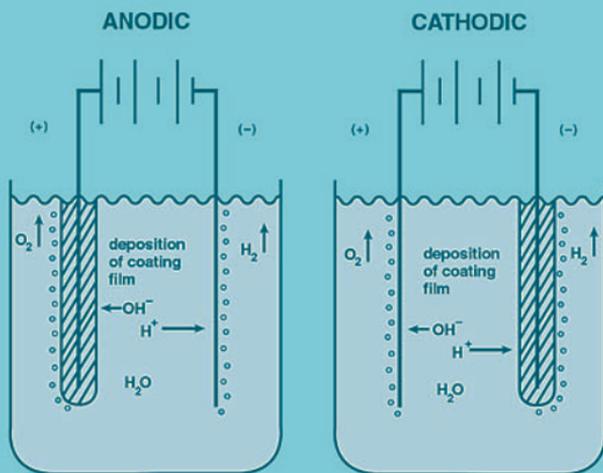


Corrosion-Resistant Linings and Coatings



Philip A. Schweitzer

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Preface

Although many corrosion-resistant metals and alloys are available, they do not always represent the most practical or economical means to combat corrosion. In many situations it is better to select a less resistant material and provide some type of coating or lining to protect it from corrosion.

Linings are generally used to protect the interior of vessels, which may be of carbon steel or synthetic construction. They may be made of sheet, glass, or cement, or may be applied in liquid form.

Coatings are normally used to protect the exterior surfaces of vessels or structures exposed to corrosive atmospheres. Some coatings may also be used as linings. Included in this category are paints, organic coatings, metallic coatings, and monolithic coatings for concrete.

This book provides a thorough introduction to the various types of linings and coatings that can be used to provide corrosion resistance. Physical, mechanical, and corrosion resistance properties—as well as areas of application—are provided for each of the materials. The effectiveness of any lining or coating is dependent on proper surface preparation and installation or application. Accordingly, these details are included for each lining and coating material. Because concrete is widely used as a construction material and is subject to corrosion, the text includes information on coatings that provide protection from atmospheric and other, more aggressive corrosive atmospheres.

For all professionals involved in design and maintenance processes, this book should serve as a valuable aid in the selection of corrosion-resistant linings and coatings.

Philip A. Schweitzer

Contents

<i>Preface</i>	<i>iii</i>
1. Introduction to Linings	1
2. Sheet Linings	19
3. Specific Thermoplastic Sheet Lining Materials	27
4. Specific Elastomeric Sheet Linings	71
5. Liquid Applied Linings	121
6. Specific Liquid Applied Lining Materials	141
7. Masonry Linings	175
8. Glass Linings	217
9. Comparative Corrosion Resistance of Lining Materials	227
10. Introduction to Coatings	265

11. Principles of Coating	281
12. Corrosion Protection by Organic Coatings	301
13. Specific Organic Coatings	331
14. Selecting a Paint System	343
15. Conversion Coatings	355
16. Metallic Coatings	363
17. Cementitious Coatings	401
18. Coatings for Concrete	407
<i>Index</i>	425

1

Introduction to Linings

Linings are barrier applications used to protect carbon steel, concrete, or other substrates from corrosion by harsh chemicals. In addition to the protection afforded, linings maintain product purity and absorb impact to maintain particle size; those having a low coefficient of friction prevent particles from hanging up and provide an easily cleanable surface. Economics plays a part in determining whether it is more advantageous to line a carbon steel vessel or to select an appropriate corrosion resistant alloy as the base metal of construction. When high temperatures and concentrations of chemicals rule out a lining system, or when downtime for repair of a lining is unacceptable, the high alloy is automatically selected.

At times external corrosion as well as internal corrosion is a problem. Under such circumstances a carbon steel vessel may have an external coating applied. Alternatively, a fiber reinforced polyester (or similar polymer) vessel may be used and lined, with the vessel shell resisting the external corrosion.

When a lining is to be used for corrosion protection, it is necessary to review the corrosion rate of the immersion environment on the substrate. Assuming that the substrate is carbon steel with a corrosion rate of less than 10 mils per year (mpy) at the operating temperature, pressure, and concentration of corrodent, then a thin film lining of less than 20 mils may be used. For general corrosion this corrosion rate is not considered severe. However, if a pinhole should be present through the lining, a concentration of the corrosion current

TABLE 1.1 Fluoropolymer Lining Systems

Lining system	Thickness, in. (mm)	Maximum size	Design limits	Installation	Repair considerations
Sheet linings—adhesive bonded					
Fabric-backed PVDF	0.06–0.09 (1.5–2.3)	No limit.	Pressure allowed. Full vacuum only at ambient temperature. Smallest nozzle size 2 in. (51 mm). Maximum temperature limited by adhesive, typically 275°F (135°C).	Neoprene or epoxy adhesive. Sheets welded with cap strips. Heads are thermoformed or welded.	Repair is possible but testing is recommended.
PTFE	0.08–0.12 (2.0–3.1)				
FEP	0.06–0.09 (1.5–2.3)				
ECTFE	0.06 (1.5)				
ETFE	0.06–0.09 (1.5–2.3)				
PFA	0.09 (2.3)				
Loose sheet lining					
FEP, PFA	0.06–0.187 (1.5–4.75)	Determined by body flange.	Pressure allowed. No vacuum. Gas-ketting required between liner and flange.	Liner with nozzles hand or machine welded, then slipped inside housing.	Difficult.

 Sprayed dispersions

FEP	0.04 (1.0)				
PFA	0.01–0.04 (0.25–1.0)				
PVDF	0.025–0.03 (0.06–0.76)				
PFA with mesh and carbon	0.08 (2.0)				
PVDF with mesh and carbon	0.04–0.09 (1.0–2.30)	8 ft (2.4 m) dia. 40 ft (12.2 m) length	Pressure al- lowed. Vac- uum rating un- determined.	Primer and multi- ple coats ap- plied with com- bination 2 psig equipment. Each coat is baked.	Hot patching is possible, but testing is rec- ommended.

Electrostatic spray powder

ETFE	Up to 0.09 (2.3)	8 ft (2.4 m)	Pressure al-	Primer and multi-	Hot patching is
FEP	0.01–(0.28)	dia. 40 ft	lowed. Vac-	ple coats ap-	possible, but
PFA	0.01 (0.28)	(12.2 m)	uum rating un-	plied with	testing is rec-
ECTFE	0.06–0.07 (1.5–1.8)	length	determined.	electrostatic	ommended.
PVDF	0.025 (0.64)			spraying	
				equipment.	
				Each coat is	
				baked.	

density occurs as a result of the large ratio of cathode to anode area. The pitting corrosion rate will rapidly increase above the 20 mpy rate and through-wall penetration can occur in months.

When the substrate exhibits a corrosion rate in excess of 20 mpy, a thick film lining exceeding 20 mils in thickness is used. These thicknesses are less susceptible to pinholes.

THIN LININGS

Thin linings are used for overall corrosion protection as well as for combating localized corrosion such as pitting and stress cracking of the substrate. Thin fluoropolymer linings are used to protect product purity and provide nonstick surfaces for easy cleaning.

Among materials available for thin linings are those based on epoxy and phenolic resins that are 0.15–0.30 mm (0.006–0.12 in.) thick. They are either chemically cured or heat baked. Baked phenolic linings are used to protect railroad tank cars transporting sulfonic acid. Tanks used to store caustic soda (sodium hydroxide) have a polyamide cured epoxy lining.

Thin linings of sprayed and baked FEP, PFA, and ETFE are also widely used. They are applied to primed surfaces as sprayed waterborne suspensions or electrostatically charged powders sprayed on a hot surface. Each coat is baked before the next is applied. Other fluoropolymers can also be applied as thin linings. These linings can be susceptible to delamination in applications where temperatures cycle frequently between ambient and steam. Table 1.1 presents details about these linings. Fluoropolymer thin lining systems can also be applied as thick linings or as sheet linings.

THICK LININGS

When the corrosion rate of the substrate exceeds 10 mpy, thick linings exceeding 25 mils (0.025 in.) are recommended. One such lining is vinyl ester reinforced with glass cloth or woven roving. Linings greater than 125 mils (0.125 in.) thick can be sprayed or trowelled. Maximum service temperature is 170°F (77°C). These linings can be applied in the field and are used in service with acids and some organics.

Another thick lining material for service with many acids and bases is plasticized PVC. This has a maximum operating temperature of 150°F (66°C).

Spray and baked electrostatic powder coating of fluoropolymers, as described under thin linings, can also be applied as thick linings. One such lining is PVDF and glass, or carbon-fiber fabric.

SHEET LININGS

Solid sheet linings can also be applied either as an adhesive-bonded lining or a loose-fitting lining. Adhesive-bonded sheet linings on steel substrates consist of fabric backed sheets bonded to steel vessel walls with neoprene or epoxy based adhesive. Linings may be applied in the field or in the shop. Joints are heat welded using a rod of the same polymer as the sheets.

Some adhesive bonded sheet lined vessels have been rated to withstand full vacuum at ambient temperature. Vacuum ratings may vary with vessel size.

Dual Laminates

Dual laminate structures are composed of fiber reinforced plastic (FRP) built with fluoropolymer sheeting that serves as a lining. This lining is fabricated by machine and hand welding of fiber backed fluoropolymer sheets, like those described above for adhesive bonded systems. The fabric aids in bonding the sheeting to the FRP.

Loose Linings

Loose linings are predominately composed of fluoropolymer sheets which are welded into lining shapes, folded, and slipped into the housing. The lining is flared over body and nozzle flanges to hold it in place. Weep holes are provided in the substrate to permit release of permeants. This is an ASME code requirement. Vacuum is permitted in vessels having diameters up to 12 in. (300 mm). Larger diameter vessels cannot be used under vacuum conditions.

PERMEATION

All materials are somewhat permeable to chemical molecules, but plastic materials tend to be an order of magnitude greater in their permeability rate than metals. Gases, vapors, or liquids will permeate polymers.

Permeation is a molecular migration either through microvoids in the polymer (if the polymer is more or less porous) or between polymer molecules. In neither case is there any attack on the polymer. This action is strictly a physical phenomenon. In lined equipment permeation can result in

1. Failure of the substrate from corrosion attack.
2. Bond failure and blistering, resulting from accumulation of fluids at the bond interface when the substrate is less permeable than the liner, or from corrosion/reaction products if the substrate is attacked by the permeant
3. Loss of contents through the substrate and liner as a result of the eventual failure of the substrate. In unbonded linings it is important that

the space between the liner and support member be vented to the atmosphere, not only to allow minute quantities of permeant vapor to escape, but also to prevent expansion of entrapped air from collapsing the liner.

Permeation is a function of two variables, one relating to diffusion between molecular chains and the other to the solubility of the permeant in the polymer. The driving force of diffusion is the partial pressure gradient for gases, and the concentration gradient for liquids. Solubility is a function of the affinity of the permeant for the polymer.

There is no relation between permeation and the passage of materials through cracks and voids, even though in both cases migrating chemicals travel through the polymer from one side to the other.

The user has some control over permeation, which is affected by

1. Temperature and pressure
2. Permeant concentration
3. Thickness of the polymer

Increasing the temperature will increase the permeation rate since the solubility of the permeant in the polymer will increase; and as the temperature rises the polymer chain movement is stimulated, permitting more permeants to diffuse among the chains more easily. For many gases the permeation rate increases linearly with the partial pressure gradient, and the same effect is experienced with the concentration gradients of liquids. If the permeant is highly soluble in the polymer, the permeability increase may be nonlinear. The thickness will generally decrease permeation by the square of the thickness. For general corrosion resistance, thicknesses of 0.010–0.020 in. are usually satisfactory.

The density of the polymer, as well as the thickness, will have an effect on the permeation rate. The greater the density of the polymer, the fewer voids through which permeation can take place. A comparison of the density of sheets produced from different polymers does not provide any indication of the relative permeation rates. However, a comparison of the density of sheets produced from the same polymer will provide an indication of the relative permeation rates. The denser the sheet, the lower the permeation rate.

Thickness of lining is a factor affecting permeation. For general corrosion resistance, thicknesses of 0.010–0.20 in. are usually satisfactory, depending upon the combination of elastomeric material and the specific corrodent. When mechanical factors such as thinning due to cold flow, mechanical abuse, and permeation rates are a consideration, thicker linings may be required.

Increasing the lining thickness will normally decrease permeation by the square of the thickness. Although this would appear to be the approach to follow

to control permeation, there are disadvantages. First, as the thickness increases, the thermal stresses on the bonding increase, which can result in bond failure. Temperature changes and large differences in coefficients of thermal expansion are the most common causes of bond failure. Thickness and modulus of elasticity of the elastomer are two of the factors that would influence these stresses. Second, as the thickness of the lining increases, installation becomes more difficult, with a resulting increase in labor costs.

The rate of permeation is also affected by temperature and temperature gradient in the lining. Lowering these will reduce the rate of permeation. Lined vessels that are used under ambient conditions, such as storage tanks, provide the best service.

Other factors affecting permeation consisting of chemical and physiochemical properties are:

1. Ease of condensation of the permeant: Chemicals that condense readily will permeate at higher rates.
2. The higher the intermolecular chain forces (e.g., Van der Waals hydrogen bonding) of the polymer, the lower the permeation rate.
3. The higher the level of crystallinity in the polymer, the lower the permeation rate.
4. The greater the degree of cross-linking in the polymer, the lower the permeation rate.
5. Chemical similarity between the polymer and permeant: When the polymer and permeant both have similar functional groups, the permeation rate will increase.
6. The smaller the molecule of the permeant, the greater the permeation rate.

The magnitude of any of the effects will be a function of the combination of the polymer and the permeant in actual service.

Vapor permeation of PTFE, FEP, and PFA are shown in Tables 1.2 to 1.4.

ABSORPTION

Polymers have the potential to absorb varying amounts of corrodents they come into contact with, particularly organic liquids. This can result in swelling, cracking, and penetration to the substrate. Swelling can cause softening of the polymer, introduce high stresses, and cause failure of the bond. If the polymer has a high absorption rate, permeation will probably take place. An approximation of the expected permeation and/or absorption of the polymer can be based on the absorption of water. These data are usually available. Table 1.5 provides the water absorption rates of the common polymers.

TABLE 1.2 Vapor Permeation of PTFE^a

Gases	Permeation (g/100 in. ² /24 h/mil) at	
	73°F (23°C)	86°F (30°C)
Carbon dioxide		0.66
Helium		0.22
Hydrogen chloride; anh.		<0.01
Nitrogen		0.11
Acetophenone	0.56	
Benzene	0.36	0.80
Carbon tetrachloride	0.06	
Ethyl alcohol	0.13	
Hydrochloric acid 20%	<0.01	
Piperdine	0.07	
Sodium hydroxide 50%	5×10^{-5}	
Sulfuric acid 98%	1.8×10^{-5}	

^aBased on PTFE having a specific gravity >2.2.

The failure due to absorption can best be understood by considering the “steam cycle” test described in the ASTM standards for lined pipe. A section of lined pipe is subjected to thermal and pressure fluctuations. This is repeated for 100 cycles. The steam creates a temperature and pressure gradient through the liner, causing absorption of a small quantity of steam, which condenses to water within the inner wall. Upon pressure release, or on reintroduction of steam, the entrapped water can expand to vapor, causing an original micropore. The repeated pressure and thermal cycling enlarges the micropores, ultimately producing visible water filled blisters within the liner.

In an actual process, the polymer may absorb process fluids, and repeated temperature or pressure cycling can cause blisters. Eventually corrodent may find its way to the substrate.

Related effects can occur when process chemicals are absorbed, which may later react, decompose, or solidify within the structure of the polymer. Prolonged retention of the chemicals may lead to their decomposition within the polymer. Although it is unusual, it is possible for absorbed monomers to polymerize.

Several steps can be taken to reduce absorption. Thermal insulation of the substrate will reduce the temperature gradient across the vessel, thereby preventing condensation and subsequent expansion of the absorbed fluids. This also reduces the rate and magnitude of temperature changes, keeping blisters to a minimum. The use of operating procedures or devices to limit the rates of process pressure reductions or temperature increases will provide additional protection.

TABLE 1.3 Vapor Permeation of FEP

	Permeation (g/100 in. ² /24 h/mil) at		
	73°F (23°C)	95°F (35°C)	122°F (50°C)
Gases			
Nitrogen	0.18		
Oxygen	0.39		
Vapors			
Acetic acid		0.42	
Acetone	0.13	0.95	3.29
Acetophenone	0.47		
Benzene	0.15	0.64	
<i>N</i> -Butyl ether	0.08		
Carbon tetrachloride	0.11	0.31	
Decane	0.72		1.03
Ethyl acetate	0.06	0.77	2.9
Ethyl alcohol	0.11	0.69	
Hexane		0.57	
Hydrochloric acid 20%	<0.01		
Methanol			5.61
Sodium hydroxide 50%	4×10^{-5}		
Sulfuric acid 98%	8×10^{-6}		
Toluene	0.37		2.93
Water	0.09	0.45	0.89

ENVIRONMENTAL STRESS CRACKING

Stress cracks develop when a tough polymer is stressed for an extended period of time under loads that are small relative to the polymer's yield point. Cracking will occur with little elongation of the material. The higher the molecular weight of the polymer, the less likelihood of environmental stress cracking, other things being equal. Molecular weight is a function of length of individual chains that

TABLE 1.4 Permeation of Various Gases in PFA at 77°F (25°C)

Gas	Permeation (cm ³ mil thickness/100 in. ² 24 h atm)
Carbon dioxide	2260
Nitrogen	291
Oxygen	881

TABLE 1.5 Water Absorption Rates of Polymers

Polymer	Water absorption 24 h at 73°F (23°C) (%)
PVC	0.05
CPVC	0.03
PP (Homo)	0.02
PP (Co)	0.03
PE (EHMW)	<0.01
E-CTFE	<0.1
PVDF	<0.04
Saran	nil
PFA	<0.03
ETFE	0.029
PTFE	<0.01
FEP	<0.01

make up the polymer. Longer-chain polymers tend to crystallize less than polymers of lower molecular weight or shorter chains and also have greater load-bearing capacity.

Crystallinity is an important factor affecting stress corrosion cracking. The less the crystallization that takes place, the less the likelihood of stress cracking. Unfortunately the lower the crystallinity, the greater the likelihood of permeation.

Resistance to stress cracking can be reduced by the absorption of substances that chemically resemble the polymer and will plasticize it. In addition, the mechanical strength will be reduced. Halogenated chemicals, particularly those consisting of small molecules containing fluorine or chlorine, are especially likely to be similar to the fluoropolymers and should be tested for their effect.

The presence of contaminants in a fluid may act as an accelerator. For example, polypropylene can safely handle sulfuric or hydrochloric acids, but iron or copper contaminants in concentrated sulfuric or hydrochloric acids can result in the stress cracking of polypropylene.

LINING SELECTION

At this stage an economic evaluation must be undertaken. There are several options which can be considered; an economic evaluation should be performed based on life-cycle costs that takes into consideration the replacement intervals and downtime associated with linings, compared to the higher costs of equipment fabricated from more expensive alloys.

Before the economic evaluation can be performed, potential lining materials must be considered. In order to determine which lining material may be suitable for the application, several broad categories must be considered, specifically materials being handled, operating conditions, and conditions external to the vessel.

The following questions must be answered about the materials being handled.

1. What are the primary chemicals being handled and at what concentrations?
2. Are there any secondary chemicals, and if so at what concentrations?
3. Are there any trace impurities or chemicals?
4. Are there any solids present, and if so what is their particle size and concentration?
5. If a vessel, will there be agitation, and to what degree? If a pipeline, what are the flow rates, minimum and maximum?
6. What are the fluid purity requirements?

The answers will narrow the selection to those lining materials that are compatible. Screening of the candidates can be accomplished by reviewing industry publications, manufacturers' data sheets, and publications listing chemical resistance data, e.g., Ref. 1. Table 1.6 will serve as a general guide for liner selection.

This next set of questions will narrow the selection still further by eliminating those materials that do not have the required physical/mechanical properties.

1. What is the normal operating temperature and temperature range?
2. What peak temperatures may be reached during shutdown, startup, process upset, etc.?
3. Will any mixing areas exist where exothermic or heat of mixing temperatures can develop?
4. What is the normal operating pressure?
5. What vacuum conditions and range are possible during startup, operation, shutdown, or upset conditions?
6. Will there be temperature cycling?
7. What cleaning methods will be used?

Finally, consideration should be given to the conditions external to the vessel or pipe.

1. What are the ambient temperature conditions?
2. What is the maximum surface temperature during operation?
3. What are the insulation requirements?
4. What is the nature of the external environment? This can dictate finish requirements and/or affect the selection of the shell material.

TABLE 1.6 Guide for Liner Selection

Acids less than 120°F/49°C	
Dilute	Concentrated
Fluoropolymer	PVC
Elastomers	Epoxy novolac
Borosilicate glass	Silicon epoxy
Silicon epoxy	Fluoropolymer
Epoxy novolac	Borosilicate glass
Furan	Baked phenolic
Polyester	Vinyl ester
Vinyl ester novolac	PP
Epoxy phenolic	
Plasticized PVC	
Epoxy amine adduct	
Baked phenolic	
Polyurethane	
Vinyl ester	
Vinyl	
PVC, CPVC, PE, PP	
Acids greater than 120°F/49°C	
Baked phenolic	Fluoropolymer
Fluoropolymer	Borosilicate glass
Epoxy novolac	Elastomers
Vinyl ester	Acid brick
Silicon epoxy	HDPE
Borosilicate glass	
Acid brick	
Solvents less than 120°F/49°C	
Aromatic	Chlorinated
Baked phenolic	Baked phenolic
Silicon epoxy	Silicon epoxy
Fluoropolymer	Fluoropolymer
Furan	Vinyl ester novolac
Vinyl ester novolac	Borosilicate glass
Epoxy amine adduct	
Borosilicate glass	
Vinyl ester	

TABLE 1.6 Continued

Solvents greater than 120°F/49°C		
Aromatic		Chlorinated
Fluoropolymer	Fluoropolymer	
Borosilicate glass	Borosilicate glass	
Baked phenolic	Baked phenolic	
Bases less than 120°F/49°C		
Dilute		Concentrated
Fluoropolymer	Fluoropolymer	
Epoxy novolac	Epoxy novolac	
Epoxy polyamide	Silicon epoxy	
Epoxy amine adduct	Epoxy phenolic	
Epoxy phenolic	Vinyl ester	
Coal tar epoxy	Elastomers	
Vinyl ester	Epoxy amine	
Elastomers	Furan	
Vinyl ester novolac	Vinyl ester novolac	
Borosilicate glass	Borosilicate glass	
Chlorinated rubber	Epoxy amine adduct	
Baked phenolic	Plasticized PVC	
Polyester	PP	
Polyurethane	PE	
Furan	PVC	
PP, PE, PVC		
Bases greater than 120°F/49°C		
Fluoropolymer	Fluoropolymer	
UHMWPE	UHMWPE	
Elastomers	PVC	
PP, PVC	Epoxy novolac	
Epoxy novolac		
Elastomers		Thermoplastic polymers
Natural rubber	HDPE	High density polyethylene
Nitrile rubber	CPVC	Chlorinated polyvinyl chloride
Butyl rubber	PE	Polyethylene
Hypalon	PP	Polypropylene
EPDM rubber	PVC	Polyvinyl chloride
SBR rubber	UHMWPE	Ultra high molecular weight
Neoprene		polyethylene