

**WATERBORNE COATINGS
FOR
MARINE APPLICATIONS**

NOVEMBER 1981

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IN COOPERATION WITH
AVONDALE SHIPYARDS, INC.

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FOREWORD

This research project was performed under the National Shipbuilding Research Program. The project, as part of that program, is a cooperative, cost shared effort between the Maritime Administration and Avondale Shipyards, Inc. The development work was accomplished by Georgia Institute of Technology (GIT) Engineering Experiment Station under subcontract to Avondale Shipyards. The overall objective of the program was improved productivity and therefore, reduced shipbuilding costs to meet the lower Construction Differential Subsidy rate goals of the Merchant Marine Act of 1970.

The studies have been undertaken with this goal in mind and have followed closely the project outline approved by the Society of Naval Architects and Marine Engineers (SNAME) Ship Production Committee.

Mr. Frank A. Rideout, of GIT, served as Project Manager and Senior Research Scientist, Dr. C. J. Ray as Senior Research Scientist and Head of the Materials Sciences Branch, Mr. Leslie E. Henton as Research Scientist and Mr. Paul M. Hawley as Technician.

On behalf of Avondale Shipyards, Inc., Mr. John Peart was the R&D Program Manager responsible for technical direction and publication of the final report. Mr. Ben Fultz of Offshore Power systems performed editorial services. Program definition and guidance was provided by the members of the 023-1 Surface Preparation Coatings Committee of SNAME, Mr. C. J. Starkenburg, Avondale Shipyards, Inc., Chairman.

Also we wish to acknowledge the support of Mr. Jack Garvey and Mr. Robert Schaffran, of the Maritime Administration. Special thanks are given to the suppliers listed below who supplied paint samples, product information, and field data where available.

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Executive Summary

The marine coatings industry is in the midst of a severe challenge to provide durable coatings responsive to current and imminent regulatory restrictions on the quantity of solvent and other volatile organic compounds (VOC) used in paints. One possible way to meet these stringent requirements is to reduce the amount of VOC by replacing organic solvent paints with waterborne paints. The overall objective of this project was to determine the state-of-the-art of waterborne coatings and their applicability for marine use.

The first part of this study consisted of a survey to determine the generic types of waterborne coatings commercially available for marine use. It was found that the number of readily available systems was disappointingly few. In fact, no really established commercial uses were found except for waterborne inorganic zinc primers.

Following the initial survey, a laboratory test program was formulated to establish the relative performance of waterborne materials. Eighteen different systems, many of them experimental, were selected for testing in simulated marine environments. The sensitivity of these materials to shipyard application conditions was also investigated. The results of these tests are as follows:

- Only a limited number of waterborne materials performed equal to solvent based materials in selected short duration tests.
- Waterborne materials are sensitive to high humidity (normal shipyard environment) which retards cure and adversely affects performance properties of the resulting dried film.
- Waterborne coatings are affected by low temperatures (50°F or less) which retard solvent evaporation. At lower temperatures (32°F) the coatings freeze usually resulting in complete destruction of film properties.

The best waterborne performers in this test program were the epoxy silicate and coal tar epoxy tank coatings. These materials should be subjected to an extended test program followed by actual shipboard testing, if warranted. An unsolicited benefit found with the epoxy silicate is improved fire resistance of the dried paint film. The commercially available waterborne inorganic zinc primers have proven to have limited application in

many shipyards due to moisture sensitivity, the exception being application in controlled environments such as Blast/Paint Facilities and interior ship areas. The one waterborne system which should be considered for use now is the acrylic latex. This material is suitable for use in interior dry spaces where a conventional primer has been applied.

In conclusion, waterborne coatings technology has not developed to the point of extensive use by the marine industry.

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SECTION 1
Conclusions

1. CONCLUSION

1.1 Project Results

As stated in the executive summary, the goal of this project was to determine the state-of-the-art of waterborne coatings and their applicability for marine use. To accomplish this goal, the following tasks were performed:

- Determination of the generic types of commercially available waterborne coatings.
- Determination of usage in related commercial applications and evaluation of their effectiveness.
- Determination of limitations and application requirements as applicable to marine use.
- Performance of limited laboratory screening test as required to verify data.

The end product of this study was the investigation of the feasibility of waterborne coatings for marine use. It was determined that with the exception of selected systems and selected ship applications, waterborne coatings have not progressed to the point where widespread usage can be effected for marine applications.

During the course of the study, only one generic category of commercially available waterborne products with many years of documented superior performance in a corrosive marine environment was identified. These materials are waterborne inorganic zinc primers. The primary reason the waterborne zinc paints have not been universally accepted by shipbuilders is the sensitivity of this material to moisture. Exterior applications (Freeboard, Underwater Hull, Superstructure, etc.) are restricted in localities of high humidity or where sudden rain showers are likely. Since these renditions are the norm for many shipyards, applications are limited to environmentally controlled areas such as interior ship tanks or enclosed Modular Blast and Paint Facilities.

During the study, it was discovered that all waterborne matings are extremely sensitive to atmospheric moisture and temperature during cure. Most require dry, warm (above 32°F) conditions. As stated earlier most shipyards are located in areas of high relative humidity and extreme temperatures; therefore, this sensitivity becomes critical. Dehumidification and ventilation equipment are available to solve the moisture problem for interior ship areas and Modular Blast/Paint Houses but adds additional costs to manufacturing operations. Water wash of the cured film to remove leached out components was also found to improve performance. Another problem inherent in waterborne coatings concerns the retention of coupling agents within the cured film. The retention of these coupling agents prolong the water solvency of the cured film and drastically decrease the resistance to water exposure particularly in immersion service.

Neither the cost of paint in roil-square-feet per gallon nor the labor cost associated with special application processes were considered in this preliminary evaluation. These costs will vary with the general business climate, technology development, field experience and competition. Material cost and application costs such as dehumidification, heat, and water wash, must be a part of the final economic evaluation.

1.2 Laboratory Test Results

During the study, a determination was made to divide the available waterborne coatings into four representative ship performance areas:

- Immersion (Interior Tenks and Underwater Hull)
- Exterior Freeboard (Hull)
 - superstructure
- Miscellaneous Interiors (Excluding Tanks and Severe Service Areas)

The test conditions for each performance area were then selected to most duplicate the conditions coatings would experience in actual service. The paragraphs which follow will discuss the test conditions and a summary of the results. When reviewing these tests, remember that the results are

based on screening tests. Even though the tests are valid, more detailed, extended testing is required prior to actual use of these materials on ships in service.

1.2.1 Immersion Test Results

The immersion tests consisted of the following:

- Immersion in deionized water under a simulated hydrostatic head of 32 psi for 30 days.
- Salt Fog (ASIM B117) for 500 hours.
- Hot Water Immersion 82°C (180°F) for 30 days.
- Diesel Immersion 65°C (150°F) for 30 days.

The best laboratory performance was exhibited by DEVRAN 258, a new proprietary waterborne coating from Devoe Marine Coatings Co., a division of Grow Group, Inc. DEVRAN 258, originally called BAR RUSI II, is identified only as an epoxy silicate and contains the least volatile organic content (VOC) of all Devoe matings offered for evaluation (66 g.VOC/liter). It is the heaviest coating (40 roils) of those tested for immersion serice and outperformed the solvent control (coal tar epoxy) in resistance to rust in the 500 hour salt fog (spray) test and resistance to softening in #2 diesel fuel. Film thickness was found to be extremely critical in the performance of this material. For example, when applied at 12 roils, Devran 258 performed worse than the control. One other characteristic of this coating Which must be considered is the hardness and resulting brittleness of the cured films.

As discussed earlier, the poor performance of the waterborne materials is due, in part, to the incomplete removal of coupling agents during cure and/or the presence of leached components. Complete ventilation and/or water wash of the cured film may improve performance.

International Paint's new epoxy coal tar carried in water, called INTERTUF X8912, gave good results under 32 psi water pressure, diesel fuel immersion, and blister resistance in the salt fog but the panels failed the

rust and scribe test in salt fog and also blistered in the 65°C (150°F) diesel fuel test. The rating of 6 was given for each of the two panels for rusting in the scribe as well as rust spots on the flat surface.

Sigma's epoxy coal tar waterborne coating performed better in the salt fog than in immersion tests.

1.2.2 Exterior Freeboard (Hull) Test Results

The following test conditions were selected for screening candidate materials.

- Salting (ASTM B117) for 500 hours.
- Humidity Chamber (ASIM D2247) for 500 hours.
- Weatherometer (ASIM G26) for 1000 hours.
- Taber Abrasion Resistance (Federal Test Standard 141a, Method 6192).

Because of the extreme atmospheric corrosion of the freeboard area, only those systems with waterborne inorganic zinc primers were selected for testing. Overall none of the waterborne systems demonstrated acceptable performance. However, of those coatings tested, the best performance in these laboratory tests was the Carboline waterborne inorganic zinc, CZ 33, with its topcoat of epoxy acrylic 288WB. The relatively poor abrasion resistance observed was unexpected and needs to be confirmed. The loss of gloss after 1000 hours in the weatherometer is substantially less than that of the straight bis-phenol A epoxy coatings.

The excellent performance of DEVRAN 258 in water immersion tests makes it also a candidate for the above-water hull and the other areas of the ship where coatings brittleness is not a factor. It now needs to be tested in the weatherometer especially in view of the excellent fire-retardant properties claimed by the manufacturer.

1.2.3 Exterior Superstructure Test Results

Exterior superstructure screening tests consisted of:

- Salt Fog (ASIM B227) for 500 hours
- Humidity (ASTM D2247) for 500 hours
- Weatherometer (ASIM G26) for 1000 hours

No waterborne system tested matched the performance of the solvent based control with the exception of the gloss retention properties of the Porter 6600/6610 epoxy acrylic system

1.2.4 Interior Areas (Excluding Tanks and Severe Service Areas) Test Results

The following test conditions were selected as being representative:

- Humidity Chamber (ASIM D2247) for 500 hours.
- Weatherometer (ASM G26) for 1000 hours.

A single coat of solvent based polyamide epoxy was selected as the control for such applications as cargo holds and work spaces. A two coat solvent based alkyd was selected as representative of miscellaneous dry area applications such as living spaces and dry storage.

Of those materials tested, two systems (Mobile Paint's Modified Acrylic and Napko's Acrylic Latex) performed satisfactorily.

1.3 Recommendations

Based on the results of these laboratory screening tests, an extended test program is now necessary to further verify the performance of those systems which passed the screening tests. The tank coating systems are the most logical choice for further testing. The epoxy silicate, the

waterborne coal tar epoxies and the untopcoated inorganic zinc should be subjected to the following tests:

- Hydrostatic salt water immersion for one year (intermittent wet and dry).
- Hydrostatic deionized water immersion for one year.
- Hut water plus detergent cleaning to simulate gas freeing of tanks.
- Diesel immersion for one year.
- Salt Fog testing for 5000 hours with intermittent wet and dry cycles.
- Cathodic disbondment (Underwater Hull Coatings only).

Coal tar epoxy, polyamide epoxy, ketimine epoxy, amine adduct epoxies and inorganic zinc systems qualified in accordance with MIL-P-23236, "Paint Coating systems, Steel Ship Tank, Fuel and Salt Water Ballast", should be selected as controls. Dry, curing times at various temperatures, humidity and ventilation rates should also be a part of the program. The procedures necessary to remove coupling agents from the curing or cured film should also be verified.

Following the successful completion of these tests, candidate materials would then be tested on ships in actual service.

During the course of the new phase of study, should new, promising waterborne coatings become available, these materials would be added to the program. The economic aspects of waterborne matings must be considered in these further studies.

Another approach which should be considered is the testing of mixed waterborne and solvent based paints within a given system. Even though not solving the total VOC problem, partial reduction in VOC's may be possible. One example would be the application of acrylic latex finish coats applied over both solvent based and waterborne inorganic zinc primers.

SECTION 2
Project Plan of Action and Results

2. PROJECT PLAN OF ACTION AND RESULTS

2.1 Background Technical Information

To become competitive with foreign shipbuilding, the U.S. shipyards' research in materials has been supported by the Merchant Marine Act of 1970. This National shipbuilding Research Program must accomplish greater productivity created by new and improved technology.

The science of painting ships both interior and exterior has a part in this program, and the applied technology has lagged behind known industrial coating technology progressing elsewhere in the U.S. economy. This is primarily due to the difficult application conditions in shipyards. Canada has found so few working days per year due to weather that are suitable for painting that they have built enclosed and conditioned dry dock facilities.

Corrosion engineers agree that the performance of every type of commercial coating is substantially enhanced by cleaning the steel to white metal. They also agree that all primers perform best when applied immediately before any rust or contamination can interfere with the binder in the primer making intimate contact with the steel surface.

Experience shows that the ticker a given paint is applied, the more protection, but the choice of generic type, the quality of the formulation and proper application technique are known to be more significant in producing economic coatings with trouble-free, long service life. It is in the search for better materials and better application methods (including surface preparation) that matings research will be most productive.

The organic coatings industry is in the midst of a severe challenge to provide durable coatings which satisfy current and imminent restrictions on the amount of solvents and other volatile organic materials traditionally used to apply paints conventionally. This Challenge started with Rule 66 instituted by the Los Angeles County Air Pollution Control District in July of 1967. Today, the emphasis has switched from the nature of the volatile

organic emissions to the quantity of the organic emissions, i.e., the photochemical reactivity of the solvents is no longer the prime concern. CARB (California Air Resources Board) is leading the way in establishing limits of volatile emissions; the Environmental Protection Agency is in the process of establishing such guidelines for the nation which most likely will be modeled after the CARB emissions rules. These regulations are being formed by the interplay of many legal, political, environmental, and safety oriented forces.

The proposed CARB standard to be fully implemented in 1985 calls for a limit of 295 grms of solvent per liter of paint.^{2,3} The exemptions granted for epoxy based coatings, polyurethanes, and vinyls are only temporary. The lead time required to confirm the performance of new mating systems and formulations by field trial makes it absolutely necessary for the marine coatings industry to start evaluating coating systems designed to meet the probable regulations of the near future.

Shipbuilding is presently exempt from existing rules. Should the rules change to include shipbuilding, this industry would pay dearly. Any anticipated productivity increase due to technology advances would be completely negated.

There are several possible avenues of compliance to meet the limits on the amount of solvent emissions in applying coatings. Add-on devices or techniques such as incineration of solvent fumes or absorption by activated carbon have the advantage of allowing the coating applicator to continue to use the materials with which he is familiar and whose performance he knows. These techniques, however, are applicable only to factory or shop applied coating operations using ovens or other enclosures in which the majority of the emissions can be contained or recovered. This is not useful for the marine coating industry since most of the painting is done outdoors.

Nationwide, there is a major effort to develop waterborne coating systems to meet and surpass the volatile organic emissions restrictions. The waterborne classification covers several types of materials.

Latex systems are best known in the field of exterior house paints. Latex systems are also used in thermosetting systems in industrial coatings (excluding marine) using, for example, water soluble or dispersible melamine type curing agents. Room temperature curing latex systems are also under development. Latex polymers are, perhaps, the most prevalent waterborne system today because of the wide latitude in monomer selection which aids in the development of specific, desired performance properties. Hence, one can find acrylic latexes (acrylic and methacrylic acid esters), vinyl-acrylic latexes, styrene-acrylic latexes, to mention a few.

Allkyd resins, polyester resins and epoxy ester resins are also found in the waterborne arena. Here, the polymers are usually designed to have excess or free carboxylic acid groups. Such resins are neutralized with a base to generate an ionized polymer. In this state, the resin is water soluble or dispersible depending on its acid number, degree of neutralization, and level of water miscible cosolvents. These materials are predominantly used in industrial finishes where they are crosslinked to tie-up the acid groups and reduce the water sensitivity of the films. The cure frequently requires heat so the use of these materials in a typical shipyard is unlikely or limited. Highly interesting crosslinking materials based on aziridine chemistry are available that react with the carboxylic acid group at room temperature. These materials can also be used in latex systems. The future of these crosslinking agents is doubtful at the present due to their probability of being carcinogenic based on the Ames test.

Epoxy resin technology is now showing promise in the waterborne approach. Epoxy esters with free acid groups can be neutralized with volatile organic bases to render them water soluble or dispersible as briefly outlined above. These materials are, subsequently, thermally cured. More germane to the marine industry which relies on coating systems that can dry and/or cure under ambient conditions is the water emulsifiable epoxy and copolymer resins.^{5,6} These materials are, largely, liquid epoxy resins blended with surfactants and cosolvents that, with sufficient shearing and agitation, can generate acceptably stable oil-in-water emulsions. Water soluble curing agents are used. The epoxy resin and

hardener will mix, as first the water, and then the cosolvents evaporate from the film and the emulsion droplets coalesce and react.

The application of the new, emerging coatings technologies to the marine industry is a demanding task. The matings used on a ship must provide protection to the steel in the midst of one of the most severely corrosive environments. In addition to this pervading corrosiveness of the seawater locale, coatings are exposed to a variety of physical and chemical stresses from the handling and carrying of cargo (solvents hydrocarbon fuels, corrosive crude oils, ore, etc.), fouling attack, and docking procedures. Because of the general severity of the marine environment to steel and the additional, localized environmental stresses on or in the various coated sections of a ship, the marine industry needs high performance, cost-effective coating systems. The application requirements for marine matings are also difficult since most of the painting is done after construction of the ship or of major, discrete sections. The surface of the steel, hull and tank interiors for example, must be blast cleaned to at least a near-hite condition to obtain the maximum performance of the coatings systems. This operation itself creates special demands in protecting the environment and workers from exposure to the blast debris and dust. Rapid turn around is also a requirement for painting in ship repair yards.

The painting of the interior of tanks and holds is especially difficult. These areas have restricted ventilation, lighting, and often, limited access. The ventilation in these areas is important to protect the workers and provide the proper conditions for the coatings to dry and cure. The use of waterborne coating systems has the potential of significantly reducing worker exposure to potentially hazardous vapors although protection must still be provided to eliminate the inhalation of the atomized paint. However, waterborne systems will require increased humidity control and ventilation to provide adequate water removal rates while the film is drying to insure a dense cured film with ultimate properties. Additionally good humidity control and high ventilation rates are required to remove Water from the film within a critical time frame. If this is not accomplished a "spongy" or less dense cured film results. The resulting film

will have reduced properties particularly water transmission and corrosion protection. This requirement leads to increased capital investment.

There can also be benefits associated with the use of high solids coatings. First, the cost of solvents would be largely eliminated; solvents are lost upon application and do not form part of the film. Secondly, the spraying of high solids film forming materials will give faster film build and require fewer applications, providing savings on the labor cost which is a major portion of the coating cost. The risk of fire and exposure to toxic materials will also be reduced with a resultant decrease in insurance costs. This is the subject of a complete MarAd Report (see reference 17).

The stove has served as a brief review of the marine coatings industry and the coating technologies potentially available to help the marine industry partially meet the imminent environmental restrictions. The pursuit of the development of waterborne coating systems is in accord with the intent of the 1970 amendments to the 1926 Merchant Marine Act to develop new technology. However, in this case, the primary impetus is not improved productivity but regulatory compliance.

2.2 Objective

The overall objective of this project was to determine the state-of-the-art of waterborne coatings and their applicability for marine use.

2.3 Plan of Action

To accomplish the above stated objective, the following plan of action was formulated:

- Determine the generic types of commercially available waterborne coatings.

TABLE I
 GENERIC TYPES OF WATERBORNE VEHICLES

<u>Generic Type</u>	<u>Example</u>	<u>source</u>
Epoxy-Polyamide Emulsion	Genepoxy M-200 Epirez WD510	General Mills Div. Henkel Celanese
Styrene-Acrylic Latex	Melon X820 ucar 4341	Ashland chemical Union Carbide
All Acrylic Copolymer Latex	Rhoplex MV-23	Rohm and Haas
Acrylic Terpolymer Latex	Ucar 4358 Rhoplex MV-9	Union Carbide Rohm and Haas
Acrylic-Vinyl Chloride Latex	Ucar 503	Union Carbide
Self-crosslinking Acrylic Latex	Ucar 4550	Union Carbide
Water-reducible Alkyd	Arolon 580	Ashland chemical
Ethylene-Vinyl Acetate Latex	Airflex 500 Elvace 1962	Air Products & chemicals DuPont
Ethylene-VA-VC Latex	Ucar 560 Airflex 728	Union Carbide Air Products & Chemicals
Vinylidene Chloride Latex	Saran Latex 143	Dow chemical
Epoxy Ester Emulsion	CEE-5	Pacific Vegetable Oil Co.
vinyl Chloride Copolymer Latex	Geon Latex Polyco 2607	B. F. Goodrich Borden Chemical

- Determine their usage in selected commercial applications and evaluate their effectiveness.
- Determine their limitations and application requirements as applicable to marine use.
- Proceed with limited laboratory testing to screen candidate materials for suitability of use in marine environments.

The laboratory tests appropriate to the coatings needs of the shipbuilding industry have been recently reviewed and assembled.⁷ The purpose of that work, supported by the National Shipbuilding Research Program, was to provide quality control tests to maximize the probability of achieving the optimum performance from a given coating system. These tests dealt mainly with checking the wet paint properties, both in the can and freshly applied. For the development of new materials or the screening of alternate materials, several tests were recommended based on the experience of several shipyards and a review of the coatings literature.

The tests used for established coatings for U. S. military fuel and seawater ballast tanks⁸ and tests for new latex primers⁹ and topcoats¹⁰ for metal surfaces used by the Naval Facilities Engineering Command were reviewed for selecting the test methods and standards most suitable for the present purpose. ASIM methods¹¹ were used in most cases as will be discussed individually in Section 2.5.

2.4 Waterborne Coatings Available for Test

2.4.1 Generic Types

Table I is a recapitulation of generic types of waterborne vehicles for air dry coatings in marine use. This list of vehicles was compiled from previous research accomplished by GIT.

2.4.2 Waterborne Coatings Recommended by Suppliers for Marine Use

To determine the usage of waterborne coatings in marine or other related commercial application, various paint manufacturers were contacted for their recommendations of suitable waterborne coatings. The names were selected from a list comprised of suppliers now working with Avondale Shipyards, suggestions made by the sources of the vehicles listed in Table I, and other major marine matings suppliers.

The number of waterborne marine coatings already in commercial use was fewer than expected. In fact, no really established commercial uses were found except waterborne inorganic zinc-rich primers. Three of these were included in this study. Disappointingly few coatings were offered from successful applications in other industrial uses with severe exposure.

At this point in the study the basis for selecting matings for testing was broadened to include developmental waterborne products that appeared promising for eventual use in marine applications. All the waterborne coatings selected were recommended by manufacturers for marine exposure renditions at the thicknesses shown and all were provided by coating suppliers except the two Celanese systems. These are newly developed epoxy/acrylic latexes with extensive industrial laboratory testing which Devoe Marine Coatings Co. has agreed to manufacture if larger quantities are required for field trials.

Several paint manufacturers replied that they were developing waterborne maintenance or marine matings but none were ready for sampling. These firms included Du Pont, Hughson, Farboil, Imperial, and Rust-Oleum. The industry contacts for waterborne candidate coatings included nine raw material suppliers and twenty-three paint manufacturers.

2.5 Results of Laboratory Testing

The candidate coating systems were spray applied to solvent washed and aluminum oxide grit blasted test panels to the manufacturers' recommended thickness as shown in Table II. Film thickness measurements were made during laboratory preparation at nine points on each panel after each coat had dried. The final topcoat was air dried in the laboratory atmosphere for 14 days before exposure to test environments.

To simulate the various ship areas, the testing was divided into four performance categories:

- Immersion Service (Interior Tanks and Underwater Bottom)
- Freeboard Areas (Hull)
- Exterior Superstructure
- Interior Areas (Excluding Tanks and Severe Service Areas)

The tests for each performance area were designed to approximate the service renditions actually existing in each respective service area.

2.5.1 Immersion Service

Four test environments were selected to evaluate waterborne coatings in simulated immersion service:

- Water Immersion at 32 PSI to Simulate a Hydrostatic Head
- Hot Water Immersion 82°C (180°F) to Simulate Tank Cleaning Processes
- Diesel Immersion 65°C (150°F) to Simulate Fuel Oil Resistance
- Salt Fog (ASIM B117) to Simulate a Corrosive Marine Environment

TABLE II
WATERBORNE COATING SYSTEMS TESTED

SUPPLIER	PRIMER PRODUCT NUMBER	GENERIC TYPE	FILM THICKNESS	TOPCOAT PRODUCT NUMBER	GENERIC TYPE	FILM THICKNESS
Bywater Sales & Service Co. 709 Engineers Road Belle Chase, LA 70037	ZINC-GUARD 108	Inorg. Zinc	3.5 roils	AQUA-POXY 370	Epoxy/acrylic	2.5 roils
Carboline Company 350 Hanley Industrial Court St. Louis, MO 36144	CARBO ZINC 33	Inorg. Zinc	3 roils	Carboline 288WB	Epoxy/acrylic	4 roils
Celanese Plastics and Specialties Company 9800 Bluegrass Parkway Louisville, KY 40299	24-192	Epoxy/acrylic	2 roils	24-146	Epoxy/acrylic	3 roils
Celanese Plastics and Specialties Company 9800 Bluegrass Parkway Louisville, KY 40299	24-194	Epoxy/acrylic	2 roils	24-178	Epoxy/acrylic	3 roils
Devoe Marine Coatings Co. Post Office Box 7600 Louisville, KY 40207	DEVFLEX Primer	Latex	6 roils	DEVFLEX I	Mod. acrylic	2 roils
Devoe Marine Coatings Co. Post Office Box 7600 Louisville, KY 40207	DEVTRAN 258	Epoxy/silicate	20 roils			
Devoe Marine Coatings Co. Post Office Box 7600 Louisville, KY 40277	DEVTRAN 259	Epoxy/acrylic	9 roils			
General Polymers Corp. 3925 Huston Avenue Cincinnati, Ohio 45212	ACRYLTEX 2500	Acrylic/cement	10 roils			
International Paint Co. Morris and Elmwood Avenue Union, NJ 07083	INTERTUF X8921	Epoxy/Coal Tar	14 roils			

TABLE II (CONTINUED)
WATERBORE COATING SYSTEMS TESTED

SUPPLIER	PRIMER PRODUCT NUMBER	GENERIC TYPE	FILM THICKNESS	TOPCOAT PRODUCT NUMBER(S)	GENERIC TYPE	FILM THICKNESS
Mobile Paint Company Post Office Box 717 Theodore, AL 36582	LP 3743	Mod. acrylic	5 roils	LP 3783		2.5 roils
Napko Corporation Post Office Box 14509 Houston, TX 77021	Pipeliner 7-2371	Epoxy/ Polyamide	6 roils			
Napko Corporation Post Office Box 14509 Houston, TX 77021	Waterborne Zinc 1371	Inorganic Zinc	2.5 roils	EPOXACRYL 5357 EPOXY PA 8-3470	Epoxy/acrylic	3 roils
Napko Corporation Post Office Box 14509 Houston, TX 77021	VERSAFLEX PN4499	Acrylic Latex	2 roils	TUX Enamel 3800	Acrylic Latex	3 roils
Napko Corporation Post Office Box 14509 Houston, TX 77021	NAPKO 5617	Epoxy/ Polyamide	2 roils	EPOXACRYL 5357	Epoxy/acrylic	3 roils
Porter Coatings 400 S B. Street Louisville, KY 40201	AQUALOCK 6600	Acrylic/Epoxy	2.5 roils	AQUALOCK 6610	Acrylic/Epoxy	5 roils
Reliance Universal, Inc. Post Office Box 1113 Houston, TX 77001	REL-ZINC 130	Zinc-Rich	3 roils	RELTEX 7633	Mod. acrylic	4 roils
Sentry Paint and Chem. Co. Mill and Lagrence Sts. Oarby, PA19023	SENTRY X5822	Epoxy Ester	2 roils			
Sigma Coatings, Inc. Post Office Box 826 Harvey, LA 70051	SIGMA 7445	Epoxy	3 roils			
Sigma Coatings, Inc. Post Office Box 826 Harvey, LA 70051	SIGMA WS-TCN	Epoxy Coal Tar	10 roils			

2.5.1.1 Water Immersion at 32 psi for 30 Days

To simulate the rendition for coatings for lining shipboard tanks that hold water, 6" x 12" panels were coated both sides as described above and suspended inside a five gallon pressure tank so that about 60% of the panel length was immersed in deionized water which was then pressurized by air and maintained at 32 ± 1 prods per square inch for 30 days at room temperature. The tank was opened for a few minutes at about 4 day intervals to check for any obvious change. The results appear in Table III.

The solventborne coating and two of the five waterborne coatings suggested for ballast tanks showed no effect. DEVRAN 258 (Epoxy Silicate), International X8912 (Coal Tar Epoxy) and Carboline CM14 (Coal Tar Epoxy Control) all passed the test. The International X8912 softened and turned white but rehardened after air dry. The Napko Pipeliner epoxy/polyamide 7-2371 which is used at only 6 roils showed no effect until the 30 day inspection. Sigma coal tar epoxy emulsion WS TCN was 10 roils thick and showed blistering at 17 days. This coating also shined whitening when removed from the water after 30 days. No rusting appeared on any panels. Figure 2.1 is a photograph of the panels after 30 days immersion.

2.5.1.2 Hot Deionized Water Immersion Tests

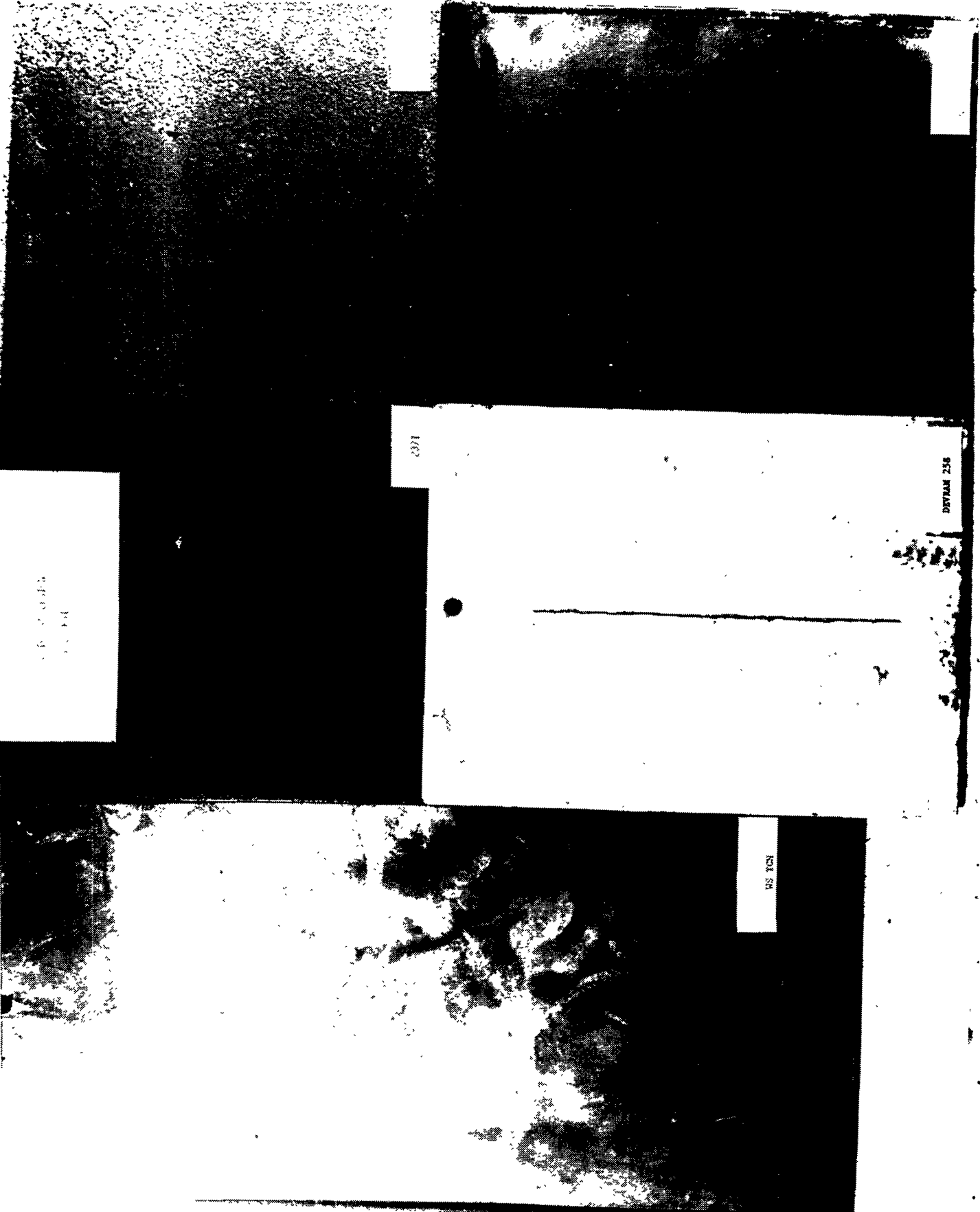
Table IV reports the blistering by ASTM Method D 714 at various intervals up to 528 hours of 4" X 8" coated panels immersed about half way in 82°C (180°F) deionized water. No panel showed rust. The only material which passed this very severe test was the Devoe DEVRAN 258 Epoxy Silicate. The second best material was the coal tar epoxy control. The waterborne coal tar epoxy materials performed almost as well as the solvent based coal tar epoxy. Each of these materials warrant further testing. See Figures 2.2 for photographic results.

TABLE III

WATER IMMERSION AT 32 PSI*

Supplier	Product	Days of Exposure							
		4	6	11	13	17	21	25	30
Devoe	DEVTRAN 258								none
General Polymer	AT 2500								complete failure
Napko	7-2371							none	6MD
Sigma	WS TON				none	8D	8D	8D	6M Whitened
International.	X-8912								none
Controls:									
Carboline	CM14								none

*Blister ratings (ASTM D 714) after immersion in deionized Water at 70°F.



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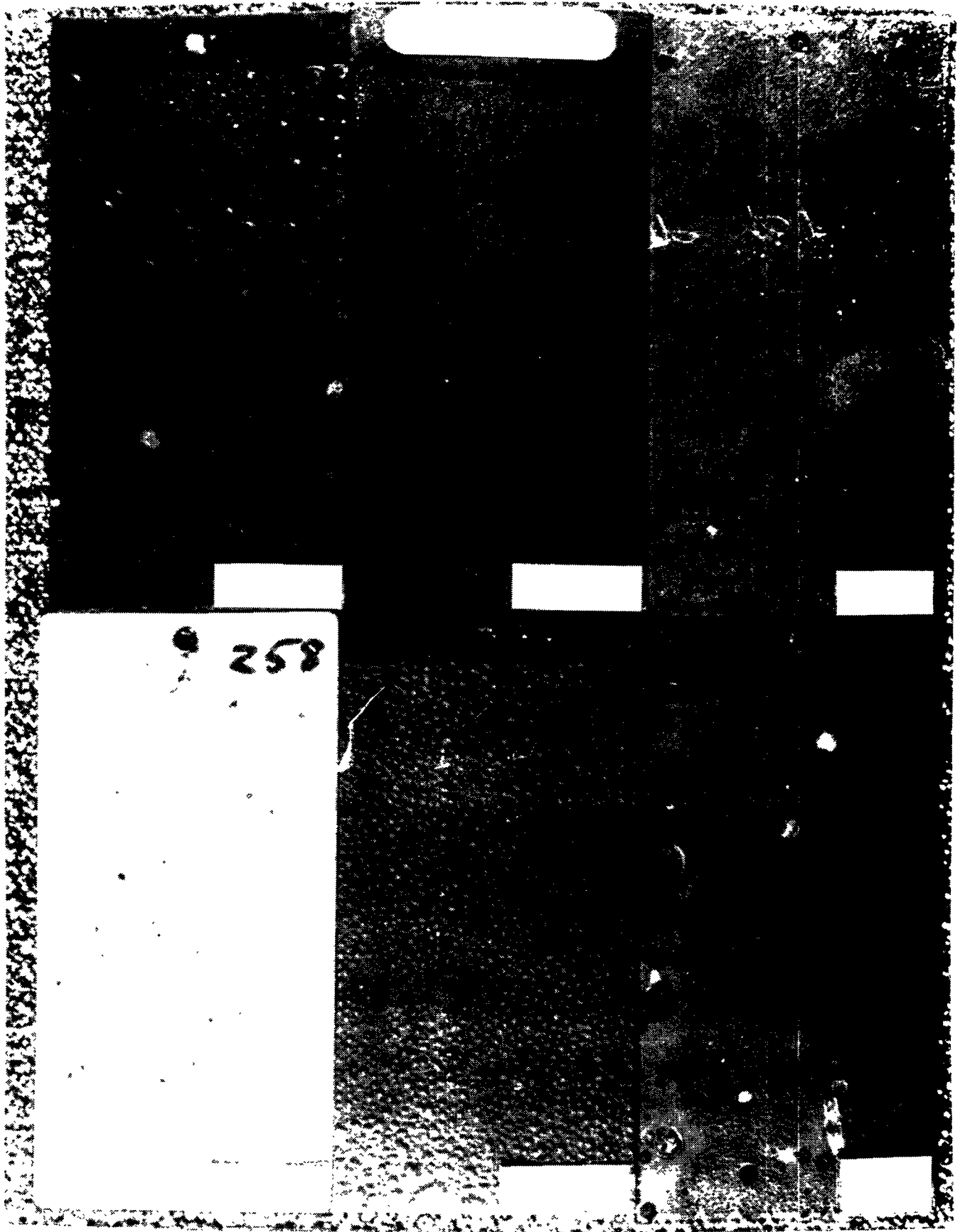
DXTMAN 235

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TABLE IV

BLISTER RATINGS (ASIM D 714) AFTER EXPOSURE TO
82°C (180°F) DEIONIZED WATER IMMERSION

Supplier	product	Hburs of Exposure									
		48	72	96	216	264	360	408	432	504	528
Devoe	DEVTRAN 258										none
General Polymer	AT 2500										complete failure
International Paint	X8912	6M	6M	6M	6m	6M	6M	6M	6M	6M	4D
Napko	7-2371	2M	2M	2M	2M	2M	2M	2M	2M	2M	complete failure
sentry	X5822										complete failure
Sigma	WS TQN	6M	6M	6M	6M	6M	2M	2M	2M	2M	2MD
Controls:											
Carboline	CM14								8M	8M	6MD



2.2 Photograph of Deionized Water Immersion Panels

2.5.1.3 Hot Oil Immersion Tests

In a similar test the panels were immersed half way in 65°C (150°F) #2 diesel fuel for 30 days. AT 2500 and DEVRAN 258 were darkened by the oil after the 30 day test. The softening effect on the coatings, shown in Table V was measured both by probing with a knife and by pencil hardness (ASTM Method D 3363), before and after the test. In this test, the waterborne coatings appear to compare well with the conventional paints.

2.5.1.4 salt Fog Tests

The salt spray (or fog) test (ASTM Method B-117¹¹) is one of the most popular laboratory tests for marine and heavy duty maintenance coating evaluations. A thorough review of the merits of the test written by Appleman and Campbell will soon be published in the Journal of Coatings Technology.¹² Duplicate 4" X 8" panels were run for 504 hours in a new cabinet conforming to ASTM B-117. The temperature was easily maintained at 35° ± 1C (95°F) and 5% C.P. sodium chloride was used. A vertical scribe was cut through the coating exposing about 1/32" of bare metal after the 14 day drying period. The panels were rated each day for the first week and then about every 4 days until removal after 21 days (504 hours) or 22 days (528 hours).

Ratings for rust on the flat panel area through intact paint and also for rust as undercutting from the scribe down the center of the panel are given in Table VI using the rating system described in ASTM Methods D 610 (Rust) and D 1654 (Creep).

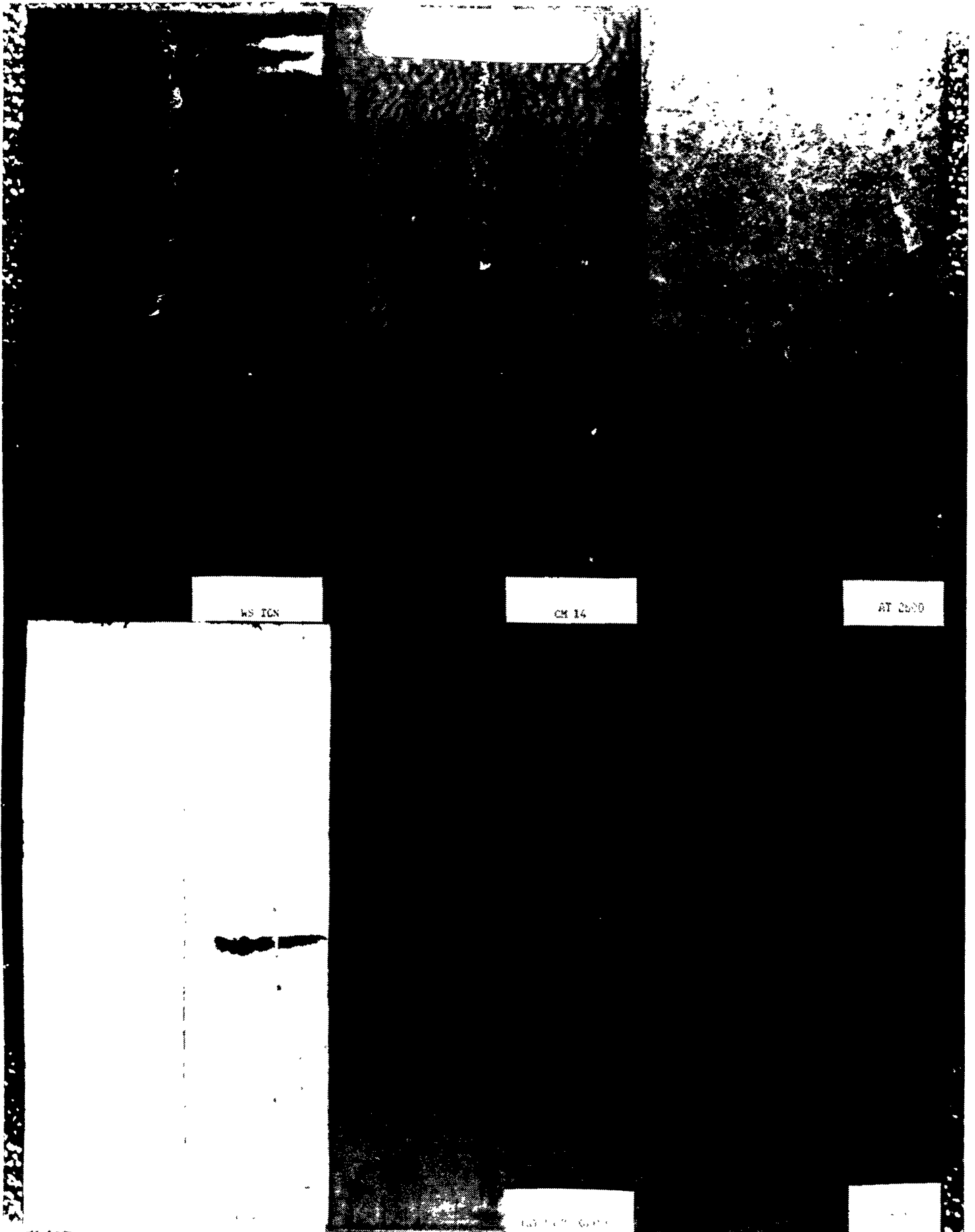
Tape adhesion test, ASTM Method D 3359 showed no loss of bond between the coating and the steel at the scribe after 504 or 528 hours on most panels which means a rating of 5. Sigma WS TON was rated 4 and Sigma 7445 was rated 3. See Figures 2.3 for photograph of Salt Fog performance.

Again the best performers were the coal tar epoxies, both the waterborne and solvent based types. Even though the performance results for duplicate panels were virtually the same, one abnormality was observed. The

TABLE V

RESISTANCE TO 30 DAYS IMMERSION IN #2 DIESEL FUEL AT 65°C (150°F)

Supplier	Product	softening	stained	<u>Pencil Hardness</u>	
				Before	After
Devoe	DEVTRAN 258	none	film	5H	5H
General Polymer	AT 2500	none	film	3B	3B
International Paint	Intertuf 8912	none		3B	3B
Napko	7-2371	slight		HB	2B
Sigma	Ws TON	none		3B	3B
Controls:					
Carboline	CM14	none		2H	2H



2.3 Photograph of Tank Coatings Salt Fog Performance.

TABLE VI

SALT FOG RUST RESULTS

ASTM B 117 (500 HRS)

Supplier	Product	Rating:	Hours to Reach Rust Rating (ASTM D 610)											
			10	9	8	7	6	5	4	3	2	1		
Int'l Paint	INTERTUF X 8912	Panel Scribe	504								504			
Napko	7-2371	Panel Scribe	96	216		336	408					Complete	Failure	
Carboline	OM 14	Panel Scribe	504									504		
Carboline	190HB	Panel Scribe	504								504			
General Polymer	AT 2500	Panel Scribe	24 72	48 96	96 216	240	336	504	504					
Sigma	WS TCN	Panel Scribe	504 72	96	240	336					504			
Sigma	7445	Panel Scribe		24 24	96 96	216			504 240	504				
Devoe	DEVTRAN 258 (12 mils)	Panel Scribe				528				528				
Devoe	DEVTRAN 258 (40 mils)	Panel Scribe	528 528											
Devoe	DEVTRAN 259	Panel Scribe	528											528
Porter	6600 6610	Panel Scribe	360 192	432 264	432							504		
Napko	1371 8-3474 5357	Panel Scribe	528 528											
Carboline	CZ33 288WB	Panel Scribe	528 528											

TABLE VI (cont'd)
 SALT FOG RUST RESULTS
 ASTM B 117 (500 HRS)

Supplier	Product	Rating:	Hours to Reach Rust Rating (ASTM D 610)										
			10	9	8	7	6	5	4	3	2	1	
By-Water	108	Panel	528										
	370	Scribe	528										
Mobile Paint	3743	Panel	24	96	264								528
	3744	Scribe	96	144	264								528
Napko	5617	Panel	528										
	5357	Scribe	480						528				
Celanese	24-194	Panel	528										
	24-178	Strike	480										528
Devoe	DEVFLEX	Panel	96	144			528						
	DEVFLEX I	scribe	96	144									
Napko	4499	Panel	96	144	264	432							528
	3801	Scribe	96	144	432								
Rel. Univ.	130	Panel	528										
	7633	Scribe	528										
Celanese	24-192	Panel	528										
	24-146	Scribe											528
Carboline	GP-10	Panel	528										
	GP-62	Strike	480		528								
sentry	X5822	Panel	480		528								
		Strike	480		528								

Note: These data are for panel A. The duplicate panel, B, had practically the same performance. The final rating varied no more than one rating number and then only in three cases.

two panels mated with DEVRAN 258 performed entirely differently. One panel had a rust grade of 7 and the other 10. Closer inspection revealed that the first panel was mated with 12 roils of material; whereas, the second panel was coated with 40 roils of material (see Figure 2.4). This demonstrates a critical film thickness requirement for acceptable performance.

2.5.1.5 Rerun of Humidity Test on Selected Materials

AS a result of the demonstrated acceptable performance of the waterborne coal tar epoxies, the humidity test was extended to 3744 hours. Table V I I summarizes the results of this test. As can be seen from the table, the waterborne coal tar epoxies warrant additional testing.

2.5.1.6 Immersion Test Sumary

Table VIII summarizes the results of these tests. When applied at the correct film thickness (20 + roils) the best performer of those systems tested was DEVRAN 258. The second best performer was the solvent based coal tar epoxy control. The waterborne coal tar epoxies were almost as good as th`e solvent based control. It must be remembered when comparing these results just as with any other test results within this report, that the tests were designed as a short duration screening test to observe relative performance. The next series of tests should be longer with additional controls such as tank matings qualified to Mil-P-23236.

2.5.2 Freeboard Areas (Hull)

Four tests were selected to investigate the relative performance of hull coatings:

- Salt Fog (ASTM B117) for 500 hours
- Humidity (ASTM D2247) for 500 hours
- Weathermeter (G26) for 1000 hours
- Taber Abrasion

SALT FOG RESULTS
ASTM B117 (500 HRS)

40 mils

DEVTRAN 258

12 mils

2.4 Photograph of Devran 258 after Salt Fog Testing
at Two Film Thicknesses.

TABLE VII

RERUN OF HUMIDITY TEST ON SELECT MATERIALS

SUPPLIER	GENERIC PRODUCT	PRODUCT NUMBER	PANEL DESIGNATION	500 HOURS RUST	500 HOURS BLISTERS	3744 HOURS RUST	3744 HOURS BLISTERS
DEVOE	EPOXY	258	A	10	NONE	10	NONE
	SILICATE		B	10	NONE	10	NONE
INTERNATIONAL	COAL TAR	X8912	A	10	NONE	10	NONE
	EPOXY		B	10	NONE	10	NONE
SOLVENT BASED CONTROLS							
CARBOLINE	EPOXY	190HB	A	10	NONE	10	NONE
	POLYAMIDE		B	10	NONE	10	NONE
CARBOLINE	COAL TAR	CM14	A	10	NONE	10	NONE
	EPOXY		B	10	NONE	10	NONE

TABLE VIII
WATERBORNE COATINGS FOR IMMERSION SERVICE

SUPPLIER	GENERIC PRODUCT	PRODUCT NUMBER	DRY FILM THICKNESS	WATER IMMERSION 32 PSI 30 DAYS		SALT FOG (ASTM B117) 500 HRS			HOT WATER IMMERSION (180°F)		DIESEL IMMERSION 150°F 30 DAYS	
				RUST	BLISTERS	RUST	CREEP	BLISTERS	RUST	BLISTERS	SOFTENS	BLISTERS
DEVOE	EPOXY SILICATE	258	12 mils 40 mils	10	NONE	7 10	6	NONE	10	NONE	8	NONE
GENERAL POLYMERS	ACRYLIC CEMENT	AT2500	10 mils	FAILED		4	4	4MD	FAILED		8	NONE
INTERNATIONAL PAINT	COAL TAR EPOXY	X8912	14 mils	10	2. NONE	10	4	NONE	7	4D	10	NONE
NAPKO	EP ACRYLIC	7-2371	6 mils	10	6MD	FAILED			FAILED		5	NONE
SIGMA	COAL TAR EPOXY	WS TCN	10 mils	10	6M	10	4	NONE	10	2MD	10	NONE
SOLVENT BASED CONTROL												
CARBOLINE	COAL TAR EPOXY	CM14	14 mils	10	NONE	10	3	NONE	10	6MD	10	NONE

NOTES:

1. The following standards were used to rate coatings performance:
 - (a) Rust - ASTM D610 (10 perfect)
 - (b) Creep - ASTM D1654 (10 perfect)
 - (c) Blisters - ASTM D714
2. Material softened in water but rehardened on removal.

2.5.2.1 Salt Fog Tests

Only waterborne inorganic zinc primed systems were tested. All the systems demonstrated acceptable corrosion protection. One system blistered (Reliance Universal 130/7633) and one system had numerous pinholes (Bywater 108/370). See Figures 2.5 for photographic results.

2.5.2.2 Humidity Chamber

The 100% humidity tests were run in a new Q-C-T Cyclic Environmental Tester using ASTM method D 2247 at $38^{\circ} \pm 1^{\circ}\text{C}$ ($100^{\circ} \pm 2^{\circ}\text{F}$) which provides continuously condensing humidity on the test surface of the panel. Panels were tested in duplicate and scribed in the same manner as for the salt fog tests. The duration was 504 hours (21 days). Panels were checked for signs of rust and blisters each day for the first week, and then about every 4 days. The ASTM tape adhesion test (D 3359) was made when exposure was terminated. All the panels failed the humidity test. Blisters ranged from 6M to 8 MD. See Figures 2.6 and 2.7 for photographs of test results.

2.5.2.3 Weatherometer Test

The Atlas 65 WR Weatherometer with 6500 watt Xenon arc and a borosilicate glass filter was operated 102 minutes of light followed by 18 minutes of deionized water spray for 1000 hours (ASTM Method G-26).

Rust ratings at 500 and 1000 hours are given in Table IX for panels A and B using ASTM Method D 610. Table X shows the blister ratings using ASIM Method D 714.

The results of blistering from water penetration would be less for some coatings if longer drying was permitted before exposure to water. Another condition that will improve some waterborne matings is a rinsing of the film with potable water after complete drying of the film and thoroughly drying again. The glycols, other slow evaporating water-coupling solvents and components of the surfactant usually present in small amounts in the pint, slowly come to the surface. The water resistance of the residual film is improved when these are removed.

SALT FOG RESULTS
ASTM B117 (500 HRS)

CE33/28945

100/370

130/7633

1371/8-3474/5357

2.5 Photograph of Exterior Freeboard Salt Fog Performance.

HUMIDITY CHAMBER

CZ33/288WB

108/370

2.6 Photograph of Exterior Freeboard Waterborne Systems
Exposed to Humidity Chamber (CZ33/288WB and 108/370).

HUMIDITY CHAMBER

1371/8-3474/5357

2.7 Photograph of Exterior Freeboard Waterborne Systems Exposed to Humidity Chamber (130/7633 and 1371/8-3474/5357).

TABLE IX
WEATHEROMETER RUST RATING

Supplier	Product	<u>Initial</u>		<u>500 Hours</u>		<u>1,000 Hours</u>	
		Panel A	Panel B	Panel A	Panel B	Panel A	Panel B
Napko	7-2371	10	10	10	10	9	8
Carboline	190HB	10	10	10	10	10	10
Gen'1 Polymer	AT 2500	10	10	3	4	Taken out at 500 hours	
Signs	7445	10	10	8	8	8	8
Devoe	DEVTRAN 259	10	10	10	10	10	10
Porter	6660/6610	10	10	10	10	9	10
Napko	1371/8-3474/5357	10	10	10	10	10	9
Carboline	CZ33/288WB	10	10	10	10	10	10
By-Water	108/370	10	10	10	10	9	9
Mobile Paint	3734/3744	10	10	10	10	10	10
Napko	5617/5357	10	10	10	10	10	10
Celanese	24-294/24-178	10	10	9	7	8	6
Devoe	DEVFLEX/DEVFLEX I	10	10	10	10	10	10
Napko	4499/3801	10	10	10	10	10	10
Rel. Univ.	130/7633	10	10	10	10	10	9
Celanese	24-192/24-146	10	10	10	10	10	10
Carboline	GP10/GP62	10	10	10	10	10	9
sentry	5822	10	10	10	10	10	10

TABLE X
WEATHEROMETER BLISTER RATINGS

Supplier	Product	500 Hours		1,000 Hours	
		Panel		Panel	
		A	B	A	B
Napko	7-2371	8D	8D	8D	8D
Carboline	190HB	2F*	None	2F*	None
General Polymer	AT 2500			Porous	Film
Sigma	7445	4F	4F	8M	8D
Devoe	DEVVRAN 259			4F	4F
Porter	6660/6610				None
Napko	1371/8-3474/5357	4F*	4F*	6 F *	6F*
Carboline	CZ33/288WB				None
By-Water	108/370	8MD	8MD	8M	8M
Mobile Paint	3734/3744	6F	6F	6F	6F
Napko	5617/5357	4MD	4MD	4D	4MD
Celanese	24-294/24-178**	2M	2M	2M	2M
Devoe	DEVFLEX/DEVEFLEX I				None
Napko	4499/3801	6F*	6F*	6F*	6F*
Rel. Univ.	130/7633				None
Celanese	24-192/24-146**	4MD	4MD	8D	8D
Carboline	GP10/GP62	6 F *	4F*	None	None
sentry	5822				None

*Fewer than 10 blisters on 3" x 9" panels.
**Failed.

Of the systems tested for exterior hull, two failed the weatherometer test by blistering, one had severe topcoat erosion and the other had minor topcoat EROSION. None performed as well as a conventional system.

2.5.2.4 Taber Abrasion Tests

The Teledyne Taber Abraser Model 505 using CS-10 Wheels and a 250 gram loading was used for 1000 cycles according to Federal. Test Method 141a, 6192. The wear index is defined as the weight loss of the film in milligrams per thousand cycles. The results are given in Table XI for panels A and B and their average. The high value for the portland cement/acrylic is not surprising in view of the roughness due to pro jetting sand particles. The reason for the high wear index of Carboline CS33/288 is not known and repeat testing is recommended. Otherwise the abrasion resistance for waterborne coatings appeared to be in the same range as for conventional marine coatings.

2.5.2.5 Freeboard Test Summary

Overall, none of the waterborne systems demonstrated acceptable performance. All failed either by blistering or erosion of the topcoat. Table XII summarizes the results of the freeboard test program.

2.5.3 Exterior Superstructure

Three test parameters were selected to evaluate exterior superstructure performance of waterborne systems. An epoxy polyamide control system was selected as the control even though in normal practice, this material would never be used alone without a rust inhibitive primer and gloss retention topcoat. However, because relative performance was the primary concern, the polyamide epoxy control was a good choice. A conventional alkyd system was also included as a second control.

- Salt Fog (ASTM B117) for 500 hours
- Humidity (ASTM D2247) for 500 hours
- Weatherometer (ASTM G26) for 1000 hours.

TABLE XI

TABER ABRADER WEAR INDE*

Federal Test Method 141a 6192

Supplier'	Product	Panel A	Panel B	Average
By-Water	108/370	42	27	35
Carboline	190 HF	33	34	34
Carboline	CZ33/288	934	957	946
Carboline	GP10/62	44	39	42
Devoe	259	27	28	28
General Polymer	AT 2500	1670	1595	1632
Napko	7-2371	23	21	22
Napko	1371/8-3474/5357	37	30	33
Porter	6600/6610	27	27	27
Sigma	7445	6	15	11

*Wear Index is loss in mg per thousand cycles using CS-20 Wheels and a 250 gram loading.

TABLE XII
WATERBORNE COATINGS FOR FREEBOARD AREAS (HULL)

SUPPLIER	GENERIC PRODUCT	PRODUCT NUMBER	DRY FILM THICKNESS	SALT FOG (ASTM B117) 500 HRS				HUMIDITY (ASTM B117) 500 HRS			WEATHEROMETER (ASTM G26) 1000 HRS				TABER ABRASION WEAR INDEX
				RUST	CREEP	BLISTER	ADHESION AT SCRIBE	RUST	CREEP	BLISTER	RUST	BLISTER	INITIAL GLOSS	FINAL GLOSS	
BYWATER	INORGANIC ZINC	108	4 mils	10	10	2. NONE	5	10	10	8MD	9	8M	41	23	35
	EP ACRYLIC	370	3 mils												
CARBOLINE	INORGANIC ZINC	33	3 mils	10	10	NONE	5	10	10	8MD	10	3. NONE	58	16	945
	EP ACRYLIC	288WB	4 mils												
NAPKO	INORGANIC ZINC	1371	2.5 mils	10	10	NONE	5	10	10	6M	10	6F	28	8	33
	EPOXY PA EP ACRYLIC	8-3470 5357	5.0 mils 3.0 mils												
RELIANCE UNIVERSAL	ZINC RICH MOD. ACY.	130 7633	3 mils 4 mils	10	10	4M	5	10	10	6M	10	4. NONE	44	9	NOT TESTED

NOTES:

1. The following standards were used to rate coatings performance:
 - (a) Rust - ASTM D610 (10 perfect)
 - (b) Creep - ASTM D1654 (10 perfect)
 - (c) Blisters - ASTM D714
 - (d) Wear index is the average of two measurements in milligrams per 1000 cycles, Federal Test Standard 141a, Method 6192.
2. Numerous Pin Holes
3. Erosion of Top Coat
4. Severe Erosion of Top Coat

2.5.3.1 Salt Fog Tests

Four of the five systems tested had as good corrosion preventive properties as the control. Three failed by blistering. See Figure 2.8 and 2.9 for photographs of salt fog performances.

2.5.3.2 Humidity Tests

The waterborne systems and the alkyd control system all blistered. The Porter Epoxy Acrylic system also demonstrated inferior rust preventive properties. No waterborne system performed as well as the solvent based polyamide epoxy. See Figure 2.10 for photograph of humidity test results.

2.5.3.3 Weatherometer Tests

Four of the five waterborne systems blistered in the Weatherometer. The only waterborne system which matched the performance of the conventional system was the Porter system which failed the humidity test.

2.5.3.4 Gloss Readings

The Weatherometer panels were measured in duplicate, A and B, for gloss readings before exposure, at 500 hours, and when terminated at 1000 hours. Measurements were made at 60° from the flat panel surface using a Gardner Glossgard and ASTM Method D 523. Table XIII reports each panel and their average readings. No requirements for gloss were requested of the supplier but same significance may be placed on the change of gloss over 1000 hours. The improvement of the epoxy/acrylic compared to the epoxy/polyamide is apparent.

2.5.3.5 Exterior Superstructure Summary

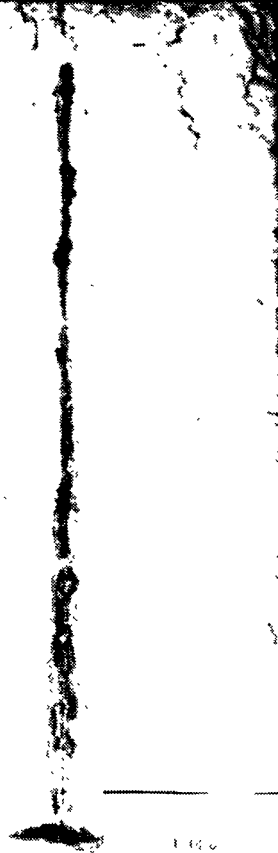
Table XIV summarizes the performance of each system tested. With the possible exception of the gloss retention properties of the Porter Epoxy Acrylic 6600/6610, no waterborne system matched the performance of the single mat of the solvent based polyamide epoxy.



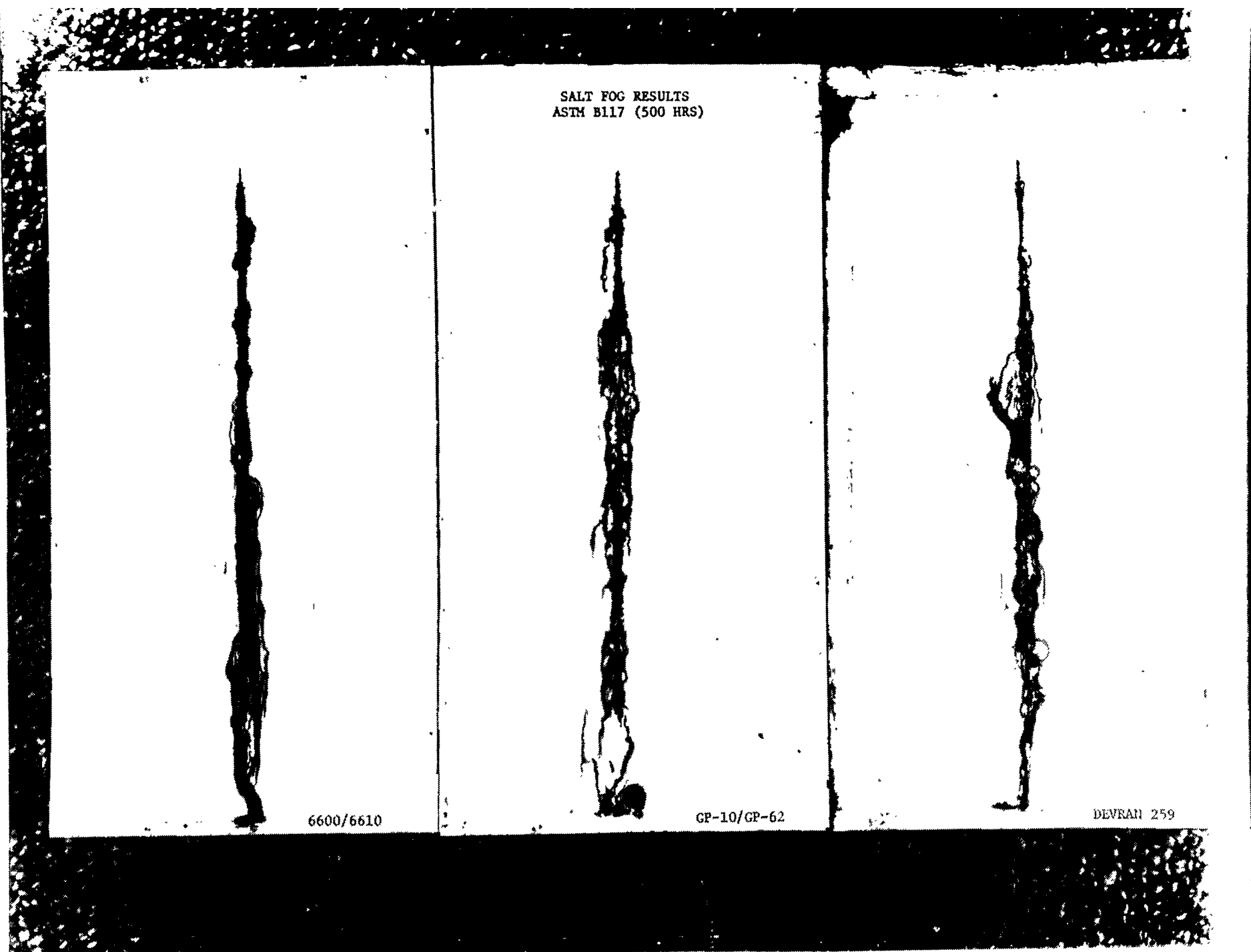
5617/5357



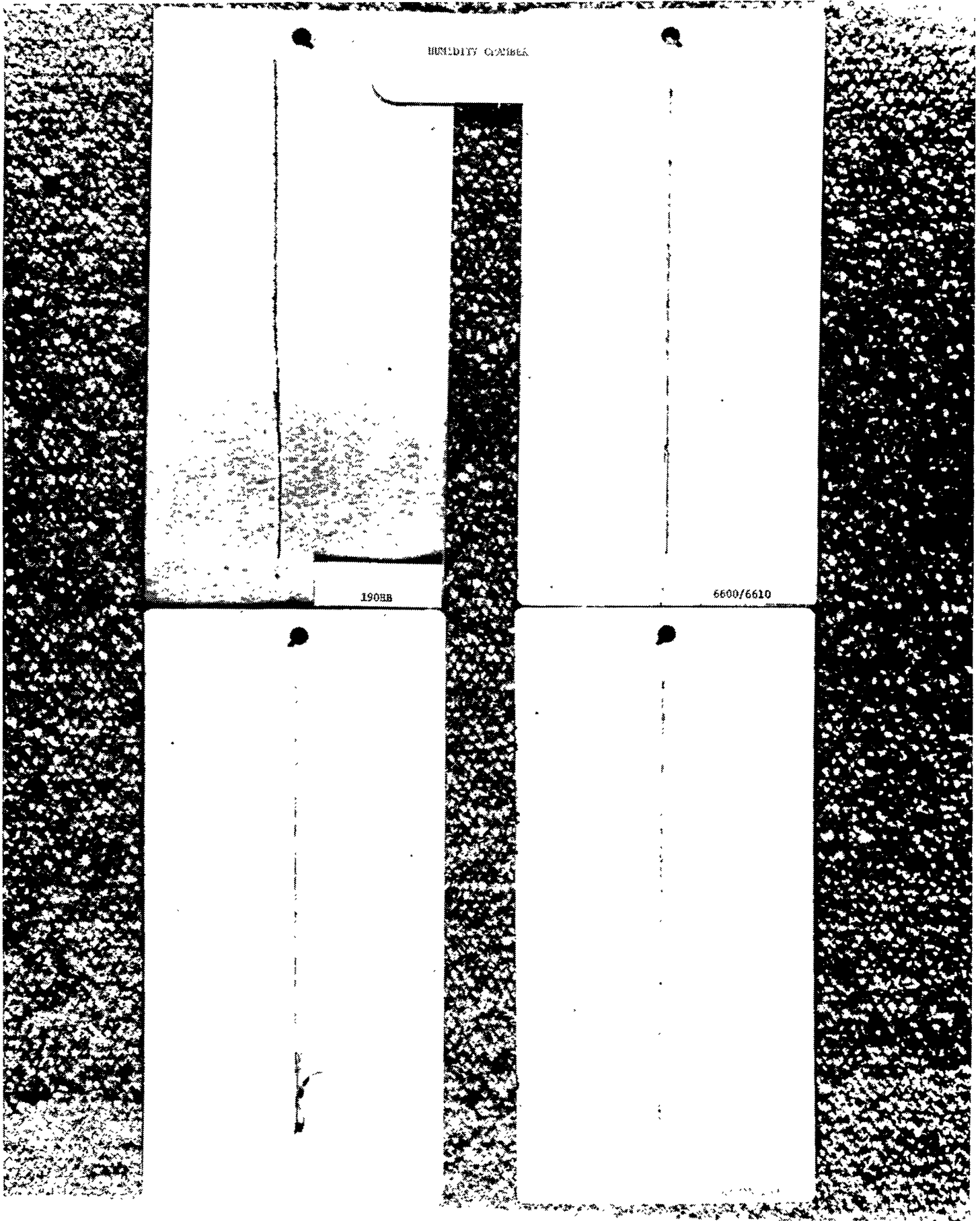
24-194/24-178



2.8 Photograph of Superstructure Salt Fog Performance
(24-192/24-146, 24-194/24-178, 5617/5357, 190HB).



2.9 Photograph of Superstructure Salt Fog Performance (259, 6600/6610, GP10/GP62).



2.10 Photograph of Superstructure Waterborne Systems Exposed to Humidity Chamber.

TABLE XIII

GLOSS READINGS (ASIM D 523) WEATHEROMETER PANELS

Supplier	Product	Initial			500 Hourse			1,000 Hours		
		Panel A	B	Avg.	Panel A	B	Avg.	Panel A	B	Avg.
By-Water	108/370	45.5	36.4	41	31.7	33.2	32	22.8	23.9	23
Carboline	GP10 GP62	60.3	58.2	59	15.7	16.9	16	9.2	11.9	11
Carboline	CZ33/288	64.4	51.3	58	44.9	43.6	44	13.2	19.3	16
Carboline	190 HB	5.0	3.0	4	2.8	2.3	3	0.9	1.5	1
Celanese	24-192 24-146	68.4	70.4	69	11.1	10.6	11	4.4	3.0	4
Devoe	DEVVRAN 259	92.7	90.0	91	9.0	9.8	9	33.4	5.2	4
Devoe	DEVFLEX DEVFLEX I	28.1	29.5	29	15.9	16.0	16	13.3	14.4	14
Mobile	3743/3744	1.5	1.4	1	0	0	0	0	0	0
Napko	5617/5357	71.2	66.9	69	19.8	20.0	20	11.0	10.6	11
Napko	4499/3801	25.9	25.4	26	4.0	5.2	5	3.7	3.9	4
Napko	1361/8- 3474/5357	28.4	28.6	28	15.4	15.6	15	8.5	8.6	8
Porter	6600/6610	66.7	61.7	64	55.3	53.5	54	46.2	43.4	45
Rel. Univ.	130/76:3	46.6	41.2	44	8.4	9.3	9	8.0	9.0	9
Sentry	X5822	30.5	49.1	40	13.1	11.8	12	8.4	9.5	9
Sigma	7445	87.1	81.9	84	17.7	17.5	18	4.2	4.2	4

TABLE XIV
WATERBORNE COATINGS FOR EXTERIOR SUPERSTRUCTURE

SUPPLIER	GENERIC PRODUCT	PRODUCT NUMBER	DRY FILM THICKNESS	SALT FOG (ASTM B117) 500 HRS				HUMIDITY (ASTM D2247) 500 HRS			WEATHEROMETER (ASTM G26) 1000 HRS			
				RUST	CREEP	BLISTERS	ADHESION AT SCRIBE	RUST	CREEP	BLISTERS	RUST	BLISTERS	INITIAL GLOSS	FINAL GLOSS
CELANESE	EP ACRYLIC EP ACRYLIC	24-192	2 mils	10	2	8D(F)	5	NR	NR	NR	10	8D(F)	69	4
		24-146	2 mils											
CELANESE	EP ACRYLIC EP ACRYLIC	24-194	2 mils	10	1	NONE	5	NR	NR	NR	6	2M(F)	93	9
		24-178	2 mils											
DEVOE	EP ACRYLIC	259	9 mils	10	1	2F	5	10	10	2D(F)	10	4F	91	4
NAPKO	EPOXY PA EP ACRYLIC	5617	2 mils	10	4	8M	5	NR	NR	NR	10	4D	69	11
		5357	3 mils											
PORTER	EP ACRYLIC EP ACRYLIC	6600	2.5 mils	9	3	NONE	10	6	10	8MD	10	NONE	63	45
		6610	5.0 mils											
SOLVENT BASED CONTROLS														
CARBOLINE	EPOXY PA	190HB	9 mils	10	4	NONE	5	10	10	NONE	10	NONE	4	1
CARBOLINE	ALKYD ALKYD	GP-10 GP-62	2 mils 2 mils	10	8	2F	5	10	9	6F	10	NONE	59	11

NOTES:

- The following standards were used to rate coatings performance:
 - Rust - ASTM D610 (10 perfect)
 - Creep - ASTM D1654 (10 perfect)
 - Blisters - ASTM D714
- N.R. - Not Rated
- (F)-Failed
- Severe erosion of top coat.

2.5.4 Interior Areas (Excluding Tanks and Severe Service Areas)

Two test conditions were selected to screen interior systems.

- Humidity (ASTM D2247) for 500 hours
- Weatherometer (ASTM G26) for 1000 hours

An alkyd and polyamide epoxy were selected as the solvent based controls.

2.5.4.1 Humidity Tests

All waterborne systems selected for test had good rust preventive properties. Four of the waterborne systems blistered and one had pin holes. Two materials (Mobile Paint 3743/3744 and Napko 4499/3801) looked as good as the alkyd control. See Figures 2.10 (190HB), 2.11, 2.12, and 2.13 for photographs of test results.

2.5.4.2 Weatherometer Tests

All but two of the waterborne systems blistered in the Weatherometer. The relative gloss retention properties were the same for all systems tested.

2.5.4.3 Interior Summary

Table XV summarizes the results of these tests.

Two of the waterborne systems, Mobile Paint 3743/3744 and Napko 4499/3801, appeared acceptable for limited use such as the interior of the house, dry storage areas and other miscellaneous interior dry areas.

HUMIDITY CHAMBER

DEVFLEX I

4499/3801

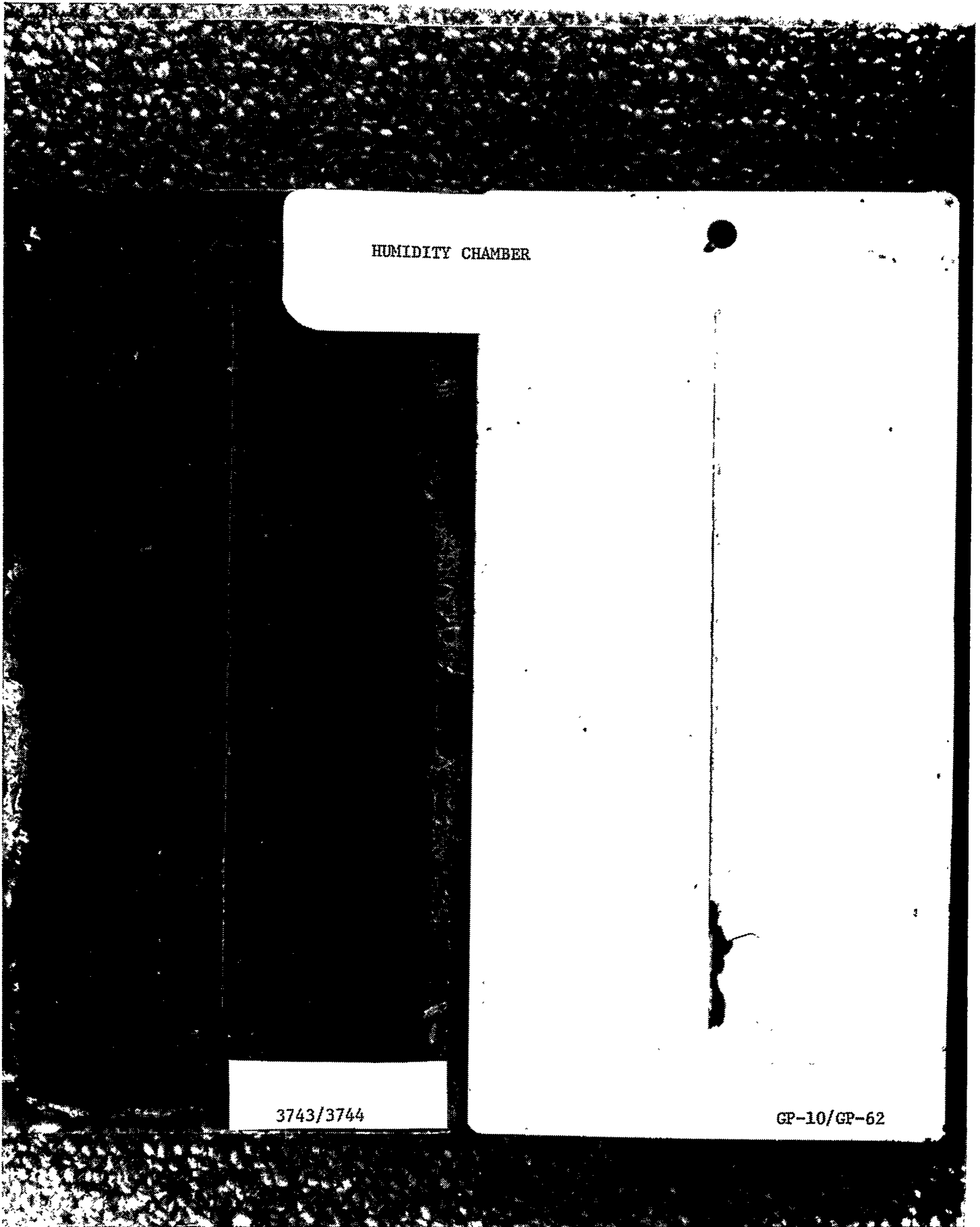
2.11 Photograph of Interior Waterborne Systems Exposed
to Humidity Chamber (Devflex/Devflex I, 4499/3801).

HUMIDITY CHAMBER

X5822

7445

2.12 Photograph of Interior Waterborne Systems Exposed to Humidity Chamber (X5822, 7445).



HUMIDITY CHAMBER

3743/3744

GP-10/GP-62

2.13 Photograph of Interior Waterborne Systems Exposed to Humidity Chamber (3743/3744, GP10/GP62).

TABLE XV
 WATERBORNE COATINGS FOR INTERIOR AREAS
 (EXCLUDING TANKS AND SEVERE SERVICE AREAS)

SUPPLIER	GENERIC PRODUCT	PRODUCT NUMBER	DRY FILM THICKNESS	HUMIDITY (ASTM D2247) 500 HRS				WEATHEROMETER (ASTM G26) 1000 HRS				PHOTO FIGURE NUMBER
				RUST	CREEP	BLISTERS	ADHESION AT SCRIBE	RUST	BLISTERS	INITIAL GLOSS	FINAL GLOSS	
DEVOE	LATEX MOD ACRYLIC	DEVFLEX DEVFLEX1	6 mils 2 mils	10	10	2. 8M	5	10	NONE	29	14	2.11
MOBILE PAINT	MOD ACRYLIC MOD ACRYLIC	3743 3744	5 mils 3 mils	10	10	3. 8F	5	10	3. 6F	1	0	2.13
NAPKO	ACRY. LATEX ACRY. LATEX	PN 4499 PN 3801	2 mils 3 mils	10	10	3. NONE	NR	10	3,4 6F	26	4	2.11
CELANESE	EP ACRYLIC EP ACRYLIC	24-192 24-146	2 mils 3 mils	NR	NR	NR	NR	10	8D(F)	69	4	
NAPKO	EPOXY P.A. EP ACRYLIC	5617 5357	2 mils 3 mils	NR	NR	NR	NR	10	3,4 4D	69	11	
SENTRY	EPOXY ESTER	X5822	2 mils	10	10	8F	NR	10	NONE	40	9	2.12
SIGMA	EPOXY	7445	3 mils	9	9	8D(F)	NR	8	4. 8D	84	4	2.12
SOLVENT BASED CONTROLS												
CARBOLINE	EPOXY P.A.	190HB	9 mils	10	10	NONE	NR	10	NONE	4	1	2.10
CARBOLINE	ALKYD ALKYD	GP-10 GP-62	2 mils 2 mils	10	9	6F	NR	10	NONE	59	11	2.13

NOTES:

1. The following standards were used to rate coatings performance:
 - (a) Rust - ASTM D610 (10 perfect)
 - (b) Creep - ASTM D1654 (10 perfect)
 - (c) Blisters - ASTM D714
2. Coating turned blueish
3. Pin holes
4. Erosion

SECTION 3
Drying Waterborne Coatings

3. DRYING WATERBORNE COATINGS

All organic coatings pick up water from a humid atmosphere, from splashing water, or immersion in water. The type of organic binder has an important influence on the water resistance, and hence durability and corrosion resistance, of any mating. A number of studies point to the superior performance of such binders as polyvinylidene chloride, hydrocarbon resins, vinyls, chlorinated rubber, acrylics, epoxy, etc., which have less chemically bound oxygen than alkyds, the old standard for most marine matings. Each component of the dried paint will have an influence on the final water resistance. Current coatings research compares these materials in an effort to formulate durable and economic paints. The organic binders have been selected from the low oxygen bearing resins for application as waterborne matings but problems remain in the choice and amount of surfactants, anti freezing additives and other chemicals necessary to furnish stable paint.

The results of this project are testimony that sane progress has been made. Some of the chemicals will slowly volatilize; others come to the surface where they can be washed or rubbed off leaving the dried mating with improved water resistance and durability. Generally, the longer the drying period and the higher temperature reached during the drying phase the better.

In addition to the problem of long term, corrosion resistance, waterborne coatings may display two other corrosion phenomena: "flash rusting" and "early rusting." Flash rusting occurs when improperly formulated waterborne matings rust the steel during the initial drying. Heavily applied pigmented matings may hide this rust so that the corrosion is not detected until months later. No flash rusting was observed to occur initially or in other testing with any of the waterborne coatings evaluated.

Early rusting, which physically appears like flash rusting, can occur after the film is dry to touch - hours to days after application.¹⁴ cool substrate steel (50°F) and high atmospheric humidity after the initial drying holds water and Water-coupling chemicals in the film and promotes early corrosion. Once these materials get out and the film fully coalesces, good water resistance is built up. The article by Grouke¹⁴ suggests tests to compare paints for this early rust resistance. This phenomenon is further discussed in a later article by Dillon¹⁵ giving a basis for selecting the type and amount of effective co-solvents.

Removing the Water from the ambient air as the coating dries is essential. Circulation and elevated temperature are obvious aids but reducing the relative humidity of the air by heating without actual removal of the water may become a disappointment if the substrate temperature merely allows the moisture to recondense from the air as it cools on contact with the paint.

Leo Crotty of Cargocair Engineering Corp. offered some solutions recently at a NPCA Marine Coating Conference.¹⁶ Waiting for good weather conditions or heating the steel surfaces are not practical answers. To prevent condensation in tanks being blasted and coated, dehumidification of the air before entering the tank is recommended so that, regardless of weather and in spite of low surface temperatures (i. e., down to 10°C (50°F) for most waterborne coatings), no condensation can recur. Raising the air temperature reduces the relative humidity (RH) but does not change the absolute humidity or actual moisture content. Table XVI is a familiar table of RH or percent of saturation. Fortunately the relationships are well defined and the thermodynamic properties of air and moisture are well documented. Efficient machines have been designed to dehumidify recirculated air to maintain the dewpoint 5°F below the surface temperature. Whenever the ambient air dewpoint is 5°F below surface temperature, dehumidification is not needed, the dehumidifier can be shut off automatically and its operating energy saved. The thermodynamics are shown in Figure 3.1 which is called a psychrometric chart. Three methods of dehumidification are illustrated in Figure 3.2.

Cargaire offers Model HC-9000 SEA designed for the marine mating industry to provide 9000 SCFM of dry air at 5 inches external static pressure with a normal drying capacity of 40 to 300 lb./hr. of moisture from the air. The volume solids for waterborne coatings is on the order 35 to 75 percent. Carboline 288 WB, a representative waterborne epoxy/acrylic, is 36% + 1% solids by volume or 64% volatiles by volume. If one assumes all of the volatiles are water, 5.3 pounds will be released per gallon. Allowing for an average overspray loss of 35%, the quantity of water evaporating would be 0.125 pounds per square foot for a 10 mil coating. Assuming that three painters can apply paint at a rate of 500 square feet per hour per painter in a tank, approximately 187.5 pounds of water ($500 \times 3 \times .125 = 187.5$) per hour would be liberated within the area. This quantity of water is well within the removal rate of the Model HC9000. Under ideal conditions, the major part of the drying would take place in 4 hours, but since the last stages of drying are so important, ideal drying conditions would be preferred at least overnight and possibly up to 14 days.

Humidity can be controlled adequately. Equipment specified to assure good waterborne performance will depend upon the area being coated at one time and how efficiently the dry air can be used with minimum loss to the atmosphere.

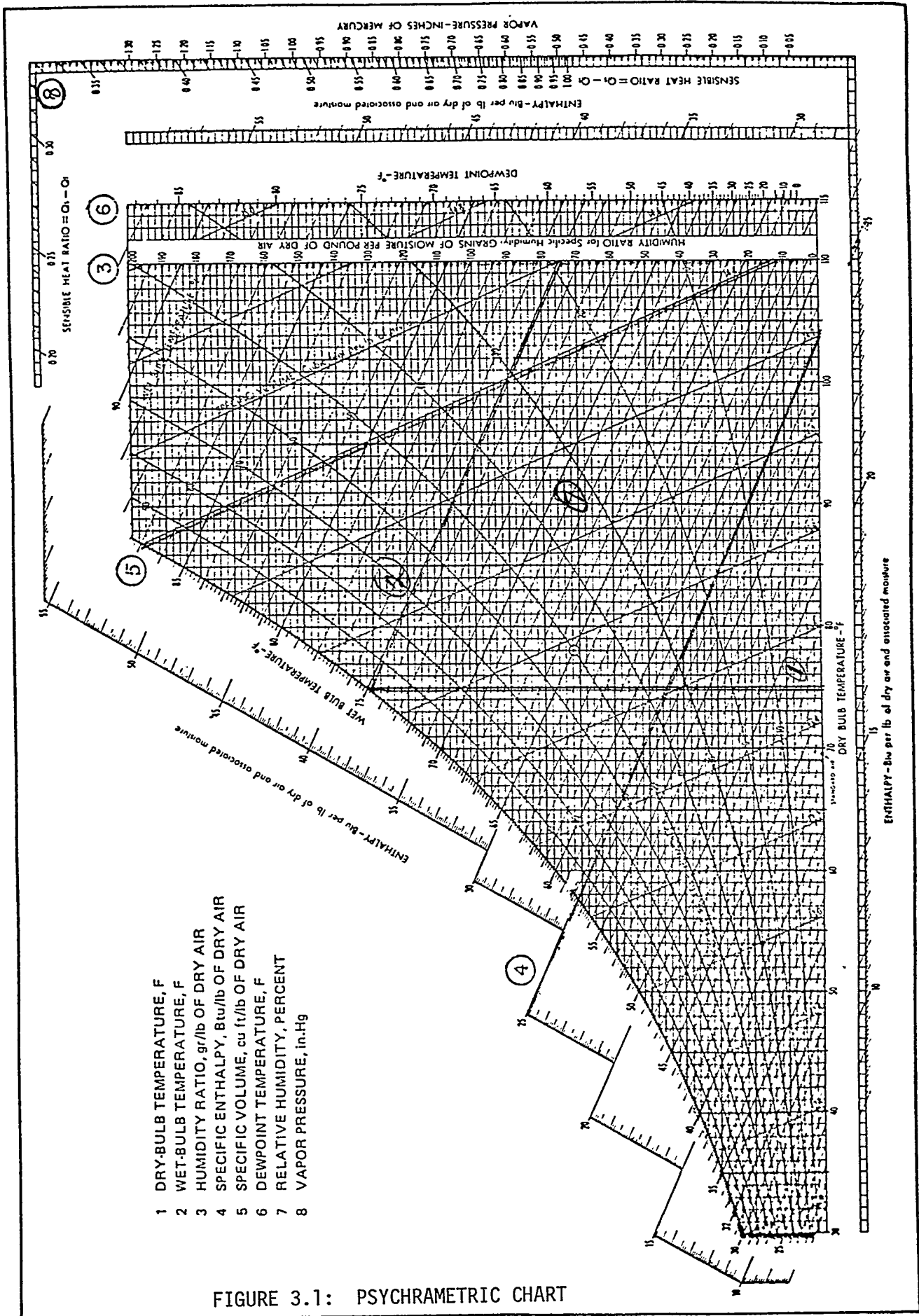
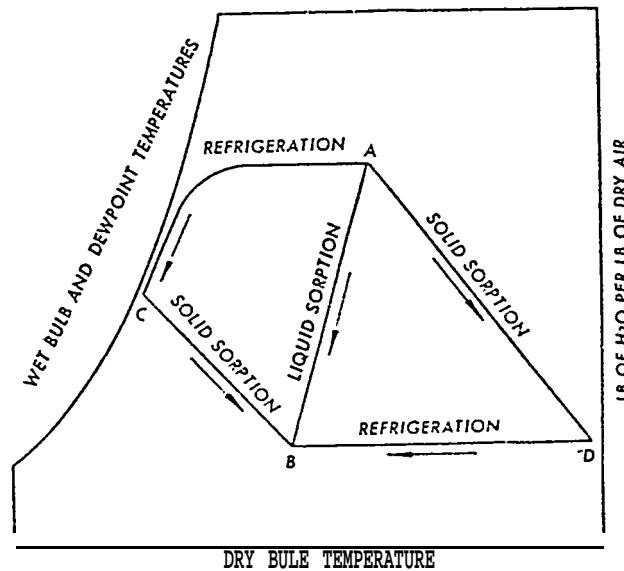


FIGURE 3.1: PSYCHRAMETRIC CHART

THREE METHODS OF DEHUMIDIFICATION'⁶

Dehumidification can be accomplished by liquid sorption, refrigeration and reheat, and solid sorption or combinations of these systems.



This represents a psychrometric chart illustrating three methods by which dehumidification with sorbent materials or sorbent equipment may be accomplished. Air at point "A" is to be dehumidified and cooled to point "B". This can be done in a liquid sorption system with inter-cooling directly, or it may be done with a solid sorption unit by pre-cooling and dehumidifying with refrigeration from point "A" to point "C" and then with solid sorption from point "C" to point "B". It could also be accomplished with solid sorption equipment by desiccating from point "A" to point "D" and then by refrigeration from point "D" to point B.

FIGURE 3.2: THREE METHODS OF DEHUMIDIFICATION

SECTION 4

References

4.0 REFERENCES

1. Anonymous, "paint Producers from Nation Advised California Emissions Rules Could Spread to 45 States, " American Paint & Coatings Journal, 63 (7), 7-8 (1978).
2. J. L. Cleveland, "CARB Makes Concessions on Marine Paint, but Producers Will Probably Still Protest," American Paint & Coatings Journal 62 (54), 7-8, 34, 36 (1978).
3. J. L. Cleveland, "CARB Gives Chief Executive Power To Perfect Model Rule for Marine Coatings." American Paint & Coatings Journal, 63 (1), 7-8, 46-47 (1978).
4. M. Hoppe, "Epoxy Resin Dispersions - New Surface Coating Possibilities," Polymer, Paint, and Colour Journal, 167 (3955/6), 634, 637-637 (1977).
5. Y. Choi et. al., "Water-Base Coatings," Final Report on AFML Contract F33615-75-C-5213, August 1976.
6. E. G. Bozzi, "Water-Borne Coatings Prepared from High Molecular Weight Epoxy Resins," Organic Coatings and Plastics Chemistry Preprints, 39, 54-56 (1978).
7. G. Rudlowski, "Prefailure Evaluation Techniques for Marine Coatings," Final Report, MA-RD 930 75072 available through NTIS accession number COM-75-10927, February 19750
8. MIL-P-23236 Military Specification Paint Coating Systems, Steel Ship Tank, Fuel and Salt Water Ballast., 28 June 1962.
9. MIL-P-28577-A (YD) Military Specification Primer, Latex, Corrosion Resistant, for Metal Surfaces. 10 June 1977.

- 10• MIL-P-28578A (TD) Military Specification Paint, Water Reducible, Semi-gloss, Exterior and Interior. 10 June 1977.
- 11• 1976 Annual Book of ASIM Standards Part 27.
12. B.R. Appleman and P. G. Campbell, "Salt Spray Testing for Short-Term Evaluation of Coatings," Corrosion Symposium in Atlanta, Federation of Societies for Coating Technology, October, 1980.
- 13• Steel Structures Painting Council, Water-thinnable Coatings Ccmmittee Reprt, April, 1973.
14. M. J. Groucke, "Formulation of Early Rust Resistance Acrylic Latex Maintenance Paints, " J. Paint Tedh. Vol. 49, Sept. 1977.
15. P. W. Dillon, "Application of Critical Relative Humidity, an Evaporation Analog of Azeotropy to the Drying of Water-Borne coatings", J. paint Tech. 49 (634), 38-49 (1977)0
16. L. J. Crotty, "Dehumidification for Coating Applications, " Marine Coating Conference, New Orleans, March 25, 1980.
- 17• L. Levine, C. Parker, B. Baum, "Solventless Coatings Evaluation and Test Program for Marine Use, " a MarAd sponsored R&D Project, October 1981.