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NAVMIRO MANUFACTURING TECHNOLOGY BULLE-TIN. NUMBER 34: EPOXY COATINGS FOR CCR-ROSION PROTECTION

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EPOXY COATINGS FOR Corrosion Protection D

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The recent Manufacturing Technology Coordination meeting held in Louisville, Kentucky in July of this year, re ealed some innovative new uses for thin-film epoxy coatings that were developed by the Portsmouth Naval Shipyard. They are being reported in this bulletin because it is felt that this process has wide application for the services.

Before beginning this report, a review of the basics of epoxy, thinfilms is presented.

Epoxies are a unique family of resins because they offer a combina-

tion of properties not found in any other class of resins. It is this combination of properties that make them so well suited for highperformance, thin-film applications.

These properties are:

- 1. Adhesion
- 2. Chemical resistance
- 3. Impact resistance
- 4. Flexibility
- 5. Heat resistance
- 6. Electrical insulation

The most outstanding quality of epoxies is probably their tenacious



adhesion to a large variety of substrates. They bond to practically everything to some degree. Most important is the property of epoxies to provide adhesion and chemical resistance without sacrificing the remainder of the above-mentioned properties.

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Powdered epoxies were introduced to the coating industry approximately 15 years ago. At that time, they were limited to the fluid bed process of coating, which does not lend itself well to the application of thin films. Since that time, many new processes have been developed which enable us to apply thin-film epoxy coatings. Consequently, the number of items that can be coated with powdered epoxy formulations has been greatly increased.

In general, epoxy coatings have excellent resistance to dilute acids and alkalies. Many organic solvents soften epoxies during long-time immersion, but they regain their excellent mechanical properties upon drying. As can be seen in TABLE 1, the epoxies offer a high degree of resistance to a broad range of chemicals and are especially suited to applications that are normally highly corrosive to other materials.

TABLE 1 CHEMICAL RESISTANCE*

Tap Water	. Unaffected	Lactic Acid	Unaffec	ted
Sea Water	. Unaffected	10% Nitric Acid	Unaffec	ted
10% Sodium Hydroxide	. Unaffected	70% Nitric Acid	Failed	at
50% Sodium Hydroxide	. Unaffected		30 days	1
30% Potassium Hydroxide	. Unaffected	10% Sulfuric Acid	Unaffec	:t_d
Ammonium Hydroxide	. Soft	36% Sulfuric Acid	Unaffec	ted
10% Hydrochloric Acid .	. Unaffected	Gasoline	Unaffec	ted
Conc. Hydrochloric Acid	. Unaffected	Acetone	Failed	at
10% Acetic Acid	. Unaffected		l day	
Glacial Acetic Acid	. Failed at	Benzene	Softene	d
	7 days	Chlorothene	Surface	2
	-	pitted,	film intact	•
		Ethanol	Soft	

*18 months exposure unless indicated. Test film of 10-14 mils cured 5 min. at 400°F.

The flexibility of these coatings enables it to expand and contract with the substrate to which it is applied, eliminating chipping, flaking, and peeling common to other type coatings. Since epoxy coatings adhere tenaciously to most substrates, primers are not required to achieve ultimate chemical resistance.

Another outstanding property of these coatings is their dielectric quality. The fluidized bed application of epoxy powders provides an even, pinhole-free film superior to other dipped insulations. Underwriters Laboratories approval has been obtained for these insulators. The availability of colored powders provides a decorative, color-coded insulation in one functional coating.

Careful surface preparation is essential to provide maximum adhesion. The method to be used will be dependent upon the type of contaminant involved, and the type of material from which the contaminant is being removed.

The proper cleaning of any surface for adhesive bonding or epoxy coating involves three basic steps:

1. Degreasing — Vapor degreasing with trichlorethylene is highly recommended. Solvent washing with a solvent such as methyl ethyl ketone is also acceptable.

2. Chemical etching or mechanical abrading — The preferred method of mechanical abrading is the use of aluminum oxide or sand blasting. The use of a medium grit emery paper to roughen the surface is frequently quite acceptable.

3. Degreasing — This final degreasing operation is very important. All mechanically abraded or sand blasted surfaces should be brushed vigorously with a stiff bristled brush to remove embedded particles prior to the final degreasing operation.

Parts should be bonded or coated as soon as possible after pretreatment.

There are numerous methods that may be used to prepare various surfaces for adhesive bonding or epoxy coating. The following are a few of the more commonly used techniques.

ALUMINUM, ALCLAD OR 24ST

1. Degrease

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2. Clean the surface with a chromic acid solution by immersion at $65-70^{\circ}C$ for 5 - 10 minutes. Prepare the solution as follows:

10 parts/wt. sodium dichromate 30 parts/wt. 96% sulfuric acid 100 parts/wt. distilled water

(Dissolve the dichromate in most of the water, add sulfuric acid, stirring carefully and then add the remaining water.)

3. Rinse the metal thoroughly with clear running water and dry well.

4. Parts should be coated or bonded immediately.

CAST IRON

Degrease, abrade, degrease again.

CONCRETE (Portland Cement Type)

1. Concrete contaminated with oil or grease must first be scrubbed with some commercially available concrete degreasing compound.

2. New or old concrete can be prepared for bonding by either sand blasting or with a chemical etch.

Concrete is chemically etched with a 15% solution by weight of hydrochloric acid. This solution is spread generously over the concrete surface with a stiff bristled broom. When bubbling subsides, rinse thoroughly with a hose until loose particles and acid have been removed. Allow surface to dry thoroughly.

COPPER AND ITS ALLOYS (Brass)

430 parts/volume sulfuric acid 72 parts/volume nitric acid 490 parts/volume water Procedure: Dip 15 seconds in above solution, rinse in running tap water $(25^{\circ}C.)$ five seconds, dip in 15% (volume) hydrochloric acid, followed by a 2-minute rinse in running tap water $(25^{\circ}C.)$

The following formula may be used:

8.0 parts/wt. ferric chloride solution
16.3 parts/wt. nitric acid
75.7 parts/wt. water

Immerse the parts 3-2 minutes at room temperature, follcwed by a thorough water rinse and air dry at $60-65^{\circ}C$.

DIALLYL PHTHALATE

Degrease, abrade the surface and degrease again.

GALVANIZED OR Z NC FINISHED METALS

Degrease, sand 'last and degrease again or use the following etching procedure:

- 20 parts/wt. concentrated hydrochloric acid
- 80 parts/wt. distilled water

Treat as follows:

- 1. Degrease
- Immorse the metal in the hydrochloric acid for 2-4 minutes at room temperature
- 3. Rinse in cold running, distilled or de-ionized water
- Dry in an oven for 20 30 minutes at 60-70°C.
- 5. Apply adhesive as soon as possible.

GLASS

For normal bonding applications, degreasing alone is sufficient for pre-treating glass surfaces. If, however, the very optimum in strength is required, the glass can be gritblasted with very fine grit until the surface appears frosted.

LEAD

Degrease, abrade and degrease again.

LEATHER

Solvent wipe, roughen with sandpaper and solvent wipe.

MAGNESIUM AND ITS ALLOYS

- 1. Vapor degrease with stabilized trichlorethylene
- 2. Immerse in 10% sodium hydroxide for 10 minutes at 76-87⁰C.
- 3. Rinse 5 minutes in a cold water spray
- 4. Immerse in a solution of 1-1/21bs. chromic acid, 1/4 lb. sodium nitrate in (gallon of water for 8 minutes at room temperature
- 5. Rinse approximately 3 minutes
- 6. Immerse in a 20% solution of hydrofluoric acid for 5 minutes at room temperature
- Rinse 1/2-1 minute
 Immerse in a boiling solution of sodium dichromate 10-15%, and calcium fluoride 0.15% for 30 minutes
- 9. Rinse 1 2 minutes
- 10. Dry in a hot air blast (71-98⁰C.) for 10 minutes
- 11. Bond immediately or apply a Zinc primer for protection of freshly etched surfaces.

SILICONE STEEL

8.0 parts/wt. hydrochloric acid
7.8 parts/wt. sulfuric acid 84.2 parts/wt. nitric acid

The parts should be immersed in the above solution (maintained at 70-75° C.) for 10-20 minutes, then rinsed with water at room temperature and brushed with a soap solution to mechanically remove scale loosened by the chemical bath. A hot water rinse (70-75°C.) followed by a hot air dry (70-75°C.) completes the preparation.

STAINLESS STEEL

Degrease

2. Etch for 10 minutes at 65-68°C. in a solution containing:

90 parts/wt. water 37 parts/wt. 96% sulfuric acid 0.2 parts/wt. Nacconol NR (National Aniline)

3. Rinse in tap water or distilled water

4. Immerse for 10 minutes at room temperature in a water solution containing:

88 parts/wt. water 15 parts/wt. concentrated nitric acid

2 parts/wt. hydrofluoric acid

5. Rinse in distilled water and dry in a 95°C. oven.

TEFLON

Teflon must be etched prior to bonding with a sodium naphthalene solution such as Bondaid. Teflon and other fluorocarbon plastics are available in a bondable form from most suppliers.

PHENOLIC RESINS, POLYESTER RESINS, POLYURETHANE RESINS

Degrease, abrade and degrease again.

CHLORINATED POLYETHER (Penton), POLYETHYLENE, POLYPROPYLENE, POLYFORMALDEHYDE (Delrin)

Either of the following formulas may be used for these plastics:

- 10 parts/wt. potassium dichromate Α. 20 parts/et. distilled water 320 parts/wt. sulfuric acid concentrated
- 15 parts/wt. sodium dichromate в. 24 parts/wt. distilled water 300 parts/wt. concentrated sulfuric acid

Prepare as follows: Dissolve the sodium dichromate or potassium dichromate in water and add the sulfuric acid carefully with constant stirring.

Treat as follows:

Degrease

2. Immerse in the chromic acid as follows:

Polyether (chlorinated) 5-10 minutes at 65-70°C

- Polyethylene & Polypropylene* 60-90 minutes at Room Temperature OR 1-2 minutes at 65-70°C
- Polyformaldehyde 10-20 seconds at Room Temperature

3. Rinse thoroughly with cold running, distilled or de-ionized water.

4. Air Dry

*25-50% longer times may be required for etching high density polyethylene and polyproplyene.

RUBBER

Surface etching cf rubber is recommended for maximum bond strength. A satisfactory bonding surface can be obtained by using the following cyclizing technique:

Immerse the rubber in concentrated sulfuric acid (sp. gr. 1.84) for 5-10 minutes in the case of natural rubber and 10-15 minutes in the case of synthetic rubber.

Many rubbers are very acid resistant and will require longer cyclizing time to reach a point where the rubber will have fine cracks when flexed.

Alternatively, a paste of concentrated sulfuric acid and Barytes can be used. The paste is made by adding Barytes to the acid to give a consistency which will not run. After washing thoroughly with water and drying, the brittle surface of the rubber should be broken by flexing so that a finely cracked surface is produced. It may be necessary to wash with dilute caustic solution to insure neutralization of residual acid which, if not removed, will consume some of the curing agent, weakening the bond strenth. The surface is then ready for application of the adhesive.

TIN

Degrease, abrade and degrease again.

TITANIUM

In general, an acid etch is the most effective surface treatment for titanium. Anodizing in 15% sulfuric acid or etching in hot sulfuric acid solution followed by cleaning in Alkanex detergent-sodium metasilicate solution produces good results. Still better results are obtained if the titanium surface is first plated with a metal such as aluminum or nickel.

WOOD

Remove any contaminating materials such as oil, rot, etc., with a sander, ax, or plane. Make certain the wood is dry. Smooth and sandpaper.

NAVY APPLICATIONS

Of general interest as previously mentioned are two applications being utilized by the Navy at Portsmouth Naval Shipyard. These are described

as follows:

SSBN (Polaris) and SSN (Attack) submarines each use several hundred ball valves in their seawater systems. The valves range in size from one inch in diameter to 21 inches in diameter. Between overhauls, these submarines operate for extended periods and the valve balls become victims of the severe environment and they badly corrode (FIGURE 1). The corrosion usually occurs in areas of stagnation and the depth of corrosion sometimes exceeds 1/8 inch.



FIGURE 1



FIGURE 2

Heretofore, normal submarine overhaul procedures have been to procure a complete replacement set of valve balls and to install these at each overhaul. All old balls are then discarded. The average cost per SSEN overhaul for the replacement of ball valves amounted to \$475,000; whereas the method of epoxy coating and replacement cut the costs in half, or approximately \$235,000 per overhaul. The economies are obvious. A finished, coated ball is shown in FIGURE 2.

The steps used in coating the ball valve are as follows:

1. The ball is turned or rough ground to at least 250 RMS finish. It is not necessary to remove all traces of corrosion — the epoxy will fill these areas.

2. The b.'l is heated to $750^{\circ}F$ for one hour to drive off any oil that may be entrapped in the pores of the metal.

3. The surface of the ball is sandblasted using No. 80 aluminum oxide grit, a one-inch nozzle, 75 to 90 pounds air pressure at a 6 to 8 inch standoff. This treatment insures good surface adherence.

4. Areas not to be coated are masked with ordinary masking tape.

5. The masked ball is heated to 410° F and dipped while 'ot, with a slow rotational motion into the fluidized bed of epoxy powder and quickly withdrawn. This process is repeated to obtain the desired thickness.

6. The dipped ball is returned to the oven at 410° F for ten minutes to cure the surface layer.

7. The ball is finished to specified dimensions using a diamond tip cutter and is hand-polished to about 16 RMS finish using No. 500 silicon carbide screening and honing oil.

Another ships repair application developed by Portsmouth Naval Shipyard is the electrostatic spray of epoxy coatings on seawater systems flexible pipe connections. Previous overhaul procedures called for the machining of the nipple to remove corrosion. This procedure is limited to the metal thickness of the nipple. In many cases, corroded nipples were discarded when the maximum allowable thickness of material had to be removed. Such a connector is shown in FIGURE 3.



FIGURE 3



FIGURE 4



The electrostatic epoxy spray method calls for the following steps:

1. The areas of the ripple which are badly corroded are col.³-patched with epoxy.

2. The excess cold patch is removed by machining.

3. The nipple is epoxy coated using the electrostatic spray method to a thickness of .002 to .003 inches.

4. The nipple is ready for reassembly (See FIGURE 4).

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A complete set of flexible connectors for a SSBN submarine cost approximately \$81,000. The epoxy repair method can be accomplished for a cost of approximately \$9,500 with a resultant savings of over \$71,000 per submarine. .

These are merely two examples of the versatility of this process. Applications are available for electrical insulation, color coding, decoration as well as protection for metallic equipment in corrosive environments.