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in cooperation with
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THE NATIONAL SHIPBUILDING RESEARCH PROGRAM

Current Project

Coating Building

DEVELOPMENT OF NON- POLLUTING, SOLVENT-FREE, LIQUID RESIN COATING SYSTEMS FOR SHIPS

**U. S. DEPARTMENT OF COMMERCE
MARITIME ADMINISTRATION**

IN COOPERATION WITH

GENERAL DYNAMICS

QUINCY SHIPBUILDING DIVISION

(275)

FOREWORD

This is a report on one of the many research projects being performed under the Maritime Administration's National Shipbuilding Research Program. The program is a cooperative, cost shared effort between the Maritime Administration and the U.S. shipbuilding industry. The objective emphasizes the development of production techniques and equipment which will result in increased productivity and reduced shipbuilding costs and thereby improve the competitive position of the U. S. shipbuilding industry.

The research effort contained herein is one of the projects in the Surface Preparation and Coatings area which was managed and cost shared by General Dynamics Quincy Shipbuilding Division. It was undertaken with the above objective in mind and has followed the guidelines established for such work by the SNAME Ship Production Committee.

We wish to acknowledge the leadership and technical expertise provided by Mr. Louis J. Nowacki of Battelle Columbus Laboratories in the development of this research.

Mr. L. M. Thorell, General Dynamics, Quincy Shipbuilding Division was the Program Manager. This report was written by Mr. W. Mirick and Mr. L. J. Nowacki, both of Battelle Columbus Laboratories.

DEVELOPMENT OF NONPOLLUTING, SOLVENT-FREE LIQUID RESIN COATING SYSTEMS FOR SHIPS

EXECUTIVE SUMMARY

The objective of this research was to develop liquid, solvent-free coating systems and practical methods for their application in the shipyards. Successful attainment of this objective would result in (1) lower cost due to elimination of solvents, faster application and fewer coats, (2) ecological advantages resulting from elimination of solvents, and (3) improved safety since elimination of solvents will decrease fire and toxicity hazards particularly in confined areas such as ship holds and tanks.

The completed research has demonstrated the feasibility of solvent-free liquid resin coatings under laboratory conditions. Several combinations of pigmented epoxy resin and pigmented polyamide resin were successfully applied to test panels using commercially available, two-component, high pressure airless spray equipment. Two pigmented polyurethane coatings were also applied successfully; one formulated for tank use and the other for topsides.

It is recommended that the coatings developed as a result of this research program be evaluated for long-term durability and ease of application in a shipyard environment as a continuation of this effort. If such evaluation proves successful, the coatings should be applied to a ship for in-service evaluation.

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Section I

INTRODUCTION

The Battelle-Columbus Laboratories (BCL) began research on nonpolluting, solvent-free, liquid resin coating systems for ships in December, 1974. The program was under the direction of General Dynamics, Quincy Shipbuilding Division, who at the time was Program Manager of Surface Preparation and Coatings Research being sponsored by the Maritime Administration (MARAD) as part of their National Shipbuilding Research Program.

The concept was to apply simultaneously both parts of a two-part reactive, liquid resin system which would interact upon the metal surface to form the protective coating. The idea was to use two high-pressure airless spray systems either with a single-mixing spray gun, or two guns set side by side.

Since the two components would be mixed at the gun nozzle or outside the gun, there would be no danger of the material setting up inside the equipment. Each component could be heated, if desired, to lower its viscosity, causing it to better wet the metal surface, and causing quicker reaction (cure) to take place. Moreover, heating could provide flexibility in adapting the application to the wide variety of temperature and humidity working conditions found in most yards. It was realized that it might be necessary to impart a degree of thixotrophy to the materials so that they would flow through the system readily under shear thinning, but recover (increase in viscosity) as soon as they were applied to prevent sagging.

Materials other than epoxies might also be handled in the way just described, and it was visualized that much of the research might be so directed.

This concept was a result of some prior research at BCL where two spray guns set side by side were used to externally mix two reactive resin components to form coatings; in one case a styrenated polyester coating which was applied 30 to 50 mils thick and set in less than one minute, and in another instance a thermal insulation coating which was applied about 75 mils thick and set in less than 5 minutes. These coatings contained styrene so did not fit the concept of coatings containing no volatile material.

1.1 ADVANTAGES FOR LIQUID RESIN SYSTEMS

The research proposal cited a number of important benefits to the American shipbuilding industry that could result from a successful research program on liquid-resin marine coatings. These are listed below.

1. Lower Costs

- a. No expensive solvents used in the coating systems. The solvents in regular coatings are wasted and do not form part of the protective film.
- b. Fast application because high build will result in lower labor costs. The build will be rapid because only film-forming material will be applied.
- c. Fewer coats will be required resulting in lower labor costs. Possibility of applying 6 to 8 mils or more of coating in a single application.
- d. Less investment in auxiliary equipment because less ventilation will be needed, and probably less protective gear for workers.

2. Ecological Advantages

The coatings contain no solvents to contribute to air pollution. EPA and OSHA standards could easily be met.

3. Improved Worker Safety

Elimination of solvents will decrease both the fire and toxicity hazards. This is especially important in the confined areas of ships such as holds and tanks.

Section 2

SUMMARY

Solvent-free liquid resin coatings have been demonstrated to be feasible under laboratory conditions. Several combinations of pigmented epoxy resin and pigmented polyamide resin were successfully applied to test panels using commercially available, two-component high-pressure air less spray equipment. Two pigmented polyurethane coatings were also applied successfully: one formulated for tank (or shipbottom use) and the other formulated for topside use.

The laboratory formulation studies included examination of (1) numerous combinations of different epoxy and polyamide resins, (2) their pigmentation, and (3) the measurement of certain physical characteristics of the coatings obtained, viscosity of components at various temperatures, cure of coatings, hardness values, and resistance to distilled water. Formulation studies were also carried out to develop the polyurethane compositions. These studies resulted in the final compositions selected for the various application trials using different commercial spray equipment. The coatings could be sprayed successfully only with equipment capable of spraying at pressures of about 3000 psi, because they contained appreciable pigment which imparted high viscosity.

Other types of liquid resins suitable for this research were sought from the U. S. companies who supply resins for the coatings industry. None were found to be available at the time the work was in progress. However, it is believed that polyester and acrylic types could be synthesized for use in solvent-free coatings. Synthesis of new resins was beyond the scope of the research.

Contacts were made with many manufacturers of marine coatings while this research was in progress. Some companies were working on solvent-free systems, but more of the U. S. companies contacted were still directing

their research efforts to high solids coatings. It appeared that the development of solvent-free coatings was further along with European coating suppliers than with the U. S. suppliers of marine coatings.

The best coatings developed at BCL need to be evaluated for long-term durability in a continuation of the current program. Assuming that the results fulfill expectations, they should then be given ship trials.

Section 3

EXPERIMENTAL WORK

3.1 BRIEF LITERATURE REVIEW AND INDUSTRY CONTACTS

A limited literature search was made during the first month of the program covering Chemical Abstracts for the prior six years. A very noteworthy article was found titled "Development of Solventless Coatings Based on Liquid Resins" by Ing. G.. Rossa* of Shell Research Ltd., Egham Research Laboratories. Rossa's article described basically the BCL idea of using a two-component spray setup. However, the article did not show that the research proceeded very far. A letter to Mr. Rossa failed to obtain any additional information regarding materials used and degree of success obtained. Consequently, contact was made with Shell Development Company, Woodbury, New Jersey.

Shell had done some development work with epoxy-type, liquid resin coating systems. The solvent-free components had been applied using Gusmer foam spray equipment. Shell's experimental coating contained low molecular weight epoxy resin with a modifier to further lower its viscosity. However, this material was not designed for a 1 to 1 mixing ratio, which was the only mixing ratio obtainable with a two-component spray unit available at BCL. The Shell representative also mentioned that Grace's Hydra-Cat and Binks' Turbulator were two pieces of equipment that could be used to apply amine-cured epoxy solventless coatings.

Contacts were then made with some major suppliers of airless spray systems for information concerning the application of two-component epoxy coatings. Binks had several systems that could be used for application of two-component materials. The output ranged from 1-1/4 to 5 gpm. Most of this equipment was designed for Gel-Coat resins and used external mixing guns. The Model 43 P Gun with internal mixing was recommended

* Paint Manufacturing, December, 1972.

for two-component epoxy since it is more versatile and since internal mixing is extremely necessary to get good reaction rates and uniform resin mixing. Nordson at the time did not have a two-component internal mixing gun. Their method of spraying two components is based on the use of two automatic guns triggered simultaneously. DeVilbiss also stated that they had equipment and two-component guns with internal mixing that would spray epoxy systems. Grace, of course, had the Hydra-Cat already mentioned.

Later in the program contacts were made with a number of resin suppliers and marine coating manufacturers, as discussed in another section of this report.

3.2 EXAMINATION OF SPRAY EQUIPMENT

Single component, high pressure, airless spray equipment could be used for applying some solvent-free coatings. However, in most instances the short pot life of the liquid resin systems would make two-component spray necessary, or at least desirable.

In order for a liquid resin system to convert to a solid coating film, it is necessary that there be a reaction between two polymers. Solution coatings of the reactive type are well known, one of the better known being epoxy-polyamide resin systems. When one attempts to use these kinds of resin systems without solvent, shorter pot life can be expected. Moreover, it will probably be desirable to lower the viscosities of the resins for easier application by heating them. This will further shorten the pot life. Thus, the desirability of using two-component spray equipment.

A number of choices of high pressure airless spray equipment were found to be available for potential use in applying the solvent-free coatings. Much of this equipment had been developed for application of two-component polyurethane foams. The maximum line pressures (and pressure of gun)

obtainable varied with the different equipment. For purposes of discussion, they are arbitrarily designated as ordinary, about 1200 to 1500 psi; intermediate, about 1800 to 2200 psi; and ultra-high, about 2500 to 3000 psi.

The two-component equipment designed for use in the 1200 to 1500 psi range is substantially lower priced than equipment designed for the ultra-high pressure range. Consequently, its use is preferred wherever the viscosities of the materials are not too high for the equipment. Since most of the polyurethane foam systems are not extremely high in viscosity, the lower priced equipment has found wide range in their application.

3.2.1 Ordinary Two-Component Airless Equipment

The first type of equipment examined for application of the two-component, solvent-free systems was a foam spray unit available at BCL. This unit was designed for maximum pressure of about 1200 to 1500 psi.

Considerable time was spent during the early months of research in improvising and modifying the equipment to try to apply the viscous epoxy systems. It would have been very helpful to have been able to use this equipment in all of the research because of the convenience of having it at BCL.

The gun produced a circular pattern because it had been designed for foam application. Therefore, another mixing gun was purchased which was designed to produce a fan-shape pattern (conventional for spray painting).

The initial trials in spraying solvent-free resins were made without pigments in the coating systems.

The most fluid materials (lowest viscosity) could be sprayed readily with good atomization. This was the combination of Epon 815 (epoxy) and

Genamid 250 (polyamide). However, " a two-component coating system formulated from these resins (based on Shell's suggestions) would require a spray system capable of mixing about two parts of the epoxy component to one part of polyamide component. The BCL spray unit was designed to mix 1 to 1 ratios, as mentioned earlier, and would have to be modified to handle 2 to 1 mixing. Therefore, attention was turned to other combinations which could be mixed in equal parts. One such system was Epon 828 (epoxy) and Versamid 125 (polyamide).

Initial attempts to spray equal parts of Epon 828 and Versamid 125 were somewhat disappointing. It was necessary to preheat the two materials in the pots (to lower viscosity) before feeding them to the proportioning pumps. Since the pumps could not be heated, it was difficult to maintain proper feed through the pumps, and thus the materials were not atomized properly. Since the problem was greatest with the Versamid 125, our attention turned to using other polyamides in combination with Epon 828. This work was very helpful in identifying some of the viscosity limitations of materials which could be used with equipment limited to the 1200 to 1500 psi range.

Before much progress could be made in spraying other liquid resins, problems were experienced with the equipment including clogging of the gun. The equipment was disassembled to determine cause of the problem. A rubber gasket in the heating unit had decomposed, and chunks of the gasket were clogging the lines. There was also a surprising amount of corrosion of the aluminum parts of the heater (especially surprising on the epoxy side). It was necessary to replace the rubber gaskets in the heating unit with Teflon gaskets. At the same time several other gaskets in the proportioning pump assembly were also changed to Teflon. The MEK used to clean the equipment was softening the rubber gaskets and then under pressure they would disintegrate resulting in leaks and loss of pressure.

After reassembling the equipment, several attempts were made to spray the following pigmented coating system:

<u>Component A</u>		<u>Component B</u>	
	<u>Weight %</u>		<u>Weight %</u>
Epon 828	67.8	Genamid 250	74
Molywhite 101	16.1	Celite 281	26
Iron Oxide	16.1		

This system was selected because (1) it was one of the lowest viscosity pigmented epoxy polyamide combinations studied earlier (see Section 3 Coatings Formulation), (2) it produced good, hard coating films, and (3) the components produced good coating films when mixed in a 1 to 1 ratio.

Both components were preheated to 140 F so they could enter the transfer pumps at the appropriate spraying temperature. This preheating was necessary since the heaters for the equipment were between the proportioning pumps and the gun.

No problems were experienced in getting the material to flow through the equipment. By using the transfer pumps for pressurizing the system both components could be driven through the proportioning pumps, heater, hose, and out the gun nozzle. However, when the proportioning pumps were turned on high pressure could be maintained only when the gun was closed. As soon as the gun was opened, the pressure would drop to that supplied by the transfer pumps. This drop in pressure, when the gun was opened, indicated that the check valves in the double-action proportioning pump may not have been seating quickly enough to maintain the high pressure. The highly viscous pigmented components were apparently retarding the seating of the check valves.

In an attempt to overcome this problem, heating tapes were placed around the proportioning pumps and check valves. Application of heat led to an improvement in spraying and pressure maintenance; however, at pressures about 800 psi, which was needed to get good atomization, the pressure could not be maintained. It was concluded that the check valves were again not seating properly.

It should be noted that the equipment was designed for nonpigmented urethane foam spraying; therefore, the check valves are ball type on metal seats. Even a small opening caused by a fine pigment particle could result in pressure loss at high pressures in the range of 800 to 1600 psi. Thus, the decision was made to discontinue the work with that equipment. Instead, the work would concentrate on using higher pressure, airless, two-component equipment.

3.2.2 Ultra-high Pressure Airless Equipment

Pigmented, epoxy-polyamide coating systems were prepared for trial application at Grace, Inc., Minneapolis, Minnesota, using their Hydra-Cat equipment which is capable of pressures up to about 3000 psi. The development and selection of the coatings for the trial application are described in Section 3.3 Coatings Formulation of this report.

All of the coatings could be sprayed satisfactorily. Ten to twelve roils of material could be applied easily in one coat (two spray passes). The lower viscosity materials produced from the combinations of epoxy and Genamid 250 sagged and the films were mottled. The coatings produced from combinations of epoxy and Versamid 140 had good appearance and showed much less tendency to sag. All panels were returned to BCL for evaluation. A chart of spraying conditions is shown in Table 3-1.

**TABLE 3-1. COATINGS APPLICATION DATA USING GRACO-HYDRA-CAT,
TWO-COMPONENT, AIRLESS-SPRAY EQUIPMENT^(a)**

SYSTEM NUMBER	MATERIAL DESCRIPTION ^(b)		MIXING RATIO A/B	FLUID PRESSURE ^(c) , psi		MATERIAL TEMPERATURE, F		COMMENTS
	Component A	Component B		A	B	A	B	
I	Epon 815	Versamid 140	1.5/1	2600 to 2800	3000 to 3200	150	150	Applied 10 mils in two passes
II	Epon 828	Genamid 250	1.5/1	2500 to 2800	2200 to 2500	150	150	Good spray pattern. However, coating had poor appearance. There seemed to be a separation of resins. Coating sagged after application.
III-A	Epon 828	Versamid 140	1/1	3400 to 3500	2400 to 2500	150	150	Borderline atomization. 10 mils in two passes. Coating film appeared to be satisfactory.
III-B	Epon 828	Versamid 140	1.5/1	2000 to 3000	3000 to 3200	150	150	Borderline atomization. 10 mils in two passes. Coating film appeared to be satisfactory.
IV	Epon 815	Genamid 250	1.5/1	1800 to 2000	1800 to 2000	150	150	Good spray pattern. However, coating had poor appearance. There seemed to be a separation of resins. The coating sagged after application. Film not acceptable.

(a) Used 208-055 gun with 616 tip. Feed pump 10 to 1 ratio President (Monark 5 to 1 could be used). Feed pump pressure was 200 psi in all cases. Minimum air pressure for feed pump 100 psi. Hose from proportioning cylinders to spray gun 3/8-inch diameter by 50-feet long. Insulated and heated.

(b) Both components were pigmented. Compositions are given in Table 3-5.

(c) Pressure required to atomize materials and obtain a spray pattern.

Near the end of the research program two polyurethane-type coatings (Formulas No. 1 and No. 6 in Polyurethane Systems, Section 3.3.2, of this report) were successfully sprayed with Graco equipment. During the same period, the Epoxy 828-Versamid 140 system (Formula III in Table 3-5) was sprayed in the following ratio: 1.25 parts Epon 828 to 1 part Versamid 140.

The two-component equipment consists of two feed pumps for forcing the high viscosity materials into the heaters and proportioning pumps. The materials are forced by the proportioning pumps through two heated hose lines to a mixing spray head. Materials can be fed from 55-gallon drums, 5-gallon pails, or other containers.

3.2.3 Equipment Capable of About 2000 psi Line Pressure

Bink's Formulator G was evaluated for spraying two polyurethane compositions and one epoxy system because it had a unique characteristic of quick change-over in ratios of the two components sprayed. However, this equipment was found to be capable of reaching maximum line pressures of only about 2000 psi, compared to the much high pressure obtainable with the Graco Hydra-Cat. The following coatings were tried:

1. Epoxy-polyamide at 1 to 1 ratio: The Epoxy 828-Versamid 140 composition described in Section 3.3 Coatings Formulation - Preliminary Coatings Evaluation.
2. Red polyurethane at 1.25 (urethane) to 1 (pigmented polyol) ratio: See Section 3.3.2 Polyurethane Systems, Page 3-18 for description (Formula No. 1).
3. White polyurethane at 1 to 1 ratio: See Section 3.3.2 Polyurethane Systems, Page 3-19 for description (Formula No. 6).

All tests were run using maximum heating of coating components (170-190 F). Heat tape in spray lines was at 200 F. Spraying pressures were also maximum 1500 to 2000 psi. Numerous tips were tried with the 43 P Gun using a wide variety of orifices and, in some cases, pre-orifices. The materials came through the gun in a stream. In no case could a satisfactory spray pattern be obtained, even though it appeared that attainment of a pattern was close in some cases. It was concluded that the viscosities of the materials were too high for the Binks equipment.

3.3 COATINGS FORMULATION -- PRELIMINARY COATINGS EVALUATION STUDIES

3.3.1 Epoxy Systems

Several epoxy-polyamide combinations were examined initially for film forming characteristics and properties. Viscosities of the components (with and without pigmentation) were measured over a range of temperatures from ambient to about 180 F. These viscosity data are in Table 3-2. It was interesting to note that viscosities of all materials (even the pigmented ones) dropped down to a reasonable range at 140 to 180 F. Representatives of two equipment suppliers had claimed that their equipment would spray materials in the 10,000 to 20, 000 cps (100 to 200-poise) range. Thus, it appeared that all the pigmented, liquid resins could be sprayed at 140 F or above.

The epoxies were pigmented with Molywhite 101 and iron oxide at the following level:

Epoxy	21 g
Molywhite 101	5 g
Iron Oxide	<u>5 g</u>
	31 g Total

TABLE 3-2. VISCOSITIES OF PIGMENTED AND UNPIGMENTED
EPOXIES AND POLYAMIDES AT HIGH AND LOW SHEAR
(Viscosities in Poises, Measured by Ferranti-Shirley Viscometer)

	LOW SHEAR				HIGH SHEAR			
	TEMPERATURE, F							
	70	100	140	180	70	100	140	180
<u>Unpigmented</u>								
Epon 828	164	26	3.9	0.75	137	17	2.4	0.60
Epon 815	8	3.2	0.8	0.26	4	2.1	0.66	0.43 ^(a)
Versamid 125	384	141	26	6	363	120	20	5.4
Versamid 140	128	58	11.5	2.8	121	41	7.2	2.6
Genamid 250	13	6.4	1.6	0.52	7	3.6	1.3	0.42
<u>Pigmented</u>								
Epon 828	256	41	5	1.3	243	31	4	1
Epon 815	12	5	1.3	0.5	6	3.0	1.2	0.6 ^(a)
Versamid 125	692	231	46	13	641	202	38	10
Versamid 140	307	103	23	6	236	78	15	4.6
Genamid 250	23	8.3	2.4	0.8	15	5.3	2.1	0.7

(a) Starting to cure.

This gave a pigment loading of 32 percent by weight and caused an increase of the initial viscosity of approximately 50 percent.

The polyamides were pigmented with silica at a ratio of 36 g polyamide to 13 g of silica. This gave a pigment loading of approximately 26 percent by weight and the resultant increase varied from 80 to 140 percent over the initial viscosity. Although the Versamid 125 has a very high viscosity (690 poise) when pigmented, by heating to 180 F, the viscosity was reduced to well within the range of the Epon 815 and Genamid 250 room temperature viscosities.

Table 3-3 lists the relative hardnesses of pigmented and unpigmented blends of epoxy and polyamide resins.

In most cases the addition of the pigments and filler increased the hardness of the systems. Two systems did not cure completely after 72 hours. These two systems used the same epoxy and polyamide (Epon 815 and Genamid 250), one at a 1 to 1 ratio and the other at a 1.5 to 1 ratio. However, at the 2 to 1 ratio, the system was well cured. From the hardness data it appeared that both Versamids gave good cure with both epoxies, at the 1 to 1 ratio, when pigmented. The Genamid 250 also showed excellent hardness with the Epon 828 when pigmented.

The hardness data seemed to indicate that it would not be necessary to hold the ratio of epoxy to polyamide resin within a very narrow range. This can be a real advantage when using two-component spray equipment.

As an aid in making the coating selections for spray trials, the 18 pigmented epoxy-polyamide combinations, for which hardness data are presented in Table 3-3, were applied to test panels by doctor blade (about 3 mils thick). These coatings were subjected to immersion studies in distilled water. Immersion in distilled water gave relatively quick indication of water

TABLE 3-3. HARDNESS ^(a) SHORE TYPE "C" OF
EPOXY-POLYAMIDE COMBINATIONS

	<u>EPON 828</u>		<u>EPON 815</u>	
	Unpigmented	Pigmented	Unpigmented	Pigmented
	<u>1:1 Ratio ^(b)</u>			
Versamid 125	73	90	83	91
Versamid 140	90	91	95	91
Genamid 250	85	92	78	N. C. ^(c)
	<u>1.5:1 Ratio ^(b)</u>			
Versamid 125	90	90	82	90
Versamid 140	86	90	85	88
Genamid 250	85	92	93	N. C. ^(c)
	<u>2:1 Ratio ^(b)</u>			
Versamid 125	92	92	80	80
Versamid 140	90	90	85	94
Genamid 250	82	94	80	90

(a) Hardness measured on small castings about 1/2-inch thick.

(b) Ratio is expressed as parts epoxy: parts polyamide.

(c) Not cured.

sensitivity of the coatings, which might be caused by inadequate cure, or improper ratio of components. It is well known that coatings blister more rapidly in distilled water than in salt water. Unfortunately, doctor blade application produced coatings with a rather wide range of film thicknesses. Nevertheless, the data (see Table 3-4) were helpful in selecting the coatings for use in the trials at Grace. The coatings selected correspond approximately to Nos. 20, 26, 27, 29, and 30 in Table 3-4, which are among the best in resistance to distilled water. Coating No. 36 was not applied at Graco because time did not permit readjusting the equipment for a 2 to 1 feed ratio.

Five-gallon quantities of two different pigmented epoxy components and two different pigmented polyamide components were then prepared for the trials. Table 3-5 shows the composition of each component and the mixing ratios used at Graco to produce the various epoxy-polyamide coating systems.

3.3.2 Polyurethane Systems

Mobay Chemical Corporation suggested a number of combinations of urethane resins and polyols for use as starting compositions for liquid resin systems. They also did some preliminary work with application of the two-component system using spray equipment capable of maximum pressures of about 2000 psi. However, none of the Mobay work was done with pigmented resins, such as would be desired in linings for ship tanks, or for topside painting.

Preliminary examinations were made of the components of polyurethane coating systems suggested by Mobay. The viscosities of these components are shown in Table 3-6. These components appeared to be readily sprayable with high pressure, airless spray equipment at 140 F or below.

TABLE 3-4. IMMERSION OF PIGMENTED EPOXY-POLYAMIDE COATINGS IN DISTILLED WATER: 14 DAYS IMMERSION DATA

COATING NO.	COMPONENT A ^(a)		COMPONENT B ^(a)		BLISTERING OF COATING	COATING THICKNESS mil
	Parts by wt	Epoxy Resin in Component	Parts by wt	Polyamide Resin in Component		
19	1	Epon 828	1	Versamid 125	Small blisters 0.5 to 1-mm dia.	4
20	1	Epon 828	1	Versamid 140	Small blisters 0.3 to 0.7-mm dia.	3
21	1	Epon 828	1	Genamid 250	Film completely removed	6.5
22	1	Epon 815	1	Versamid 125	Blisters 1 to 1.5-mm dia.	3.5
23	1	Epon 815	1	Versamid 140	Blisters 1 to 1.5-mm dia.	6
24	1	Epon 815	1	Genamid 250	Blisters 1.5 to 2-mm dia.	12
25	1.5	Epon 828	1	Versamid 125	Heavy blisters up to 5-mm dia.	4.5
26	1.5	Epon 828	1	Versamid 140	No evidence of blistering	6
27	1.5	Epon 828	1	Genamid 250	Few small blisters 0.2 to 0.7-mm dia.	4.5
28	1.5	Epon 815	1	Versamid 125	Blisters several 5 to 6-mm, rest 1.5 to 2.0-mm dia.	2
29	1.5	Epon 815	1	Versamid 140	No evidence of blistering	4
30	1.5	Epon 815	1	Genamid 250	No evidence of blistering	4.5
31	2	Epon 828	1	Versamid 125	Lightly blistered 0.5 to 2.0-mm dia.	4
32	2	Epon 828	1	Versamid 140	Well dispersed blisters 0.1 to 0.3-mm dia.	1.5
33	2	Epon 828	1	Genamid 250	Covered with small blisters 0.3 to 0.7-mm dia.	1.5
34	2	Epon 815	1	Versamid 125	Blisters just below water line 0.3 to 0.8-mm dia.	3
35	2	Epon 815	1	Versamid 140	6 or 7 blisters 0.3 to 0.5-mm dia.	4.5
36	2	Epon 815	1	Genamid 250 ^(b)	No evidence of blistering	5.5
37	1	Epon 828	1	Genamid 250 ^(b)	Multiple blisters 0.5 to 2.0-mm dia.	4.5
38	1	Epon 828	1	Genamid 250 ^(c)	Multiple blisters 0.5 to 2.0-mm dia.	4

(a) Compositions of pigmented components

Epon 828	315 g	Epon 815	315 g	Versamid 125	270 g	Versamid 140	270 g
Molywhite 101	75 g	Molywhite 101	75 g	Silica 1160	98 g	Silica 1160	98 g
Iron Oxide B-5095	75 g	Iron Oxide B-5095	75 g				
Genamid 250	270 g						
Silica 1160	98 g						

(b) Double the normal pigment loading.

(c) Triple the normal pigment loading.

TABLE 3-5. EPOXY-POLYAMIDE SYSTEMS PREPARED FOR COATING TRIALS AT GRACO

EPOXY-POLYAMIDE SYSTEM NO.	COMPONENT A			COMPONENT B			VOLUME MIXING RATIO, A to B
	Material	Wt, lb	Gal.	Material	Wt, lb	Gal.	
I	Epon 815	42.85	4.51	Versamid 140	35.72	4.41	1.5 to 1
	Molywhite 101	10.10	0.24	Silica 1160	13.02	0.59	
	Iron-Oxide B-5095	10.03	0.25				
		<u>62.98</u>	<u>5.00</u>		<u>48.74</u>	<u>5.00</u>	
II	Epon 828	43.60	4.495	Genamid 250	34.96	4.425	1.5 to 1
	Molywhite 101	10.31	0.245	Silica 1160	12.69	0.575	
	Iron Oxide B-5095	10.43	0.26				
		<u>64.34</u>	<u>5.000</u>		<u>47.64</u>	<u>5.000</u>	
III-A	Epon 828 pigmented same as II			Versamid 140 pigmented same as I			1 to 1
III-B	Ditto			Ditto			1.5 to 1
IV	Epon 815 pigmented same as I			Genamid 250 pigmented same as II			1.5 to 1

TABLE 3.6 VISCOSITIES OF UNPIGMENTED COMPONENTS FOR HIGH BUILD SOLVENTLESS AROMATIC POLYISOCYANATE TANK LINERS AND SOLVENTLESS ALIPHATIC TOPCOATS OF HIGH AND LOW SHEAR
(Viscosities in Poises, Measured by Ferranti-Shirley Viscometer)

COATING COMPONENTS	% / WT	LOW SHEAR		HIGH SHEAR			
		75	100	TEMPERATURE, F		100	140
				140	75		
<u>Tank Liner Components</u>							
I Multranol M4012 Zeolith L. Paste (a)	91 9	8.0	2.9	0.67	5.2	2.4	0.57
II Polycaprolactone PCP-0301 Zeolith L. Paste (a)	91 9	23.4	9.1	2.24	19.9	6.4	2.09
III Multranol M4012 Castor Oil DB Zeolith L. Paste (a)	45.5 45.4 9	8.2	3.2	0.82	4.4	2.4	0.67
<u>Topcoat Components</u>							
VI Polycaprolactone PCP-0301		25.0	9.0	2.26	20.3	5.5	2.0
VII Polycaprolactone PCP-0301 Multron R-16 Zeolith L. Paste (a)	73 18 9	32.7	12.2	3.17	28.5	8.2	2.86
VIII Polycaprolactone PCP-0301 Multron R-12A Zeolith L. Paste (a)	45.5 45.5 9	57.1	22.1	5.22	53.5	18.2	4.87

(a) The Isocyanates Desmodur E-21 and Desmodur N-100, also recommended by Mobay, were not measured because of their reaction to moisture in the air. The Ferranti-Shirley viscometer

was used so that these components can be kept under a nitrogen atmosphere

After further conversations with a Mobay chemist, two starting formulas were chosen for the BCL formulation studies. A combination of Desmodur E-21 (aromatic type isocyanate) and Multronol 4012 was selected as the start for a tank lining composition. A combination of Desmodur N-100 (aliphatic-type isocyanate), Multron-R-12A, and PCP 0301 was selected for development into a topside coating.

The formulation work involved study of pigmentation and accelerators, the latter to provide fast gelation and cure times. It soon became evident that foaming was a problem with these urethane-type coatings. The foaming occurred because the isocyanate group reacts with moisture, liberating CO_2 . The pigments brought moisture into the system and there are no special dry pigments available commercially for urethane coatings.

Mobay suggested incorporation of Zeolith L Paste, which acts as a moisture scavenger. The paste contains 50 parts synthetic zeolite (molecular sieves to absorb moisture) dispersed in 50 parts castor oil. Levels of addition were studied which would be just sufficient to prevent the foaming because incorporation of an excessive amount of castor oil would soften the coating films unduly.

The curing catalyst type and amount was varied in each case to find a level that would assure that the coating would become nonfluid in less than 10 minutes.

During the course of this work, the polyurethane coatings were found to lack the high degree of adhesion to steel which is desirable for marine coatings. These observations were made on smooth steel surfaces. It is recognized that the apparent bond will be improved by blasting the steel. However, improvement in the true adhesion of the polyurethane coatings would be desirable for best performance. Thus, the addition of small

amounts of epoxy resin was studied in the attempt to improve adhesion of the polyurethane coatings. There appeared to be some improvement when 10 percent epoxy was added. However, there was also some evidence of incompatibility of the polyurethane compositions with the epoxy resin. Thus, epoxy was not used in the final formulas. The formulas shown below were selected for spray trials at Binks and subsequently for trials at Grace.

Polyurethane Formula No. 1 - Red (For Tank Lining)

<u>Component A</u>	lb	<u>Kg</u>
Midtranol 4012	32.6	14.768
Molywhite 101	24.4	11.074
Iron Oxide B-5095	24.4	11.074
Cab-O-Sil M-5	0.5	0.225
Zeolith L Paste	6.5	1.477
33LV Accelerator	0.2	0.109
T-12 Accelerator	0.1	0.055

Viscosity of Component A at 140 F was about 7 poises.

Component B

Desmodur E-21

Spray Ratio: 1 Part Component A to
1.25 Parts Component B (by volume).

Polyurethane Formula No. 6- White (For Topsides)

<u>Component A</u>	<u>lb</u>	Kg
PCP0301	14.5	6.577
Multron R-12A	14.5	6.577
TiO ₂ R-960	43.5	19.731
Cab-O-Sil M-5	0.4	0.181
Zeolith L Paste	2.9	1.315
33LV Accelerator	0.2	0.104
T-12 Accelerator	0.1	0.052

Viscosity of Component A at 140 F was about 44 poises.

Component B

Desmodur N-100

Spray Ratio: 1 Part Component A to
1 Part Component B (by volume).

Difficulty was experienced in getting a spray pattern with the above composition during the final coating trials at Grace. Additional resin and catalyst were therefore added to decrease the amount of pigment in the mix and thus lower the viscosity for easier spraying. This resulted in Formula 6A, which follows:

Formula No. 6A
(Modification of Formula 6)

<u>Component A</u>	<u>lb</u>	Kg
PCP0301	15.75	7.144
Multron R-12A	15.75	7.144
TiO ₂ R-960	31.37	14.230
Cab-O-Sil M-5	0.18	0.083

Formula No. 6A (Cont'd)

<u>Component A</u>	<u>lb</u>	<u>Kg</u>
Zeolith L Paste	2.09	0.946
33LV Accelerator	0.24	0.107
T-12 Accelerator	0.12	0.054

Viscosity of Component A at 140 F was
about 24 poises;

<u>Component B</u>	<u>lb</u>	<u>Kg</u>
Desmodur N-100	47.5	21.545

3.3.3 Coatings Preparation

Two methods were used to disperse the pigments into the liquid resins. All but the three final batches of coating had pigment incorporated into the mix with the aid of a high shear mixer (Cowles Dissolver). For the final batches sprayed at Graco (one epoxy and two polyurethanes) the pigment and resin were premixed in a pony mixer (kneader) and then passed over a three-roll paint mill. This technique was used in the attempt to incorporate less air into the mix than had been experienced with the Cowles Dissolver. This method did mix in less air, but did not eliminate it entirely. Entrapped air can be harmful both in spraying with high pressure equipment and in bubble formation in the applied coating.

3.3.4 Other Liquid Resin Systems

Other liquid resin systems were sought for inclusion in the BCL research program, The resins had to be either commercially available or already developed in other laboratories. It was not the intent of the program that new polymers be synthesized at BCL.

Rohm & Haas and Du Pont were contacted with respect to 100 percent solids acrylic coatings. The DuPont representatives said they do not offer a 100 percent solids coating. Du Pont has sold an acrylic syrup that uses an acrylic monomer for dilution which is 100 percent reactive. The monomer is flammable and toxic, and the syrup must be handled with precautions at least as strict as solvent systems.

The Rohm & Haas representative also mentioned a monomer-polymer syrup. They are developing high solids (70-90%) systems, but do not have a 100 percent solids coating. Workably high viscosity appears to be a major problem.

At the annual meeting of the Federation of Societies for Coatings Technology in Los Angeles, numerous suppliers of coatings materials were interviewed regarding availability of solvent-free, liquid resin coating systems. During the last two years Dow Chemical has worked on 100 percent solids coatings using EP 75.02 resin. To this they have added some rubber polymer to improve the flexibility and adhesion.

Pacific Anchor Chemical Corporation has worked in the field of solvent-less coatings and their representative recommended one aliphatic curing agent Ancamine 1617, and several other curing agents such as Ancamine LT, Ancamine LO, and Ancamine MCA. The Pacific Anchor representative also said that he would send some starting formulas using these products.

Other suppliers that were contacted were Rohm & Haas, Amoco Chemicals, Ashland Chemical, Celanese Chemical, Eastman Chemical, General Mills, and Neville Chemical.

Amoco Chemicals has high solids coating systems with no information concerning 100 percent solids coatings. Ashland Chemical does not appear to be working in this area.

Celanese Chemical is working with multifunctional acrylates in the areas of high solids, but have not yet developed 100 percent solids coatings.

Eastman has some high solids polyester/melamine and polyester/urethane coatings based on NPG and TMPD glycols. They are sending further information.

General Mills is featuring G-Cure acrylic resins for acrylic/urethane coatings that have high gloss and require only minimum or no oven time. They are to send technical and support literature covering G-Cure acrylic resins.

Neville Chemical is not working in the field of 100 percent solids resins or coatings.

Some work was done in the BCL laboratories with a low molecular weight acrylic-type polymer which had been designed for curing by UV radiation. Attempts to cure this resin with peroxides and catalysts were unsuccessful. It is believed that nonvolatile, unsaturated polyesters, or acrylics might be developed which could be cured with peroxide and catalyst. However, none are known to be commercially available at present. The available polyester types contain styrene, which is volatile. Most of it does become part of the coating when cured, but a substantial portion also volatilizes during application.

3.4 STATUS OF SOLVENT-FREE COATINGS DEVELOPMENT BY COATING SUPPLIERS

Besides searching among the raw materials suppliers for new types of liquid resins which might be included in the BCL research, most of the leading suppliers of marine coatings in the U. S. were contacted for

information. Many of them were contacted by Georg Rudlowski (Project Engineer for General Dynamics) during the early part of the program. This met with little success. Later, BCL personnel talked by telephone with technical representatives of the following companies:

Ameron, Inc.
Brea, California

Celanese Coatings and Specialties Company
Louisville, Kentucky

Exxon Chemical Company
Houston, Texas

Du Pont
Philadelphia, Pennsylvania

International Paint Company, Inc.
Union, New Jersey

Hempel's Marine Paints, Inc.
New York, New York

Mobil Chemical Company
Edison, New Jersey

Carboline Company
St. Louis, Missouri

In most instances, the developments by these companies have been in high solids coatings. However, some were doing development work with solvent-free systems.

The International Paint Company, Ltd., has done substantial work in Europe with solvent-free liquid resin systems. They have developed epoxy and epoxy-tar types of solvent-free coatings and are using them on an experimental basis. Hempel's has also been using epoxy-type systems in Europe.

One U. S. company had developed liquid resin systems for their own use in a specialty coatings application. They had not offered the coatings to the trade because they are tricky to apply. They were also doing

some work in Europe on the pilot coating of ship tanks with a liquid resin system. It is a single-component material applied by high pressure air-less spray. However, it has not been proven sufficiently for offer to the trade.

Carboline was the only company contacted which was far enough along in solvent-free coatings to offer samples for evaluation in the BCL program. They had developed an epoxy-polyamide system for potential use in tanks, but had not offered it to the shipbuilders. We told them that we would examine the suitability of their coating for use as ship tank linings using a procedure similar to that described in Specification MIL-P-23236-Ships.

Subsequent to reaching the above agreement with Carboline, they informed us that they had been working on a solvent-free polyurethane coating system. Because of its poor adhesion a water-dispersed primer had been developed for use with it. We agreed to include this new system in our future evaluations. I

In addition to the above, a news announcement by H. B. Fuller Company was noted regarding a solvent-free polyurethane coating. H. B. Fuller Company was contacted for more information on their Senotex 100 percent solids, polyurethane coating systems.

The coatings were developed in Europe, along with a special, two-component spray unit, "Spray-Q". It is a low-pressure system.. The pigmented polyol side is heated, but normally the isocyanate side is not heated because of its lower viscosity.

The coating can be made very fast curing (a few minutes to set) by addition of accelerators. Because of the fast cure, little or no sagging takes place even though the coating components are relatively low in viscosity.

The isocyanate component is an aromatic type. Therefore, outdoor durability (especially color retention) is not especially good. However, the Fuller representative thought that some compositions would make good tank linings. He offered to coat some test panels for our evaluation. Panels were blasted at BCL and sent to Fuller. These coating samples can be included in a subsequent extended evaluation program.

Section 4

FUTURE WORK

4.1 RECOMMENDATIONS FOR SUBSEQUENT EVALUATION OF SOLVENT-FREE COATINGS

Coating systems which appear to be suitable for use as ship tank linings should be evaluated by a procedure similar to that described in Specification ML-P-23236 - Ships. The actual procedure suggested is as follows:

1. Immerse coated test panels in salt water (simulated seawater) for one week at room temperature.
2. Remove from salt water and immerse in a mixture of hydrocarbons (heptane, toluene, xylene, and benzene) for one week at room temperature.
3. Remove from hydrocarbon mixture and immerse in hot salt water (175 F) for two hours.
4. Remove from hot salt water and spray panels for 10 seconds with hot salt water (175 F).

Steps 3 and 4 are to simulate tank cleaning. The four tests above constitute one cycle. The testing is to continue for 10 cycles unless the coatings fail sooner. A solvent-type coating approved according to MIL-P-23236 should be tested alongside the experimental coatings as a control. Moreover, a coating of the same composition as the solvent-free coating, but applied with the use of solvent, should be used as a control.

The coatings which are being evaluated for use on the ship hull should be tested by immersion in synthetic seawater. These same coatings should be evaluated on the Cleveland Condensing Cabinet, which subjects the coatings to continuous exposure to condensate. This is a quicker way of determining water sensitivity than exposure to salt water. Again, solvent coatings should be used as controls.

Coatings which are believed to be suitable for exterior topside use should be exposed outdoors on racks near the beach at the BCL Daytona Beach test site. They, too, should be evaluated on the Cleveland Condensing Cabinet. Solvent coatings designed for topside use should be tested alongside as controls.

All coatings should be given additional physical tests such as hardness and impact resistance.