29C contain epoxy resin 324 (Dow) and curing agents 956 (Ciba), 955 (Ciba), and

TABLE 5. EVALUATION OF NONEMISSIVE PAINTS PREPARED FROM EPOXY RESINS

Ingredients	BCL Formula No. (a)						(b) (Ingredients, Parts by Weight)			
	10A	10B	10C	11A	11B	11C	12A	12B	13A	14A
D.E.R. 736 (epoxy resin)	10.0	10.0	10.0						10.0	
TiO ₂ R901 (pigment)	6.3	6.3	6.3	6.3			12.5		6.3	
Epofuf 37-610 (hardener)	5.0									
Iron Oxide R0-6097 (pigment)	4.5	4.3	2.1	.7	1.3	1.3	.3	.3	5.6	.4
Epi-Cure 855 (hardener)		4.7					.3		4.7	.4
TiO ₂ OR 600 (pigment)					6.3	3.3		6.3	6.3	
Epi-Cure 826 (hardener)			2.4	.8	1.5	1.5			1.5	
MicroTalc MP 15-38 (extender)						3.3				
Epi-Rez 505 (epoxy resin)				10.0	10.0		20.0	10.0	10.0	10.0
Epi-Rez 50727 (epoxy resin)										6.3
D.E.R. 324 (epoxy resin)						10.0				
TiO ₂ R960 (pigment)										
Epi-Rez 5027 (epoxy resin)										
Odor	Mild	Mild	Mild	Mild	Mild	Mild	Very Mild	Very Mild	Mild	Mild
Pot Life (Hours)	2	<18	<18	<18	1/4	1 1/4	--	>48	<1	>24
Dry to Touch (Hours)	~22	~40	~44	--	1 1/4	26	--	--	1-2	--
Dry Hard (Hours)	~40	--	--	--	<8	--	--	--	<8	--
Adhesion(c)	poor (d)	poor	ex.	poor	ex.	ex.	--	--	good	poor
Flexibility	ex.	ex.	ex.	ex.	ex.	ex.	--	--	good	ex.
Overall Rating	poor	poor	poor	poor	ex.	good	poor	poor	good	poor

(a) Original data are recorded in Battelle Laboratory Record Book No. 37062.

(b) See Appendix B for identification.

(c) Over standard Q panel

(d) ex = Excellent.

TABLE 6. FORMULATIONS FOR EXPERIMENTAL BILGE PAINTS

Ingredients	BCL Formula Number ^(a) (Ingredients, Parts by Weight) ^(b)				
	29A	29B	29C	30A	30B
TiO ₂ R960	45.0	45.0	45.0	45.0	45.0
Lampblack	0.675	0.675	0.675	0.675	0.675
Genamid 250	--	--	--	135.0	135.0
D.E.R. 324	450.0	450.0	450.0	--	--
Hardener 956	225.0	--	--	--	--
Hardener 955	--	225.0	--	--	--
Epotuf 37-610 (Hardener)	--	--	225.0	--	--
Araldite 507 (epoxy resin)	--	--	--	225.0	--
Araldite GY9513 (epoxy resin)	--	--	--	--	225.0
Adhesion ^(c) :	ex. ^(d)	ex.	ex.	ex.	ex.
Flexibility ^(c) :	ex.	ex.	ex.	ex.	ex.
Hours Drying Time:	<8	<8	<8	≥8	≥8

(a) Original data are recorded in Battelle Laboratory Record Book No. 37062.

(b) See Appendix B for identification.

(c) Over standard Q panel.

(d) ex = Excellent.

37-610 (Reichhold). These three formulas had excellent drying times and excellent physical properties. Formulas 30A and 30B contain epoxy resin 507 (Ciba) and GY9513 (Ciba) together with hardener 250 (Henkel). These two paints had excellent physical properties but an excessive drying time. With slight modification, the drying times could be improved but other properties such as water resistance would have to be superior to justify further work with these formulas.

Studies Based on Low Viscosity Epoxy Resins
Coupled With Low Emissivity Curing Agents

In order to obtain low emissive epoxy paints, it may be necessary to react selected curing agents with materials such as alpha-olefin epoxides to tie up the low molecular weight species contained therein without affecting the subsequent reaction of the curing agent with the epoxy resins. Therefore, two epoxides were obtained and reacted with a selected curing agent. Table 7 lists the ingredients used in Formulas 25A and 25B. The epoxides (alpha-olefin epoxide - C16, and 1,2-epoxy-3-phenoxypropane) were added in the amount of 10% to epoxy curing agent Genamide 250 in Formulas 25A and 25B, heated to 100 C in a three necked flask with agitation for 1 hour, and then cooled. These two samples were then mixed with epoxy resin D.E.R. 324 as shown in Formulas 26A, 26B, and 26C (Table 7). The control sample 26A and the experimental sample 26C had similar drying times. The second experimental sample Formula 26B was still slightly tacky after an overnight dry. Since these experimental curing agents still showed reactivity with the epoxy resin it was important to check the emissivity of these materials. Therefore, samples of Formulas 25A and 25B as well as a sample of the control (Genamide 250) were sent to NSRDC for emission testing.

Further work was done with these experimental curing agents by incorporating them into paints as shown in Table 8 (Formulas 27A, 27B, 28A, 28B). Formulas 27A and 27B are similar except that in 27A the curing agent (Genamide 250) was pigmented and in 27B the epoxy resin (D.E.R. 324) was pigmented. (These paints were pigmented to match either the red or gray bilge paint.) The film properties of both paints were similar so there is apparently no advantage for pigmenting either the curing agent or the epoxy resin. In production, each

TABLE 7. FORMULATIONS FOR EXPERIMENTAL EPOXY RESINS

Ingredients	BCL Formula Number ^(a) (Ingredients, Parts by Weight) ^(b)				
	25A	25B	26A	26B	26C
Genamid 250	135.0	135.0	5.5	4.95	4.95
α -Olefin Epoxide C-16	15.0	--	--	0.55	--
1,2-Epoxy-3-Phenoxypropane	--	15.0	--	--	0.55
D.E.R. 324	--	--	10.0	10.0	10.0
Adhesion ^(c) :			ex. ^(d)	ex.	ex.
Flexibility ^(c) :			ex.	ex.	ex.
Hours Drying Time:			8	>8	8

(a) Original data are recorded in Battelle Laboratory Record Notebook No. 37062.

(b) See Appendix B for identification.

(c) Over standard Q panel.

(d) ex = Excellent.

TABLE 8. FORMULATIONS FOR EXPERIMENTAL BILGE PAINTS

Ingredients	BCL Formula Number(a) (Ingredients, parts by weight)(b)			
	27A	27B	28A	28B
TiO ₂ R960	45.0	45.0	45.0	45.0
Lampblack	0.675	0.675	0.675	0.675
Genamid 250	135.0	135.0	121.5	121.5
D.E.R. 324	225.0	225.0	225.0	225.0
α -Olefin Epoxide C-16	--	--	13.5	--
1,2-Epoxy-3-Phenoxypropane	--	--	--	13.5
Adhesion ^(c) :	ex. (d)	ex.	ex.	ex.
Flexibility ^(c) :	ex.	ex.	ex.	ex.
Hours Drying Time:	8	8	8	8

(a) Original data are recorded in Battelle Laboratory Record Book No. 37062.

(b) See Appendix B for identification.

(c) Over standard Q panel.

(d) ex = Excellent.

component would be pigmented for easier dispersion. Formulas 28A and 28B are pigmented versions of Formulas 25A and 25B (Table 7). These paints were pigmented gray to match one of the colors used in the bilge. Comparisons were made against non-pigmented formulas to determine if drying times or physical properties were different. Formulas 28A and 28B should be compared against the control, either 27A or 27B. The pigmented versions of these four paints (27A, 27B, 28A, 28B) were very similar in drying times and in physical properties. These paints will be evaluated further if their emissivity is considered adequate. Preliminary results on the emissions tests from NSRDC indicate that there was no outgassing present in the above samples.

Studies Based on Low Viscosity Epoxy Resins Coupled With Modified Curing Agents

To develop a successful, 100% solids bilge paint from epoxy resins and hardeners, the paints developed must undoubtedly be two-package systems consisting of resin and activator. The activators must have a low, or equivalent viscosity in order to mix well and uniformly with the epoxy resin. The types of curing agents or activators to be used will consist mainly of amines, and amido-amines, amine adducts, and polyamides. The latter may need to be modified due to their viscous nature. Therefore, four experimental epoxy curing agent modifiers were evaluated using Emerex 1512 polyamide resin as a common hardener and each was incorporated into a clear coating and a gray pigmented paint using a selected epoxy resin (D.E.R. 324). These modifiers were used to lower viscosity of the Emerex 1512 without sacrificing film properties. Table 9 shows formulas and physical properties of cured clear films from these experimental curing agent modifiers (31A, 31B, 31C, 31D) along with a control formula, 31E, for comparison. The film properties of each were similar to those of the control except that the control possessed better adhesion. The drying times of these five unpigmented resin systems were equivalent. The drying times and physical properties of the pigmented versions of these four paints (32A, 32B, 32C, and 32D) were very similar to those of the unpigmented

TABLE 9. FORMULATIONS UTILIZING EXPERIMENTAL EPOXY CURING AGENTS

Ingredients	BCL Formula Number ^(a) (Ingredients, Parts by Weight) ^(b)				
	31A	31B	31C	31D	31E
Emerez 1512 Polyamide Resin	2.0	2.0	2.0	2.0	1.0
Emerest 2660	1.0				
Emerest 2650		1.0			
Emerest 2616			1.0		
Emerest 2622				1.0	
D.E.R. 324	3.0	3.0	3.0	3.0	1.0
Adhesion ^(c) :	good	good	good	good	ex.
Flexibility ^(c) :	ex. ^(d)	ex.	ex.	ex.	ex.
Hours Drying Time:	8	8	8	8	8

(a) Original data are recorded in Battelle Laboratory Record Book No. 37062.

(b) See Appendix B for identification.

(c) Over standard Q panel.

(d) ex = Excellent.

paints (See Table 10). These paints will be evaluated further at different modifier levels to improve their adhesion. Two additional gray paints (33A and 33B) were developed using Emerest 2660 and Emerest 2662 experimental curing agent modifiers in combination with Ganamid 250. Both paints had good physical properties and acceptable drying times (Table 10). The viscosity of the above paints was acceptable for adequate brushing. These paints will be evaluated further.

Studies Based on Low Viscosity Epoxy Resins and Curing Agents Utilizing Zinc Pigments

In a slightly different approach to epoxy paint development, two zinc rich paints using 3M's 2216 epoxy resin and hardener were prepared. The 2216 resin system was suggested at the February, 1982, meeting at NAVSEA. Since the curing agent in the 2216 epoxy package is a modified detergent of the amide type, it may be nonemissive. Formula 35A (Table 10) was unworkable due to high viscosity when the normal ratio of 19 parts zinc was stirred into 2 parts resin. In Formulas 35B and 35C, 9.5 parts zinc dust were added each to 2 parts curing agent and 2 parts resin, and then the curing agent and resin were combined. Formula 35D was a combination of 2 parts D.E.R. 324 and 2 parts of 2216. These were first mixed together and 1/2 of the zinc was added. These three formulas were also too viscous to be considered practical bilge paints. The results of these evaluations show that the quantity of pigment necessary to formulate a zinc rich epoxy paint when mixed with the required amount of 2216 epoxy resin produces a paint too viscous for application by any technique.

Studies Based on Proprietary Water-Based Epoxy Paints

Four water-based epoxy paints were examined; "Magic Lux High Build Water Base Epoxy Coating" (Hoboken), and "Chem-tar Epoxy High Build Coating" (Devoe and Raynolds). Both yielded noxious vapors due to solvent content and thus were eliminated from further consideration as potential bilge paints. In addition, water-based zinc-rich paints obtained from a commercial supplier

TABLE 10. FORMULATIONS FOR EXPERIMENTAL BILGE PAINTS

Ingredients	BCL Formula Number (a)					(Ingredient, Parts by Weight) (b)							
	32A	32B	32C	32D	33A	33B	34A	34B	34C	35A	35B	35C	35D
TiO ₂ R960	45.0	45.0	45.0	45.0	45.0	45.0							
Lampblack	0.675	0.675	0.675	0.675	0.675	0.675							
D.E.R. 324	225.0	225.0	225.0	225.0	225.0	225.0							
Emerez 1512 Polyamide Resin	150.0	150.0	150.0	150.0									
Emerez 2660	75.0					28.12							
Emerez 2650		75.0											
Emerez 2622			75.0		28.12								
Emerez 2616				75.0									
Genamid 250					84.38	84.38							
IMSIL-A-108							66.3	66.3					
Portland cement							66.3	66.3					
Whitcon-L-169							17.7	17.7					
Molywhite 212							33.2	33.2					
R06097 Kroma Red Oxide							33.2	33.2					
Rhoplex MC76							65.0	65.0					
Distilled water							50.0	100.0	50.0				
BYCO versa-kote 3-WB										19.0	2.0	9.5	2.0
3M epoxy 2216A										2.0	9.5	2.0	
Zinc 555													
3M epoxy 2216B													
Adhesion (c);	good	good	good	good	good	good	--	poor	poor	--	--	--	--
Flexibility (c);	ex. (d)	ex.	ex.	ex.	ex.	ex.	--	poor	poor	--	--	--	--
Hours Drying Time:	10	10	8	10	8-10	8-10	--	1.5	0.5	--	--	--	--

(a) Original data are recorded in Battelle Laboratory Record Book No. 37062.

(b) See Appendix B for identification.

(c) Over standard Q panels.

(d) ex = Excellent.

(Devoe and Raynolds) were evaluated for physical properties by drawing down samples on steel panels, and checking for drying time and odor. These paints, "Zincprime 800" and "Zincprime 900" (Devoe and Raynolds) were two-component systems requiring the addition of a dust portion to a liquid immediately prior to use. Both were eliminated due to high solvent content.

Preparation and Evaluation of Cementitious Paints

Cementitious paints could be good candidates for a superior bilge paint if their emissions prove to be acceptable and if marginal paint flexibility is acceptable. During a conversation with Mr. Bob Supcoe of NSRDC on March 25, 1982, formulas and suppliers were obtained for cementitious paints that would be applicable for producing satisfactory bilge coatings. Mr. Supcoe was of the opinion that, since the cementitious paints that he has worked with all contain ammonia, this may present an insurmountable emission problem unless an ammonia-free formula can be developed. The coatings that Mr. Supcoe has worked with are also lacking in flexibility. Since the amount of flexibility required for this program has not been determined, this lack of flexibility may not be an important consideration at this time.

Cementitious Paints Prepared in the Laboratory and Proprietary Cementitious Paints

Cementitious paints were evaluated for physical properties, odor, and drying times. The paints evaluated were obtained from commercial suppliers or developed from formulas obtained from Mr. Bob Supcoe. Important considerations for cementitious paints as practical bilge paints are durability and chemical resistance. However, evaluations of three formulas (34A, 34B, 34C) showed a definite lack of film integrity (Table 10). Adhesion and flexibility were poor and therefore unacceptable. All three formulas were two-part systems requiring the addition of a dry powder component (Portland cement) immediately prior to use which poses the question of atmospheric contamination if used on submarines while under way. Additionally, all commercially supplied cementitious coatings which have been considered yielded noxious ammonia vapors or contained solvent as part of the system. It may be necessary to develop an ammonia-free, dust-

less system to meet emissions requirements. Application of cementitious paints by roller or brush appears unlikely due to high viscosity and rapid setting time. Spray application seems the probable application method of choice. If spray application of paints is prohibited on submarines while underway then the cementitious paint research will be discontinued.

Formulas 34B and 34C (Table 10) were re-examined using spray application. Spray application did show that the quality of the resultant coatings was more acceptable and it was easier to build thicker films. Formula 34B applied by spraying (5 mils dry thickness) applied on bare steel and also on primed panels had good adhesion and excellent flexibility when flexed over the conical mandril. Formula 34C (20 mils dry thickness) over both bare steel and primed panels had poor adhesion but excellent flexibility when flexed over the conical mandril. Both 34B and 34C coatings had fair to poor film integrity. More work needs to be done to develop cementitious paints into viable bilge coatings.

Effects of Surface Preparation on Various Physical Properties of Bilge Paints

One of the prime considerations in developing a bilge paint is the limited surface preparation measures which are possible and how this adversely impacts on ultimate paint adhesion. Since one of the major bilge contaminants is oil and ideal surface preparation is impossible, it is necessary that any bilge paint developed should be adherent to oily surfaces or detergent cleaned oily surfaces.

Table 11 shows the results of experimental paints applied over treated and untreated surfaces and over primed and unprimed surfaces. The surfaces were:

- | | | |
|---------------------------|--|--|
| (1) oiled steel | | excess oil removed with rag |
| (2) oiled on primed steel | | |
| (3) oiled steel | | washed with approved detergent
to remove oil before coating |
| (4) oil on primed steel | | |
| (5) clean steel | | |
| (6) primed steel | | |

TABLE 11. PHYSICAL TEST RESULTS OF FILMS ON SELECTED SUBSTRATES(a)

Properties(c)	BCL Formula Number (b)						
	17A	21C	23A	23B	23C	23D	23E
Bare steel adhesion flexibility	(d) ex. ex.	good ex.	good ex.	good ex.	good good	good ex.	good ex.
Formula 156 coated steel adhesion flexibility	ex. ex.	ex.	good ex.	good to ex. ex.	ex. ex.	ex. ex.	ex. ex.
Bare steel oiled adhesion flexibility	ex. ex.						
Formula 156 coated steel-oiled adhesion flexibility		good ex.	good ex.				
Formula 156 coated steel-oiled & washed adhesion flexibility		good ex.	good ex.				

- (a) Original data are recorded in BCL Laboratory Record Notebook No. 37062.
 (b) Formulas will be found in Tables 1, 2, and 4.
 (c) Over standard Q panel.
 (d) ex = Excellent.

Formula 156 was used to prime the indicated panels. As shown in the table, the adhesion of the paints to the oily surface is equal to that observed on the clean steel. This is very encouraging as it means that not all the oil will have to be removed from the surfaces in the bilge spaces to obtain good adhesion. As the paints are developed they will be evaluated over rusty surfaces as well as oily surfaces and their performances checked against a standard.

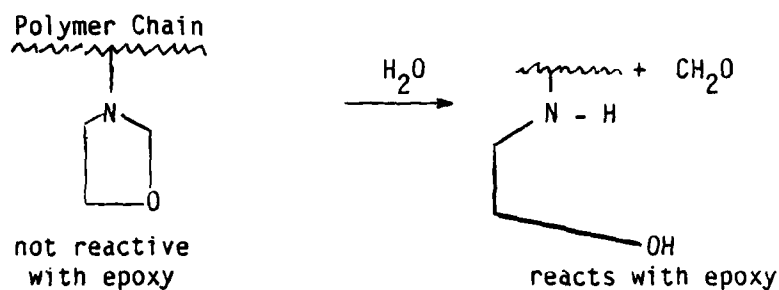
Miscellaneous Studies

Other Methods Used to Reduce Emissions

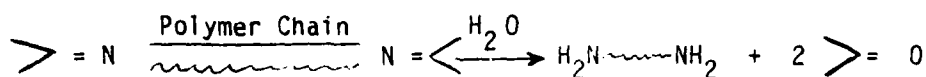
At the start of this program there was considerable interest in developing one-package epoxy coating systems. As noted previously, the majority of epoxy coatings are two-component systems. If the crosslinking agent is stored together with the epoxy prepolymer, gelation will occur. Battelle attempted to obtain latent crosslinking agents which have the possibility of being mixed and stored with the epoxy prepolymer without the danger of premature gelation. However, no suitable agents could be identified. The U.S. Navy would gain two distinct advantages from such a coating system.

- (1) Less storage space is required for a one-component coating system.
- (2) The complexities introduced through mixing of components and using the mixed system prior to the end of its suggested pot life are eliminated.

Two examples of such latent crosslinking agents are oxazolidines and ketimines.

1. Oxazolidine

Upon exposure to water, the oxazolidine ring (which will not react with an epoxy prepolymer) will open to give a hydroxyl and amine group both of which will react with and crosslink the epoxy prepolymer. The water is provided by moisture in the air or on the bilge walls (i.e., after surface preparation by detergent washing). These resins can be made with low vapor pressure aldehydes that will reduce or eliminate any emissions from the paint during drying.

2. Ketimine

Again, the ketimine will not react with the epoxy prepolymer. However, upon exposure to water the ketimine will form a diamine which is very active with epoxies and will crosslink the epoxy prepolymer.

One-component epoxy systems based on oxazolidine and ketimine crosslinking agents could be formulated to provide 100% solids systems. From the standpoint of nonemissivity, this is very important. If a one-component coating system cannot be obtained, there still remains the advantage that a two-component system based on ketimine or oxazolidine crosslinking agents will have a much longer pot life as compared to conventional two-component epoxy systems.

Both of these polymers were to be investigated briefly to determine their worth in relation to time and money needed to develop their properties to suit our purpose. The emissivity of both systems has not been evaluated.

These polymers have not been investigated as yet because no source has been determined for polymers made with low vapor pressure ketones and aldehydes. All materials located to date use high vapor pressure materials which may contribute to air pollution in the submarine.

Water Resistance of Selected Bilge Paints. Experimental bilge paints were evaluated for water resistance using procedure ASTM D1308. Steel panels coated with a 5-mil dry film of the experimental coatings were one-half immersed in a tank of distilled water for 5 days. After 5 days the panels were removed and immediately observed for blistering, peeling, and wrinkling. After 2 hours the coatings were rechecked for recovery by comparing them to the non-immersed half of the panel. After 24 hours air drying the panels were tested again for adhesion and hardness. The formulas tested and their results appear in Table 12.

The water resistance test results on the unpigmented epoxy coatings (26B and 26C) make them excellent bilge paint candidates. However, some work will be necessary to improve the pigmentation of the epoxy paints, Formulas 32A, 33A, and 33B (due to their poor water resistance), to qualify them as acceptable bilge paints. Also, the water resistance of the cementitious paints, Formulas 34B and 34C, needs to be improved before they can be considered as acceptable bilge paints. The above formulas will be optimized in the follow-on third-year program.

STUDIES FOR PROGRAM YEARS THREE AND FOUR

The present program (described herein) is considered Year Two (Contract No. N00167-81-C-0248) and runs from September 28, 1981, to September 27, 1982. This contract has been concurrent with Program Year One until December 30, 1981, when contract Year One expired.

The requirements for years Three and Four are listed in the following work program.

TABLE 12. WATER RESISTANCE TEST RESULTS OF (a)
EXPERIMENTAL BILGE PAINTS

		BCL Formula No. (b)							
		26R	26C	32A	33A	33B	34B	34C	
Thickness, mils	5	5	5	5	5	5	5	5	
Immediate Appearance	No Change	No Change	No Change	Heavy Tiny Blistering	Dense Tiny Blistering	Sparse Tiny Blistering	Softened Coating	Softened Coating	
2-Hr. Appearance	No Change	No Change	No Change	Blisters	Blisters	Blisters	Slight Recovery	Full Recovery	
Initial Adhesion	Excellent	Excellent	Good	Good	Good	Good	Poor	Poor	
24-Hr. Adhesion	Excellent	Excellent	Poor	Poor	Poor	Poor	Poor	Poor	
Initial Hardness	Excellent	Excellent	Good	Good	Good	Good	Fair	Fair	
24-Hr. Hardness	Excellent	Excellent	Good	Good	Good	Good	Fair	Fair	
Clear or Pigmented	Clear	Clear	Pigmented	Pigmented	Pigmented	Pigmented	Pigmented	Pigmented	
Type	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy	Cementitious	Cementitious	

(a) Original data are recorded in Battelle Laboratory Record Notebook No. 37062.

(b) The formulas for these paints are listed in Tables No. 7 and 10.

1. Requirements

Battelle will continue the research, development, and test program began under Contract N00167-81-C-0047, continued under Contract N00167-81-C-0248, and described in the following portions of this program plan that will result in a paint qualified for the intended use. The specific goal of the work to be performed herein will be to develop formulations that will qualify the paint for fleet use.

Studies planned for Program Year Three and Four include: (1) optimization of preliminary formulations identified in Year Two; (2) substantiating surface preparation requirements; and (3) qualifying selected coatings to program requirements.

2. Optimization of Preliminary Formulations

To date, formulations appearing attractive are based on low viscosity epoxy resins and hardeners. Cementitious paints deserve to be evaluated further but appear to be marginal candidates. No effort has been made to refine a specific resin, pigment, dispersion, or blend (paint), to optimize its properties or performance.

The low viscosity epoxy resins and hardeners appear to be the best candidates for developing a superior nonemissive bilge paint. The resinous materials must be combined with selected pigments to produce a corrosion resistant paint that can be brushed onto metal surfaces. These paints must not only be corrosion resistant, but must have good physical properties as well.

Cementitious paints are also two-component systems that must be combined immediately prior to use. One of the components must be a powder (Portland cement). Combining this powder with a liquid would present a hazard on a closed submarine and would not be allowed. A method would have to be developed to insure a dustless mixture. The physical properties of these paints must be improved (specifically adhesion) in the early months of Program Year Three or these paints will be dropped from further evaluations.

3. Substantiation of Surface Preparation Requirements

The second part of the proposed bilge paint development research is concerned with identifying and substantiating surface preparation techniques which are compatible with the paints identified in the second year studies. As noted above, these studies will proceed concurrently with the optimization efforts. In general, these studies will be limited to state-of-the-art methods and not include research to develop new surface preparation methods. The determination of what techniques are applicable to submarine environments will be generally considered early in the program year. If no technique can be identified in an acceptable time period, it may be necessary to specify something as simple as a rigorous detergent wash.

Surfaces to be considered include bare metal and primed metal (MIL-P-24441). Emphasis will be placed on the MIL-P-24441 coated surface as this will undoubtedly represent the bulk of the substrates encountered. Primary considerations will include, (a) compatibility of the procedure with submarine environment, and (b) ultimate adhesion of new paint to the primed surface. Beyond these limitations it will be necessary to consider the restrictions imposed by submarine crew labor being supplied from unskilled ship's personnel.

4. Qualification of Selected Coatings to Program Requirements

The primary objective of the bilge paint third and fourth-year studies is to optimize the acceptable formulations identified in the second year studies. Optimized formulations will be rigorously evaluated to insure their conformance to all requirements listed below MIL-P-24441 is being considered as a control throughout the program, and test results from both control and experimental materials will be reported. Reporting will also include a comparison analysis of performance.

Specific evaluations which will be performed on optimized formulations during the third and fourth year include the following.

<u>Item</u>	<u>Applicable Test Method</u>	
	<u>FED-STD-141</u>	<u>ASTM</u>
Pigment Content	4021	
Volatiles		D2369
Nonvolatile vehicle	4053	
Water		D1364
Coarse particles	4092	
Consistency		D562
Weight per gallon		D1475
Set-to-touch time	4061	
Dry-hard time	4061	
Fineness of grind		D1210
Flash point		D93
Adhesion	6301	
Gloss		D523
Hiding power (contrast ratio)		D2805
Sag		D2801
Epoxy content of vehicle (determined as weight per epoxy)		D1652
Amine nitrogen content of non- volatile vehicle	7391	
Brushing properties	4321	
Spraying properties	4331	
Flexibility	6221	
Water resistance		D1308
Stability in partially full container	3021	
Dilution stability	4203	
Odor		D1296
Condition in container	3011	

Battelle will conduct a test program ultimately leading to a paint having the following characteristics.

- (1) Gloss of 25 minimum
- (2) Be red in color, Federal Standard 595, Color No. 20109

- (3) Have service characteristics (cure, flexibility, recoatability, durability, corrosion resistance, washability, and serviceability) equal to MIL-P-24441 Formula 156 or better, as authorized by ACN No. 2-78.
- (4) Paint must be capable of being applied by brush, roller, or other conventional means to an acceptable finish (i.e., minimum brush marks). Unconventional methods will be accepted only if compatible to atmosphere requirements and can be used by unskilled ship's force.
- (5) Paint must be adherent to the following type of substrates: steel and aluminum: unpainted, primed with Navy Formula 23 (MIL-P-18210), MIL-P-24441, or MIL-P-23236 Type 1 Class 1 coatings). This corresponds to new construction and maintenance conditions of use.
- (6) Paint must have a shelf life of at least two years.
- (7) Set-to-touch time at 40 F of no more than 6 hours.
- (8) Set-to-touch time at 73 F of no more than 2 hours.
- (9) Paint shall be free of mercury or mercury compounds.
- (10) Dry hard time at 40 F of no more than 24 hours.
- (11) Dry hard time at 73 F of no more than 8 hours.
- (12) If a multicomponent paint, the mixed paint ready for application shall have a pot life of at least 6 hours at 73 F.
- (13) If a multicomponent paint, no single component will comprise less than 5% by volume of the total volume of mixed paint.
- (14) If a multicomponent paint, each component shall differ markedly in color from each other component. When mixed, the paint should have a color different from any of its components.
- (15) Have a flash point of 100 F or higher (Pensky Martin or Setaflash Closed cup).
- (16) Have a sag resistance of at least 4 mils.
- (17) Meet the requirements of the bilge environmental test developed under Contract N00167-81-C-0047.

APPENDIX A

METHODS USED TO PREPARE PAINTS

APPENDIX A

METHODS USED TO PREPARE PAINTS

When preparing any paints, different dispersing methods should be compared to determine which one or ones provide the most efficient dispersion of the pigments needed to obtain the proper color. This work was done before any paint preparation or evaluation was begun. Some pigments are hard to disperse, but by using the attritor⁽¹⁾ rather than the Premier mill⁽²⁾ the pigment dispersion was performed quickly and efficiently. Once the pigment dispersing method was established, then preparation and evaluation of paints was begun. Materials were carefully selected for nonemissivity and both 100% solids and emulsion paints were prepared that were thought to be effective. Evaluation of these paints showed that some were very tough and adhesive to steel substrates. The following work describes in detail the work done and the results obtained from this initial study.

Comparison of Different Mixers

First, two different means of dispersing the pigments used to prepare the red bilge paint were compared; these methods used a laboratory attritor and a Premier dispersator. The attritor has a chamber that is approximately one pint in capacity. A mixing shaft of 1/2" in diameter which has eight arms of 1/4" diameter spaced uniformly about the main shaft on two levels is inserted into the chamber. Stainless steel or ceramic balls are added to the chamber so that they fill about 3/4 of the volume. Battelle used ceramic balls in this

(1) Type 01, Union Process, Inc.

(2) Laboratory model, Premier Mill Company.

study. To this was added 250-350 g of ingredients comprising a typical paint formulation. The speed of rotation of the mixing shaft can be varied but there is usually a narrow speed range where best grinding results are obtained. The rotational speed is governed by a variac voltage setting. Battelle generally uses a setting of 60 which corresponds to 72 volts input. Excellent grinds can usually be obtained in 30 minutes or less.

The Premier mill or dispersator is a high speed mixer similar to a Cowles dissolver. A blade with serrated edges is attached to a shaft that can turn at a very high speed to disperse pigment particles. The viscosity of the batch is very important when using this mixer. The quality of dispersion is viscosity dependent. Some pigments are difficult to disperse using this unit. Pigment grinds prepared using the two dispersing methods are shown in Table A-1. All six of the attritor grinds have very good dispersions as shown in the table while only one of the 12 dispersator grinds resulted in a good pigment dispersion. Most of the dispersator grinds were very poor after 30 minutes so most were ground for a longer time to obtain the results shown in Table A-1. In the interest of efficiency and good reproducibility it appears necessary to use the laboratory attritor to obtain best results.

TABLE A-1. COMPARISON OF GRIND RESULTS FROM LABORATORY ATTRITOR VS. PREMIER MILL

Ingredients	(a) BCL Formula No. (Ingredients, Parts by Weight)									
	3A	4A	4B	5A	6A	6B	7A	8A	8B	8C
Epi-Res 5027 (epoxy resin)	150.0	200.0								9C
Epi-Res 50727 (epoxy resin)			200.0	200.0						
Epi-Res 505 (epoxy resin)					200.0					
D.E.R. 736 (epoxy resin)						200.0	200.0			
Epi-Cure 826 (hardener)								200.0		
Epi-Cure 855 (hardener)									200.0	
Epotuf 37-610 (hardener)										200.0
MicroTalc MP 15-38 (extender)	50.0				50.0					
TiO ₂ OR600 (pigment)	50.0	62.5	125.0	125.0						
TiO ₂ R901 (pigment)				125.0	125.0	125.0	125.0			
Iron Oxide R06097 (pigment)								180.0	180.0	180.0
Cap Cure 711 (hardener)									200.0	
ANCAWINE 1171 (hardener)										200.0
HY 2969 (hardener)										150.0
Pigment dispersed using										
Attritor = A or Dispersator = D	A	A	A	A	A	A	D	D	D	D
Fineness of Grind = G, F, or P (b)	G	G	G	G	G	G	G	F	F	P

(a) Original data are recorded in Battelle Laboratory Record Book No. 37062.

(b) G = Good, F = Fair, P = Poor.

TABLE A-1. (Continued)

Ingredients	BCL Formula No. (a)				(Ingredients, Parts by Weight)	
	15B	16A	16B	18A	19A	
D.E.R. 324 (epoxy resin)	200.0					
Genamid 250 (hardener)		200.0		102.2		
Genamid 747 (hardener)			200.0		100	
Iron Oxide R06097 (pigment)		180.0	180.0	61.4	60.0	
TiO ₂ R960 (pigment)	125.0			16.2	15.8	
Iron Oxide Y03587 (pigment)				10.2	10.0	
Aluminum Trihydrate 632-ST (pigment)				4.3		
Aluminum Trihydrate SB-632 (pigment)					4.2	
Pigment dispersed using Attritor = A or Dispersator = D	D	D	D	D	D	D
Fineness of Grind = G, F, or P (b)	F	F	F	F	P	P

(a) Original data are recorded in Battelle Laboratory Record Book No. 37062.

(b) G = Good, F = Fair, P = Poor.

APPENDIX B

RAW MATERIALS INDEX

APPENDIX B

TABLE B-1. INGREDIENT IDENTIFICATION CHART

Ingredient	Function	Supplier
TiO ₂ R960	Pigment	Du Pont
Y03587 Iron Oxide	Pigment	Pfizer Minerals, Pigments & Metals Division
R06097 Iron Oxide	Pigment	Pfizer Minerals, Pigments & Metals Division
Distilled Water	Thinner	Various
Tamol 850	Dispersant	Rohm and Haas
Colloid 691	Defoamer	Colloids
Texanol	Coalescing agent	Ashland
Propylene glycol	Stabilizer	J.T. Baker Chemical Company
Surfactol ^R 365	Wetting agent	N.L. Industries
NeoCryl A621	Acrylic emulsion	Polyvinyl Chemical Industries
NeoCryl A622	Acrylic emulsion	" " "
NeoCryl A623	Acrylic emulsion	" " "
NeoRez R966	Polyurethane emulsion	" " "
NeoRez R967	Polyurethane emulsion	" " "
Aluminum Trihydrate 632-ST	Pigment	Salem Industries
Aluminum Trihydrate SB-632	Pigment	" "
TiO ₂ R901	Pigment	Du Pont
AMSCO P777	Resin	Union 76
Neoprene Latex 101	Resin	Du Pont
Lampblack	Pigment	Smithko
D.E.R. 324	Epoxy Resin	Dow
Genamid 250	Curing Agent	Henkel
Emerez 1512 Polyamide Resin	Curing Agent	Emery
Emerest 2660	Flexibilizer	"
Emerest 2650	Flexibilizer	"
Emerest 2622	Flexibilizer	"
Emerest 2616	Flexibilizer	"

TABLE B-1. (Continued)

Ingredient	Function	Supplier
IMSIL-A-108	Filler	Illinois Mineral Company
Portland Cement	Binder	Columbia Cement Corporation
Witcon-L-169 PTFE Powder	Cement modifier	ICI Americas, Inc.
Molywhite 212	Pigment	Sherwin Williams
Rhoplex MC76	Acrylic cement modifier	Rohm and Haas
Distilled Water	Solvent	Various
BYCO Vesa-Kote 3WB	Cementitious coating	Bywater Coatings
2216A Epoxy	Epoxy curing agent	3M
2216B Epoxy	Epoxy resin	3M
Zinc 555	Pigment	Federated Metals Corporation
α -Olefin Epoxide C-16	Epoxy resin	Union Carbide
1,2-Epoxy-3-Phenoxypropane	Epoxy resin	Polysciences
Hardener 956	Curing agent	Ciba-Giegy
Hardener 955	Curing agent	" "
Araldite Epoxy 507	Epoxy resin	" "
Alaldite Epoxy GY9513	Epoxy resin	" "
37610 Epotuf Hardener	Curing agent	Reichhold Chemicals
Epi-Rez 5027	Epoxy resin	Celanese
Epi-Rez 50727	Epoxy resin	"
Epi-Rez 505	Epoxy resin	"
D.E.R. 736	Epoxy resin	Dow
Epi-Cure 826	Curing agent	Celanese
Cpi-Cure 855	Curing agent	"
MicroTalc MP 15-38	Pigment extender	"
TiO ₂ OR600	Pigment extender	Du Pont
Capcure 711	Hardener	Diamond Shamrock
Ancamine 1171	Hardener	Pacific Anchor
Hy 2969	Hardener	Ciba-Giegy
Genamid 747	Hardener	Henkel