Properties and Characteristics of Third Generation , U nderwater Applied , Anti-Corrosive, Epoxy Coatings

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ABSTRACT:

The ability to apply protective coatings on metal and other surfaces underwater has long been recognized as a much desired function. Epoxy coating and epoxy repairs performed underwater save both time and money, potentially even delaying the need for drydocking.

First generation underwater coatings were generally 'bubble gum' type products literally pushed into place one handful at a time. Second generation underwater coatings were much closer to the true perception of a paint. However, these products suffered from poor storage stability, high toxicity, and other user unfriendly features.
While first and second generation underwater coatings are still common, the latest third generation underwater coatings are much improved over their predecessors. These new epoxies are typically much less toxic, have a long shelf life, and do not require special haz-mat shipping. Being more user friendly, they typically result in higher application productivity.

Introduction

First formulated in the late 1930's in the U.S. and Switzerland, epoxies can be considered a two-part, thermoset plastic. Mix two liquid components together, a heat producing reaction (known as 'Exotherm') occurs, and a hard product results. Some basic and general characteristics of epoxies are: 1) 10w viscosity base and curing agents are available; 2) easy cure temperatures, generally from 5-150 degrees C; 3) 10w shrinkage; 4) high adhesive strengths; 5) high mechanical properties; 6) high electrical insulation; and 7) good chemical resistance.

With so much going for it, epoxies were produced as commercial adhesives in 1946 and as commercial coatings by 1947. The versatility of epoxies was further advanced with the early formulations of epoxies that could be applied in an uncured state to underwater (or wet) surfaces. Applications for such epoxies are wide spread and include; boat/ship repair;
dock/piling and sheet piling repair; and the coating of concrete, wood, or metallic surfaces at near, or below the waterline or splash zone. This paper examines the development of such underwater epoxies.

II Chemistry of Epoxies

Epoxies consist of two components that react with each other forming a hard, inert material. Part A consists of an epoxy resin and Part B is the epoxy curing agent, sometimes called hardener. Let's begin with taking a closer look at the epoxy resin.

Epoxy resin begins with the reaction of two compounds, bisphenol A (or bisphenol F) and epichlorohydrin. Bisphenol A is the chemical product of combining one acetone unit with two phenol groups. Phenol is a man-made chemical, although it is also found naturally in animal waste and decomposing organic material. It was originally produced from coal tar and was named carbolic acid. Structurally it contains a benzene ring with an attached hydroxyl (a carbon ring with an attached OH). Acetone is a organic ketone (.i.e. it contains a carbonyl C=0 group attached to two organic methyl groups) primarily used as a solvent or chemical intermediate or raw material for many other products.

Nearly 70% of all epichlorohydrin is used in the production of epoxy resin. This colorless liquid with its irritating chloroform like odor finds it way into the production process of various synthetic materials. Leading producers are Dow Chemical (Texas) and Shell Chemical (Texas and Louisiana).

The reaction between bisphenol A and epichlorohydrin removes unreacted phenol and acetone and attaches two glycidyl groups to the ends of the bisphenol A, creating a `diglycidyl ether of bisphenol A' (called DGEBA), which is standard epoxy resin. The glycidyl group on both ends of the bisphenol A are also referred to as an oxirane or 'epoxy group'. The size of

the resulting molecule (and hence its molecular weight) depends upon the ratio of epichlorohydrin to bisphenol A.

The 'amine' curing agent has a molecular structure which typically consists of four hydrogen 'arms and legs'. These hydrogens react with the oxirane (epoxy group) ring unit on the ends of the epoxy resin. The result is a new carbon-hydrogen bond, this time using the hydrogen from the curing agent and freeing the epoxy group's hydrogen to unit with the group's oxygen to form an OH (hydroxyl) pendant. This hydroxyl group contributes to the epoxy's outstanding adhesion to may substrates. The aromatic ring unit, which the hydroxyls are attached to, helps provide the epoxies positive thermal and corrosion properties.

Because there are at least four hydrogens on the curing agent they can react with four epoxy resin groups, which causes giant interlocking structures (in a process known as 'crosslinking').

III Epoxy curing agents

The curing agent selection plays the major role in determining many of the properties of the final cured epoxy. These properties include pot life, dry time, penetration and wetting ability. Curing agents come in many different chemical flavors, generally based upon amines or amides. Some of the more common amines and amides often listed in Material Data Safety Sheets (MSDS) include:

1) Aliphatic (carbon atoms forming open chains) and cycloaliphatic (ring structured aliphatics) amines and polyamines. Amines are basically ammonia with one or more hydrogen atoms replaced by organic groups;

2) Amides and polyamides. Amides are basically ammonia with a hydrogen atom replaced by a carbon/oxygen and organic group.

Amine based curing agents are considered to more durable and chemical resistant than amide based curing agents but most have a tendency to 'blush' in moist conditions. Blushing produces a waxy surface film on actively curing epoxy, the result a reaction with the curing agent and moisture in the air. Other potentially toxic chemicals within the curing agent can also be released in the same manner, thus amines are often viewed in light of these potential shortcomings. Amides, on the other hand, are more surface tolerant and less troubled by moisture.

Fortunately for epoxy end-users involved with underwater applications, there is a small subgroup of non-benzene ring structured amines that maintain all the benefits of amines while removing the toxic leachability and moisture attracting properties of typical amines. These special polyamines form the basis for today's cutting edge underwater epoxies.

IV How epoxies work

The well known adhesion of epoxies is due to the strong polar bonds it forms with the surfaces it comes in contact with. On dry surfaces the bond between the surface and the epoxy displaces the air, which is a fluid. The same is true underwater. As on dry surfaces, the polar bond attraction is strong enough to displace the fluid, in this case the water, and produce an strong bond even underwater. Thus, painting underwater is, in theory, no different that painting above the water. The crosslinking reaction of epoxies should be independent of the surrounding environment. Still, as mentioned above, many or most curing agents will react with water molecules rather than the epoxy base, resulting in a waxy film, also mentioned above, commonly known as amine blush. This makes them unsuitable for underwater application.

At least one modern hydrophobic, underwater epoxy goes one step farther to ensure a strong underwater polar bond with the introduction of a proprietary 'bond enhancer'. This is important because many marine structures are subjected to active cathodic protection systems. Such systems place an electrical charge on the structure's surface that will literally and actively repel the epoxy's existing polar bonding surfaces. The enhancer provides additional polar bond surfaces that are also firmly anchored into the crosslinking epoxy structure.

V Epoxy evolution

In general terms, three generations of apply underwater epoxies have emerged over the years. Each has pushed the technology window forward. The success of first generation epoxies seems to be in their ability to be applied and cured underwater. The next generation moved these epoxies into true coating status, albeit with issues of user friendliness and chemical safety issues still to be addressed. The new third generation epoxies have addressed those issues successfully.

V.a First Generation Underwater Epoxy Coatings

• *Sticky, like Bubble Gum '*- similar to a thick putty

• *Hard to mix and apply* - knead the two parts together in hand-sized amounts and literally push on to the surface

• *Expensive on a tost per square foot'*- @ 1/4 thick and $50 gallon = $7.80 per square foot material cost

• *Potentially difficult to ship and/or store* - may require hazmat shipping (Corrosive Liquid N.O.S.), may have short shelf life

V.b Second Generation Underwater Epoxy Coatings

• Good *underwater adhesion* - true bonding instead of 'sticking'

• *Poor storage stability (heating required)* - products tended to crystalize over time

• *Toxic - MDA and possible solvents (see footnote)*

● *Hazmat shipping required* - keep away from foodstuffs

● *Problem with cathodically protected surfaces* - interference with the polar bonding

V c Third Generation Underwater Epoxy Coatings

● *Low cost* - $2.50 per sq. ft. for 40 mils, $5.00 per sq. ft. for 80 mils ($100 per gallon)

● *Stable storage* - will not crystalize over time

● *Basically Non-toxic, 100% solids (0% VOC), no MDA*

● *Non-hazmat* - unregulated shipping

● *Good application on cathodically protected surfaces* - additives to overcome polar bonding interference, easy application results in productivity increase

VI Applications and examples of underwater coatings

The unique properties of these coatings have many practical applications outside of those commonly associated with traditional dry surface epoxies and paints. They offer an expanded set of solutions to corrosion related problems in difficult areas. Common uses of underwater epoxy coatings include:

● Quick field repairs of ships (no drydocking required for minor repairs)

● One step pier, piling, dock repair - (no need for cofferdams, dryout, or large volumes of annulus filling materials and epoxies

*Hull collision and emergency repair kits - (such kits can be found in the 2000 Round the World Sailboat Race. Also pipe repair/wrap kits for use in industrial facilities and plants)

● Adhesive properties (bond and/or remove underwater devices such as meters or gauges. Already tested and approved for use in underwater bomb removal)

● Follow-up to underwater welding - (corrosion protection of surfaces after welding)

● At sea, flooded ballast tank re-coating/repair - (saving drydock downtime)

● Bonding to wet, damp, saturated surfaces not actually underwater - (such as sumps, pits, tanks, pipes with active condensation forming)

● Adhesion and bonding unaffected by high humidity - (tropical conditions such as coastal industrial sites where humidity conditions adversely affect the performance of many coating products)

VI.a Examples of third generation epoxies

Underwater epoxy repair - case study one

On June 24, 1998 divers from Underwater Construction Corporation performed an underwater video and ultrasonic thickness inspection of a water intake barge located on the Hiwassee River.

The ultrasonic inspection of the hull revealed plate thickness ranging between 0.360 and 0.380 of an inch. These measurements are consistent with the as-built drawings that indicate the full was constructed from 3/8" steel plate. During the inspection, a pattern emerged showing reduced wall thickness (0.005 - 0.010) on the starboard side. Upon inspection of the inner hull, approximately 2" of standing water was found on the starboard side. The port side was dry.

The hull coating was found to be about 90% - 95% intact, although rust nodules were found over the entire submerged surface of the hull. These nodules were concentrated near the bow at a frequency of 12-17 per square meter. Upon removal of several of the rust nodules, pitting was found. Pit depths ranged between 1/16" to 1/8". A majority of the rust nodules appeared to be concentrated along the weld seams. Several inches of water were found in the bilge. It was believed that at least some of the leakage was caused by pinhole perforations of the hull at pitting corrosion sites.

The barge was permanently moored and could not be dry-docked. It was decided to use underwater epoxies to coat and repair the pitted areas, with hopes that the epoxy would not only arrest corrosion but plug any pin hole leaks as well.

Diver cleaned the surface with a 3,500 p.s.i. pressure washer. This was followed by a mechanical surface prep to SP 1 1 using a 3M Clean N' Strip to remove any remaining corrosion and roughened the coating around the pit.
Epoxy was applied at 40 - 50 mils.
Approximately 500 repairs were made ranging in size from 1/2" to 3' in diameter. The

work was performed in a 1 knot current. Water temperature was 50°F. Visibility was approximately 2'. After the coating was fully cured, the main compartment was sealed and pressure tested to 5 p.s.i. No pressure loss was detected over 30 minutes. Subsequent inspections indicate there has been no additional leakage.

Underwater epoxy repair - case study two

A large oil fueled power station located on the Gulf of California in Mexico receives fuel oil from tankers which unload at a deep water terminal. The discharge terminal is built at the end of a 1 .2 Km long concrete pier built on 30" and 36" diameter steel pilings.

The pier was suffering from advanced corrosion in the "wind and water" area at its waterline. The pilings were fouled with marine growth, corrosion products and the residues of the failed coating applied at construction. Repair of the coating system had to be accomplished in the water using divers.

Epoxy was applied over the steel piling surface which had been freshly blasted using 4,000 psi water entrained river sand abrasive. The surface obtained was a mixture of white metal with islands of roughened, tightly adhering existing coating which is highly satisfactory for this application.

The divers and other workers employed in this project had little previous experience of this type of work but were immediately able to properly mix and apply the modern, third generation, underwater epoxy and obtain an excellent result. Under the conditions of application in approximately 65 - 85°F (18 - 29°C) water the epoxy cured to a firm 30-50 mil film thickness after 6-3 hours,

respectively, and hard overnight. Wave action had no effect whatsoever even immediately after application before any curing had taken place.

The modern epoxy showed tenacious adhesion compared to the traditional "splash zone putty" type products. Diver productivity was also markedly better when using modern underwater epoxies that are applied with a spreading action rather than using "pattycake" type action of pushing and sticking handful by handful amounts of early generation putty type underwater epoxies.

Later inspections showed that the epoxy coatings were still in perfect condition after two years salt water service in cold and stormy winters and hot and humid summers.

Underwater epoxy repair - case study three

The largest aquarium in Australia is located in Canberra. The centerpiece attraction in this facility is a large 'shark encounter' type tank in which visitors walk through a plexiglass tunnel set inside the tank so that the fish are on the outside and the visitors are on the inside.

After some years of service there were several slow leaks inside the visitor tunnel which appeared to come from fiber optic lighting fixtures exiting the 'rocks' at the base of the tunnel. Short of draining the entire tank it was not possible to seal these fixtures using conventional materials or techniques.

Two aquarium divers entered the aquarium equipped with a third generation underwater epoxy and abrasive pads for cleaning the fiber optic terminals. After scouring the immediate area the epoxy was applied over and around five terminals using spatulas. Adhesion to the 'rock' and glass surfaces was strong and immediate. The one repair which could be seen by visitors was hidden by sprinkling sand and debris on the uncured epoxy repair before leaving the tank. The repairs were accomplished with no distress to the fish living in the tank.

VI.b Potential application for underwater epoxy - in-service ballast tank re air/coatinq

Ship ballast tanks are large structures with limited access. A VLCC wing tank for example may be over 70' high from tank top to overhead. Examination of tank surfaces for corrosion generally requires extensive scaffolding in order to work safely and effectively. Scaffolding is time consuming, expensive and damages existing sound coatings because of impacts during erection and teardown.

Vessels built using reduced scantlings have little safety margin available to accommodate steel lost by corrosion. The underwater repair treatment proposed below offers the opportunity for early repair to isolated steel corrosion which could prevent more costly repairs or even steel replacement if repair is deferred until a future scheduled drydocking.

Professional diving services and technically advanced underwater epoxies would enable permanent repairs to be made to ballast tank linings without disrupting normal operating schedules. Drydock expenses related to ballast tank repairs would be reduced by eliminating costs of scaffolding and possibly by reducing time in dock. Future costs would be reduced by eliminating scaffolding damage during current work.

During the course of normal vessel operations it is possible to press up ballast tanks to the overhead using clean ocean water. With a tank filled with clear water it is possible to gain close access to all immersed surfaces using a diver supported with surface supplied air and electricity for lights, closed circuit TV and communications. The illumination, absence of currents, clear water, known environment and the close support of a well equipped colleague would ensure safety and excellent productivity in the ballast tank.

The working divers would be able to thoroughly inspect every part of the ballast tank surface in ideal diving conditions. Steel loss would be measured using underwater ultrasound gauging. Working with underwater TV in real time it is possible to communicate with Owners or Classification Society representatives to accurately convey existing conditions. A video recording would be made as a permanent record.

Coated areas seen to the damaged could easily be repaired using pneumatic needle gun or grinder surface preparation followed by application of a modern underwater epoxy for permanent underwater anti-corrosive protection. Repairs on a particular voyage could be carried out with underwater epoxy of a specific color to allow easy reference in future surveys.

In-water ballast tank repairs could be made as a vessel is alongside discharging or during voyaging. Working while voyaging would offer the most advantage to a vessel operator since it would incur the minimum disruption to normal operations. Generators which allow the safe use of electricity for lights, instruments and CCTV are available. Professional divers adhering to the highest standards would assure safe working in the enclosed tank environment.

A work crew would travel with a vessel during a suitable voyaging leg. The size of such a crew would be governed by the amount of work anticipated and the ships

accommodations. A small crew would be, for example, include two divers (includes supervisor), one tender, and one laborer/paint mixer.Production rate estimates are: Underwater needle gun surface preparation - 7 - 10 sq. ft./hr./diver; underwater application of the epoxy at 30 - 50 sq.
ft./hr./diver. These production rates are for the working diver, additional costs will be incurred for the support personnel such as diver tenders, machine operators and so on.

It is anticipated that such a group would be able to repair at least 150 sq. ft. of scattered corrosion per day. This would correspond to completely rehabilitating a 30,000 sq.ft. tank with 5% scattered corrosion during a 10 day voyage.

VII Closing

The underwater applied coating market remains a small niche within the much larger industrial and marine maintenance marketplace. Both first and second generation underwater coatings
are still widely in use, primarily because of the conservative nature of the industry and the acceptance of 'less than user friendly' underwater products. Too few users and potential users/applicators of underwater coatings are aware of the advances made in recent years.
This is changing as the shift toward environmentally friendlier, and easier to use coatings are slowly causing the reelvaluation of old familiar products and the introduction into the limelight of new companies with new products that better meet today's expectations.

The ability of a single product to be effectively used on dry surfaces, underwater, or on saturated or dripping metal/concrete surfaces, while being both environmentally and user friendly, represents a technology that will continue to

gain acceptance. The savings associated with in-situ underwater repairs and coating projects is often easy to document, as are the potential benefits from even more ambitious applications of this maturing coating technology.

APPENDIX A:

The Dangers of Methyleneadianiline (MDA) in Epoxies

A number of commercially available epoxy coatings designed for underwater application contain a very dangerous chemical in their curing agents. That chemical is 4,4' Methylenedianiline commonly called MDA. Users of epoxy coatings should check their MSDS sheets for mention of this chemical.

Medical concerns over MDA regards its liver toxicity and carcinogenicity. OSHA exposure limits are set at only 8 parts per billion. Coating concerns with MDA are that it tends to crystallize sold and is very brittle. Additionally, it requires not just hazmat shipping but also special 'Keep away from foodstuffs' labels.

Below is the actual text from OSHA regards MDA:

The Department of Labor (OSHA) has published 29 CFR Parts 1910 and 1926, Occupational Exposure to 4,4' Methylenedianiline (MDA) which classifies MDA as a dangerous substance
and a carcinogen.

The basis for 'promulgating new standards regulating exposure to MDA. ..is a *determination by the Assistant Secretary, based on animal and human data, that exposure to MDA at the current occupational exposure levels causes adverse effects on employee health including an increased risk of cancer and that limiting occupational exposure to MDA to an eight-hour timeweighted average (TWA) of 10 parts per billion (ppb), establishing a short-term exposure limit (STEL) of 100 ppb" In addition to establishing permissible exposure limits (PELs) for MDA, this regulation includes requirements such as medical surveillance, exposure monitoring, hygiene facilities, engineering controls and work practices, proper respirator use, and record keeping.*

The *standards apply to all industries covered by the OSHA Act including general industry, construction, and maritime. These final rules shall become effective on September 9, 1992.*

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