A NEW INNOVATION IN COATINGS

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Abstract

For a number of decades the deionization of water has been accomplished with polishing and mixed beds vessels lined with rubber or some type of elastomeric lining. These linings, though inexpensive and widely used, suffer from a number of difficulties and challenges. They have relatively short life spans and high levels of extractables and TOC levels. Joint failure, blistering and disbonding of the elastomeric lining is not uncommon. Because of these challenges device manufacturers and their suppliers seeking higher purity water began using fluoropolymer sheet linings. Though the water quality improved exponentially the linings were expensive and difficult to install. The next development in lining technology was thick electrostatically applied fluoropolymer coatings. Though slightly less expensive and much more efficient than sheet linings the relative cost is still significantly higher than traditional rubber or elastomeric linings. Our goal was to find a substitute thermoplastic resin, probably non-fluorinated because of raw material costs, to be a viable replacement for traditional rubber and synthetic rubber linings.

After some testing and evaluation over a period of years, our company has developed a replacement coating for elastomeric linings. It is a copolymer of polyethylene and polypropylene and offers the industry a number of advantages. First of all, it is competitive in price to an elastomeric lining. Extraction studies were done by a west coast testing laboratory (Balaz) and confirmed the relative cleanliness of this type of lining. This new coating makes rubber and elastomeric linings obsolete by offering greater service life, lower extractables, smoother surface and greater adhesion to the metal substrate.

Introduction- Lining History

Early in the development and manufacture of semiconductor devices, materials and methods of construction or lining for various applications were borrowed or modified from allied fields. Boiler water purification technology for steam generation plants was borrowed using a variety of deionizers having rubber or synthetic rubber linings. These types of vessels are found in nearly everyone's water purification plants, including device manufacturers.

Because of the demands for higher purity water and perceived increased service life and at the urging of fluoropolymer sheet manufacturers, a variety of fabric backed and non-backed sheet materials have been applied as vessel linings. These first attempts at lining offered both impressive results in improvement of water quality and some very impressive failures. Early sheet lining materials were either too rigid or brittle resulting in cracking, or had poor adhesion to the substrate resulting in disbonding. The delamination could occur at either the interface between the metal substrate and the fabric backing, or detachment of the fabric from the fluoropolymer sheet.

Plastic liners, fluoropolymers included, require welding to complete a leak free monolithic and impervious lining. These materials, like steel and other metals, possess heat-affected zones (HAZ) when welded. These areas can be prone to cracking and separation. On one installation in which our company participated, a rigid fluoropolymer sheet lined deionizer was accidentally dropped from only a few feet above the pavement by a forklift operator. However it was enough to cause major weld failures in the HAZ due to stresses inherent in the weld joints. These cracks had to be rewelded at the installation site. In another instance a large sheet lined degasifier was being unloaded and in the process of removing the vessel from the trailer it was picked up by a crane from either end and went into a beam-bending mode. This caused the liner, a rigid fluoropolymer sheet material, to separate and tear. Again the vessel required repairs in the field, delaying the installation and challenging the confidence of all concerned.

Fabric backed fluoropolymer sheet linings are used less for high purity water vessels in the United States than they once were, though they are still to be found in Europe and Asia. The reason for this was the development of thick, high purity, bonded electrostatically deposited coatings a little more than a decade ago by our company. These coatings have overcome many of the challenges and difficulties of sheet linings. In addition to achieving weld free and smooth interiors, (with no HAZ), at about the same thickness as a sheet lining, 0.060 to 0.090 inches (1.5 to 2.3mm), they are or can be adhered at strengths equal to or greater than current adhesive systems for fabric backed materials associated with sheet linings. Bond strengths of 4,000 to 5,000 psi have been achieved with these coatings, essentially equaling the tensile strength of the resin. Tensile elongation of an electrostatically applied lining equals that of the resin or between 400 and 450% thus overcoming some of the early problems with sheet linings and weld failures.

Another of the advantages of these thick, bonded, coatings is the ability to be repaired in the field should they be damaged during installation. Early on and with some types of coatings any puncture or leak would require returning the entire vessel into an oven to be reheated to the melt temperature of the coating resin. With these thick bonded coatings repairs can be made with a hand held welding gun and a little filler rod without disbonding the coating or lining.

Elastomeric Linings

Though these thick fluoropolymer coatings have essentially redefined the standard for vessel linings in high purity water and chemical applications, because of high raw material costs and moderate investment in time to coat, they still do not compete with the most commonly used linings, rubber and synthetic elastomers.

The choices for lining with rubber or synthetic elastomers are numerous in searching for a suitable lining candidate. Selection of a suitable elastomeric liner, like other materials, is based upon cost and performance. The chemical resistance of the material, for the short term and for long-term aging are key factors in the decision making process. However, according to several industry experts more attention should be given to the choice of compatible materials for ultra pure water (UPW) applications. From an article in November 1987 in Ultrapure Water magazine we find the following "The most ignored of all materials in a deionized water supply system are the seals and *elastomeric materials* (italics added). Often the piping materials are carefully investigated and selected. The selection of elastomers, however, is typically only an afterthought." [1]

It is also the opinion of the authors of the article that, "In noncritical applications, cost is usually the overriding factor in selection. In critical applications such as deionized water, however the choice of elastomers should be a compromise for the best balance of required properties." [2]

The following table[3] illustrates resistance of common elastomeric linings to selective oxidizers or sanitizing agents.

Elastomer	Ozone (2 ppm)	5% H_2O_2 (5 ppm)	Chlorine
NR	Poor	Good	Poor
NBR	Poor	Good	Poor
EDPM	Fair-Good	Excellent	Fair
CR	Fair	Excellent	Fair
FPM	Good	Excellent	Good
CSM	Fair-Good	Excellent	Good
FFR	Excellent	Excellent	Good

Resistance of PCP to the agents in the above table:

PCP	Fair-Good	Excellent	Fair

[1] Hanselka,Reinhard; Williams,Ralph; and Bukay,Michael. UltraPure Water, "Materials of Construction for Water Systems, Part 3: Proper Selection of Elastomers." November 1987, p. 52.

[2] Ibid

[3] Ibid

In addition to susceptibility to sanitizing agents, namely chemical attack, failure modes for elastomeric linings also include incomplete cure, blistering and disbonding from the substrate.

There are three methods outlined by the industry for the curing of rubber linings to take place.

Autoclave cure – this is a pressure cure up to 270° F for a period of time up to 5 hours.

Exhaust steam cure – this is a process of introducing steam into a rubber lined product that is too large for an autoclave.

Chemical cure – This is typically used in the repairs and field lined vessels. Catalytic agents are required to achieve a cure and complete cure may require 7 to 14 days depending on temperature and other conditions.[1]

Because elastomeric lining materials are modified and filled with other compounds and process aids including mold release agents, plasticizers and extenders, there are some challenges in achieving a lining that will perform over an extended service life. "Solvent washing and abrading are common treatments required in adhering elastomeric linings. Chemical treatment is required for maximum properties. Many synthetic and natural rubbers require 'cyclizing' with concentrated sulfuric acid until hairline fractures are evident on the surface."[2] In addition, organic primers are often used to enhance bonding and adhesion. These primers and solvent wipes are readily absorbed into the elastomer and cause the liner to swell and soften. This necessitates further drying times in an oven. Surface treatments may also include mixtures of sulfuric acid and barium sulphate. Though inexpensive, elastomers as a group are not had without their own problems associated with installation and the potential as sources of contaminants both organic and inorganic.

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[1] Bittner Industries Technical Brochure, "Rubber Linings," www.bittner.thomasregister.com, no date given.

[2] Harper, Charles A., editor in chief. Handbook of Plastics and Elastomers, McGraw-Hill, 1975, p. 10-52.

A New Innovation in Coatings and Linings

The challenge in providing a lining competitive to common elastomeric linings is to select a material that will reduce the level of leachants and contaminants and to develop a system offering the promise of enhanced longevity and performance.

The appeal of a weld and crevice free polymeric thick coating is significant. A smoother interior surface mitigating attachment of microorganisms would also be important. The coating ought to be robust and able to withstand mechanical loads, such as internal installation of piping and headers by technicians. It should be easy to repair should the lining be punctured, without returning the entire vessel into an autoclave or oven. Neither should it require solvent-based primers or sulfuric acid washes.

A number of candidate resins, thermoplastic and non-fluorinated types were evaluated. After some extensive testing including ease of application, adhesion to substrate, thermal cycling and the ability to achieve a thick coating (approximately 0.090" or 2.3mm) at lower oven temperatures than a fluoropolymer, we selected a polyethylene/polypropylene copolymer. We refer to this as a polyolefinic copolymer or PCP.

Relative Costs of Linings

Lining Material and Method:	Cost Factor:
White Rubber	1.0
PCP, 60 mil nominal coating	1.3
Flex Kynar, 90 mil sheet lining	9.5
ETFE, 60 mil nominal coating	5.5

Having done the math in time and costs associated with energy required in the oven as well as raw material costs the next step was to evaluate this material in a real test. Not just exposing pellets, tubing or piping to circulating or static DI water but actually test lined and coated stainless steel containers. We contacted an important testing laboratory on the west coast and performed a seven day static test using Mass spec, ICP etc. etc. on several lined and coated vessels including chlorobutyl, pharmaceutical grade synthetic rubber.

Extraction Test Results*

	White Rubber	Fluoropolymer Resin #1	Fluoropolymer Resin #2	PCP
TOC	5300	**	**	46
Anions:				
Sulphate	1200	**	**	11
Chloride	130	**	0.8	3.8
Cations:				
Sodium	77	**	1.5	0.9
Trace Metals:				
Zinc	350	**	13	3
Barium	1300	**	**	0.20
Calcium	270	**	**	21

*77°F, Seven Day Static Soak, Units in PPB, from actual coated and lined vessels

**Extractables below detectable levels

The process of applying this type of polymeric lining is typical of other electrostatically applied powder coatings. The first step is to prepare a clean substrate, which is done by grit blasting that removes contaminants, oxidation and scale. The blasting also creates a surface profile of 2 to 3 mils, which increases the surface area for adhering the polymer and enhances adhesion. The vessel is put into an oven and brought to approximately 500°F where it is allowed to soak for a period of time to flash of any organics and bring the entire vessel to a constant temperature throughout. The vessel is then removed hot from the oven and a primer layer is applied. This layer is approximately 5 to 10 mils in thickness. The primered vessel is then placed back into the oven to allow the primer layer to melt and to adhere to the substrate. Several successive applications then follow at reduced temperatures of the PCP topcoat until the desired thickness is reached.

After the coating is fully melted and has a very glossy appearance it is removed from the oven and allowed to cool. The lining is measured to insure adequate thickness has been achieved and then it is spark tested at approximate 3,000 volts DC. It is important AC testers are not used as they can damage the lining.

The vessel exterior is cleaned and coated with some type of epoxy or urethane coating per customer's requirements and color choice. The vessel interior is cleaned with DI water, dried with N2 gas and prepared for shipment having all of the openings covered with protective flanges.

Summary

This new innovation in the coating or lining of equipment for UPW service offers advantages to the traditional elastomeric linings common in the industry. It is inherently cleaner with much lower extractables including organics. The bond or adhesive strength to the substrate is much greater than can be achieved through vulcanizing or using rubber cements and adhesives. Irregularities such as weld girth seams and internal projections are more easily accommodated with this process. It possesses the best balance of properties and is cost effective in competing with traditional elastomeric linings. This lower cost non fluorinated coating system will not meet all of the demands of high purity, performance or chemical resistance, but offers UPW engineers a viable alternative to less than satisfactory traditional elastomeric linings with the promise of enhanced longevity and performance.