Novel “Novolac Epoxy/Polyurethane-Hybrid” Coatings for Industrial and Municipal Applications

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Introduction

The protective coatings industry has seen vast changes over the last several years. The constant demand for lowering Volatile Organic Compounds (i.e. V.O.C.’s) and meeting the ever changing environmental regulations has forced many coatings manufacturers to concentrate on managing their formulations to “fit” within the regulations instead of concentrating on improvements in their formulation technology. A few manufacturers continue to progress their technologies to improve application techniques and formulation compatibility. One of these improvements has been the constant development and improvement of polyurethanes and polyurea chemistry. With new technology, it is now possible to utilize the benefits of polyurethane combined with the chemical resistance of epoxy-based formulations.

A Brief History

It is widely accepted in the municipal industry that an “epoxy system” is the coating product of choice when it comes to coating municipal concrete or steel structures that are “underground” or in constant immersion. This is due to the epoxy chemical structure allowing less reactivity with moisture-laden substrates, excellent adhesion, and the low permeability of epoxy systems. Additionally, epoxy shows excellent chemical resistance and the chemical resistance can be altered to suite a particular application (i.e. standard bis-A epoxy, novolac epoxy, etc.). Over the last few decades, other coating systems have shown promise in similar applications. Polyurethane systems are well known for their flexibility and color fastness (depending on formulation). Polyurea systems are well known for their speed and fast return to service time. Included in the polyurethane group are many hybrid systems that combine polyurethane functionality and polyurea speed and low-temperature cure. However, many of the products in the polyurethane/polyurea group have not performed well in immersion conditions and especially on underground structures. This is disheartening, due to the fact that many coating applicators embrace the idea of applying polyurethanes/polyurea, however, the long term performance has not made the specification of these products appealing.

Polyurethane

Polyurethane chemistry was invented in the 1937 by Otto Bayer. Polyurethane chemistry is nearly 80 years old, and new inventions are still being discovered every day. A polyurethane is generally known as the reaction of an isocyanate with hydroxyl functional polyols. It is common knowledge that polyurethanes perform very well in several applications, however, until recently polyurethanes have not been the product of choice when it comes to coating underground concrete or steel structures. This is due to the fact that the isocyanate portion of the polyurethane is sensitive to moisture and can cause blistering in the coating. The issue of “blistering” or “foaming” is usually caused by the reaction of isocyanate with moisture that is enhanced in some cases by formulators utilizing older technology metal catalysts that have tendency to catalyze the isocyanate/water reaction and the isocyanate/polyol reaction at different reaction rates. Additionally, the exothermic portion of the reaction can exacerbate the foaming. Recent advances in polyurethane catalyst chemistry has dramatically improved this issue making polyurethanes a viable option in the underground municipal coating and lining market.

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Polyurea

Approximately 30 years ago, polyurea coating chemistry was invented by Texaco Chemical's Dudley Primeaux and other staff. This technology is superb for several coating applications including concrete, steel, and many others. Today's polyurea formulas have improved dramatically over the original formulations. Several large chemical companies are now manufacturing raw materials specifically for polyurea chemistry and the technology has grown in volume as a result. Polyurea chemistry can be a bit misleading as there are several types of formulas that get lumped into the polyurea category.

- "Pure" polyurea is the reaction between and isocyanate and amines (and only amine functionality). It is safe to say that many manufacturers also include hydroxyl-functional pigment dispersions, fillers, and some other items that may be not considered "reactive".
- "Hybrid" polyurea typically includes the reaction of hydroxyl and amine functionality.
- "Polyaspartic" polyurea is a "pure" polyurea based on a molecule formed by reacting a maleate and PACM (an epoxy hardener) to yield an amine. It performs similar to an epoxy with excellent color stability when utilizing an aliphatic isocyanate.

Polyurea has been used with varying success when coating underground structures. Polyurea can provide a fast cure, good adhesion and fast return to service when applied correctly. One issue that can arise when using polyurea is applying the coating on damp or wet concrete or steel (which is a common problem with underground structures). Even though the polyurea reaction rate appears to be unaffected by moisture, micro foaming at the substrate surface can occur. This usually occurs on the very first "pass" of the polyurea coating to the substrate. When several "passes" are applied, the resulting coating looks acceptable from the applicators standpoint. However, when reviewed with a microscope, the polyurea can be "sponge like" at the substrate/coating interface and this can cause unfavorable moisture vapor transmission rates which could ultimately cause premature failure. Proper primer selection is important when applying polyurea systems.

Epoxy

For years, epoxy has been the choice when coating underground concrete or steel structures. This is due to the ease of application and the moisture tolerance that epoxy systems display. When properly formulated, epoxies can react under water and adhere quite tenaciously. There are several drawbacks to epoxy technology some of which include long cure times, temperature sensitivity and brittleness. Furthermore, epoxies usually display better chemical resistance properties than the softer polyurea's and polyurethanes.

The Best of All Worlds

It seems that the ideal situation for coating underground concrete or steel structures would be a hybrid epoxy/polyurethane/polyurea. This could provide a relatively fast cure, moisture insensitivity, and excellent resistance to acids, bases, water and municipal water treatment chemicals. This technology now exists. This new technology is a "tri-hybrid" based on a polymer backbone of "novolac" epoxy chemistry. The coating was designed specifically for use in water and wastewater applications. It utilizes "oleo-chemical" technology which includes a "novolac" epoxy structure for chemical resistance. This coating is "green" technology and grown naturally due to the fact that the formula contains technology based on Bio-Based technology.

AquataFlex…A "Tri-Hybrid "

The use of non-petroleum based polyols (i.e. natural oils-soy, castor, cashew nut shell oil) has become very popular. They are especially useful when applied on concrete or steel in immersion conditions due to the fact that they are extremely hydrophobic. The AquataFlex 505 and 506 series product combines assets from several chemistries: an initial quick gel for applying up to 125 mils per application (similar to

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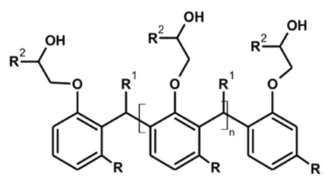
a polyurea), hydrophobicity, chemical resistance and adhesion (similar to an epoxy), flexibility, and impact resistance (similar to a polyurethane). Additionally, the polarity and surface tension of the "natural oils" are very low allowing for excellent flow and adhesion to difficult substrates.

The Problem with Some Natural-Based Polyols and Their Use in Immersion Conditions

Several years ago, many natural-based polyols were introduced into the formulator's toolbox. Some of these were based on Castor oil and Soy Oil. While these polyols showed initial improvement in immersion conditions due to their hydrophobicity, they are built upon "triglycerides" or tri-esters. Although fairly stable, triglycerides will hydrolyze in "basic" solutions and begin to break down.

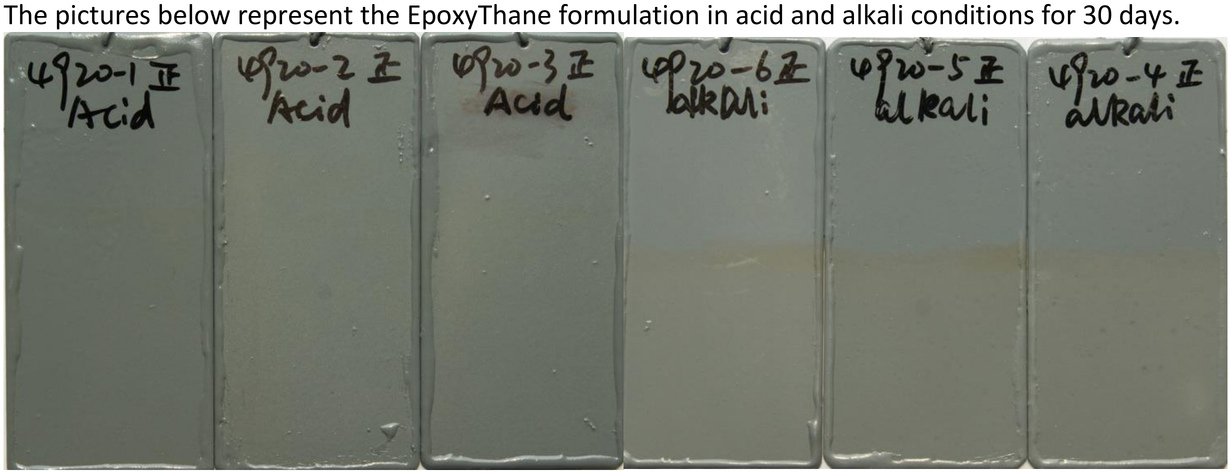
Recently developed technology allows hydroxyl functionality of Cashew Nut Shell Liquid (i.e. CNSL). This technology offers several advantages over Soy and Castor oil technology in immersion conditions. CNSL is superior to Soy or Castor oil for immersion conditions due to the resulting structure. The polyol is based on epoxy "novolac" chemistry based on the following structure:



The structure contains aromatic rings which greatly increase the heat resistance, chemical resistance and continuity of the molecule. Additionally, the polyol contains a side chain of C15 (a fatty acid) which increases the flexibility and hydrophobicity while decreasing surface tension resulting in excellent adhesion properties. Furthermore, the functionality is approximately 4.3 resulting in much greater crosslink density. The structure contains no "ester" functionality to allow for hydrolyzation in basic solutions.

Chemical Resistance

The pictures below represent the EpoxyThane formulation in acid and alkali conditions for 30 days.



The pictures below represent a "castor oil"- based formula in acid and alkali conditions. The alkali solution was immersed for only 6 days.

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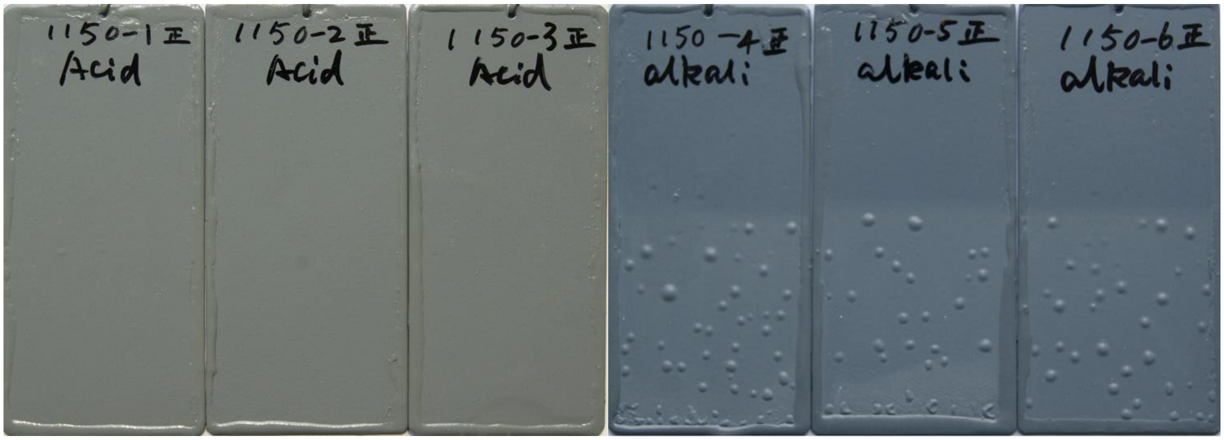
Castor Oil Based Formula in Acid Solution

Castor-Oil Formula in Basic Solution

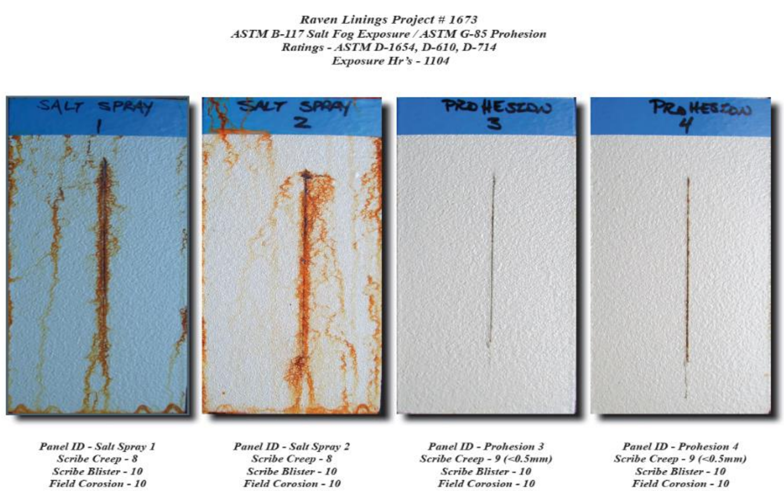


"EpoxyThane" in Salt Water -30 Days

Castor Oil-based formula in Salt Water 30 days

Potable Water Certification and Excellent Corrosion Protection

In addition to being an excellent coating for corrosion protection in wastewater environments, AquataFlex 506 and 506 has also passed the rigorous ANSI 61.5 Certification for use in potable water tanks and pipes with a 24 hour return to service. For municipalities, AquatFlex 505 and 506 are truly coatings that can be specified in multiple applications and substrates. The picture to the right illustrates the performance of the AquataFlex 505 and 506 in Salt Spray testing and Prohesion testing



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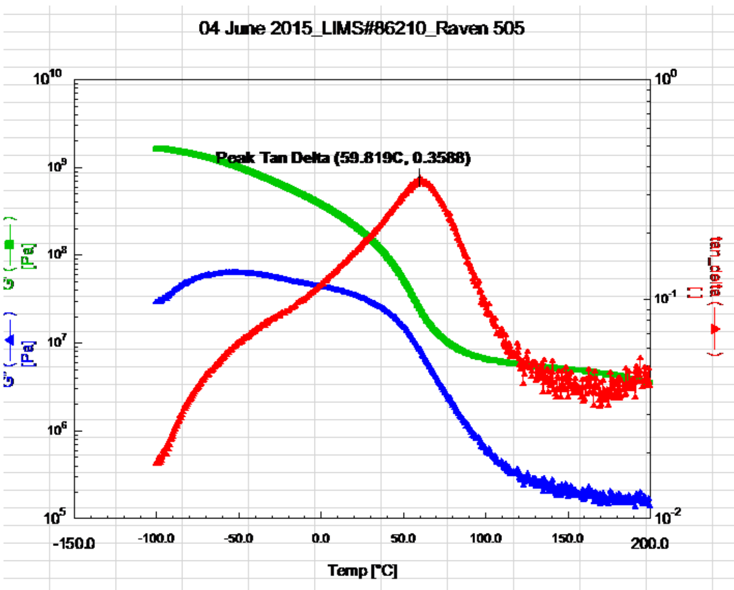


DMTA analysis shows glass transition temperature (i.e. 59°C) exceeding wastewater and potable water application requirements.

Formula Availability

The AquataFlex series has been formulated in two versions to satisfy different types of application equipment. One version (AquataFlex 505) is a 1:3 by volume mix ratio and is applied using heated plural component equipment that utilizes "in-line" static mixers and a whip hose. Examples of acceptable equipment for applying this coating are the Graco Hydracat© or XP50 type pumps. This formulation version utilizes and standard airless spray gun. The second version (AquataFlex 506) is 1:1 by volume and sprayed like a polyurea that utilizes a heated plural component pump such as a Graco Reactor© HXP2 or EXP 2 using a high pressure impingement gun. Both systems require heaters and heated hose. For specific application recommendations, see the technical data sheets.

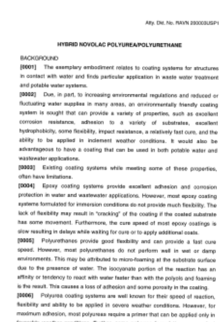
AquataFlex Certifications

The AquataFlex series of products has been tested and is certified as a U.S.D.A "Bio-Based" Product. This signifies that the coating contains at least 37% "natural" based materials as tested by an independent laboratory according to ASTM D-6866.

USDA CERTIFIED BIOBASED PRODUCT
PRODUCT 38%

Additionally, the AquataFlex products have obtained ANSI/NSF 61.5 drinking water certification. This certification allows the coating to be applied to tanks as small as five gallons and for pipe diameter as low as ½ inch. This is the highest safety level a coating product can test for drinking water applications.

The technology utilized for this coating is protected under United States "Patent Pending" law. The concept of an epoxy/polyurethane hybrid is not new, however, placing hydroxyl functionality on an epoxy novolac backbone is novel. Additionally, combining this "novel" backbone chain into a user-friendly, effective formulation requires hours of dedicated research and tremendous creativity.



Atty. Dkt. No. RAVN 200003USP1

HYBRID NOVOLAC POLYUREA/POLYURETHANE

BACKGROUND

[0001] The exemplary embodiment relates to coating systems for structures in contact with water and finds particular application in waste water treatment and potable water systems.

[0002] Due, in part, to increasing environmental regulations and reduced or fluctuating water supplies in many areas, an environmentally friendly coating system is sought that can provide a variety of properties, such as excellent corrosion resistance, adhesion to a variety of substrates, excellent hydrophobicity, some flexibility, impact resistance, a relatively fast cure, and the ability to be applied in inclement weather conditions. It would also be advantageous to have a coating that can be used in both potable water and wastewater applications.

[0003] Existing coating systems while meeting some of these properties, often have limitations.

[0004] Epoxy coating systems provide excellent adhesion and corrosion protection in water and wastewater applications. However, most epoxy coating systems formulated for immersion conditions do not provide much flexibility. The lack of flexibility may result in "cracking" of the coating if the coated substrate has some movement. Furthermore, the cure speed of most epoxy coatings is slow resulting in delays while waiting for cure or to apply additional coats.

[0005] Polyurethanes provide good flexibility and can provide a fast cure speed. However, most polyurethanes do not perform well in wet or damp environments. This may be attributed to micro-foaming at the substrate surface due to the presence of water. The isocyanate portion of the reaction has an affinity or tendency to react with water faster than with the polyols and foaming is the result. This causes a loss of adhesion and some porosity in the coating.

[0006] Polyurea coating systems are well known for their speed of reaction, flexibility and ability to be applied in severe weather conditions. However, for maximum adhesion, most polyureas require a primer that can be applied only in favorable weather conditions. Further, some polyurea formulations are so fast

Summary

AquataFlex 505 and 506 represent a long history of a continued commitment to research and development for the municipal industry by Raven Lining Systems. These two novel coating systems are "next generation" products that provide excellent corrosion protection and give specifying engineer's confidence that Raven Lining Systems continues to manufacture the highest quality product on the market.

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