



# FRP Material Selection Guide

An Engineer's Guide to  
FRP Technology

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# FRP Material Selection Guide

An Engineer's Guide  
to FRP Technology

Reichhold's *FRP Technology Guides Series*, of which *The FRP Materials Selection Guide* is a part, is intended to give practicing engineers an understanding of composites technology in order that they may be able to effectively incorporate FRP, polymer concrete, and other polymer materials in their designs.

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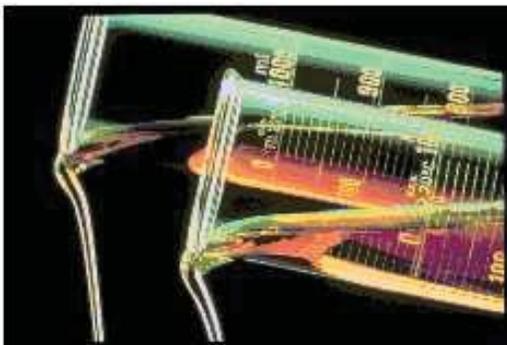
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## **Introduction**



### **An Engineer's Guide to FRP Technology**

One of the great advances of the Twentieth Century in Materials Technology was the advent of unsaturated polyester and vinyl ester resins and their use in engineered composites. These versatile polymer materials immediately found acceptance in aerospace, construction, transportation, the infrastructure, and industrial process equipment, where their unique properties brought value and new solutions to the practicing engineer.

Because of its superb corrosion resistant properties, composite fiber reinforced plastic (FRP) has displaced other more costly metals in many industrial process equipment, e.g. tanks, piping, duct and hood systems, reaction vessels, etc. Because of its fast cure, polymer concrete has displaced Portland cement concrete in highway bridge deck overlays where traffic can resume within hours instead of a week. Special resins using advanced thickening technology have revolutionized the rehabilitation of municipal and industrial process sewers using cured-in-place pipe (CIPP).

However, the availability of good engineering information and data regarding composites has not kept pace with the advances in the technology. Reichhold's *FRP Technology Guides Series*, of which *The FRP Materials Selection Guide* is a part, is intended to give practicing engineers an understanding of composites technology in order that they may be able to effectively incorporate FRP, polymer concrete, and other polymer materials in their designs.

*The Materials Selection Guide* is a step-by-step guide to selecting resins for use in these applications. Resin selection is different for the corrosion barrier than for the structural laminate. This Guide focuses the resin selection for the corrosion barrier and the structural laminate.

#### ***CORROSION HOTLINE***

Chemical attack will alter the structural performance of laminates and environmental effects must be considered in the selection of an appropriate resin. Reichhold provides technical assistance for the selection of the proper resin and will provide test coupons prepared according to ASTM C-581 for in-plant testing.

To obtain assistance, contact the **Reichhold Corrosion Hotline at 1-800-752-0060, or email us at [corrosion@reichhold.com](mailto:corrosion@reichhold.com)**. When you do so, please have the following information ready:

- Precise composition of the chemical environment
- Chemical concentration(s)
- Operating temperature (including potential temperature fluctuations, upsets, or cycling conditions)
- Trace materials
- Potential need for flame-retardant material
- Type and size of equipment
- Fabrication process

## **FRP Technology Guide Series**

In addition to the *Materials Selection Guide for Fiber Reinforced Plastics*, Reichhold has also published the following FRP Technology Guides

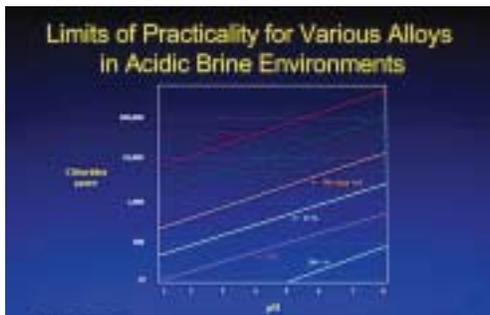
DION® Application Guide

Quality Assurance and Preventive Maintenance Inspection Guide for Fiber Reinforced Plastics

DION® Corrosion Guide

DION CIPP® – Cured-in-Place Pipe Resin Systems Guide

These Guides are available free of charge from Reichhold, Inc. To receive copies, call the **Reichhold Corrosion Hotline at 1-800-752-0060, email [corrosion@reichhold.com](mailto:corrosion@reichhold.com), or visit [www.reichhold.com/corrosion](http://www.reichhold.com/corrosion).**



### ***Industrial Applications of FRP Process Equipment***

Corrosion costs Industry billions of dollars each year and an important task of the design engineer is to seek ways of eliminating or reducing corrosion of industrial equipment. Much of the corrosive attack to industrial equipment comes from chlorides. The Figure shows the range of suitability for many important metals in the presence of chlorides. The ranges are limited to narrow bands above which more and more exotic materials are required. FRP, however, is

suitable across the entire spectrum of chloride concentration and pH.

DION® resins have over 55 years of field service in the most severe corrosive environments. The design versatility offered by FRP fabrications has produced a wide variety of industrial products that have established dominant positions in many segments of the process markets.

### ***Industrial Process Equipment***

FRP process equipment is used in many industrial applications. A few include:

#### **Chemical Storage Tanks**



Carbon steel, stainless steel, rubber-lined steel, and premium alloys, once standard materials of construction for chemical storage tanks, are more and more being replaced by fiber reinforced plastics (FRP) as engineers begin to realize the advantages of FRP, e.g. increased corrosion resistance, light weight, higher strength to weight ratio, low life cycle costs, etc.

## Underground Fuel Storage Tanks

The same advantages of FRP for chemical storage tanks apply to underground fuel storage tanks with the corrosion resistance of FRP taking particular prominence. Highly cross-linked terephthalic resins are particularly successful in containing gasoline and gasoline blends and resisting the corrosion that results from water condensation inside the tank and corrosion from ground water on the exterior of the tank. Secondary containment systems are easily incorporated into the fabrication of FRP tank shells.



## Pickling and Plating Tanks

Among the best applications for FRP are pickling tanks or electrowinning tanks in minerals processing plants. These applications illustrate the advantage of FRP in an environment typified by high concentrations of chlorides. Metal alloys have limited practicality in acidic brine environments in contrast to FRP, which is applicable across this entire range of conditions.

## Chemical Piping Systems



FRP piping is used extensively in process piping systems, stock and effluent piping in pulp bleach plants, chemical waste and municipal waste sewer piping, cooling tower piping, leach field acid piping, irrigation piping, etc.

## Sewer Pipe

The formation of hydrogen sulfide and its successor, sulfuric acid, in sewer pipe aggressively attacks concrete sewer piping leading to reduced service life and degraded hydraulic performance when compared with FRP. The light weight of FRP is a special advantage in installing large diameter piping. A smaller capacity crane can be used in most cases, and, in the case of smaller diameter piping, a crane can be eliminated by two laborers handling pipe spoils.

The formation of hydrogen sulfide and its successor,



## Fume Ducts and Scrubbers

The Clean Air Act has created increasing demand for scrubbers and collection ductwork systems that will resist the corrosive effects of industrial fumes drawn from process streams. Duct and scrubbers for pulp bleach plants, ducting from clean rooms in semiconductor fabrication plants, odor control ducts, carbon absorbers, and scrubbers in municipal waste water treatment plants: all use FRP as a key material of construction to combat corrosion. The smooth inside surface of FRP piping also greatly reduces the accumulation of biomass in duct systems transporting organo-chemical fumes.

## Chimney Stacks and Stack Liners

As the demand for electrical generation capacity increases, new coal and natural gas-fired generating plants come on line, flue gas desulfurization systems will be needed to scrub NO<sub>x</sub> and SO<sub>x</sub> gases. Large diameter FRP stack liners and transport ducting for power generation stations are already a proven technology for this growing application.



## Fans, Blowers, and Hoods



FRP impellers and fan housings are used in municipal waste water treatment plants. Hoods are used to capture chlorine dioxide fumes coming off pulp washers in bleach plants. And FRP pump housings are used to protect submersible sump pumps in industrial applications.

## Chlorine Cell Covers and Collectors

The chlor-alkali industry is one of the most important, albeit, toxic and corrosive environments in industry. Chlorine gas, sodium hydroxide, and sodium chlorate are chemicals found in this process. Cell covers and headers capture and transport highly corrosive (and dangerous) chlorine gas, and FRP is used for the storage of highly flammable sodium chlorate. The corrosion potential is so great in cell headers, for example, that special thick corrosion barriers are specified to extend the service life of the equipment.

## Pulp Washer Drums and Up-flow Tubes



FRP has long been a material of construction for pulp washer drums used to extract residual chlorine dioxide or caustic chemical carryover from pulp. FRP is also used in large diameter up-flow tubes and retention towers where digested wood chips are first chlorinated and then bleached in the pulping process.

## Secondary Containment Systems

The process of FRP fabrication lends itself to the creation of outer skins, or secondary containment systems, separated from the inner wall by three dimensional glass fabrics. These interstitial spaces can then be incorporated with sensors to detect and locate leaks or drain to a sump where discharge can be detected.



## Grating and Structural Shapes

Steel gratings used in catwalks around industrial process equipment provide a lot of surface area vulnerable to corrosion and small openings which make painting difficult. Likewise, carbon steel structural shapes are quickly attacked by corrosive fumes rising from process vessels, etc. In each case, FRP resists

the corrosive attack and extends the service life of the structure by a significant time.

## **Cooling Tower Elements**

The moisture and oxygen rich environment of cooling towers creates a corrosion-prone environment for louvers, structural elements, distributors, sumps, and piping. FRP has long been used in these applications to extend the life of the cooling towers. Similarly, large diameter steel cooling water intake and discharge piping systems are often clogged by zebra shells. The use of FRP piping decreases, and in some instances, eliminates this severe maintenance problem.



## **Highway Bridge Deck Overlays**

Highways in the northern climes are subject to chloride attack from deicing salts used in the winter, roadways in coastal areas are subject to chloride attack from ocean spray, and highways in large metropolitan areas become “political lightning rods” when lanes are taken out of service for any reason. The use of polyester polymer concrete to overlay deteriorated wearing surfaces has become the method of choice where chloride

attack is severe and traffic delays are not an option. Polymer concrete will allow a traffic lane to be returned to service in 2 to 4 hours, instead of the 1 to 4 days required for the more traditional concrete. Friction values remain high and chloride permeability is now zero.

## **Floor Coatings and Mortars**

FDA regulations require that many food processing plants keep their floors clean. Polymer floor coatings and mortars seal the surface and prevent the accumulation of biomass, which is often present in the pores of Portland cement concrete.

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## ***Industrial Process Environments***

### **General**

Although general resin selection data are presented in the Corrosion Resistance Guide, some of the more common and more aggressive environments deserve elaboration with attention to specialized concerns regarding fabrication or associated process conditions.

### **Acids**

Polyesters and vinyl esters, in general, have excellent acid resistance, even those resins which are ordinarily used for general purpose or aesthetic applications. In most cases an isophthalic or terephthalic resin may be used, but if dealing with high concentrations or temperatures, premium resins should be considered. Moreover, acids can have other chemical properties, such as oxidizing or reducing abilities, and these properties must be properly considered.

Apart from acid solutions themselves, acidic attack to metals can come indirectly in soil, especially from anaerobic sulfate-reducing bacteria, which form hydrogen sulfide (H<sub>2</sub>S) and ferrous ion (Fe<sup>2+</sup>). Buried steel commonly experiences such microbiological attack and FRP has been used extensively to protect underground pipe as well as fuel tanks. Similar attack can occur to lower grade stainless steel

from metal-reducing bacteria which may be present in various industrial, soil, or marine environments.

If the FRP is intended for applications involving neutralization with caustic or other bases it is advisable to use either a bis-A polyester or a vinyl ester, since a poorly controlled process can often result in very alkaline conditions. The same would apply to cases where caustic or other bases might be used for neutralization as part of periodic maintenance or cleaning.

If acids are to be diluted, careful recognition should be given to the heat of dilution. Safe and accepted practices should be used in the dilution procedure to avoid high exotherms or splattering of the acid. The tanks and foundation design should also recognize that many inorganic acids can have high specific gravities.

It is advisable not to use fillers in FRP composites intended for acid service. These can increase permeation and detract from corrosion resistance. Furthermore, many types of filler, such as carbonates, can react very readily with acids to generate carbon dioxide.

## **Sulfuric Acid**

In dilute form sulfuric acid is extremely corrosive to carbon steel, yet FRP is highly resistive. Some FRP tanks based on DION<sup>®</sup> 382 have contained sulfuric acid for over 40 years without problems.

However, in concentrated form (>76%), sulfuric acid displays reducing properties which makes it more aggressive toward FRP. The SO<sub>3</sub> associated with concentrated sulfuric acid has a very high affinity for water, and can actually chemically dehydrate polyesters or vinyl esters to yield a charred surface. Ironically, very concentrated or fuming sulfuric acid (oleum) is commonly handled by carbon steel or passive alloys.

Special concerns can arise in cases where there might be a transition in the sulfuric acid concentration. An example would involve combustion gas ducting where traces of sulfur trioxide are present. The SO<sub>3</sub> serves to raise the dew point, and owing to the affinity of SO<sub>3</sub> for water, the first drop which condenses may contain as much as 82% sulfuric acid. Fortunately, when this happens the acid becomes rapidly diluted, but the process must be carefully analyzed to be sure there are no areas where concentrated acid may be allowed to accumulate. Dew point corrosion tends to be a bigger problem for metals than for FRP.

## **Hydrochloric Acid**

HCl is a reducing acid which is very corrosive to carbon steel and most passive alloys. FRP on the other hand has provided exceptional service even at high temperatures and concentrations, up to the maximum commercial concentration of about 37% (23° Bè). Concentrated HCl should be kept below 110°F, but temperatures can go up to 200°F for the dilute or muriatic grades.

Prolonged exposure to hydrochloric acid typically turns the FRP to a green color, and the depth of this color increases with age. This is normal and is not a concern with a properly constructed corrosion barrier. Additionally, concentrated acid can induce reactions with glass reinforcement to yield wicking or blistering. This is due to an ion migration mechanism, along with reactions between HCl and soda ash present in E-glass which yields carbon dioxide, which in turn creates a blister. The blistering is a normal expectation for concentrated HCl especially at temperatures in excess of 100°F, yet FRP has provided extended service after the blisters have formed. However, the FRP should be inspected

frequently.

Inexpensive grades of HCl or muriatic acid are often produced as by-products, and at times may contain chlorinated hydrocarbons. Although HCl solutions are relatively dense, these hydrocarbons can be denser and at the same time display very low solubility. There have been cases where they may separate and accumulate at the bottom. Since many chlorinated hydrocarbons can attack FRP, care should always be taken in consideration of impurities.

## **Nitric and Chromic Acids**

Concentrated nitric acid and chromic acid are strongly oxidizing acids commonly encountered in metal plating, pickling, or ore processing. These acids can gradually attack FRP, and in extreme cases a yellow crust can develop along with simultaneous micro-cracking. In dealing with oxidizing acids, the same general precautions should be observed as if dealing with a bleach environment. A good, complete cure is very important.

Nitric acid concentrations of up to 15% are readily accommodated, but in dealing with concentrations of up to 50% there can be significant temperature limitations (see corrosion resistant tables). Since nitric acid is a powerful oxidizer, be sure to always heed the general precautions associated with general handling of nitric acid. Organic chemicals should never be introduced into the same tank where nitric acid is stored. Spills should be diluted and promptly cleaned, and sawdust should not be used for absorbing spills. Any NO<sub>x</sub> fumes should be properly vented.

Dilute chromic acid (5% or less) is readily handled, but the concentrated forms can attack FRP. Very dilute concentrations of chromic acid are ordinarily not oxidizing. The valency of the chromium also affects its properties, but the ordinary hexavalent form does not become oxidizing unless used in conjunction with a relatively high excess of acid. Thus, most situations involving chromic acid, such as plating liquors, also involves chromic with a mixture of other acids. FRP has a very good history with plating liquors, but the chromic acid based types are among the most aggressive (see corrosion resistance tables).

Most of the premium polyesters and vinyl esters are used with nitric acid, but if dealing with concentrated chromic acid, consideration should be given to DION<sup>®</sup> 797, which is a chlorendic anhydride based polyester with a dense structure which features exceptional oxidizing acid resistance.

## **Hydrofluoric Acid and Hydrofluosilicic Acid**

Hydrofluoric acid is actually a very weak acid, yet can be a very powerful oxidizing agent. As such it is commonly used in plating applications in conjunction with other acids. It also finds use in pickling, oil recovery, and refinery alkylation processes. Hydrofluosilicic acid (aka fluorsilicic acid) has similar properties, and is commonly used in water fluoridation and assorted industrial applications.

Premium resins have been used for HF concentrations up to 20% and hydrofluosilicic acid up to 35%. FRP has also been used for other fluorinated acids and salts, such as fluoroboric acid.

The ability for HF and related acids to attack glass is well-known. Most often, fabricators will use synthetic surfacing veils in these environments, but experience has been equally as good with C-veils as long as the corrosion barrier is properly constructed. Silica based thixotropic agents should not be used in these environments.

When considering FRP for HF or fluoride service it should be recognized that fluorides may induce crevice corrosion to stainless steels. Likewise, titanium can be corroded by fluorides even at trace levels.

## Organic Acids

FRP is routinely used with many organic acids, but some of these require special attention since they can have other chemical properties or solvating characteristics.

Glacial acetic acid (99+ % purity) can cause rapid blister formation and laminate deterioration. This is believed to be related to the solvent properties, since many thermoplastics will swell with the concentrated acid. When it is diluted below about 75% concentration FRP can be used quite successfully. Often FRP is favored with some forms of dilute acetic acid since it is not affected electrolytically to thereby pick up metallic impurities. Historically copper and stainless steel have been used with acetic acid, but much of the applications of acetic acid are related to fibers and other polymers which are sensitive to trace metal contamination. Often passive alloys are attacked by acetic acid due to its mildly reducing properties.

Strong organic acids, such as toluene sulfonic acid or sulfamic acids, can be accommodated with FRP, whereas they are often very corrosive to steel and many passive alloys.

Certain reducing acids or antioxidants, such as formic or oxalic acids, may also be used successfully with FRP, while passive alloys can be often attacked with concentrated forms of these acids

## Phosphoric Acid

Phosphoric acid is a reducing acid, which may attack metals, including titanium and other passive alloys, when in concentrated forms. It can also act as a sequestering agent with some metals. FRP has a long history of success with phosphoric acid at all concentrations, including superphosphoric acid.

Often phosphorous deposits (mainly calcium phosphate) occur in nature along with fluoride containing minerals, e.g., fluorapatite. Some technical grades of phosphoric acid may contain fluorides, which can influence the ability to digest glass. However, there has been no known case of fluoride attack to FRP in phosphoric acid applications.

## Perchloric Acid

FRP may be used to store stable solutions of perchloric acid of up to 30% concentration. However, if solutions are allowed to evaporate, concentrated perchloric acid becomes unstable and in some cases is subject to detonation. Care should be taken in dealing with venting, draining, or any other conditions which may allow stagnant areas of concentrated perchloric acid to form. Similar considerations apply to a variety of other bleaching agents, e.g., sodium chlorate (see bleach section).

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NaOH Concentration, wt%	Calculated pH
0.0004	10.0
0.0013	10.5
0.0040	11.0
0.0126	11.5
0.0400	12.0
0.1265	12.5
1.0000	13.4
2.0000	13.7
3.0000	13.9

## Alkaline

Ordinary polyesters are not resistive to basic or alkaline environments since the ester linkages of polyester are subject to hydrolysis. Once the resin is attacked, deterioration can be rapid, since strong bases can digest glass. Alkaline deterioration is very distinct and is characterized by a fiber bloom and a very “cheesy” appearance.

Isophthalic and terephthalic resins should not be used continuously in environments where the pH exceeds about 10.5, which corresponds to a very low concentration in the case of a strong base such as caustic. On the other hand, polyesters based on alkoxyated adducts of bisphenol-A, e.g., DION<sup>®</sup> 382 or DION<sup>®</sup> 6694, feature chemistry where the ester linkage is sterically hindered from hydrolysis. These resins have excellent alkaline resistance, with very good case histories.

Vinyl esters based on bisphenol-A epoxy also have quite good alkaline resistance, for example DION<sup>®</sup> 9100, 9200, or 9102. Care should be taken with vinyl esters based on novolac epoxy. The alkaline resistance of novolac resins is fair, but with strong bases at high temperature phenolate salts can form which lead to laminate destruction. This

deterioration of a novolac vinyl ester in caustic is often preceded by development of a pinkish color.

Many fabricators will employ a synthetic veil for alkaline environments, which makes sense in view of potential attack to glass. However, C-veil has also been used successfully, provided accepted practices are used for the corrosion barrier. Likewise, it is advisable to not use silica based thixotropic agents.

## Sodium Hydroxide

Sodium Hydroxide is a very strong base, which completely dissociates at dilute concentrations. Very low levels can give a high pH.

Beyond about 2% concentration, there is an equilibrium which exists between dissolved NaOH and a hydrated solid phase, but at higher concentrations the pH is very close to 14 for all practical purposes. Actually, very concentrated caustic solutions of caustic, e.g. 50%, are somewhat less aggressive to FRP than dilute concentrations (refer to corrosion resistance tables) due to the presence of solid phase caustic which seems to protect the FRP surface. In dealing with concentrations beyond 50% FRP is not recommended. Many steels and passive alloys can become embrittled by caustic at high concentrations and temperatures, and nickel is commonly used for caustic concentrates.

Care should always be given to impurities, especially if dealing with chloro-alkali intermediates, which may contain traces of chlorates or hypochlorite.

Caustic is often sold in the form of solid pellets or flakes, as well as in the form of 50% and 73% solutions. Very often these solutions are diluted before use in the process. The heat of solution for

dilutions is considerable, and care must be taken to ensure proper heat removal along with all other safety precautions recommended by the supplier.

Sodium hydroxide can form soda ash upon prolonged exposure to carbon dioxide from the atmosphere. For high purity applications, a slight amount of pressurization is sometimes used to keep air from infiltrating the tank. If so, the tank must be designed for this possibility. Likewise, NaOH solutions can display a high specific gravity which must be reckoned in the design.

## Potassium Hydroxide

Like sodium hydroxide, potassium hydroxide is a strong base and has many similar chemical properties to that of NaOH. However, KOH tends to be more aggressive than NaOH toward FRP. Refer to the Corrosion Resistance Charts.

## Calcium Hydroxide, Magnesium Hydroxide, Other Weak Bases

Oxides and hydroxides of alkali earths, such as calcium and magnesium, tend to be weak bases due to their limited solubility into water. Other compounds are weak bases due to their dissociation properties, such as sodium or potassium carbonates and bicarbonates. In most cases, the pH will be less than 10, but saturated lime solutions or residual lime in concrete may at times exceed a pH of 12, which can be high enough to significantly affect glass. Some less expensive isophthalic or terephthalic resins may be practical for use (consult chemical resistance tables), but if there are doubts about the expected pH or available alkalinity, then premium resins should be used, such as alkoxyated bisphenol-A fumarates or vinyl esters

Most calcium compounds will display inverse solubility properties, i.e., they can become less soluble as temperature increases. Common scale in hot water systems is an example. If saturated lime solutions are contained or piped by FRP equipment scale formation may be possible if the solutions are heated, and this should be recognized in the design. If the solutions are acidified or buffered, this will increase the solubility.

Certain heavy metal hydroxides encountered in ore processing, or electroplating, such as those of nickel, tend to have low solubility unless the solutions are acidified. By-and-large premium resins are quite suitable for these applications.

Weak or moderately alkaline solutions associated with Kraft pulping, such as black, green, and white liquors, are readily accommodated by the alkaline-resistant premium resins. In some cases, high cross-link density terephthalic resins, such as DION<sup>®</sup> 490, might be practical to consider, but this must be carefully reviewed to fully understand the range of conditions.

## Ammonia/Ammonium Hydroxide

Ammonia is an active compound which readily dissolves in water to form ammonium hydroxide, sometimes called aqua ammonia. It is a moderately strong base, and most commercial solutions are in the 10-12 pH range. The alkaline resistant premium resins are all suitable for practical use (refer to chemical resistance guides). Isophthalic and terephthalic resins should not be used.

Although ammonia has a high degree of solubility in water, solutions nonetheless have a distinct vapor pressure depending on concentration and temperature. Since ammonia is noxious, tanks are often kept

under pressure to minimize ammonia loss. If FRP tanks are used, the appropriate vapor pressure must be considered. Likewise, if tanks are not properly vented or pressure controlled and the tanks are cooled, ammonia in the vapor can dissolve to create a vacuum or negative pressure in the tank. An FRP tank is difficult to design for vacuum service, so the processing and storage operating procedures must be carefully reviewed.

Anhydrous ammonia (boiling point  $-33^{\circ}\text{C}$ ) is used in large volumes in the chemical and agricultural industry. It should not be used with FRP, other than in the preparation of dilute solutions of ammonium hydroxide. Adding ammonia gas to water can be hazardous, and this must be carefully reviewed.

## Lewis Bases

Many organic or inorganic compounds or their derivatives display reducing properties which can effectively make them function as strong bases. Examples include amines, quaternary ammonium salts, phosphines, and phosphites. Since some of these are corrosive to passive alloys, FRP at times is considered.

Amines by themselves can also function as powerful solvents, and ordinarily FRP is wholly not suitable other than for incidental or temporary containment. However, most amines are soluble in water, and it is common to employ solutions containing relatively low levels. Often premium resins may be used for aqueous solutions, but resistance is difficult to generalize and environments should be examined case-by-case.

Quaternary ammonium salts can be used with FRP (see chemical resistance tables), but the premium alkaline resistant resins are ordinarily suggested. The same applies to other Lewis bases, but once again, case by case examination is suggested.

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## Bleach

Bleaches are oxidizing agents, and those which are chlorine based are especially aggressive to metals. FRP has hence been used extensively in such environments, particularly in the pulp and paper industry. Bleaches are electrophilic and are active receptors of electrons from the materials which are to be oxidized. A potential electron source in an FRP laminate can originate with residual unsaturation resulting from an incomplete cure. Consequently, the resistance of composites to bleach environments can be greatly improved by ensuring the highest practical extent of cure. Post-curing is always suggested, and it is advisable to also consider the use of a high temperature co-initiator, e.g., tert-butylperbenzoate (TBPB), which can be used in conjunction with the regular curing agents in order to further increase the extent of cure. Air-inhibited surfaces are particularly susceptible to attack by bleaches, so the corrosion barrier should preferably be prepared on a mold surface, and a paraffinated topcoat is recommended for exterior surfaces that may come into incidental contact with the bleach.

BPO/DMA curing systems are sometimes advocated for FRP intended for service with chlorine based bleaches, since cobalt used in MEKP/Co/DMA systems can potentially react with chlorine or otherwise serve to promote oxidation-reduction reactions which accelerate the bleaching process. Although BPO/DMA cures can often yield improved results on a laboratory scale, there can be many practical problems when a BPO based cure is applied to actual shop or field fabrication. BPO crystals can be difficult to dissolve into styrene and are also difficult to uniformly disperse. This can lead to hot spots in the laminate, or in extreme cases may yield permanent under-cure. While BPO is usually found to

	<b>Oxidation Potential volts (Can be influenced by pH)</b>
Fluorine	3.06
Ozone	2.07
Hydrogen Peroxide	1.77
Permanganate ion	1.67
Chlorine dioxide	1.50
Hypochlorous acid	1.49
Chlorine	1.36
Bromine	1.09
Oxygen	0.40

offer appearance advantages, there is no evidence that it offers corrosion resistant advantages. Provided that a good extent of cure is achieved along with proper attention to construction of the corrosion barrier, Reichhold ordinarily suggests use of the more conventional and reliable MEKP/Co/DMA systems from the standpoint of practicality, preferably in conjunction with a high temperature co-initiator such as TBPB.

When stored at low temperature, bleaches such as sodium hypochlorite, chlorine dioxide, or hydrogen peroxide should be kept stable by avoiding conditions of pH, temperature, UV radiation, or any other factors which can activate the oxidation potential of the bleach. By-and-large, FRP has had a good history in the storage of such bleaching agents when they are stabilized. Nonetheless it should be recognized that many bleaching agents are inherently unstable and start to decompose as soon as they are made. This means that stability is a relative term which really means that the decomposition rate is slow for practical purposes. Some bleaches also require attention to the composite construction, so careful review should be made of the following considerations to specific beaches.

## Sodium Hypochlorite

Sodium hypochlorite is widely used in both dilute (about 5%) or more concentrated forms (10-15%) for a variety of household bleaching agents, swimming pools, textiles, water purification, and pulp bleaching. FRP has been used in processes associated with generation or storage of hypochlorite, as well as in related bleach plant equipment such as piping, caustic extraction, seal tanks, bleach towers, washer hoods & drums, dechlorinators, and scrubbers.

In the case of Kraft based pulp, hypochlorite historically has been used in the final brightening stages in association with chlorine, which is used in the first stage delignification steps of the bleaching operation. Its use is diminishing in view of trends or mandated use of elemental chlorine-free (ECF) bleaching processes which favor chlorine dioxide in conjunction with extended delignification technologies.

Most commonly, sodium hypochlorite is made by the direct reaction between chlorine gas and sodium hydroxide, although more active forms can be based on soda ash. The final concentration depends on the initial caustic concentration. Stability of the hypochlorite solution depends on concentration, pH, temperature, concentrations of certain impurities, and exposure to light. The pH or available alkalinity has a very pronounced effect, and the most stable solutions are in the 9.5-10.5 pH range, but for practical reasons it is ordinarily suggested to always keep the pH at 10.5 or greater (up to 12.5) when dealing with FRP. Resins with combined oxidation and alkali resistance are necessary, and include

vinyl esters and bisphenol-A fumarate polyesters, e.g., DION<sup>®</sup> 9100, DION<sup>®</sup> 382, DION<sup>®</sup> 9800, or DION<sup>®</sup> 6694.

Some people advocate the use of aromatically substituted halogenated resins, e.g. DION<sup>®</sup> FR 9300, for increased bleach resistance. The halogen at least theoretically stabilizes the resin or otherwise retards chlorination. The higher specific gravity will also have a tendency to physically reduce permeation. However, it is believed that good curing is one of the most important factors to consider for any given resin which might be selected.

Beyond concentrations of about 15% available chlorine, the pH can drop rapidly, which makes the hypochlorite very aggressive to FRP and other materials of construction due to formation of hypochlorous acid or active nascent chlorine. When preparing or storing concentrated solutions the circumstances must be carefully reviewed to ensure that the solutions are never over-chlorinated or otherwise deficient in excess caustic. At low pH, FRP will not be resistive to concentrated hypochlorite, regardless of the resin selected.

When producing or storing dilute hypochlorite solutions, the temperature should be kept below about 85°F. More concentrated solutions should be kept below 70°F and due consideration must be given to the heat of reaction. Often refrigerated storage is used. In the preparation of hypochlorite, the velocity of the incoming chlorine gas has been known to induce vibration, stress, or potential fatigue on the chlorination tanks, and this should be recognized in the design. Likewise, due consideration must be given to potential leaks in view of chlorine's toxicity.

When employed in the bleaching process of a pulp mill, the hypochlorite is activated by reducing concentration to 40 gm/l or less by means of dilution rings or towers, and the temperature is elevated by the brown stock and the associated heat of reaction. Concentration of active chlorine subsequently drops, but for acceptable life of the FRP it is advisable never to exceed 125°F if the FRP is associated with the active bleaching process.

Thixotropic agents based on silica should never be used in the construction or repair of composite equipment, or in the use of paraffinated resin exterior topcoats which may contact the bleach. Attack can be rapid from silica due to both alkalinity and oxidation effects. Due to the adverse effect of light on stability of hypochlorite solutions, any equipment intended for outdoor service should be exteriorly coated with a suitable UV absorber or pigment.

## Chlorine Dioxide

Chlorine dioxide (ClO<sub>2</sub>) usage has increased in recent years. It tends to be a more selective bleaching agent and yields brighter pulps without undue sacrifice of paper strength. Typically it is used in conjunction or in series with oxygen enhanced delignification processing.

Furthermore, ClO<sub>2</sub> significantly reduces the quantity of absorbable organically bound halides (AOX) along with chlorinated dioxins or furans. It also allows an overall tighter water balance, which serves to reduce aqueous effluents. For these reasons it is favored in elemental chlorine free (ECF) bleaching related to EPA integrated combined water and air pollution standards...the so-called cluster rules. In 1998 toxic air pollutants were regulated in 155 of the 565 US paper mills, and water discharges were regulated for 96 of these. All mills were additionally required to file notifications, and any expansions are expected to be specifically regulated.

Chlorine dioxide is ordinarily generated on-site by a variety of processes, such as the Mathieson process. Chlorate solution is prepared electrochemically from brine and then reacted with SO<sub>2</sub> in a series of generators, usually at 105°F or less. The ClO<sub>2</sub> containing gas is then scrubbed, absorbed into water or chlorate solution, and then placed into storage. The absorbing solution is chilled in the 40-65°F range, and typical concentrations are 4-10 g/l (10-25 g/l based on active chlorine).

FRP, among other materials, has been successfully used for generators, strippers, chlorate storage tanks, SO<sub>2</sub> piping, effluent tanks, absorbers, solution piping, and ClO<sub>2</sub> solution storage tanks. Often thermoplastic piping is used, such as PVC, CPVC, polypropylene, PTFE, or PVDF. Many times, the thermoplastic piping is externally filament wound with FRP for added strength. In some instances dual laminate FRP/thermoplastic tanks have been used as well.

There are other ClO<sub>2</sub> generation process, such as the Hooker process, which is based on chlorate solution, sodium chloride, and sulfuric acid. Once again, FRP has been successfully used in the various process components.

ClO<sub>2</sub> has been used at concentrations ranging from 4-10 g/l within C/D and D stage bleaching operations. Temperatures are preferably kept below 150°F, and like all bleaching operations, the lower the temperature and/or bleach concentration... the longer the FRP life. In some cases, the heat of reaction has raised temperature to as much as 190°F.

Modern ClO<sub>2</sub> bleaching often employs a very tall up-flow tube processing stage, wherein caustic washed pulp slurry at 6-12% concentration is transported upward and simultaneously bleached. The pulp enters at about 65°F, but the heat of reaction will raise the temperature considerably. This is a very demanding application for all materials of construction due to corrosion, high temperature, high pressures, and abrasion from the brown stock pulp. When FRP is attacked it may form a yellow so-called “butter layer” on the surface which can be abraded off to thereby expose more surface which accelerates attack. A soundly constructed corrosion barrier and structural layer are always necessary. DION<sup>®</sup> 6694 has some impressively good histories in up-flow tube applications. Often the up-flow tube uses a premium flame-retardant resin within portions of the construction.

<b>Equilibrium Ozone Concentrations in Distilled Water @ 760mm Hg</b>	
Volume Ozone in gas, %	Ozone in Water, ppm
1	3.3
4	13.1
6	19.6

### Ozone

Ozone is second only to fluorine in oxidation potential and is hence becoming increasingly used in diverse bleach applications such as water treatment, odor control, disinfection, sludge treatment, food processing, or pulp bleaching.

Ozone is generated on-site by an electric corona process. For air feeds to the generator, the O<sub>3</sub> concentration ranges from 2-4%, but with oxygen feed, the concentration is 6-15%. Apart from oxidation potential, ozone is regarded as safer

since the generation can be terminated quickly in an emergency. Temporary high doses of ozone, although quite irritating, are usually not fatal, as would be the case with chlorine, ClO<sub>2</sub> or many other bleaches. In the case of water treatment, the waters tend to clear and have better taste. Often ozone can disinfect certain strains of protozoan cysts or other microorganisms (including some viruses) which are difficult to kill with chlorine. In wastewater treatment, ozone also tends to be more effective in heavy

metal ion recovery.

Ozone will attack nearly all organic materials, including FRP. The attack on FRP is typified as a uniform gradual etching of the surface which gives a dull appearance. The rate at which this occurs depends on the concentration of ozone in the water phase, but since ozone is a very active oxidizing agent, any dissolved ozone gets rapidly depleted as it contacts the organic matter for which it is intended to be used. Most ozone related applications for FRP keep active ozone levels at less than 3 ppm in the water phase. Ideally, the operation should be well managed to avoid high levels of excess ozone; in fact this is necessary anyway to control ozone levels released to the atmosphere.

Currently, most ozonators tend to be inefficient due to the limited solubility of ozone into water. Thus, the actual concentrations in the water can be much lower than predicted from equilibrium. However, newer counter-current contactors are being introduced in the electronics and other industries. These types of units are expected to improve the dissolution of ozone and the overall efficiency of the process.

Stainless steel and other passive alloys are used successfully with ozone. The piping and associated sparging should be kept as far away as possible from FRP walls. Since the etching is gradual, it has been found that the life can be extended by periodically applying a fresh paraffinated topcoat to the surface in conjunction with Atrime<sup>®</sup> in order to obtain a good chemical bond to the exposed surface. Successful use depends on good planning, close control of the process, and regularly scheduled inspections and repairs.

In the case of pulp bleaching, ozone is receiving increased attention due to future emphasis on totally chlorine free bleaching technology (TCF). Since ozone has such a strong oxidation potential it can attack the cellulose more readily, which makes it difficult to maintain paper strengths or the selectivity necessary for brightness. Nonetheless, it still has a potential to be used on a supplemental basis with other oxidizers such as peroxides or ClO<sub>2</sub>. Often the ozonation is conducted under acid conditions. Although passive alloys have ozone resistance, there may still be problems with chlorides, or other process chemicals which might be associated with ozone bleaching, such as certain chelates. Thus there can still be a good role for FRP.

## Hydrogen Peroxide

Like ozone, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is becoming increasingly used as a chlorine-free bleach agent in water disinfection, wastewater, odor control, denitrification, hypochlorite reduction, and a variety of industrial processes. Not only is it an oxidizer, but in some cases it can serve as a reductant as well. In some processes the hydrogen peroxide is used in conjunction with ozone.

H<sub>2</sub>O<sub>2</sub> is supplied in a variety of concentrations such as 3%, 35%, 52%, and some grades as high as 70%. It can decompose to form water and oxygen gas, so most grades are stabilized with acetanilide or other organic compounds.

FRP can be used to store stabilized hydrogen peroxide at up to 30-35% concentration. Tanks should be well-vented and any exterior topcoats should be pigmented since UV light will readily decompose the peroxide. If the tank is to be used for dilution of any commercial grades, due consideration should be given to accommodate the heat of dilution in order to prevent excessive temperatures which can promote decomposition. Care must be taken to avoid any contaminants or alkali materials which can activate decomposition.

The activated peroxide can be corrosive to carbon steel since it is a source of oxygen, and the corrosion can be significant especially if dealing with sulfide or other sour waters. FRP can be a good substitute for the steel.

Hydrogen peroxide is finding increased use in pulp bleaching in part due to interest in totally chlorine free (TCF) bleaching. It is estimated that as many as 150 mills in North America employ some embodiment of peroxide bleaching. Usually this is done in conjunction with oxygen under high temperature alkaline conditions. Although passive alloys like austenitic stainless steel and titanium are ordinarily resistive to hydrogen peroxide, there can be severe attack at elevated temperature. This is especially likely if chlorides are present, which can be the case whenever the peroxide is used on a chlorine substitution basis. In the case of titanium, hot, strongly alkaline media can induce embrittlement at temperatures in excess of about 175°F. Thus FRP can find favor in many of these processes.

### Other Bleaching Agents

There are numerous miscellaneous bleaching agents used historically in the pulp, textile, and other industrial processes. Examples are sodium chlorate, sodium hydrosulfide, potassium perchlorate, potassium permanganate, and sodium hydrosulfite. FRP is widely used to store stable solutions of most of these compounds.

Special attention should be paid to chlorate, perchlorate, or perchloric acid solutions. When dissolved, these compounds can be quite stable but when dried to a solid form they can be extremely hazardous and subject to detonation in the presence of organic materials. This is possible, for example in ducting or vapor spaces, and the hazards can be irrespective of the material of construction for the process equipment. Care should always be taken in regard to spills, draining, venting, or any other conditions which may allow the bleaches to concentrate.

In the pulp and textile industry many other new bleaches are being used in efforts to improve bleaching selectivity and/or for environmental purposes. These include miscellaneous peroxygenates and Caro's acid, which is made from hydrogen peroxide and sulfuric acid. To further reduce the need for bleaching, technology is evolving in enzymatic delignification as well as in genetic engineering of plant species whose lignin structures are more amenable to decomposition. Again, FRP can find favor in these emerging areas.

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### Chlor-Alkali

Chlorine and sodium hydroxide are commercially co-produced by the electrolysis of brine, which also yields by-product hydrogen. Historically the most common types of electrolytic cells have been the mercury and diaphragm types. In the mercury cell sodium forms an amalgam that is converted to NaOH by treatment in a separate cell which co-produces hydrogen. In the diaphragm cell, 10-15% concentration NaOH is produced directly, but is separated and kept from reacting with the chlorine by a porous diaphragm usually made of asbestos onto mild steel. The mercury cells are disfavored for environmental concerns and high energy consumption, but they are used when high purity salt-free caustic is required, such as in Rayon production. Newer membrane type cells are now becoming more widely used.

Unlike the porous gas separators associated with diaphragm cells, the membrane cells employ fluorinated type ion exchange separators which are perm-selective and reject all negative ions. Caustic solutions from the membrane cells are more concentrated than those from the diaphragm cells and are essentially salt-free. Among other economic advantages, this results in less overall energy consumption in the plant.

Chlorine cells operate at temperatures of up to 200°F. The hot/wet chlorine within the cell and associated headers is a very aggressive environment to all materials of construction.

## Cell Covers and Headers

The mercury cells have used flexible covers, which rules out FRP construction, but diaphragm and membrane cells require the use of a rigid cover due to the use of dimensionally stable graphite anodes, or in newer designs, alloy titanium anodes. Originally the rigid cell covers were made of concrete, which typically lasts only 10-18 months. As the concrete erodes in service, debris tends to clog the diaphragm or membranes, which lowers efficiency and requires frequent repairs. This problem has been solved by the use of FRP. DION<sup>®</sup> 6694 has been one of the most widely used resins for the corrosion barrier, with an extensive service history. Lifetimes of 10 years are common and older cells are often relined and returned to service.

The cell covers are manufactured under well-controlled shop conditions. The mold is usually designed to avoid sharp contours to prevent corner cracking, and good surface smoothness and hard mold release agents have been shown to improve corrosion resistance. Silica based thixotropic agents should not be used. Most often a beefed-up corrosion barrier is used with 4 plies of 1½ oz mat. Proper wet-out and air release is important. If more than one veil layer is used, the fabricator must have good experience to lay in the veils without obtaining resin-rich areas subject to cracking. As is the case with all bleach or oxidizing environments, a good cure is essential, followed by post-curing at temperatures of at least 150°F. Preferably, a high temperature co-initiator (such as tert-butylperbenzoate) should be used in conjunction with the regular curing agents.

Care should be given to the choice of curing components. Many times a cobalt free cure system (BPO/DMA or DEA) is specified since cobalt can act as a redox coupling agent in the presence of chlorine. While there is some merit to this approach, there can be many practical problems associated with the use of BPO in large scale operation. BPO crystals are difficult to disperse and dissolve into styrene, and there have been consequential problems with hot spots and/or permanent undercure, which can cause rapid corrosive attack. There have been several reported cases where BPO cured cell covers deteriorated very rapidly and exposed the veil layer, which subsequently floated free into the anode liquor. BPO cures usually give excellent properties when used in the laboratory. Unfortunately, these advantages are usually not realized in the field, although there are indeed some fabricators who have good large scale experience with BPO. However, a conventional MEKP/Co/DMA cure system is a much more reliable and time-proven system, and if used properly can in reality give superior performance to a cobalt-free system.

Often a flame-retardant resin is used in the structural portion of the cell cover for incidental fire protection. DION<sup>®</sup> FR 9300 vinyl ester is a good candidate.

In some high amperage cells, there have been reports of accelerated corrosion on the analyte liquor exposed surfaces as well as on flange knuckles. Sometimes, the chlorinated brine piping may show similar effects. It is believed this is a combination of abrasion and electrolysis effects. More abrasion-

resistant synthetic veils can be considered.

Apart from cell covers, FRP has a good history with the associated headers and hot/wet chlorine piping. Many of the same fabrication considerations used for the covers would apply. Titanium is being used more commonly for the chlorine piping. Titanium holds up well provided the chlorine is wet, but if the chlorine is dry it can potentially induce dangerous ignition reactions with the titanium.

## Piping



Regardless of the particular cells or associated processing, there are basic similarities. In all cases, it is necessary to pre-treat the saturated brine feed to reduce hardness. Hydrochloric acid is also added to neutralize a portion of back-migrating NaOH. This minimizes the potential formation of chlorates, hypochlorites, and oxygen impurities.

Dilute saturated chlorinated brine from the cells is cooled and then de-chlorinated. The de-chlorinated brine (depleted brine) is then recycled to the salt dissolving tanks. A common problem with diaphragm or membrane cells is that they can leak as they get older. This can cause more formation of traces of hypochlorite or chlorate in the chlorinated or depleted

brines. At elevated temperature, these impurities are extremely corrosive and must be carefully considered, even though modern plants do their best to monitor and reduce hypochlorite impurities to low levels.

Although FRP has been used in chlorinated and depleted brine service, thermoplastic piping has been increasingly used. The choice of thermoplastic is a subject unto itself but has included PVC, CPVC, polypropylene, PVDC, PTFE, PVDF, ABS, and probably many others. Often FRP is used in an over-wrapped filament wound layer to give strength to the thermoplastic piping at the temperatures involved.

Metal piping is used, but apart from corrosion, metals can contaminate the caustic product. Iron, copper, and nickel impurities are especially undesirable.

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## Plating Solutions, Pickling Liquors, and Anodizing Solutions

FRP has been used for many years to accommodate hot acidic salt solutions associated with plating, electro-winning, or anodizing involving zinc, tin, silver, gold, lead, copper, nickel, platinum, and chrome. Often this is done at temperatures of 200°F or higher, so the premium resins with high heat distortion properties are ordinarily suggested. These resins also tend to have good dielectric properties.

As is the case with most materials, corrosion resistance life is a function of temperature and concentration. It is difficult to generalize aspects of the numerous plating solutions which might have been encountered, so it is always good to test solutions in advance if there are concerns. Temperature limitations given in the tables are only intended to be general guidelines. Some plating solutions, such as those associated with chrome, lead, or zinc may contain HF or fluoride salts along with other acid ingredients. Most fabricators will use synthetic veils for these solutions. Those solutions which employ

oxidizing acid, such as chromic acid tend to be the most aggressive.

Sound construction and corrosion resistance is important since many plating operations cannot tolerate debris or impurities in the plating solutions. If the operations entail use of large parts or ingots, care must be taken to avoid physical damage to the FRP construction.

Plating is usually done by a dipping operation. The baths have been made of total composite constructions, but they have also entailed laminate lined concrete or steel. Good surface preparation, priming, bonding, and surface cure are important. Laminate thicknesses of up to ¼" are commonly used.

Apart from the baths per se, plating operations require a great deal of ducting as well as scrubbers and mist eliminators. FRP is widely used. In almost any plating plant, acid drift will eventually induce corrosion to surrounding equipment, such as concrete flooring, grating, roofing, conduit trays, or cooling towers. It is very common to use polymer concrete, FRP protected concrete, fiberglass grating & handrails, and various pultruded composites for corrosion protection.

Picking is a commonly used process to remove rust or mill scale from steel and other metals. It is also used to affect a more uniform surface on the steel to minimize compositional gradients which can contribute to oxygen cell corrosion. Normally dilute sulfuric acid (2-5%) is used, but more concentrated acids are also used, such as 15% HCl. The temperatures range from ambient up to about 200°F. FRP has a long history of successful application.

## **Ore Extraction and Electro-winning**

Many modern and evolving ore extraction processes employ extractive metallurgy processes (sometimes called hydrometallurgy) where equipment contacts acids, organic solvents, and various combinations of inorganic salts. This generally involves converting the metal to a water soluble form which can be subsequently extracted or leached to a more highly refined product. Alternatively, the technology can be used to remove the more soluble waste or gangue minerals from the ore to yield an insoluble concentrate of the ore. After the ores are concentrated they can then be refined by a more conventional pyrometallurgical process.

Ores commonly suited for these processes have included bauxite, copper sulfide ore, gold, molybdenum, nickel, uranium, zinc, and rare earths. Leachants have included things like caustic, sulfuric acid, ammonia, soda ash, hydrochloric acid, nitric acid, and phosphoric acid. Purification methods include solvent recovery, electro-winning, and ion exchange. In the case of solvent extraction, the solvents are usually middle distillates, such as kerosene, or isodecanol. For precious metals, more expensive solvents are sometimes used.

Most often the ores are digested under acidic conditions, but some ore processing entails alkalinity. Examples involve gold (or silver), which employ cyanidation processes which employ sodium cyanide to form NaOH along with cyanoaurite. Aluminum metal is sometimes digested in caustic as part of some refining or anodizing processes. Alkaline resistant FRP has been used in such applications.

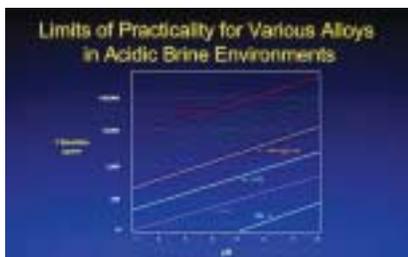
Many of these environments are extremely aggressive to even the most expensive alloys, yet moderately priced FRP has had a good history of successful use. As an example, DION<sup>®</sup> 382 has been used extensively in uranium and vanadium recovery at the Atlas Mineral plant in Moab, Utah, as well

as in a similar plant in Colorado. More recently FRP is being used in zinc recovery in the Salton Sea area of California. DION<sup>®</sup> resins have also been used for uranium extraction from phosphate rock in Florida. FRP has also been used in the production of alum from bauxite and sulfuric acid.

Related to hydrometallurgy is in-situ extraction. Instead of physically mining the ore, the ore is extracted by a series of injection wells. Then follows an acidic solvent extraction process, which in the case of uranium, involves sulfuric acid, isodecanol, kerosene, and traces of tertiary amine. DION<sup>®</sup> 382 has been used very successfully. Apart from the extraction equipment per se, FRP is used for most of the ancillary equipment, such as ducting.

Obviously, the types of environments used in these applications are diverse and difficult to generalize, but FRP is one of the best considerations for construction of process equipment.

## Brine



FRP is widely used in saltwater and brine applications, such as those associated with oil drilling. In general the resistance of FRP to inorganic and organic salts is good (see Corrosion Resistance Tables). Special attention should be given to chlorinated brines which may contain traces of chlorates or hypochlorites (refer to section on bleaching agents).

## Solvents

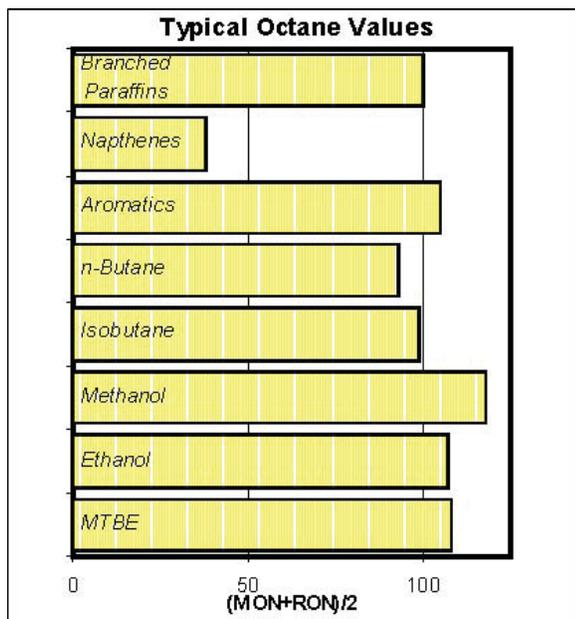
Since the resins used in FRP composites are organic themselves they are subject to swelling or severe attack by a variety of organic solvents. On the other hand there are many solvents to which FRP is quite resistive, such as gasoline, alcohol, middle distillates, and a variety of natural oils.

The mechanism of attack involves a gradual permeation of the corrosion barrier. If this occurs continuously or in accordance with Fick's law, failure will occur. On the other hand, many solvents will permeate the corrosion barrier to only a limited asymptotic extent (non Fickian diffusion), and as such the use of FRP is very practical. At times, swelling of the laminates can cause irreversible damage, but often the permeation can be reversed. For example, gasoline may slightly permeate and soften the corrosion barrier to give a reduced Barcol hardness, yet when the laminate is removed and allowed to dry, the Barcol will often recover to nearly the original value. This can vary with the particular solvent and the resin used, so each situation must be carefully considered.

As a general rule, the following classes of solvents are not practical to consider with FRP when at full concentration, other than for incidental or temporary containment:

- Chlorinated hydrocarbons, e.g., dichloroethylene, methylene chloride, chlorobenzene, chloroform
- Various acetates and acrylates, e.g., ethyl Acetate, ethyl acrylate, methyl methacrylate
- Certain aromatic hydrocarbons, e.g., benzene, styrene. Other substituted aromatics such as toluene or xylene can be accommodated by the higher cross-link density (see corrosion resistance tables). Blends of aromatics with other hydrocarbons, such as in what typifies gasoline, can also be handled.
- Acetone and other ketones

- Furfural and tetrahydrofuran
- Most amines, as well as dimethylformamide
- Carbon disulfide and sulfuryl chloride
- Liquid bromine



Some of these solvents, for example acetone, are water soluble. Such solvents are much less aggressive when in water solution and are often very practically handled by FRP. Some solvents have only slight solubility in water. Care must be taken in examining these environments, since the solvent (owing to its density) may phase separate from saturated solutions.

This could happen for example in ground water remediation, where small amounts of chlorinated degreasing solvents may have an opportunity to settle out over a long period of time, such that the bottom of the tank sees a localized concentrated amount of solvent which could damage the tank. The same can happen when dealing with impurities in some other commodity chemicals such as hydrochloric acid, which at times contains chlorinated hydrocarbon impurities.

Resins with high cross-link densities give the best solvent performance. These include most epoxy based vinyl esters, novolac vinyl esters, many epoxy resins, and DION<sup>®</sup> 490 terephthalic resin. However, isophthalic and other terephthalic resins are used very extensively in less aggressive solvents such as fuel oil. For good performance, the resins must be well cured, along with post-curing. If not prepared on a mold surface, a good paraffinated topcoat must be used.

## Gasoline and Alcohol Containing Fuels

Distributed gasoline is usually stored underground for safety and fire protection, as well as to make more efficient use of property assets. When steel underground tanks are used, corrosion is a major problem, especially in wet acidic soils. Most soils harbor sulfate reducing anaerobic bacteria (mostly of the genus *desulfovibrio*), which react indirectly with the steel to form sulfide and ferrous ions. This biologically induced corrosion is the most common cause of external corrosion to steel.

FRP has been used for many decades for the underground storage of steel, both as a glass-reinforced external laminate to steel, as well as in the form of total composite tanks. FRP tanks exhumed after many years of service have essentially shown no attack. By-and-large the earlier FRP tanks have been made of isophthalic resins, but trends toward higher octane gasoline, alternate fuel compositions, and specific federal regulations have led to the introduction of resins with improved performance at economical prices, such as DION<sup>®</sup> 490.

Gasoline is a mixture of various branched paraffin, olefin, naphthene (saturated cyclics), and aromatic

hydrocarbons which collectively boil in the 85-400°F range. To avoid knocking, it is necessary to maintain a sufficiently high octane value, and yet keep the Reid vapor pressure within a proper range. Octane values can vary with composition as well as chemical structure. Iso-octane (the reference for octane determinations) has a motor octane number of 100, while other constituents, such as naphthenes, are much lower. Therefore, refineries incorporate aromatics and butane into the gasoline to the extent which is necessary or economical. For many years, the additional approach was to add tetraethyl or tetramethyl lead to boost the octane values.



In the last two decades significant trends have occurred which have influenced the octane and constituency requirements of gasoline. Section 211 of the Clean Air Act of 1970 required reduced hydrocarbon emissions (hence catalytic converters), the phase out of lead and other toxins, and at the same time allowed waivers to use alcohols, which by themselves have good octane values and allowed some extension to production due to gasoline shortages. At the same time, Department of Transportation mandates required improvements in fleet economies, which have led to higher engine compression ratios and the need for good octane values on a larger scale.

The phase-out of lead took a long time, but by 1990 the use of lead was limited to only small volume of specialized gasoline. Meeting the octane requirements was a challenge. Refineries have gradually modified their operations to increase the yield through more severe fluid cat cracking and isomerization, but the workhorse process involves reforming, wherein hydrogen is catalytically abstracted from naphthenes and other hydrocarbons to produce high octane aromatics consisting of benzene, toluene, and mixed xylenes (BTX). In leaded gasoline the aromatic content ranged from 15-25 volume percent, now averages an estimated 32%, and in excess of 40% for super premium grades. Since aromatics tend to be more aggressive than other hydrocarbon gasoline constituents, it was felt that improved resins should be considered, which prompted Reichhold to initiate evaluations and qualifications.

Increased usage also began of alcohols as well as methyl-tertiarybutylether (MTBE), which is made in the refinery from methanol and isobutylene. Each has a very good octane rating, but also serves to reduce carbon monoxide and other hydrocarbon emissions. Of course there are some down-sides to the use of these fuels insofar as drivability and other aspects are concerned, but they have been largely accommodated. When the Clean Air Act was amended in 1990, the use of alcohols, MTBE, or other oxygenated fuels was actually mandated to contain about 2.7 wt% oxygen in 41 US cities. Lately, however, MTBE has received controversy due to its water solubility which can lead to groundwater contamination, and MTBE is expected to be gradually phased-out, and will quite likely be largely replaced with ethanol and increased refinery alkylate levels. In a nutshell, these changes have made it difficult to plan for the best resins to use to accommodate reformulated gasoline in the future, but superior cross-link density resins will receive favored attention.

Apart from air quality issues which affected gasoline consistency, leaking underground tanks and resulting ground water contamination issues led to adoption of federal regulations (40CFR280) for leak detection, monitoring, reporting, and corrosion protections of underground petroleum tanks. Specific programs were outlined with a compliant deadline of December 1998, although it is believed that many tanks are still not in compliance.

The most germane aspect of 40CRF280 was that the tanks must feature cathodic protection of other suitable corrosion resistance. In the case of FRP wrapped steel tanks they must conform to industry standards such as UL-1746 or ACT-100 of the American Steel Tank Institute. For total FRP construction they must conform to the requirements of UL-1316.

UL-1316 is a very comprehensive standard and involves accelerated testing at 100°F of FRP in a variety of fuels ranging from toluene to various methanol and ethanol blends with Fuel-C (a 50/50 mixture of toluene and iso-octane). Flexural retention and appearance properties are monitored, and in most solutions a 50% minimum is required after 270 days of exposure.

Conventional isophthalic resins would fall short of the some of the UL-1316 requirements. Thus much focus was given on higher cross-link density resins such as novolac based vinyl esters. Since novolac resins are expensive, Reichhold also introduced DION<sup>®</sup> 490, which is an economically priced high cross-link density terephthalic resin. Basically, it was found that DION<sup>®</sup> 490 held up very well as shown by some of the typical data below. It has been approved by Underwriters Laboratories as conformant to UL-1316 for a variety of manufacturers of composite tanks.

The appearance of the DION<sup>®</sup> 490, after prolonged exposure to UL-1316 fluids remains good. It was also found that when removed from solution, the Barcol values can recover much faster than those of vinyl esters. Apart from novolac vinyl esters, ordinary epoxy based vinyl esters were tested extensively. By-and-large these vinyl esters retain very good appearance, yet retention of flexural properties are often sub-standard.

In the case of FRP over-wrapped steel tanks, a variety of isophthalic polyesters are approved, such as Reichhold's PolyLite<sup>®</sup> 33402-00. The linings are applied promptly to blasted steel, and are usually of chopped glass construction of about 100 mils thickness, with a paraffinated topcoat. Some manufacturers use a design where the over-wrap is not bonded to the steel, such that the small resulting gap serves as part of the leak detection scheme.

Most steel tanks fail from external soil corrosion, but internal corrosion is sometimes addressed. Saline water can accumulate on the bottom of the tank where it can be corrosive. Even though the tank bottom would contain low levels of dissolved oxygen, the frequent filling of the tank allows some oxygen infiltration. Oxygenated fuels may also influence corrosion. Many times debris and other hydrocarbon sat the bottom of a steel tank may induce corrosive damage. For example, a penny dropped into a steel tank can induce galvanic corrosion of the steel to generate a sizable hole.

More data and detailed information on gasoline applications can be obtained by contacting us directly at **corrosion@reichhold.com**, **www.reichhold.com/corrosion**, or **1-800-752-0060**.

## **MTBE**

Methyl tertiarybutyl ether (MTBE) has throughout the 1990s been a common additive to gasoline, especially in winter months. It is made in the refinery from methanol and isobutylene. MTBE features a good octane value and when blended with gasoline gives good driving performance. Its use became widespread when oxygenated fuels were mandated under the 1990 Clean Air Act Amendments, since it reduced CO and hydrocarbon emissions.

A down-side has been that MTBE is more water soluble than other gasoline constituents, and leaks can travel a long way through the groundwater supply. Critics also argue that the emission reductions may

not be actually as large as first portrayed. Consequently, California is expected to ban its use, and this may begin nationwide. However, this phase-out (if it occurs) could take a long period of time. In the meantime, there is speculation that MTBE will be largely replaced by ethanol and increased amounts of refinery branched alkylates.

Resins such as DION<sup>®</sup> 490 are extremely resistant to 100% MTBE as well as to gasoline which contains MTBE. Some refiners have reported that MTBE will attack elastomers, such as Viton, so this must be considered in selection of gasketing materials.

## Fuel Oil, Middle Distillates, and Aliphatic Hydrocarbons

Middle distillates, such as #2 fuel oil, jet fuel, lubricants, and kerosene, have been stored extensively with FRP. Most often, these are accommodated by isophthalic and terephthalic based resins, but the more premium resins are used if dealing with some residual fuels which require heating to keep the oil at a tolerable viscosity.

A very common application involves the bottom lining of large above ground fuel tanks, some of which are as large as 3 million gallons. Water and other saline raffinates, due to their higher density, can settle to the bottom of the tank where they can induce severe oxygen cell corrosion/tubercle formation to steel, especially if they contain sulfur. Laminations range from 30-100 mils, depending on the fuel and age of the tank. The steel surface must be blasted, repaired, and free of chlorides. It should then be promptly primed and then laid-up with the FRP. When done properly, these tank bottoms have lasted a long time. Often it is difficult to schedule such repairs in a tank farm, but it is advised not to do the linings when temperature drops below about 50°F. Good cure and application of a paraffinated topcoat are important to obtain maximum corrosion resistance. Since the metal represents a conductive heat sink, high reactivity resins which can yield high exotherms are advantageous to consider. An example is DION<sup>®</sup> 490, which also gives excellent resistance to various fuels, including gasoline.

New and proposed regulations relating to above ground tanks are introducing new corrosion problems for steel, and this may afford more future opportunities for novel applications of FRP. For example, tanks now must usually employ a leak detection system, which often entails retrofitting older tanks with a new steel bottom, while allowing the older bottom to serve as the containment barrier. It has been reported that in some cases the old bottom will shield the newer bottom from impressed current galvanic protection, and as such will accelerate corrosion to the steel. Alternative bottoms based on FRP composites have been suggested. Some studies suggest that as much as 25% of the approximately 1-1.2 million above ground petroleum tanks currently experience some type of leakage.

The Clean Air Act Amendments of 1990 have placed restrictions on floating roofs commonly used for large fuel storage tanks. Consequently, these tanks are fitted with large geodesic covers made from either aluminum or FRP. In some cases it is advantageous to rapidly monitor and alert to strain or ruptures which might occur due to tank settling from a leak, or from seismic activity. Some FRP composites equipped with strain gauges or microprocessors (so-called smart composites) have been suggested. Field fabricated FRP tanks have evolved to large sizes; Some field fabricated FRP tanks and other process equipment have been made in excess of 50 feet, and many industry specialists feel that the technology exists to make tanks in excess of 100 feet in diameter. Compared to steel, this gives the advantage of seamless construction along with inherent corrosion resistance.

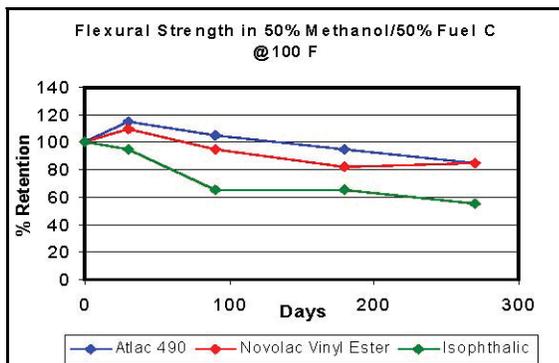
Aliphatic and most cycloaliphatic and naphthenic hydrocarbons can be accommodated by FRP. Examples include naphtha, hexane, or cyclohexane (consult corrosion resistant tables). The vapor

pressure of these fluids must be duly considered in venting or possible pressure requirements. FRP is also suitable for use for various synthetic oils, such as hydraulic fluid. It is also very well suited for many naturally derived oils such as tall oil, castor oil, corn oil, etc. Consult the section on FDA and USDA requirements, if applicable, for some of these materials.

## Alcohols

FRP is very resistive and widely used for alcohols and alcohol/fuel mixtures. Generally, the higher the chain length of the alcohol, the less aggressive it becomes. Alcohols are water soluble, and FRP is often favored over metals when dealing with aqueous solutions. Sometimes the effects of methanol on metals are surprising. For example, titanium is resistive to many materials, yet reports have been made that it can be attacked significantly by anhydrous methanol.

Methanol and ethanol deserve special attention due to their wide-scale industrial use, along with their increasing use in reformulated gasoline. Apart from their use in gasoline blends, methanol by itself makes a good fuel, and may be used in future automobiles specially designed for methanol.



It takes less air per unit volume of piston displacement to burn methanol, which can improve the power output and efficiency. Furthermore, methanol has a very high octane number, which can allow high compression ratios to improve engine efficiency. It is also clean burning, and there has even been some work done with methanol to improve the Cetane rating of diesel fuel. Some fuel cells being designed for electric or hybrid vehicles are designed to operate directly on methanol, with potentially high efficiency. Methanol has the further advantage that it can be made from carbon

monoxide and hydrogen associated with the gasification of coal, an abundant US energy reserve. In the case of ethanol, it can be made synthetically as well as by fermentation processes involving grain or other organic matter. Many people expect ethanol to largely replace MTBE in many gasoline blends, and already accelerated production is planned.

Most isophthalic and terephthalic resins, as well as the more premium resins, are suitable for anhydrous methanol or ethanol (refer to chemical resistance tables). If dealing with alcohol/gasoline blends, DION<sup>®</sup> 490 is suggested. Review should be made of vapor pressure data to ensure that any tank is properly designed or vented.

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## Water

FRP is used very extensively in contact with many grades of water. Most applications involve general purpose resins, but if dealing with hot water, more chemically resistant resins with appropriate heat distortion properties must be used (consult chemical resistance charts).

Unlike the case of metals, higher salt or electrolyte content represents less potential attack to FRP. This is because dissolved salts diminish ion migration effects which can allow reactions with the fiberglass reinforcement. Distilled water is actually more aggressive than tap water, and the distilled water can

effectively act like a solvent.

Permeation problems are especially likely with gel-coated decorative laminates, such as used with boat hulls. If the resin barrier is permeated, blisters can form when gas is trapped behind the gel coat layer.

Acids can contribute to this effect due to reactions with residual soda ash in E-glass, but higher pH levels can affect the hydrolytic stability of ester linkages in the polyester. The specific isomer used in general purpose polyesters can affect water resistance, and the order of improved resistance is terephthalic > isophthalic > orthophthalic. In marine applications, excellent resistance to blisters has been obtained with skins made of DION<sup>®</sup> 9800 or those of vinyl esters, such as the Reichhold Hydrex<sup>®</sup> line. In industrial applications, gel coats are of course not used.

Temperature and density of glass construction can greatly affect the permeation rate. In general, resins which display good alkaline resistance, such as DION<sup>®</sup> 382, will also display good resistance to water permeation.

## Potable Water

Potable (drinking) water has been a longstanding use for FRP. Apart from corrosion resistance which prevents damage or rust tastes, FRP surfaces are smooth to reduce areas which may harbor growth of algae or microorganisms. FRP can also avoid problems with certain potentially harmful trace metals.

The most important considerations for potable water is to use a resin with a composition deemed acceptable from a health or regulatory standpoint. The curing technique is extremely important, along with a good extent of cure to minimize styrene and other compounds which can infiltrate the water. Apart from resin selection, the general considerations are:

- Use enough catalyst to achieve a good cure, yet try to minimize the use of MEK peroxide, since some of the catalyst plasticizers, such as dibutyl phthalate, are water soluble. This mainly involved using a resin which is not overly inhibited.
- In addition to the normal curing components a high temperature co-initiator, such as TBPB (tertiary butylperbenzoate) is suggested at a typical level of 0.5%. The resin should be post-cured with hot air (180-200°F) for 4-8 hours, or with hot water at 150-180°F (or steam) for 6-8 hours. Before placing the tank into service the inside should preferably be steam cleaned with a wand type nozzle with an exposure time of about 5 minutes.
- The surface should then be washed with a warm non-ionic detergent and thoroughly rinsed before placing it into service.

Standards relating to drinking water have long been under the domain of federal and state environmental authorities, along with independent organizations such as Underwriters Laboratories (UL), National Sanitary Foundation (NSF), American National Standards Institute (ANSI) and the American Water Works Association (AWWA).

Cure System, wt. %				Secondary	% Residual
% Cobalt	MEKP	TBPB	Post Cure	Steam Treatment	Styrene
1.0	2.0				3.55
1.0	2.0		4Hrs @100C		0.06
1.0	2.0		4Hrs@100C	15 minutes	0.06
1.0	2.0			60 minutes	0.05
1.0	2.0	0.5			2.21
1.0	2.0	0.5	4Hrs@100C		0.01
1.0	2.0	0.5	4Hrs@100C	15 minutes	0.01
1.0	2.0	1.0			2.50
1.0	2.0	1.0	4Hrs@100C		0.01
1.0	2.0	1.0	4Hrs@100C	15 minutes	0.01
1.0	2.0		15 min@300F/4Hrs@100C		0.03
1.0	2.0	0.5	15 min@300F/4Hrs@100C		0.01
1.0	2.0	0.5	15 min @ 300F	60 minutes	0.01
1.0	2.0		6 Hrs @80C		0.11
<b>Effects of using high temperature co-initiator in conjunction with post-curing. (DION® 4010)</b>					

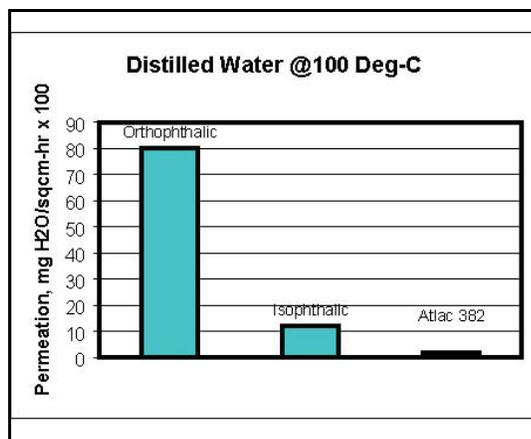
With the passage of the federal Clean Drinking Water Act, standards have become more stringent as well as more complicated to understand. Even though many certified standardized tests are used, the emphasis is now on risk assessment, where components and fabrication methods are scrutinized by third parties, such as NSF. The risk assessment involves not only resin constituents and extractables, but potential toxicity, mutagenicity, and carcinogenic aspects.

Increasingly, states are adopting the requirements of ANSI/NSF Standard 61. Currently DION® Impact 9102-00 holds a certified listing for use as a barrier material in accordance with Standard 61. This relates to tanks >10 gallons or piping > 6 inches in diameter at ambient temperature. Among other things, the requirements entail post-curing for 4 hours at 160°F, followed by 2 hours at 180°F.

Additionally DION® 9100 vinyl ester as well DION® 6631 series and Polylite® 33433-01 isophthalic

resins, are approved in accordance with British Standard BS 6920. This standard is very stringent and tests effect of taste, appearance, growth of aquatic microorganisms, effects of organic extractions (monkey kidney cell vero), and trace metals. DION<sup>®</sup> 382 and DION<sup>®</sup> 9800 have also been approved by in Norway by Folkehelsa for use in drinking water applications involving North Sea oil platforms and ships.

## Deionized Water



Distilled and deionized water can effectively be a power solvent, and special attention must be given, especially to those applications involving high purity or high electrical resistivity deionized water, such as might be associated with the electronics industry, steam generation, or certain pharmaceutical applications. These systems employ sophisticated mixed cationic and anionic stratified ion exchange systems.

Even though these are demanding applications a variety of Reichhold's products have been used in deionized water applications where resistivities are maintained up to 17-18 mega-ohm/cm. Most of the case histories have involved DION<sup>®</sup> 490 terephthalic resin and DION<sup>®</sup> 4010

flexible bisphenol-A fumarate, but other resins may be used. A very good cure must be obtained, and in general the cure and fabrication techniques are similar to those of potable water (see potable water section). In addition, some systems may require periodic temporary high dosage hypochlorite treatment for disinfection, and if so a resin with appropriate hypochlorite resistance must be used.

Ozone is also used at times. Glass can contribute conductive ions like sodium, which can affect the purity, so a good corrosion barrier should be used, and no silica containing thixotropic agents or fillers should be used. Synthetic surfacing veils are commonly used for corrosion barrier construction. In some DI water applications, such as steam generation, there are usually stringent limitations on dissolved silica. In nuclear applications, any trace metals which are subject to neutron activation are also important to control.

If a closed loop system is used it is expected that any FRP storage tanks or piping will be used in conjunction with appropriate maintenance devices, such as organic polishers, ultra-filtration, nitrogen blanketing, and blow-down.

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## Food and Agricultural

### FDA Compliance

Resins used for repeated contact with food items must meet the requirements of FDA Title 21, CFR177.2420, which pertains to thermosetting resin composites. Strictly speaking, this is not an approval, but entails using resins and curing agents which are listed in §177.2420, since when properly used these ingredients are judged not to introduce undue health risks. It is strictly the responsibility of the composite manufacturer to ensure all of the relevant FDA requirements are met.

DION<sup>®</sup> 382, DION<sup>®</sup> 4010, DION<sup>®</sup> 6631, and DION<sup>®</sup> 6334 are resins which comply with the FDA formulation guidelines. The fabrication procedures are the same as those which generally apply to potable water (see potable water section). The main features involve good curing, post-curing, use of a co-initiator like TBPB, and properly washing the equipment before placing it into service.

In the dairy industry, the 3-A Sanitary Standards Program has been jointly developed by a number of agencies to consider materials exposed to dairy products. Specific approval procedures should be investigated by the fabricator. Historically, various DION<sup>®</sup> 382 and DION<sup>®</sup> 4010 have appeared on the lists of approved materials.

FRP has also received a variety of international approvals for food related applications. The standard scans vary significantly. For example, DION<sup>®</sup> 490 is approved, without objection, to its use in food packaging and utensil applications by the Central Institute for Nutrition and Food Research of The Netherlands.

### USDA Requirements

USDA approvals must be petitioned directly from the USDA by the composite manufacturer. Typically, those resins which comply with the requirements of §177.2420 are easily approved.

The meat Inspection Division of the Department of Agriculture also approves applications on an individual basis, but again the approvals are ordinarily straightforward as long as the requirements of §177.2420 are met. DION<sup>®</sup> 382 has been used in meat processing, usually in such items as brine tanks.

Many meat and food processing operations require periodic disinfection with bleaching agents or caustic. They may also be subjected to periodic steam cleaning. The premium FDA compliant resins, such as DION<sup>®</sup> 382, are well-suited.

### Beer, Wine, and Other

FRP has an extensive history in the storage and manufacture of fruit juices, wines, and beer. The requirements vary throughout the world, so it is important to understand them on an individual basis.

The same procedures as apply to FDA applications should be followed. Even so, in discriminating applications like wine, taste is very important and can be influenced by factors difficult to measure by other means. Nonetheless various isophthalic and terephthalic resins as well as DION<sup>®</sup> 382 have been used in wine and beer applications. For example, DION<sup>®</sup> 490 (high crosslink density terephthalic resin) has been determined to be entirely suitable for wine storage by the Wine Laboratories Ltd. of London. Most of the beer related applications have involved steep tanks.

In the case of fruit juices, liquid SO<sub>2</sub> or other reducing agents like sulfites may be used to control color or to inhibit fermentation. If SO<sub>2</sub> is to be used, it must be injected at a point where no liquid may temporarily settle and subsequently evaporate upon any FRP surface.

### Duct and Scrubbers

FRP is frequently used for large diameter ducting and scrubbers, not only for its corrosion resistance, but also for properties such as noise dampening, good strength/weight ratio, low thermal conductivity, and electrical insulation.



Often FRP ducting can accommodate chemicals or temperatures which might otherwise be too aggressive in their concentrated or liquid states. This is because there is ordinarily a good deal of air flow which serves to keep the materials at low concentration. Even with unusual oxidizing agents, such as found in the electronics industry, products like DION<sup>®</sup> FR 9300 have displayed excellent ducting service.

Solvents and other volatile materials are not very aggressive in gaseous form, and in most cases the concentrations correspond to a dew point which is well below the normal operating temperature of the duct. When considering the venting of vapors it is always advisable to estimate the dew points to be sure the duct remains warm enough to prevent condensation. Usually this is not a problem, unless the vented gases in the ducting are subsequently exposed to very low temperatures, or when dealing with high boiling impurities, such as tars, which may tend to accumulate in the duct.

Drift or splashing might occur at times, especially in acid plating or pickling operations where large parts are being continuously moved. Corrosion resistance to such possibilities should be considered.

In most cases, a key consideration to ducting relates to flame, self-extinguishing properties, fire, or smoke in the event of accidental fires. When a fire begins in a duct it can propagate faster due to air flow associated with either forced or natural drafts. For this reason, brominated flame-retardant resins, such as DION<sup>®</sup> FR 9300 are used. These resins burn very slowly when exposed to a flame and can self-extinguish when an external flame is removed.

Flame spread properties are usually tested in accordance in the ASTM E-84 fire tunnel although many insurance underwriters or testing agencies may have their own specific designation or embodiments of the tunnel test. For example, Underwriters Laboratories version of the test is designated UL-723. Flame spread is a relative index and basically represents the rate at which the testing material burns in comparison to a reference material, usually red oak. The long-standing Uniform Building Code (UBC) requires a Class I flame spread rating of <25. A number of Reichhold's brominated resins conform to Class I requirements. Most of these resins require the addition of a few percent of antimony trioxide or pentoxide, which acts in synergy with bromine to suppress flame propagation. Others, such as DION<sup>®</sup> FR 7767 and the soon to be introduced DION<sup>®</sup> FR 9310 series can meet a Class I flame spread without use of antimony based synergists.

Self-extinguishing properties are ordinarily measured by UL-94, which involves measuring the time for a flame to extinguish (usually a few seconds for FR resins) once a flame is removed. Of course, specific tests do not necessarily simulate every possible actual fire situation, but the industry tries to do its best to give proper attention to public safety while still benefiting from the corrosion resistance and other properties of the FRP ducting. Often self-extinguishing properties are the most desirable properties, since they can serve to prevent the evolution of fires.

Many standards, codes, and evaluation procedures have evolved pertaining to FRP ducting, and many of these are subsequently adopted or relied upon by government and regulatory agencies. A common one is NFPA (National Fire Protection Association) Code 91, but other evaluations, specific designs, and procedures are set forth by Factory Mutual and ICBO (International Congress of Building Officials) Evaluation Services. Factory Mutual considers the use of FRP ducting with fusible-link fire-

stop dampers which close off the air flow automatically in the event of fire. ICBO considers the use of internal fused automatic sprinklers. All of these systems give due recognition to the UBC requirements.

The big disadvantage to flame-retardant resins relates to smoke generation. The same mechanisms which are responsible for slow flame spread or self-extinguishing properties will also yield a higher smoke density due to incomplete combustion at the flame front which gives carbon black and other colloidal pyrolysis products. The smoke density is measured optically by the same tunnel associated with ASTM E-84 flame testing, and is also measured by a smoke chamber, such as described by NBS method 258 or ASTM E-662.

In some cases, toxicity of the combustion products is also an issue. Numerous ways have been used to evaluate toxicity, but a common one (so-called Pittsburgh Protocol) involves monitoring the amount of material which must be burned to induce mortality (usually 50%) of a mice population. In these tests, the predominant lethal gas is carbon monoxide, which also occurs from wood or other common building products.

Smoke generation can often be the most hazardous feature of a fire, and the UBC specifies a smoke density of 50 or less for many building products, as measured by ASTM E-84, including ducting which runs through concealed spaces. Often (but not always) this smoke density requirement is relaxed for outdoor installations (such as in sewage treatment plants), high elevations, or where there might be sufficient escape routes. However, none of these requirements can be generalized, and in the final analysis approval ordinarily rests with the local fire marshal, regardless of the standards which might otherwise be met by the installation.

Low flame spread laminates can yield smoke densities typically in the 500-1000 range. This can be reduced to <450 by use of fillers, at times in conjunction with use of methyl methacrylate monomer added to the resin mix. Data described in the product bulletin for DION<sup>®</sup> 7704 will illustrate this.

A practical solution to obtaining low smoke generation is to paint the outside of the duct with a thick coating of intumescent paint. These are usually phosphorous containing and have the property of swelling and ablating during a fire to seal off the flame front. This allows achieving <50 smoke density, and more details can be seen in ICBO Evaluation Report 4055 associated with Class V ducting in conjunction with internal automatic sprinklers. These intumescent paints have poor corrosion resistance and should not be used for outdoor installations, but as previously noted, the smoke requirements are often relaxed for outdoor installations. DION<sup>®</sup> FR 9300 has been listed by ICBO as a conforming resin when used for Class V ducting as described in ICBO Evaluation Services Report 4055. More details can be obtained at [www.reichhold.com/corrosion](http://www.reichhold.com/corrosion), [corrosion@reichhold.com](mailto:corrosion@reichhold.com) or by calling the Reichhold corrosion hotline at 1-800-752-0060.

## Flue Gas Desulfurization



FRP has been used extensively in chimney liners exposed to sulfur dioxide and sulfur trioxide. Wet scrubbers and ancillary equipment associated with flue gas desulfurization processes can represent extremely corrosive environments to carbon and stainless steels, whereas FRP is quite resistive.

Since accidental fires can occur, brominated flame-retardant resins are commonly used for stacks. Fires can be

accelerated in a stack due to the draft which develops. Coal tars or pitch which may accumulate can contribute to the fire, but this can be the case regardless of the stack construction. Calcium sulfate or other hydrated deposits may retard fire propagation.

Normally flame-retardant resins such as DION<sup>®</sup> FR 9300 are used in these applications to reduce the potential for fire, but other high temperature resins such as DION<sup>®</sup> 6694 or DION<sup>®</sup> 490 will handle this environment. Resins having high temperature properties are usually selected to accommodate uncontrolled temperature excursions that can occur if there is a loss of quenching water. FRP can withstand temperatures of up to 350°F without serious impairment of the structural properties and can operate at up to 220°F on a continuous basis.

FGD systems were first introduced upon promulgation of the 1970 Clean Air Act, after which about 150 systems were installed in the United States. In 1990 the Act was amended (CAAA), and Title IV of the amendments deals with the specific acid rain precursors, SO<sub>2</sub> and NO<sub>x</sub>, it was broken into two phases: Phase I began in 1995 and was directed at 110 specific utility companies. Phase II began in 2000, and calls for sulfur dioxide to be controlled to less than 1.2 lbs./MM Btu. There are 785 utility companies affected in Phase II, and this involves in excess of 2100 stations.

A novel feature of the CAAA is that it represents a departure from traditional command and control strategies. Utilities can meet the requirements in ways which are ostensibly designed to be the most economical. Installing scrubbers is one of the approaches, but most company decisions at the end of the 20<sup>th</sup> century focused on other options, such as use of lower sulfur coal or allowance trading. Critics argue that only FGD affords the Best Available Control Technology (BACT). They also argue that Title IV does not address air toxin issues, which are better accommodated by scrubbers than by other options. These environmental factors, along with the current shortfall of generating plants, are expected to accelerate power related applications of FRP.

Although there are many embodiments of the various processes, most commonly they involve the ultimate conversion of the SO<sub>2</sub> to calcium sulfite or sulfate sludge (or by-products) by absorption and reaction with limestone, dolomite, or calcined lime. Within the scrubber, SO<sub>2</sub> is selectively absorbed by active sulfite, bicarbonate, and carbonate ions to form bisulfite ion. Due to the fact that combustion gas contains free oxygen associated with the level of excess air used for combustion, much of the bisulfite is effectively converted to dilute sulfuric acid. Most scrubbers are operated in the 4-5 pH range, but excursions as low as 2 have been reported. If pH is allowed to rise about 5.5, then scaling can become a problem, and an elevated pH also serves to reduce solubility of the calcium based absorbent.

The acidity combined with free oxygen represents a very aggressive environment to carbon steel, and steel cannot be used unless lined with rubber or a composite coating. There has been good experience with Flakeglass coatings, provided the steel surface is properly blasted to a high profile (6 mil. gives the best results). The coating must also be properly applied and spark tested. Total FRP construction has also been used instead of lined steel.

Stainless steel is also used in FGD, but the big problem with passive alloys is their inherent lack of resistance to chlorides which accumulate in the system. These chlorides originate mainly with make-up water to the system, which is necessary to compensate for the net evaporation which occurs when the flue gas is simultaneously scrubbed and humidified. Due to restrictions on blow-down and aqueous effluents, the chlorides levels can be quite high, and levels around 15000 ppm are not unusual. Chlorides, fluorides, and other salts may also enter the system from coal fly ash.

High chloride concentrations in conjunction with acidity make stainless steels very subject to stress corrosion. Usually only expensive, high nickel content stainless steels, including Haynes C-276, are used in FGD systems (see the Alternate Materials Section). Stainless steels are also subjected to intergranular corrosion, especially in weld areas. Even though welding is carefully controlled and inspected, there have still been enormous problems with welds in FGD equipment. Crevice corrosion has also been reported from localized oxygen-starved fly ash deposits, as well as from biologically induced corrosion due to certain species of sulfur-loving or sulfate reducing bacteria which can thrive in some FGD environments.

Some FGD systems introduce other factors which need to be considered. For example, dibasic organic acids are sometimes added to the absorbers to buffer or otherwise inhibit scale formation. Since the acids have reducing properties, they have been known to affect passive alloys like stainless steel.

FRP is not affected by the acid or oxygen cell corrosion mechanisms which affect metals, and is consequently used extensively for stack lining, slurry piping, concrete protection, mist eliminators, and process equipment. More extensive information can be found in the application guide, DION<sup>®</sup> Resins for Power Generation Applications. This guide is included in the Reichhold corrosion literature package on CD or flash drive and may also be found at [www.reichhold.com/corrosion](http://www.reichhold.com/corrosion).

Wet chimneys can be one of the most corrosive areas of an FGD system. There are always traces of sulfur trioxide present in combustion gas, and SO<sub>3</sub> serves to raise the dew point considerably. If the acid dew point is reached, sulfuric acid can condense at concentrations very corrosive to steel. Likewise, chimneys will often contain localized deposits from coal fly ash; this leads to oxygen-deficient areas which can cause stainless steel to lose its passive chromium film. Stacks made with FRP tend to be less prone to such fly ash deposits due to smoothness, but even if deposits form they do not affect the FRP corrosion-wise. FRP chimney liners have represented some of the largest FRP structures in the world. Compared to dry stacks, the wet stacks associated with FGD are larger in diameter to minimize pressure drop and energy required for induced draft fans, which can be considerable since the gas loses its buoyancy when it is cooled in the course of SO<sub>2</sub> absorption.

Due to the size of FRP equipment it is at least theoretically possible to build up static charge gradients due to flow of combustion gas, especially if it is dry or laden with fly ash. It is common practice to use a light weight grounded carbon surfacing veil in the corrosion barrier to dissipate static charge. At times, natural graphite (about 30 wt%) is used for the same purpose, but this takes careful consideration, since graphite increases the resin mix viscosity, may affect curing, and if not properly dispersed can result in loss of electrical continuity.

Acid drift from chimneys is another common problem with wet FGD systems. The acid drift from a tall stack can corrode surrounding areas to a wide extent. Often FRP is used for the wind cap at the top of the stack, along with mist eliminators and a means of collecting and draining acid condensate to minimize release to the atmosphere.



## Sewers

The advent of Resin Thickening Technology (DION CIPP<sup>®</sup>) at Reichhold revolutionized the installation of cured-in-place pipe (CIPP). DION CIPP<sup>®</sup> resin systems utilize a patent-pending resin thickening

chemistry that provides an array of unique benefits not previously available during wet out, installation and curing of CIPP. Very low initial viscosity permits fast, thorough liner impregnation, with uniform wet out. After the liner has been fully saturated, DION CIPP<sup>®</sup> resins controllably thicken over a 24 hour period to a viscosity greater than 1.5 million centipoise. Cured in place pipe made with DION CIPP<sup>®</sup> resin has superior felt or fiberglass wet out, more consistent and reliable installation properties, and dramatically improved curing performance. Thickened DION CIPP<sup>®</sup> resins are water-repellent, and remain intact under heavy infiltration and/or tracking.



## Miscellaneous

### Abrasive Materials

Even though FRP pipes and ducts are smooth to allow low pressure drop, abrasive materials can present problems. Abrasion can actually be a complex phenomenon, which depends on the angle of incidence, hardness, and velocity.

If the abrasion is occurring from inertial effects of hard materials impinging on the surface, good success has been obtained by incorporating about 30% of 120 grit silicon carbide or ceramic beads into the surface of the composite. Generally this is done when corrosion is fairly mild, such as in slurry piping associated with flue gas desulfurization. Moreover, the filler must have hardness greater than the abrading material. Lime or limestones, for example, are relatively soft materials with a Mohs hardness of 2 or so. A down-side to use of silicon carbide is that repairs to the piping are difficult since even a diamond saw may be impractical to use. In some cases involving high velocity fly ash there has been reported success in controlling localized abrasion by bonding thermoplastic urethane sheet stock to the composite.

For sliding abrasion, where the force is parallel to the surface, there has been good success in some instances with the use of synthetic veils, not only the polyester type, but those based on nylon or Dacron. Carbon or graphite surfacing veils can also show improvements. Sliding abrasion is most commonly predicted by laboratory Taber type abrasion instruments. Further details can be provided at [www.reichhold.com/corrosion](http://www.reichhold.com/corrosion).

Sometimes a more resilient resin is preferred since it will elastically absorb more energy. However, this cannot be generalized.

### High Energy Radiation

Since thermosetting resins are primarily comprised of carbon, hydrogen, and oxygen, they represent low neutron cross-section capture efficiency to resist high energy radiation. Uncured DION<sup>®</sup> 382 has been tested at dosages of up to  $15 \times 10^6$  rads. No degradation was observed in molecular weight or other properties. Experts have offered the opinion that cured 382 laminates would probably be practical for use up to the  $50\text{-}100 \times 10^6$  rad range. As a frame of reference, only 400 rads is regarded as a lethal dosage to humans.

DION<sup>®</sup> 382 has been used in various nuclear related applications, such as ducting or left-in-place concrete forms. It is expected that FRP could be a good candidate for containment of certain low level wastes. FRP has also been used in X-ray exposure, such as cat-scan devices.

A usual requirement for ducting it that the surface be well cured and spark tested to be sure it is free of holidays, which are microscopic holes in the laminate. This is necessary in the event of an accident which may require decontamination. Likewise, a strippable exterior paint may be used in the event decontamination is ever necessary.

Since nuclear radiation represents important issues affecting public health and safety it is always advisable to contact experts before proceeding with any specifications or installations.

### Electrical Considerations/Static Electricity

FRP has good electrical insulation and dissipation properties which makes it well-suited for numerous applications. Many of these applications do not deal with corrosion resistance, but there are instances

Property	Test Method	
Dielectric Constant	ASTM D150	4.18
Dissipation Factor	ASTM D 150	0.0078
Dielectric Strength, v/min	ASTM D149	>350
Surface resistivity, ohm	ASTM D257	8 x 10 <sup>14</sup>

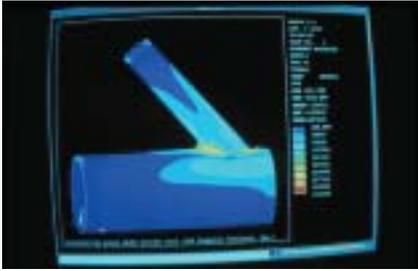
when the combined corrosion resistance and electrical properties are an advantage. FRP has been used for such things as underground transformer housings, electrostatic precipitator plates, electrochemically processing, or in cases where low electrical interference is required near sensitive electronic equipment.

In general, resins with high heat distortion properties tend to display improved electrical attributes. Moreover, complete curing and post-curing is necessary to obtain the best performance. In high frequency applications, the fiberglass reinforcement can affect dielectric or dissipation values. Some typical electrical properties for DION<sup>®</sup> 382 laminates are given below:

- In some cases, the electrical insulation properties may be a disadvantage. For example, this can allow static charge potential to develop in the laminate, although this is ordinarily not even considered unless dealing with large equipment, such as stack liners, or where the FRP is exposed to dry or rapidly flowing fluids. Care should also be exercised if FRP is installed underground near to impressed current galvanic protection systems used for metal, since the FRP may shield the protection.
- In some cases, graphite fillers (usually at 30%) or carbon surfacing veils are used to impart some surface conductivity if necessary. The carbon should be connected to a stainless buss embedded into the laminate and then appropriately grounded. Copper conductors should not be used, since copper may inhibit cure and lead to wire pull-out. If using graphite fillers, care should be taken to properly disperse the graphite and to avoid cracking which results in electrical discontinuity. Graphite may also retard cure and will make glass wet-out more difficult.

### Surface Conductivity

Resin/glass composites are non-conductive materials, and high static electric charges can develop in ducting and piping. Such static build-up can be reduced by using conductive graphite fillers or graphite veils and continuous carbon filaments in the surface layer.



## **Why Use Fiber Reinforced Plastics (FRP)?**

Engineered composites have properties and capabilities that metals lack and they usually cost less than their metals counterparts: austenitic stainless steels, high nickel content alloys, or titanium.

FRP is one-fourth the density of steel, which means that in many instances, equipment can be handled manually instead of renting a crane. FRP is easy to repair and does not necessitate arc welding in hazardous areas.

The dielectric properties of FRP means that it can be used safely where electrical conductivity cannot be tolerated. The anisotropic nature of FRP (different physical properties in different directions) enables the engineer to align the fiber reinforcement with the principal strain field, thus making the equipment stronger and lighter than a corresponding steel fabrication.

The applications of composites are not limited to fiber reinforced plastics, either. In another important application, and by no means the only other example, polymer concrete bridge deck overlays provide chloride protection for bridge deck reinforcement steel while restoring roadway profile, durability, and ride quality. The overlays can be placed under a variety of extreme environmental conditions and, as a result, two to four-hour cure times are achievable allowing a rapid return to public traffic.

Whether it is the material itself or its corrosion resistance, all of these advantages translate into better engineered systems that perform better, last longer, and cost less.

### ***Material Advantages of FRP***

Proper applications of FRP often require an understanding or appreciation of the physical and corrosion resistant properties of metals and other common materials of construction. In the case of metals, the table below lists some of typical properties in comparison to those of FRP reinforced composites. The properties of FRP can vary with the type of resin and the construction employed for the reinforcement. Likewise, metal properties may vary considerably depending on the particular alloy or the manner in which the metals have been annealed or pre-processed.

Reinforced composites are not as stiff as most metals, and obviously can be limited in applications requiring high modulus of elasticity. FRP also does not display other favorable properties of metals such as ductility or malleability. On the other hand, FRP features a low density, which can often give a good strength to weight ratio, which is important in transportation and many structural applications. FRP is also a relatively good thermal as well as an electrical insulator. Fabrication or repairs can be made easily, and without the need for arc welding in hazardous areas

<b>Material Advantages of FRP</b>							
	<b>FRP</b>		<b>Carb on Steel</b>	<b>Stainless Steel</b>	<b>Hastelloy</b>	<b>Aluminum</b>	<b>Titanium</b>
<b>Property</b>	<b>With glass mat roving</b>	<b>All glass mat</b>	<b>AISI 1020</b>	<b>316L</b>	<b>C</b>	<b>1050-O</b>	<b>Grade 12</b>
Density, lb/in <sup>3</sup>	0.065	0.050	0.284	0.286	0.324	0.098	0.163
Tensile Strength, psi x 10 <sup>3</sup>	12-20	1020	55	80	80	11	89
Yield Strength, psi x 10 <sup>3</sup>	10-20	9-15	33	34	51	4	69
Modulus of Elasticity psi x 10 <sup>6</sup>	0.8-1.5	0.7-1.0	30	30	26	10	14
Coefficient Thermal Expansion in/in°F x 10 <sup>-6</sup>	13	17	7	9	6	13	6
Thermal Conductivity, btu/hr/ft <sup>2</sup> /ft/°F	0.15	0.15	3	9	7	135	11

In addition to physical properties, corrosion resistant properties differ greatly between FRP and metals or other materials of construction. In the context of this guide, some brief elaboration is presented on comparative corrosion related properties, at least within the domain of temperatures and environments in which FRP is usually considered.

This table compares the principal material properties of FRP to those of various metals. The light weight (density) and the strength to weight ratio of FRP are clear advantages in transportation and in handling. The thermal conductivity is a clear advantage when storing, using, or transporting fluids at elevated temperature. With a thermal conductivity only 1/187 that of carbon steel and 1/900 that of aluminum, heat loss is much less and the hazard that hot equipment poses for workers is reduced.

The reduced tensile strength, coefficient of thermal expansion (at twice that of carbon steel), and modulus of elasticity introduce design considerations that may, at first, appear to be disadvantages to design engineers more familiar with steel, but are, in fact, advantages. The coefficient of thermal expansion (at twice that of carbon steel) may be seen as a disadvantage in the case of applying an FRP liner to a steel substrate, e.g. as in relining a steel tank, but with a modulus 1/30<sup>th</sup> that of steel, resultant thermal forces in a piping system are only 1/15<sup>th</sup> that of carbon steel (because of the lower modulus of elasticity). An actual calculation is necessary to weigh this advantage for thrust blocks in restrained piping systems, since the wall thickness and pipe size also enter into the calculation of the thrust force. Conversely, the lower modulus of elasticity means that pipe guides will be closer together due to the earlier onset of elastic instability.

The key to realizing the inherent advantages of FRP is to remember that while some material properties may, at first glance, appear to be disadvantages; these are parameters that can be accommodated in the design of the equipment. No amount of design finesse will make steel lighter than FRP or even equal to FRP in thermal or electrical conductivity.

### **Corrosion Resistance of FRP**

Materials	<i>OK = Unaffected</i>				<i>X = Corroded</i>		
	Dilute H <sub>2</sub> SO <sub>4</sub>	Conc. H <sub>2</sub> SO <sub>4</sub>	Dilute HCl	Conc. HCl	Dilute HNO <sub>3</sub>	Chloride Salts	Dilute NaOH
FRP Laminate	<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>
Carbon Steel (1020)	<i>OK</i>	<i>OK</i>	<i>X</i>	<i>X</i>	<i>OK</i>	<i>X</i>	<i>OK</i>
316 Stainless	<i>OK</i>	<i>OK</i>	<i>X</i>	<i>X</i>	<i>OK</i>	<i>X</i>	<i>OK</i>
Hastelloy C	<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>

The superb corrosion resistance of FRP is well known. FRP is ordinarily made using polyester or vinyl ester resins which possess excellent corrosion resistance as well as good thermal and physical properties. The table above presents a generalized comparison of the corrosion resistance of premium grade FRP laminates, carbon steel, stainless steel and Hastelloy. For additional corrosion information, call the **Reichhold corrosion hotline at 1-800-752-0060**.

In almost all cases, styrene is the crosslinking monomer and the cure is initiated with various peroxides in conjunction with accelerators and promoters. All of the rigid forms of these resins have excellent water and acid resistance, but the less expensive polyesters do not feature good alkali resistance. However, bisphenol-A based polyesters as well as vinyl esters have excellent combined acid and alkali resistance.

## Alternate Materials

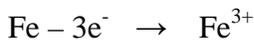
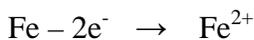
### Carbon Steel



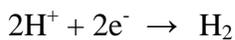
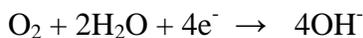
There are many corrosion mechanisms which affect ordinary carbon and low alloy steels, but by far the most common is that induced by the so-called oxygen cell, which occurs in the combined presence of acid, water, and air. Both hydrogen ions and molecular oxygen can function as electron acceptors to form an oxidation/reduction galvanic cell, and the steel functions as an anode to thereby become oxidized.

The corrosion can be accelerated if the steel is electrically coupled to a cathodic material (such as copper) which is listed lower than iron in the galvanic series. The presence of salts or other conductive electrolytes can accelerate the process. Variability in the steel or dissimilarities in the surrounding materials or respective oxygen concentrations can lead to complex electrochemical gradients which often make the corrosion of steel difficult to predict or to control. Stray galvanic currents, such as from adjacent DC power sources can also contribute to this type of corrosion.

#### *Oxidation (anode)*



#### *Reduction (cathode)*



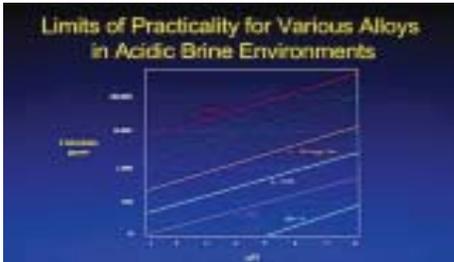
There are many common ways to prevent or to minimize the galvanically related corrosion of carbon steel. The most common is to paint or coat the steel with a suitable dielectric coating to isolate it from the environment. Proper surface preparation is necessary to obtain good adhesion to the steel. Since organic coatings can be permeable in harsh environments, it is desirable to make the coating as thick as possible, although the coatings themselves can have comparatively poor physical strength. Thus a thick coating is often used in conjunction with fiberglass reinforcement. Polyesters and vinyl esters characteristically have excellent acid resistance, and as such they are commonly used in protection of steel and other substrates, both as reinforced laminates or as flaked glass type composites.

To avoid oxidation, it is also common practice to employ materials in the vicinity of the steel which are more anodic than iron (for example, magnesium metal), such that the steel can effectively function as a cathode. These anodes can be used either sacrificially, or else permanently as electrodes which are continuously charged to a higher oxidation potential voltage than the steel to thereby cathodically protect the steel by impressed current.

Galvanic attack to steel can also be manifested as biological attack, usually from species of sulfate-reducing bacteria (SRB) commonly found in soil. In the presence of iron, these bacteria can generate hydrogen sulfide along with ferrous iron. Biological attack is very distinctive and is perhaps the most common form of corrosion to buried steel. FRP is frequently used for external protection of underground piping or fuel tanks. Analogous to SRB are species of metal reducing bacterial which can affect some stainless steels in certain industrial and marine environments.

The mechanisms associated with galvanic oxygen cell corrosion do not come into play with FRP.

## Stainless Steel



The oxidation attack of steel can be greatly reduced by effectively passivating the surface, most commonly by alloying with >10.5% chromium to yield a wide family of stainless steels which are classified by structure into austenitic, ferritic, or martensitic types. The chromium combines with oxygen to form a thin, transparent oxide protective film. This passive film must be preserved for the stainless steel to maintain its oxidation resistance. In normal atmospheric or mild aqueous environments the film is quite stable, but can be

improved by other alloying elements. Increased levels of chromium and molybdenum improve the resistance to chloride penetration, while nickel improves resistance in strong acid environments.

Stainless steels resist corrosion over a broad range of conditions, but they are by no means immune to severe attack. For example, they perform poorly in reducing environments, such as concentrated sulfuric or hydrochloric acid at elevated temperature, due to the breakdown of the passive film over the entire metal surface. Of even more commercial significance is the lack of resistance to chloride and other halide salts, which can penetrate the passive film and lead to pitting, crevice attack, stress-corrosion cracking, or inter-granular corrosion.

Pitting occurs when the protective film breaks down in small isolated spots, which cause the attack to accelerate due to gradients in electrical potential between the passive surface and the active pit. Once initiated, the attack can be rapid.

Crevice corrosion results from localized differences in oxygen concentration associated with deposits or stagnant areas of liquid. A wide variety of common materials, including even microorganisms, can be responsible for crevice formation, and the attack can be especially intense and rapid in chloride environments.

Stress-corrosion cracking results from the combined effects of tensile stress and corrosion, and stainless steels are especially susceptible to stress corrosion in the presence of chlorides. Inter-granular corrosion occurs at high temperature whenever the chromium along grain boundaries combines with carbon to form carbides, as so-called carbide precipitation or sensitization. The net effect is a depletion of chromium in areas adjacent to the grain boundaries which leads to rapid attack.

Most commonly, susceptibility to inter-granular corrosion is induced during the welding process, and welds are often the most troublesome areas in dealing with corrosion resistance with stainless steels. Although annealing and various alloy stabilization techniques can be used to mitigate inter-granular corrosion, many of these methods are not practical to employ in field applications. Reliance must be made upon skilled fabrication and rigorous inspections of welds.

Often it is necessary to employ high nickel content alloys, such as Hastelloy or the Haynes series C-276 alloy, or increased molybdenum content 900 series super-austenites. This is especially likely in severe acid and chloride environments, which are present in a typical flue gas desulfurization process. Many of these alloys can be exceedingly expensive, and yet are not without problems.

The mechanisms associated with corrosive attack of stainless steels do not apply to FRP, and FRP has had a long and successful history in a wide variety of acid and chloride containing environments.

## Aluminum

FRP is often used competitively with aluminum due to comparable advantages in cost, weight, and similar physical properties. Examples include solids storage bins, grating, and other parts of 2-dimensional symmetry made by pultrusion of FRP or extrusion of the aluminum. Such pultruded parts are often used in chemical plants for hand rails, grating, conduit trays, or cooling tower components.

Aluminum weathers well and tends to have good corrosion resistance in mild environments in the 4-10 pH range. This is due to passivity of the aluminum with results from an oxide film less than 10Å thick on the surface.

However, aluminum and its numerous alloys are unsuitable for a wide variety of industrial applications, where FRP otherwise may be used quite successfully. Aluminum lacks resistance to strong acids, especially reducing acids like phosphoric. In the case of HCl or HF, the reactions can be violent, so care must always be given in selecting or placing of aluminum. Caustic and other strong alkalis are extremely corrosive to aluminum, even at concentrations of <2%. Even free lime in concrete can attack aluminum, so it is advisable not to embed it into concrete foundations.

## Titanium

Titanium has been finding increased use for certain severe corrosion related applications, where it is usually alloyed with chromium, molybdenum, nickel, or other elements, and then stabilized with palladium to improve its resistance to stress and crevice corrosion. Like stainless steel, it features passivity from an oxide film. Thus it can have some of the same limitations when it comes to chlorides at low pH or to reducing environments, such as concentrated HCl, phosphoric acid, or sulfuric acid. Nonetheless, the corrosion resistance is improved considerably over many grades of austenitic stainless steels. The good strength/weight properties of titanium are also often an advantage.

However, titanium can be rapidly attacked by HF and certain other halide salts, especially when hot, even at dilute concentration. When titanium is used in such environments, corrosion inhibitors are often added to the process environment. Although titanium is widely used with chlorine gas, care must be taken not to expose it to completely dry chlorine, which can cause rapid attack, and possibly even ignition of the metal. It has good resistance to organic materials, but a notable exception has been stress corrosion frequently observed with anhydrous methanol. Certain concentrated organic acids, such as oxalic or formic acid, may also tend to be corrosive to titanium.

Titanium is a combustible material, so care must be taken if dealing with strongly oxidizing environments where there may be a source of potential ignition. Likewise, inert gas welding is often necessary. Few problems are expected as long as experienced fabricators are used.

Both FRP and titanium have been used in chloride or bleaching environments where stainless steel is impractical. Of course, titanium is considerably more expensive than FRP.



## Concrete

Concrete is by far the world's largest and most widely used material of construction. Corrosion wise, the biggest

problems have related to resistance to acids, sulfites, and sulfates. For many years, glass-reinforced FRP laminates have been applied to concrete surfaces for corrosion resistance in diverse applications such as flooring, acid dipping baths, or flue gas desulfurization plants.

Furthermore, concrete is a porous material, so there are always problems when water, acids, or salts permeate the concrete to induce galvanic corrosion of the steel reinforcement. This can lead to rapid spalling or cavitation of the concrete. Numerous protective resins and latex coatings are used for sealing. Moreover, there has been increased use of so-called polymer concrete, wherein polyesters or vinyl esters are used to replace all or a portion of the Portland cement, sometimes along with alternative aggregates. This can greatly improve the strength and chemical resistance compared to ordinary concrete. Applications have ranged from bridge decking to special composites used in acid based electrochemical or electro-winning processes. Reichhold specializes in the supply of resins suitable for such applications.

Because of the potential corrosion problems to the reinforcing rebar, specialized pultruded FRP reinforcement has been considered. As is the case with ordinary laminations, care must be taken to ensure that the fiberglass reinforcement is properly protected by an alkaline-resistant resin, since fiberglass itself can be gradually attacked by concrete.

In the case of sewer pipe, anaerobic bacteria can lead to generation of H<sub>2</sub>S, which can attack older concrete, especially if highly porous. FRP piping is unaffected by this type of corrosion, just as it is not affected by sulfate reducing bacteria, which are common in soil and notoriously corrosive to steel. Additionally, polyesters and vinyl esters are commonly used with felts as part of sewer line rehabilitation projects. A resin used for this purpose is DION CIPP® 2000.

## **Rubber and Various Elastomers**

The elastic and abrasion resistant properties of rubber and other elastomers have made these materials indispensable in many industrial applications. Since many grades have good resistance to acids and other chemicals they are often used as linings onto steel in competition with FRP and other materials for SO<sub>2</sub> absorbers, slurry piping, bleach towers, storage tanks, and railcar linings.

In the case of large vessels, a big disadvantage to rubber linings is that it takes very skilled and specialized fabrication, which often makes them expensive. They can also be difficult to bond to steel, so there can be potential problems if the lining is damaged or penetrated. Many linings are also difficult if not impossible to use around restrictive geometries, and repairs are not always easy. The considerable weight of the linings often makes field bonding extremely difficult onto vertical or inverted surfaces.

Rubber inherently has a low T<sub>g</sub>, which restrict many of the applications. At high temperature, rubbers may become too flexible, and below the T<sub>g</sub> they can be excessively rigid. Properties of many rubbers are quite different than most materials, for example they may contract upon heating, and as such these differences need to be recognized.

Despite good acid resistance, rubbers can become embrittled if subjected to cyclic wet and dry conditions. They also can swell or become attacked appreciably in the presence of many solvents.

Since most hydrocarbon rubbers have corrosion limitations, reliance is often made on synthetic elastomers, such as Viton, thermoplastic urethanes, and various bisphenol-A vulcanized

fluoroelastomers. Even so, these materials can be subject to water absorption, and specialists should always be consulted.

Occasionally, FRP has been used for the structural wall in conjunction with elastomer sheet lined vessels, often referred to as dual-laminate construction. Ordinarily, this is done in cases where the use of the elastomer has been specified due to some type of ultra- high purity requirement.

## **Acid Resistant Brick and Refractories**

Both castable and masonry block brick and ceramics have been used for many years in corrosive environments. Examples include bleach towers, absorbers, sulfite pulp digesters, sulfuric acid plants, ducts, and chimneys.

Construction consists of the structural pressure envelope, which is ordinarily steel or concrete. A primary corrosion barrier, such as reinforced FRP is then applied to the steel, followed by the brick or tile lining. The bricks or tiles can be installed as-is with the appropriate mortar, but they may also be used with a Portland cement and sand grout backing. Reinforced concrete backing has also been used.

Bricks can be up to 3-inches in thickness, and the commonly used types display good acid resistance, which can be improved by using refractories with dense spinel structures. The types have ranged from expensive silica carbide or fused alumina down to ordinary glazed firebrick. One advantage to their use is that the materials are thick, which allows a designer to factor in an appropriate corrosion and abrasion allowance. In bleach plants the mortar frequently incorporates bisphenol-A or chlorendic anhydride based polyesters and vinyl esters. In power plants, the bricks are often borosilicate glass, with inorganic mortars. If glazed, the permeation is low, but close consideration must be given to the environment, since some refractories can be rapidly attacked by certain materials, such as fluorides or phosphates, especially if silica based.

Installation costs tend to be high, and skilled personnel are required. Castable materials must be well-bonded or anchored to the steel structure by use of Y-anchors or studs. Refractory materials are not ductile and concern always exists over expansion, cracking, and thermal cycling. Ordinarily, the linings will exhibit irreversible physical growth due to chemical hydration, swelling, and water absorption, which is independent of thermal expansion. Sometimes this growth aids in the stability and is factored into the design, but if the swelling is progressive it can induce damage. For example, swelling can cause disbonding or induce a tall structure like a stack to lean. Frequently, the mortar can be preferentially attacked.

The high weight can be a big disadvantage, and there can also be restrictions to use of bricks in seismic design areas. Failures, when they occur, can be catastrophic. Some private industry surveys have indicated that there are more than 100 tall brick stacks in the US which are leaning or otherwise in need of replacement.

## **Thermoplastics**

Like FRP, many thermoplastics share the corrosion resistant properties which are not possible with metals and other materials of construction. Examples include polypropylene, ABS, PVC, Teflon, Kynar, and CPVC, but there are many others, including expensive specialized grades. Manufacturers should always be consulted for specific corrosion resistance properties.

Perhaps the most common corrosion related applications for thermoplastics deal with piping. For example, various grades of fluorinated thermoplastics, e.g. PVDF as well as PVC, have been used in aggressive chlorine generation and bleach environments. In view of the pressure requirements for the piping, the thermoplastics are often used as liners for steel pipe, and on some occasions, FRP has been over-wrapped onto thermoplastic pipe for the necessary strength.

Some thermoplastics can be sprayed, extruded, or applied by powder coating technology onto steel. Specially extruded thermoplastic sheet stock has also been used for the linings of FRP vessels, as so-called dual laminates. Usually such laminates are used when there are special purity requirements, or if there is reason to believe the thermoplastic liner will give even further improved chemical resistance. Nothing should be taken for granted, since thermoplastics can have drawbacks. For example, everyone well recognizes the chemical resistance of Teflon, yet Teflon tends to display water permeation properties which can affect the laminate. Welding and bonding of the thermoplastic also requires a good deal of expertise.

FRP and thermoplastics have quite different thermal properties. Thermoplastics are high in molecular weight, but they have distinct glass transition points, which mean they can essentially melt or flow at temperatures above the transition. On the other hand, the polyesters and vinyl esters used in composites are crosslinked during the curing process and are thermosetting in nature, which give them much higher thermal resistance. Additionally, FRP is reinforced with fiberglass to restrict any distortion and to yield high stiffness. Although an increasing amount of glass reinforced thermoplastics are becoming available, the reinforcement is limited to factory extrusion and molding processes, and the sizes and available geometries of glass reinforced thermoplastics are limited. Thus, in high temperature applications, such as mist eliminators, thermoplastics may be impractical to consider.

Most thermoplastics have coefficients of thermal expansion higher than most metals. This can present many restrictions or difficulties in their use. Although FRP shares some of these problems, properly designed placement of glass reinforcement serves to greatly restrict the expansion. At low temperature, thermoplastics lose a lot of their ductile properties, and most people have first-hand experience with cracking of thermoplastics under cold conditions. In the case of FRP, the fiberglass actually becomes stronger at low temperature, and FRP has had a good history in cold applications.

Often crosslinked polyethylene is used economically in the production of some reasonably large storage tanks which are made by a roto-molding process. This involves polyethylene or other polyolefins which are specially formulated with diene monomers and extruded and milled into powders along with a high temperature peroxide initiator. The powder is injected into the mold cavity, and then melts to conformance of the mold, and after prolonged heating, the polymer crosslinks. Such tanks have good physical properties and chemical resistance, and are used in diverse applications, such as hypochlorite storage associated with municipal water treatment. A significant problem occurs if these tanks crack or otherwise need repairs or modifications. Due to water absorption and the need for thermoplastic welding materials, the tanks are regarded to be impractical to repair. FRP on the other hand is easily repaired.

## **Epoxy Resins**

Epoxy resins have been used for many years as functional protective coatings as well as for composites ranging from filament wound pipe to sophisticated aerospace applications. Nearly all are based on the diglycidal ether of bisphenol-A, which in turn is crosslinked or cured with a variety of agents including aliphatic amines, cycloaliphatic amines, amidoamines, or polyamides. The choice of the curing agent

greatly affects the final physical and chemical properties. Some epoxies use a novolac or cresol-novolac base, which can yield a good deal of crosslinking and further improved chemical resistance.

Advantages to epoxies include excellent resistance to alkali, solvents, and many reducing media. They also are fairly easy to use and have good adhesion properties to metals and other substrates. Very little shrinkage occurs during cure.

On the other hand epoxies generally tend to have poor acid resistance, especially at a pH less than about three. In contrast, specialty polyesters and vinyl esters can have combined good alkali and acid resistance. Epoxies also tend to yellow and chalk considerably during weathering. They also in general do not have high heat distortion properties compared to those attainable with polyesters and vinyl esters, and care should always be taken when considering epoxies for elevated temperature use.

Epoxies are also notoriously slow to cure and develop hardness. This can be a big drawback in many field applications. In the case of polyesters or vinyl esters, fast cures are possible and good control can be achieved over the rate at which hardness develops.

In the case of composite applications, a big draw-back is that most epoxy resins have high viscosities. A simple bis-A epoxy base typically has a viscosity of over 12000 cps before adding the curing agent. A novolac base is typically around 16000 cps. This obviously presents problems in glass wet-out or film forming. There are a number of solvents or reactive diluents which can be used to reduce viscosity, but these present limitations to practicality. Some epoxies are based on bisphenol-F, which tends to give reduced viscosity and may further improve final properties. In contrast, most polyesters and vinyl ester resins are sold in the 400-600 cps range.

Reichhold supplies a wide variety of epoxy resins and curing agents, including various epoxy-polyester hybrids. Interest in such products would be welcomed.

## **Phenolic Resins**

Phenolics are perhaps the oldest family of synthetic polymers and are used in diverse applications including household items, plywood, tires, and brake pads, often with inexpensive fillers. They are made from phenol and formaldehyde or paraformaldehyde, and some versions use cresol or resorcinol. The reactant ratio can be altered to produce both novolac or resole grades. They are usually cured with strong organic acids, but some modern acid-free cure systems are now used.

A big advantage to phenolics is that they carbonize upon combustion to yield very low rates of smoke generation. This has led to obvious increasing applications in ducting, transportation, and building materials. However, by far the biggest disadvantage is their lack of corrosion resistance, especially when compared to FRP. A secondary disadvantage is that they can continue to cure for a long time, which may make it difficult to control dimensional properties. Glass compatibility has also been an historic problem in the use of phenolics, although glass products are now available for specific use with phenolics.

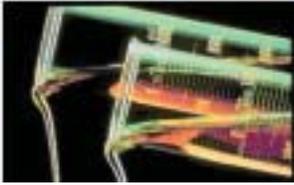
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## **Fiber Reinforced Plastic (FRP) Technology**

The engineering process is well-established and applies the same when using FRP. It begins with process definition, moves on to materials selection, engineering design and analysis, the preparation of

drawings and specifications, quality assurance inspection, and finally, throughout the service life of the equipment, preventive maintenance inspection.

## ***Resins***



Resins can be divided into two broad classes: thermosetting and thermoplastic. This document discusses composite materials formed using thermosetting resins combined with fiber reinforcement. Thermoplastic resins have a definite melting point, whereas thermosetting resins cure to produce an infusible solid material that does not melt when heated. They soften, but they do not liquefy.

Thermosetting resins used for FRP are typically purchased in liquid form and are reacted to a solid with chemical additives. The most commonly used thermosetting resin systems:

- Vinyl ester
- Bisphenol-A fumarate polyester
- Terephthalic polyester
- Isophthalic polyester

These resin families have unique usefulness depending upon the specific corrosive process, temperature, and engineering requirements of the application.

Resin Casting	Tensile Strength psi	Tensile Modulus 10 <sup>5</sup> psi	Elongation @ Break	Flexural Strength psi	Flexural Modulus 10 <sup>5</sup> psi	Barcol Hardness	HDT °F
DION <sup>®</sup> 9800	13,100	4.6	4.2	22,600	4.9	38	244
DION <sup>®</sup> 9100/9102	11,600	4.6	5.2	23,000	5.0	35	220
DION <sup>®</sup> FR 9300	10,900	5.1	4.0	21,900	5.2	40	230
DION <sup>®</sup> 9420	7,400		1.8	16,100	5.0	45	>320
DION <sup>®</sup> 9480	9,000	5.0	3.0	20,500	5.1	38	260
DION <sup>®</sup> 6694	8,200	3.4	2.4	14,600	4.9	38	270
DION <sup>®</sup> 382-05	10,000	4.3	2.5	17,000	4.3	38	270
DION <sup>®</sup> 4010	9,900	4.2	4.0	17,000	4.6	32	205
DION <sup>®</sup> 490	8,700	4.8	2.1	16,700	5.2	40	260
DION <sup>®</sup> 6631	9,300	5.9	2.4	16,600	5.2	40	225
DION <sup>®</sup> 400	10,900	5.0	2.5	17,500	5.2	37	240
DION <sup>®</sup> 797	7,800	5.0	1.6	17,100	9.6	45	280
DION <sup>®</sup> FR 7704	6,200	5.3	1.3	6,200	5.1	40	171
DION <sup>®</sup> FR 7709	8,300	5.3	1.8	16,500	6.1	47	167
DION <sup>®</sup> FR 7767	8,000	5.4	1.6	8,000	5.4	48	172

## Resin Casting Performance

Resin casting performance is important in two ways: the resin casting physical properties play an important role in the mechanical performance of the resin-rich corrosion barrier, e.g. resisting thermal shock. In the structural wall, the resin transfers loads to and between the fiber reinforcements. The resin properties play an important role in the performance of the overall FRP laminate. The table below lists the physical properties of clear castings of Reichhold corrosion and flame-retardant resins.

## Resin Performance at Elevated Temperatures

At elevated temperatures, the structural performance of all polymeric materials decreases. This is not a problem; only a factor that the design engineer must take into account in the design of the equipment. The physical properties used in the design of equipment intended to operate at, say, 200°F will need to be adjusted to take into account this loss. The loss of physical properties at elevated temperature is

dependent, among other factors, on the glass content. It is the design engineer's responsibility to assure that proper account has been taken of this critically important design decision.

	Tensile Modulus, x 10 <sup>6</sup> psi				
	75°F	150°F	200°F	250°F	300°F
DION <sup>®</sup> 9800-05					
DION <sup>®</sup> 9100/9102	1.70	1.70	1.39	0.80	0.80
DION <sup>®</sup> FR 9300	2.16	1.94	1.82	1.62	1.18
DION <sup>®</sup> 9480	2.13	2.23	2.00	1.61	1.47
DION <sup>®</sup> 6694	1.95	2.14	1.86	1.86	1.62
DION <sup>®</sup> 382	1.45	1.40	1.35	1.20	
DION <sup>®</sup> 797	1.39	1.36	1.21	0.98	0.59
DION <sup>®</sup> 6631	1.43		0.86		
DION <sup>®</sup> 490	1.15	0.90	0.76	0.58	0.47

	Flexural Modulus, x 10 <sup>6</sup> psi				
	75°F	150°F	200°F	250°F	300°F
DION <sup>®</sup> 9800-05	1.01	0.87	0.74	0.58	0.32
DION <sup>®</sup> 9100/9102	1.04	1.23	1.07	0.89	0.42
DION <sup>®</sup> FR 9300	1.07	1.02	0.86	0.78	0.52
DION <sup>®</sup> 9480	1.10	1.02	1.00	0.97	0.86
DION <sup>®</sup> 6694	1.20	1.04	0.96	0.83	0.74
DION <sup>®</sup> 382	1.20	1.00	0.97	0.83	0.62
DION <sup>®</sup> 797	1.50	1.35	1.16	0.91	0.48
DION <sup>®</sup> 6631	1.28	1.20	0.85	0.50	0.30
DION <sup>®</sup> 490	1.07	0.98	0.81	0.61	0.41
* Construction -V MM WR M WR MM, Glass Content -42%, Thickness 0.250 inches					

	Flexural Strength psi				
	75°F	150°F	200°F	250°F	300°F
DION <sup>®</sup> 9800-05	26,300	25,600	23,100	19,200	740
DION <sup>®</sup> 9100/9102	32,800	35,300	31,400	26,600	11,600
DION <sup>®</sup> FR 9300	29,700	27,300	26,400	18,400	8,200
DION <sup>®</sup> 9480	28,400	27,500	27,200	26,400	18,600
DION <sup>®</sup> 6694	29,700	26,500	26,100	24,300	21,900
DION <sup>®</sup> 382	25,400	27,500	23,200	17,800	10,200
DION <sup>®</sup> 797	30,100	30,100	29,600	25,200	15,400
DION <sup>®</sup> 6631	31,000	28,600	24,000	14,700	4,280
DION <sup>®</sup> 490	23,800	25,800	25,400	22,700	17,200
* Construction -V MM WR M WR MM, Glass Content -42%, Thickness 0.250 inches					

	Tensile Strength psi				
	75°F	150°F	200°F	250°F	300°F
DION <sup>®</sup> 9800-05	19,500	19,500	19,500	13,000	9,000
DION <sup>®</sup> 9100/9102	19,200	22,100	22,700	14,600	9,900
DION <sup>®</sup> FR 9300	26,600	29,100	30,100	21,200	13,700
DION <sup>®</sup> 9480	23,900	25,000	27,700	26,700	20,900
DION <sup>®</sup> 6694	22,000	22,400	24,800	27,700	25,000
DION <sup>®</sup> 382	18,000	21,500	21,500	20,000	
DION <sup>®</sup> 797	16,800	17,800	19,400	20,200	15,800
DION <sup>®</sup> 6631	20,100		20,200		
DION <sup>®</sup> 490	14,300	16,200	16,600	15,300	11,700

## **Reinforcements**



Fiber reinforcements that are used in the corrosion fiberglass industry include various forms of glass fiber, such as E-glass and a newer, more corrosion-resistant version, called ECR-glass. Synthetic fibers, such as polyester surfacing veil or carbon veil (for abrasion resistance and conductivity) are also available. Occasionally, aramid, or carbon fibers may be used in the structural laminates to improve the strength-to-weight ratio. The most common forms of glass reinforcement are:

### **Surfacing Veil**

Surfacing veil is a very thin sheet material formed from either synthetic polyester fiber of random lengths or very fine C-glass fibers.



Veil is most commonly used on the surface of FRP equipment that is intended to come into contact with a corrosive environment, whether it is on the interior molded surface or on the exterior of the equipment. Polyester synthetic veil is more difficult to work with, but it may improve corrosion resistance in services such as chlorine dioxide, hydrofluoric acid or hydrofluosilicic acid. Polyester veils can also impart abrasion resistance. The use of double synthetic veils is not necessary, nor is it recommended. Should a double veil construction be deemed appropriate, use of a combination of synthetic and C-glass veil is suggested. This makes it easier to fabricate high-quality components and reduces the risk of cracking in resin-rich areas.

### **Fiberglass Roving**

Spooled fiberglass roving is commonly used in the corrosion industry for filament winding and as feedstock for chopper-guns (fiberglass and resin spray guns). Various weights and treatments are used for each and they cannot be interchanged. The weight of filament-winding strand varies from 113 ft/lb to 450ft/lb. Roving weight has a significant effect on the strength and flexibility of the finished laminate. For large filament-wound pipe, 113 ft/lb roving is generally used. The most commonly used weight is 250ft/lb, while 450 ft/lb is used for small (2") diameter pipe. Generally, finer roving is more time consuming to work with but will reduce ply thickness and increase strength. It is also less likely to leave voids in the laminate behind the corrosion barrier.

### **Fiberglass Cloth and Woven Roving**

When fiberglass strand is woven into a fabric, it is called cloth or woven roving depending upon its weight. Woven roving is a heavy fabric that is the primary structural component of most hand lay-up laminates. 18 and 24 oz./sq. yd. woven roving are commonly used. Six and 8 oz./sq. yd. fiberglass cloths or exotic directional fiberglass reinforcements may be used where strong, thin laminates are needed.



**Random Chopped Glass**

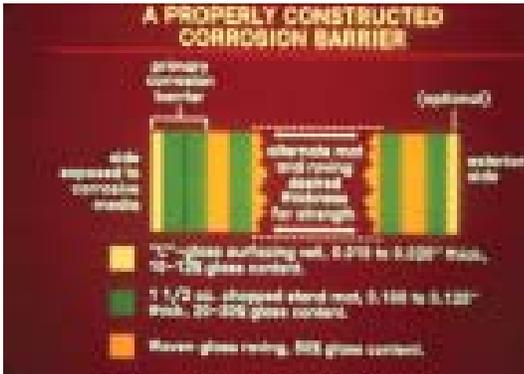
Roving strand is cut into approximately 2” lengths and formed into a sheet using various resin binders.

Chopped-strand mat is available in thickness ranging from 3/4 to 3oz/sq. ft. The most commonly used mats are 1.5 oz/sq. ft.

## **Laminate Types**

FRP is referred to as a composite material because it combines the widely divergent properties of its constituents— reinforcing fibers and resin— into a unique material. Reinforcing fibers contribute virtually all of the material’s strength; resin channels stress into the fibers and provide corrosion resistance. Because of this, corrosion-resistant FRP uses two basic laminate types: a corrosion barrier and a structural laminate.

### Corrosion Barrier



The corrosion resistance of FRP process equipment is in the resin, while strength is realized by the glass reinforcement. Corrosion barrier laminates are usually made starting with one or more plies of resin-saturated C-glass or synthetic veil against the process surface, followed by two or more plies of 1.5 oz. random chopped mat. The resin-rich veil plies in the corrosion barrier contain approximately 90% resin by weight, making them effective barriers to permeation and corrosion. The mat layers contain about 70% - 75% resin by weight and also function as a permeation and corrosion barrier. The high resin content of the corrosion barrier effectively shields the structural laminate from chemical attack.

### Inner Layer

The Inner Layer is constructed of a surfacing veil, generally 10 mils in thickness. The principal purpose of the veil is to provide moderate reinforcement to the comparatively weak resin used in the corrosion barrier. It is important to avoid excess resin which can lead to cracking. Veils made from C-glass fiber are normally used since they are easy to work with and provide excellent corrosion resistance. Synthetic veil allows the corrosion barrier to have higher resin content, but care must be taken to avoid excessive resin-rich areas. Historically, some specifications have required multiple veils. However, the practical problems associated with fabricating with multiple veils, e.g. excessive resin-rich areas, often outweigh the advantage gained.

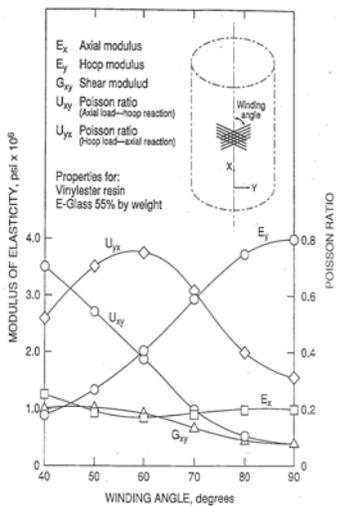
### Mat Layers

Chopped strand mat is widely used in the fabrication of corrosion structures to obtain consistent resin/glass lamination ratios. The mat is made from E-type glass fiber with sizing/film former which provides excellent structural reinforcement, good wet out characteristics, and sufficient clarity to observe entrained defects. ECR glass fiber mat is sometimes specified for acidic environments.

A “standard” ASTM C 582 corrosion barrier has two 1.5 oz. /sq. ft. mats behind the C-veil. In severe corrosion, say in chlorine cell headers, or when the process temperature exceeds 200°F, these mats can be increased to four or more for additional protection. Beyond these mat layers, the consideration to type of reinforcement and the construction method are based on overall structural requirements. In most FRP standards, the structural contribution from the corrosion barrier is excluded.

ASTM C 581 and ASTM C 582 are the industry standards for corrosion barriers and these standards have been adopted by various other equipment standards, e.g. ASME RTP-1, ASTM D 3299, ASTM D 3982, etc.

## Structural Wall



Shell Properties vs. Winding Angle

The structural laminate follows the corrosion barrier. The structural wall gains its strength from glass fiber, and therefore maximum glass content of the structural wall is sought. The fiberglass may be filament-wound or hand lay-up, or may use another arrangement wherein plies of continuous, directional fiber are placed to provide specific strength and stiffness as required by the engineer. The fiber content of structural wall laminates may range from 35% by weight for hand lay-up to 70% or more for filament winding. This high fiber content permits FRP structures to combine high strength, light weight and low cost.

FRP materials are products of both the raw materials and the construction process used. The most commonly used processes for producing corrosion-grade FRP parts are filament winding, contact molding, centrifugal molding, matched die compression molding, and pultrusion. Specialized resins are used in each of these methods of construction.

## Laminate Construction

FRP laminates for corrosion service are constructed using a variety of processes and materials as noted below. Although they appear to be different, these processes have many similarities. Most corrosion-grade laminates have a corrosion barrier and a structural wall.

The corrosion barrier is dedicated to resisting surface corrosion and to preventing the process environment from permeating into the structural wall. The structural wall is that portion of the laminate dedicated to mechanical support. In some cases, such as ducting or hoods intended for mildly corrosive service conditions, the laminate may be manufactured using only random chopped glass and therefore have no separately defined corrosion barrier and structural wall.

## Construction Methods

FRP materials are products of both the raw materials and the construction process used. The most commonly used processes for producing corrosion-grade FRP parts are filament winding, contact molding, centrifugal molding, matched die compression molding, and pultrusion.

## Filament Winding



Although it is possible to wind complex structural shapes, filament winding in the corrosion industry is generally limited to cylindrical shells. It is used to produce small to very large diameter tank shells and straight pipe.

Filament-wound parts are relatively inexpensive to make and are characterized by a high strength-to-weight ratio. The strength and stiffness are gained by winding tapes, random chopped glass, or glass roving in a spiral pattern,

commonly referred to by its helix angle (the angle between the longitudinal axis and the spiral pattern).

For helically wound laminates, the primary strength and stiffness can be varied between the hoop and axial direction by altering the helix angle of the wind. A good corrosion barrier is necessary to protect the continuous filament-wound structural laminate from the effects of permeation or “wicking” by the process fluids should the corrosion liner be breached.

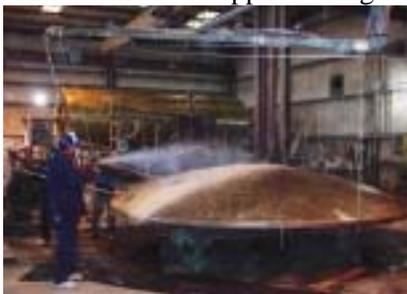
DION<sup>®</sup> 9800 and DION<sup>®</sup> 9102 are particularly good resins for filament-wound applications.

**Important Note:** It is important to assure that a good corrosion barrier is in place to protect the continuous filament-wound structural laminate from the effects of permeation or “wicking” by the process fluids should the corrosion barrier be breached.

## Contact Molding

Contact molding refers to a process by which layers of glass saturated with resin are applied sequentially to a form or mold.

The laminate produced by contact molding is often referred to as “hand lay-up”. Hand lay-up may also refer to any laminate that is composed of plies of fiber reinforcement in sheet form where the resin and reinforcement are applied using a spray gun, a bucket and brush, or a special spray system, one called a chopper –gun and the other called a flow-coater, each of which simultaneously applies chopped glass and resin.



Contact molding is used to produce ancillary parts for tank shells, such as nozzles, elbows, and flat, conical, or dished heads and bottoms. It is also used for complete tanks and pipe.

Normally, hand lay-up parts are very tough and resistant to permeation and wicking. While not as strong as filament-wound FRP for a given thickness, contact molding is one of the best

ways to manufacture the most highly corrosion-resistant equipment intended for challenging corrosive services. ASTM C582 gives typical construction and properties of corrosion-resistant hand lay-up laminates.

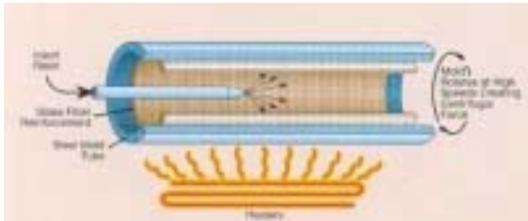
Normally the same resin used in the primary structure is used in the ancillary parts. In the case of a contact-molded primary structure, either a Bisphenol fumarate resin, e.g. DION<sup>®</sup> 382 or DION<sup>®</sup> 6694, or a vinyl ester resin, e.g. DION<sup>®</sup> 9800 and DION<sup>®</sup> 9102, can be used, depending if added corrosion

resistance or added structural performance is preferred. For mild corrosion service at ambient temperature, an Isophthalic or Terephthalic resin may be used.

ASTM C582 gives typical construction and properties of corrosion-resistant hand lay-up laminates.

## Other Molding Processes

### *Centrifugal Molding*



This process is used for round parts, such as lengths of pipe and tank shells. Resin and reinforcement are placed against the inside surface of a mold that is rotating about its long axis, forcing the resin and reinforcement to evenly disperse.

### *Matched Die Compression Molding*

Compression molding is used for small parts, such as flanges, elbows and fittings. Dry reinforcement is placed in a cavity, then resin is added and the cavity is closed, distributing the resin through the reinforcement.

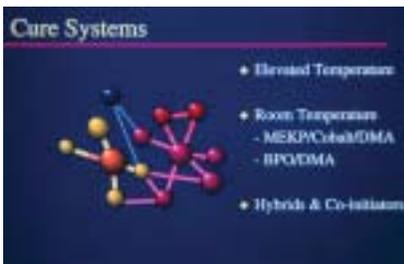
### *Pultrusion*



This process is used to create long parts with constant, often complex, cross-sections, such as FRP rebar and I-beams. Reinforcement and resin are forced through a heated die and rapidly cured into a fixed cross-section. The continuously pultruded section is then cut to desired lengths.

### Significance of Molding Technique

It is important to be familiar with and able to recognize the products of various materials and production methods because of the properties that they impart to the finished product. For instance, filament-wound flanges were available for a period of time and some are still in service. Because filament winding imparts hoop-directional strength but lacks axial reinforcement, these products may be unable to withstand axial loads placed on them by bolting and bending. Similarly, short-fiber press molded flanges may be prone to cracking and may not be suitable for severe services. By recognizing the FRP molding techniques employed to produce specific products, the inspector is more able to assess the overall condition of the equipment.



### **Catalysts and Cure Systems**

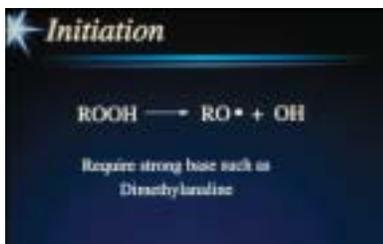
Polyester resins are transformed from a low-viscosity liquid into a thermoset solid when mixed with an initiator (often called a catalyst), in conjunction with appropriate promoters and accelerators. Peroxide catalysts need activation to be effective at room temperature. This is generally accomplished by adding dimethyl aniline (DMA) to the resin. The rate of cure is

increased with promoters, most commonly cobalt compounds, such as cobalt naphthenate.

With pre-promoted resins, only an initiator (often called a catalyst) is required to initiate the cure reaction. However, resins are often available in non-promoted form, requiring addition of carefully measured quantities of promoter(s) and thoroughly blending them into the resin before initiator is added to effect curing.

Catalysts generally used for fabricating corrosion-resistant equipment are methylethylketone peroxide (MEKP), benzoyl peroxide (BPO) and cumene hydro-peroxide (CHP). Promoters are very selective in their function with peroxide catalysts and care must be taken to use the correct combinations.

## Peroxide Initiators



Initiators are typically the final additive required to initiate a cure reaction. Promoters and/or inhibitors may be added to prepare the resin hours, days, or weeks before it will be used. The initiator is added immediately prior to use, and the amount employed is one factor that determines the working life of the resin.

The most commonly used initiator systems for the resins listed above include:

### Methyl Ethyl Ketone Peroxide (MEKP)

Methyl ethyl ketone peroxide is the workhorse initiator system. It is generally the easiest to use, especially in adverse conditions. It provides excellent curing performance, and responds well to post-curing.

MEKP is activated by DMA, or other strong base, and cure is further promoted by cobalt naphthenate, cobalt octoate or other cobalt solutions at room temperature. The percentage of each component determines the gelation time of the resin. Gelation or gel time is usually defined as the time lapse in minutes between the addition of the catalyst to the liquid resin and the point at which the liquid resin becomes gelatinous.

In preparing catalyzed resin for a fabrication, the gel time is the maximum working time allowed to complete the task. Generally, most resins will require 0.3-1.0% of cobalt naphthenate, 0.1-0.3% DMA and 1.0-1.5% of MEKP to obtain a gel time of 30-40 minutes. To obtain faster gelation characteristics, it is usually more effective to add additional DMA or cobalt naphthenate solution to the resin, but in some cases, excessive amounts will retard cure. Always refer to the product bulletins which give cure guidelines.

Because working life will vary from resin to resin, gel and cure tables are provided for each resin to obtain precise times. Temperatures also have a pronounced influence on gel time. Catalyst systems providing 30-40 minutes at 70°F may only allow 20-25 minutes at 80°F, so it is important to check the resin gel time at the working temperature before starting a fabrication. The addition of 0.1% of DMA to the resin will greatly speed gel and cure rate, and Barcol readings usually will be registered in under two hours.

It is important to note that cobalt solutions and DMA should not be mixed together before being added to the resin; they should be added to the resin separately and mixed in thoroughly. MEKP is not activated by DMA alone, so if the cobalt naphthenate is not added to the resin, no gelation or cure will occur. MEKP must always be added to the resin as the last component and dispersed, preferably with a propeller-type mixer.

**Warning: Care must be taken to avoid direct mixing of any organic peroxide with metal soaps (such as cobalt naphthenate), amines (such as DMA) or any other polymerization accelerator or promoter, as violent decomposition will result!**

Accelerators and promoters should be used with caution to avoid undesirable cure problems. Excessive levels of cobalt naphthenate may tend to cause foaming and extended cure rates. Higher levels of DMA will increase exothermic heat generated as the resin cures and may cause scorching, warpage and fiber whitening in thick laminate sections.

While Cobalt Naphthenate and DMA are already added to pre-accelerated resins, in some cases, e.g. unusually hot or cold fabrication conditions, the fabricator may wish to increase the amounts. In some cases, resins are supplied free of accelerators and promoters and the fabricator must add them.

Generally, levels of addition of each component should be within the following ranges:

Cobalt Naphthenate 0.3-1.0 phr\* (%)

DMA 0.1-0.3 phr (%)

MEKP 1.0-1.5 phr (%)

\*per hundred parts of resin by weight

### Cumene Hydroperoxide (CHP)

Cumene hydroperoxide (CHP) is used when a more controlled reaction rate is required. When used in conjunction with MEKP, it can eliminate foaming in vinyl ester resins, and reduce the laminate exotherm temperature of bisphenol fumarate resins.

CHP is normally used to reduce exotherm problems in thick laminates (½ inch-1 inch) where sequential lamination is not appropriate. It is substituted for a part of the MEKP in the cobalt naphthenate activated system. The result is a slower release of heat as the section cures, avoiding scorching or delamination. We recommend consultation with our technical specialist to discuss use of CHP in specific applications. Please call the Reichhold **corrosion hotline at 1-800-752-0060** or email **corrosion@reichhold.com** to contact a technical expert.

### Benzoyl Peroxide (BPO)

Although not considered as reliable as the DMA/CO/MEKP system, BPO can be used as an alternative system for curing resins. It is activated at room temperature by DMA and provides very fast gelation and cure. Benzoyl peroxide is available in concentrated powder or liquid diluted paste forms. For safety and convenience, the 50 percent paste concentrates are available for both in-house and in-field fabrications.

Typically used in paste form, benzoyl peroxide may be more difficult to evenly disperse in resin than MEKP. It also requires special care to ensure that the correct ratio of BPO to dimethylaniline (see below) is maintained throughout the resin. This initiator is sometimes specified in the mistaken belief that it enhances the corrosion resistance of FRP. Given the mixing issues, the need for more precise measurements, and its post-cure insensitivity, use of BPO for enhanced corrosion resistance is questionable in all applications.

BPO/DMA catalyst systems should be used only in fabrications that specifically require its use. Before using BPO/DMA, we recommend cure trials. BPO, whether in powder or paste form, is difficult to mix thoroughly in styrene, especially under field conditions. Improperly dispersed BPO can lead to a wide range of conditions, such as hot spots or permanent undercure.

MEKP actually will vary depending on grade and supplier, and resin gel times will vary accordingly. Refer to the product bulletin for the specific resin for further information on cure systems. Like all peroxides, MEKP can lose its activity upon storage. It should be kept cooled or refrigerated, and if there is evidence of lost activity it should be replaced.

Vinyl ester resins are very sensitive to MEKP activity and some grades of MEKP will cause excessive foaming. MEKP grades which contain amounts of CHP, such as Triganox 239, greatly reduce the foaming. With some versions we recommend that MEKP grades with high peroxide dimer content, such as HiPoint 90 and Superox 46748, be used with vinyl esters, such as DION<sup>®</sup> 9100 and DION<sup>®</sup> 9420. Foaming will not occur with the urethane vinyl ester resin DION<sup>®</sup> 9800-05A, which has been modified to alleviate foaming.

## Other

Some catalysts are activated by heat, and can be used to extend cure. An example is TBPB.

## Flame-Retardant Resins and Cure Systems Using MEKP Catalysts

Flame-retardant resins cure well with MEKP catalyst systems. Antimony trioxide is normally added to the resin to optimize flame retardance and some varieties have been found to adversely affect gel time. It is advisable to check small sample of the mix prior to beginning fabrication. All additive levels on the labels are expressed as parts per hundred by weight of resin. Some fabricators may establish volumetric equivalents for in-house use. It must be noted that flame-retardant resins have a higher specific gravity and will require corresponding increases in volumetric additions of about 20 percent. Antimony involves some health hazards and these should be recognized before using. Antimony trioxide can be difficult to disperse. Some antimony pentoxide is available in pre-dispersed form, e.g. Nyacol, APE 3040.

## Promoters, Inhibitors, and Accelerators

These materials are used to prepare the resin for reaction with the initiator and to alter rheology, flame-retardance and other specialized resin or laminate properties. They are often added by the resin manufacturer.

## Promoters



Cobalt naphthenate (CoNap) is typically used to adjust the gel time of the cure reaction.

## Inhibitors

MEKP catalyst systems will gel very quickly when fabricating at high ambient temperatures (90°F), even when the minimum levels of cobalt naphthenate and MEKP are used. Hydroquinone (HQ) and tertiary-butyl catechol (TBC) are used to stabilize polyester and vinyl ester resins after manufacture. They are seldom added in the field but may be useful in conditions where the reaction time and rate cannot be controlled by adjusting other additives. In many vinyl ester resins, 2,4-pentanedione (PDO) is sometimes used to achieve very long gel times. This effect is not consistently observed with other types of resin.

The gel time can be extended by adding inhibitors such as tert-butyl catechol in the form of a 10 percent solution in styrene (TBC-10). To maximize effectiveness and obtain stable gel times, sufficient mix time should be allowed when adding TBC-10.

Other inhibitor solutions of hydroquinone or toluhydroquinone are available. 2,5 ditert-butyl hydroquinone is a specialized inhibitor that can be used to both lengthen gel time and reduce exotherm development in very thick sections.

**Caution: All inhibitors influence the final cure of the laminate, and levels in excess of the maximum recommended should be avoided to maintain essential corrosion performance.**

## Accelerators

Dimethylaniline (DMA) has a significant effect on the hardness development and peak exotherm temperature of the reaction and can be used to reduce gel time.

## ***Degree of Cure***

To gain the ultimate performance from an FRP laminate in corrosion service, the resin must cure completely. ASTM\_D 2583, *Test Method for Indentation Hardness of Rigid Plastics by Means of a Barcol Impressor*, specifies that the laminate reach a minimum of 90% of its ultimate Barcol value. It may take 24 hours or more to reach ultimate Barcol hardness.

In highly aggressive service conditions, post-cure of the laminate shortly after it has gelled and completed its exotherm will assure the highest degree of cure—and corrosion resistance—possible.

Use of secondary catalysts, such as TBPB, and/or postcure, can extend the degree of cure. While many FRP components have been made using the BPO/DMA system under shop fabrication conditions, BPO/DMA has not always performed as well as expected. In some instances, resins using BPO/DMA have demonstrated a permanent undercure.

High quality FRP components can be fabricated using any of the promoter/catalyst combinations described above. For end-users, it is recommended that the preferences of the fabricator be taken into account when specifying resins and catalyst systems.

## Cure Exotherm

DION® high-performance corrosion resistant resins are generally of high reactivity in order to provide maximum performance. The high reactivity, although desirable at lower fabricating temperatures (70°F), can present some problems at temperatures between 80-90°F. Laminate exotherm is a normal sequence of the gelation and cure cycle and is beneficial in laminations of low cross-section thickness to assist cure rate. However, as laminate thickness increases, laminate exotherm will also increase dramatically, causing scorching, warpage, discoloration and delamination in extreme cases.

This condition is aggravated at high fabrication temperatures and caution is required in selecting appropriate cures systems for fabricating under such conditions. BPO-DMA catalyst systems will exacerbate laminate exotherm development and can produce variable cure development in thick sections, especially if the BPO is improperly dispersed. Delamination can also occur when using this system in sequential lamination if previous layers are allowed to cure completely.

MEKP/cobalt naphthenate cure systems are more reliable and time-proven than BPO-DMA in the fabrication of corrosion-resistant equipment and provide a low-viscosity liquid system that can be readily measured and dispersed in the resin.

## Low Temperatures

The activity of MEKP catalyst systems is adversely influenced by low temperatures. Fabrication should not be attempted below 40°F.

## Air Inhibition

All polyester resins are subject to air inhibition, which influences the cure in the outer surface of the laminate, leading to a tacky surface or a surface that can be softened by acetone. Cure systems can overcome this surface inhibition by incorporating a paraffin wax additive in the resin for the final lamination. The wax works to prevent air inhibition due to its incompatibility. If the temperature is too hot, the wax dissolves and becomes ineffective. Usually, the topcoat should not be applied if the laminate surface is over 100°F.

## ***Thixotropes, Antimony Oxides, and Other Additives***



Fillers are used to enhance a specific property of a laminate, e.g. the addition of antimony trioxide to develop flame retardance, but they can also be used to bulk the resin with cheap filler at the expense of the finished laminate properties. It is important to assure that fillers are used wisely. In general, fillers detract from the performance of resin.

Common fillers include silica flour, glass micro-balloons, milled fiber, graphite, carbon, metallized fibers, silicon carbide, and ceramic beads. These materials may be added to extend resin or to add other properties, such as electrical conductivity or abrasion resistance. Pigments are added to modify the color and opacity of the resin. Fillers and pigments are not commonly used in the corrosion barrier.

The following Table lists commonly used fillers, the normal amounts that are used, and the purpose for which they are used. Some amounts will be determined by the resin manufacturer, e.g. a certain percentage of antimony trioxide to match the amount used in ASTM E-84 tests; other amounts will be determined by the fabricator.

<b>Filler</b>	<b>Amount</b>	<b>Purpose</b>
Fumed silica	1-2phr*	Thixotropy (viscosity control)
Antimony trioxide	1-5phr	Fire retardant synergist
Antimony pentoxide	3-5phr	Fire retardant synergist
Aluminum trihydrate	50-120phr	Low smoke formulation
Carbon black/graphite	1-30phr	Electrical conductivity
Silica carbide	1-30phr	Abrasion resistance
Pigments/UV stabilizer	1-2phr	Cosmetics/UV protection
* parts per hundred parts resin		

## Thixotropes

Fumed silica is added to resin to prevent it from flowing out of the reinforcement before cure. It can also be used to formulate resin putties. Fillers, pigments and thixotropes are typically not used in the corrosion barrier due to their adverse effect on corrosion resistance.

## Antimony Oxides

Antimony trioxide and antimony pentoxide are added to halogenated resins at 1.5% to 5% by weight. In a fire, these compounds exert a synergistic effect with chlorine and bromine by forming antimony oxychlorides or oxybromides, which are effective snuffing compounds. Use of Antimony compounds has no effect on flame retardance in resins that do not contain chlorine or bromine.

Other Additives

Intumescent Coatings (Flame Barriers)

*Intumescent Paint*

*Technofire*

Air Release Agents

SAG 47, by Witco Corp, provides surface tension release of air in fillers. It has been shown to have no adverse effect on corrosion resistance.

Styrene Suppressants

Surfactants and Anti-Foam Agents

Ultraviolet (UV) Stabilizers

Tinuvin P

Wax Topcoats

**Resin additives are typically highly reactive and must be stored and handled according to manufacturers' recommendations. NEVER MIX PROMOTERS WITH INITIATORS, SINCE VIOLENT DECOMPOSITION (EXPLOSION) MAY RESULT.**

***Codes and Standards***

A quality assurance inspection program is intended to verify that the level of quality inherent in the specifications is, in fact, delivered to the purchaser. In order to make this happen, that level of quality must be detailed clearly and quantitatively in the specifications, or elsewhere in the purchase documents.

**Reminder: A poorly written specification with conflicts, errors, and omissions is the most frequent cause of disputes during inspection.**

The specification writer must also be aware that existing standards for FRP may not always be sufficiently rigorous to assure a given level of quality. It is often necessary for the specification writer to add further descriptive language.

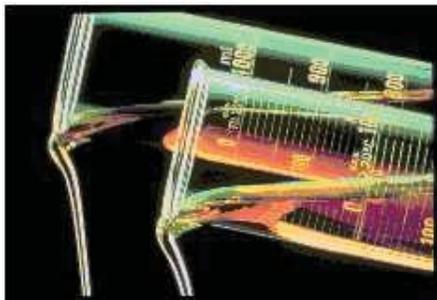
**Reminder: It is the specification writer's responsibility to ensure that the language of the specification is sufficiently rigorous to establish the desired level of quality.**

The following commonly used codes and standards have related content:

ASTM C 582	Standard Specification for Contact-Molded Reinforced Thermosetting Plastic (RTP) Laminates for Corrosion-Resistant Equipment
ASTM D 2310	Standard Classification for Machine-Made “Fiberglass” (Glass-Reinforced Thermosetting-Resin) Pipe
ASTM D 2471-71	Standard Test Method for Gel Time and Peak Exothermic Temperature of Reacting Thermosetting Resins
ASTM D 2517	Standard Specification for Reinforced Epoxy Resin Gas Pressure Pipe and Fittings
ASTM D 2563	Standard Practice for Classifying Visual Defects in Glass-Reinforced Plastic Laminate Parts
ASTM D 2583	Standard Test Method for Indentation Hardness of Rigid Plastics by means of a Barcol Impressor
ASTM D 2584	Standard Test Method for Ignition Loss of Cured Reinforced Resins(Burn Test)
ASTM D 2996	Standard Specification for Filament-Wound “Fiberglass” (Glass-Fiber-Reinforced Thermosetting-Resin) Pipe
ASTM D 3299	Standard Specification for Filament-Wound Glass-Fiber-Reinforced Thermoset Resin Corrosion-Resistant Tanks
ASTM D 3982	Standard Specification for Custom Contact Molded “Fiberglass” (Glass Fiber Reinforced Thermosetting Resin) Duct and Hoods
ASTM D 4021	Standard Specification for Glass-Fiber-Reinforced Polyester Underground Petroleum Storage Tanks
ASTM D 4097	Standard Specification for Contact-Molded Glass-Fiber-Reinforced Thermoset Resin Corrosion-Resistant Tanks
ASME Section X	Vessel Code
ASME/ANSI RTP-1-1995	Reinforced Thermoset Plastic Corrosion Resistant Equipment, 1995 Edition
ASME	Code for Pressure Piping B31.3, Non-Metallic Section

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## Resin Selection



The process of selecting a resin begins with the definition of the chemical process, specifically the chemical composition, concentrations, and temperatures. The required mechanical elongation and heat distortion temperature of the resin are then defined. If the fabrication is to be done in the field, or if the fabrication conditions are unusual, these factors will be considered. Lastly, the cost of the resin is considered.

Resin cost, while a measurable portion of the system, is generally a relatively small portion of the overall system cost, and it is usually considered subordinate to a resin system that will give the best life cycle performance.

## General Resin Capabilities

The following table lists the general resin capabilities of Reichhold corrosion resins:

Resin	Flame-Retardant	Thermal Performance	Impact & Stress Properties	Alkaline Resistance	Chlorine & Hypochlorite Resistance	Solvent Resistance	Strong Oxidizer Resistance
DION <sup>®</sup> 9800		<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>		<i>OK</i>
DION <sup>®</sup> 9100/9102		<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>
DION <sup>®</sup> FR 9300	<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>
DION <sup>®</sup> 9420		<i>OK</i>		<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>
DION <sup>®</sup> 9480		<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>
DION <sup>®</sup> 6694		<i>OK</i>		<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>
DION <sup>®</sup> 797	<i>OK</i>	<i>OK</i>			<i>OK</i>		<i>OK</i>
DION <sup>®</sup> 382-05		<i>OK</i>		<i>OK</i>	<i>OK</i>	<i>OK</i>	<i>OK</i>
DION <sup>®</sup> 4010			<i>OK</i>	<i>OK</i>	<i>OK</i>		<i>OK</i>
DION <sup>®</sup> 400		<i>OK</i>				<i>OK</i>	
DION <sup>®</sup> 490		<i>OK</i>				<i>OK</i>	
DION <sup>®</sup> 6631		<i>OK</i>				<i>OK</i>	

***OK* = Acceptable**

## ***Selecting a Resin for the Corrosion Barrier***

The first step in selecting a resin for the corrosion barrier is to define the chemical process. There are several process conditions that affect resin selection: process chemistry, process temperature, abrasive materials in the process, and mechanical forces that are imparted to the equipment. Keep in mind that small details that are overlooked can later lead to problems.

Since corrosion is a complex and often unpredictable phenomenon, it is recommended that premium corrosion grade resins, e.g. bisphenol fumarate or vinyl ester resins, be specified in the most aggressive environments. The urethane-modified vinyl ester, DION<sup>®</sup> 9800, is the best premium corrosion resistant resin available today. There are a few specialized applications where other “special use” resins are preferred; however, the exceptional corrosion resistance, high heat distortion temperature (244°F), and excellent fracture toughness of DION<sup>®</sup> 9800 make it the preferred resin for corrosion barrier service over all other bisphenol epoxy vinyl ester resins.

Because applications differ, tests and case histories should also be examined in all cases. Consult with the **Reichhold Technical Staff**, [corrosion@reichhold.com](mailto:corrosion@reichhold.com) or **1-800-752-0060**, for additional assistance.

### **Chemical Composition and Concentration**

The most obvious, but not always the most critical condition, is the chemical composition and concentration of the process. This includes trace elements and upset conditions where exposures will be relatively short, e.g. caustic wash during wash down.

If the chemical composition of the process is a single chemical, refer to the Corrosion Resistance Charts. Find the applicable concentration and then read across to identify those resins that have a temperature limitation that is equal to or greater than the process temperature.

If there is more than one chemical in the process (which is often the case) or if the concentration is greater than the maximum concentration listed, contact the **Reichhold Technical Support Group** at [corrosion@reichhold.com](mailto:corrosion@reichhold.com) or call the **Reichhold Corrosion Hotline** at **1-800-752-0060**.

### **Process Temperature**

Polyester and vinyl ester resins provide excellent structural performance when reinforced with glass fiber. In all cases, the normal operating range of temperature and short term thermal upset conditions and its duration must be defined. At higher temperatures, the mechanical properties of FRP tend to fall off and the chemical environment tends to become more aggressive. Good physical properties will generally be retained at temperatures of 200°F or higher. Each generic category of resin will respond somewhat differently to increasing temperature (Refer to the chart below). Typically the bisphenol fumarate, novolac vinyl esters, and the highly crosslinked terephthalic resins provide the best high temperature physical properties.

The suggested temperature limits shown in the Corrosion Resistance Chart provide service guidelines based on ASTM C-581 coupon testing and real world experience. These do not necessarily represent the highest temperature at which these resins may be employed in a given environment. Laminate construction, the details of the process, and the required life span of the equipment to be fabricated are significant factors which may permit a higher temperature than that listed. If none of the temperature

limits shown on the Corrosion Resistance Chart equal or exceed the process temperature, again, contact the Reichhold Technical Staff.

Appropriate DION<sup>®</sup> resin systems may be considered for use in relatively non-aggressive gas phase environments at temperatures up to 300°F.

## **Mechanical Forces**

Mechanical forces resulting from agitators or high pressure injections can lead to significant dynamic loads carried by the FRP equipment. Knowledge of mechanical forces, therefore, is important to assuring impact resistance, fatigue properties and toughness. The vinyl ester resin family is recognized as having the best fatigue resistance compared to isophthalic and bisphenol fumarate resins.

While not a direct influence in the selection of resin, high pressure, or the existence of negative pressure, often requires special design considerations that favor one resin over another. Negative pressure, for example, can lead to elastic instability, i.e. buckling modes of failure. Buckling is governed by the modulus of elasticity of the laminate, rather than by its rupture strength. A resin with a high modulus of elasticity is therefore preferred for an application subject to buckling.

## **Flame Retardance**

Is flame retardance required? If so, ASTM E-84 Flame Spread class I ratings are achieved using special “brominated” resins, sometimes, but not always, employing antimony trioxide. See *Use of Fillers* next.



## **Abrasion**

Composite pipe and ducting offer significant air and fluid flow improvement due to the smooth surfaces obtained with FRP. However, FRP is not “hard” compared to steel. FRP can abrade in the presence of high loadings of suspended materials,

especially when moving at high velocities. Slurries and coarse particulates will cause abrasion - a point that should be considered in the design process.

Abrasion resistance can be enhanced by the sliding abrasion resistance of synthetic veil or, for extreme cases, the impact abrasion resistance of silicon carbide or ceramic beads as fillers in the surface layer. Resilient liners based on rubber modified vinyl esters have also demonstrated enhanced resistance to a wide range of slurries.



## **Selecting a Resin for the Structural Wall**

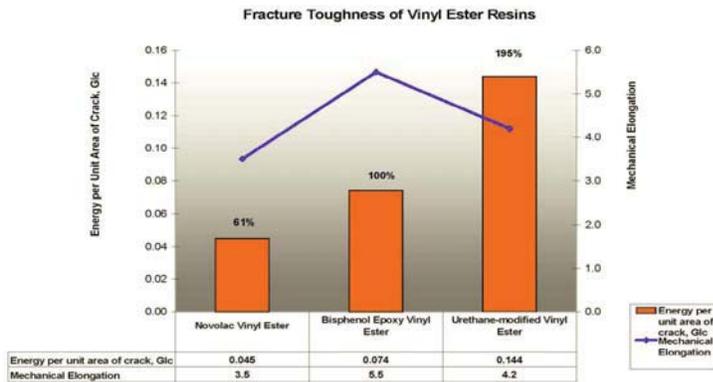
The primary strength of the structural wall comes from its fiber reinforcement, generally glass fiber. Consequently, the primary factors to consider in the resin selection for the structural wall are: 1) ease of fiber wet-out and 2) its resiliency, or toughness. In addition to creating a more robust laminate for industrial service, a resin with toughness will help avoid cracking of the resin during curing due to an excessively hot exotherm. A resin that is easy to wet-out the fiber reinforcement will result in a stronger, higher quality laminate, much as packing concrete around a steel rebar cage

will maximize its strength and structural integrity. Not only will ease of wet-out lead to more effective use of the reinforcement, it will also allow the use of a higher glass content, which will increase the strength of the laminate.

Decades ago, during the developing stage of FRP Technology and when both engineers and fabricators were working out the best and most reliable procedures to design and fabricate FRP process equipment, using the same resin in the structural wall as in the corrosion barrier was normally considered “good insurance” against a failure of the corrosion barrier and attack by the process fluids to the structural wall. And, in extremely aggressive applications, this is still a wise practice.

However, design and fabrication techniques have now evolved to the stage where competent engineers and fabricators can consistently produce high quality FRP equipment. Today, using a more expensive resin in the structural wall, because of its corrosion resistance—and not because of its better mechanical properties—is simply an unnecessary added expense.

For applications involving aggressive corrosive process materials, one of the premium vinyl ester or bisphenol fumarate resins should be specified. In many situations where a more premium corrosion resistant resin is preferred for the structural laminate, DION<sup>®</sup> 9800 is the preferred choice.



The Chart is taken from the following study: Staffan Nyström\* and Peter Vens\*\*, Studies of fracture toughness of some vinyl ester polyester resin, Swedish Institute for Materials Technology\* and University of Delft, Holland\*\*. It illustrates the important contribution that the high elasticity of a urethane can make in the storage modulus of a resin and its subsequent fracture toughness.

For more information on the use of DION<sup>®</sup> 9800 in specific applications, contact the **Reichhold Technical Support Group at 1-800-752-0060 or by email at [corrosion@reichhold.com](mailto:corrosion@reichhold.com)**.

## Resin Technologies

Reichhold, Inc. has assembled a comprehensive product line to provide an optimal resin selection for each of the diverse needs encountered in the corrosion related equipment industries. These high performance resin systems are arranged by generic resin families, or groups, much the same as metals.

See Table at right.

Those new to FRP Technology often think of FRP as a singular material made from resin and glass fibers, failing to understand that there are many different resins and resin families to choose from much as there are many different metals and metals families to choose from. The Table illustrates this very important parallel.

Note: this table shows the transition among materials of differing corrosion resistance. It does not purport to show a relationship between the corrosion resistances of metals versus that of FRP.

### ***Vinyl Ester Group***

Vinyl ester resins offer excellent structural properties and very good corrosion resistance in many acid, alkaline, oxidizing environments, and other common chemical environments. These resins are based on epoxy adducts which are extended in molecular weight and reacted with methacrylate end groups. The high elongation and resilience of these resins provides enhanced impact resistance as well as improved stress fatigue properties in systems subject to extreme thermal cycling conditions.

### **DION® 9800**

A unique non-promoted, urethane modified vinyl ester with several distinguishing features. It does not foam when catalyzed with ordinary MEKP, and provides excellent glass wetting characteristics. This makes it easier for fabricators to produce high quality, void free laminates. It also has outstanding chemical resistance and physical properties. It possesses 95% more fracture toughness than any member of the bisphenol epoxy vinyl ester resin family. DION® 9800-05AS is a low styrene emissions version of this resin.

DION® 9800 is the preferred resin for engineered equipment subjected to harsh and demanding service.

### **DION® 9100/9102**

A pre-promoted, generic bisphenol epoxy vinyl ester resin used in filament wound tanks and pipes for a wide range of acidic, alkaline, and other chemicals. A non-promoted version is also available. DION® 9102 is a lower viscosity, reduced molecular weight versions of DION® 9100, which has similar corrosion performance.

Resilient corrosion resistant bisphenol epoxy vinyl ester is particularly suited to high stress/fatigue and thermal cycling situations where optimum structural properties are desired. It is used extensively in filament wound FRP tanks and piping.

<u>Metals</u>	<u>Premium Corrosion Resins</u>
▪Carbon Steel	▪ <u>Isophthalic</u> Polyester
▪Stainless Steel	▪ <u>Terephthalic</u> Polyester
304 Stainless	▪ <u>Vinyl Polyester</u>
316L Stainless	▪ <u>Bisphenol Epoxy Vinyl Ester</u>
317L Stainless	▪ <u>Epoxy Novolac Vinyl Ester</u>
▪904 High Molybdenum	▪ <u>Urethane-modified Vinyl Ester</u>
▪Inconel 625	▪ <u>Bisphenol Fumarate</u>
▪C 276	

## DION® IMPACT 9102-70 (US)

A special version of DION® 9102-70 which offers lower color, reduced viscosity and improved curing at lower promoter levels. This resin is particularly suited for filament winding applications which require fast and efficient wet-out of reinforcement material. It is certified to NSF/ANSI standard 61 for potable water tanks and piping at ambient temperature.

## DION® 9160

DION® 9160 is a low styrene (<35%) version of DION® 9100 vinyl ester resin.

## DION® 9420

DION® 9420 is a specialty vinyl ester resin that features additional cross-linking sites on the polymer chain and in the monomer system. Ultra-high cross-link-density yields a resin with an exceptionally high HDT (325°F), excellent resistance to solvents and very good retention of physical properties at elevated temperatures.

## ***Epoxy Novolac Vinyl Ester Group***

### DION® 9400

DION® 9400 is a premium epoxy novolac vinyl ester resin that has been specially modified for improved fabrication properties. This high crosslink density resin provides excellent retention of mechanical properties at elevated temperatures, offers a high resistance to solvents, chemicals, acidic, alkaline, and oxidizing environments.

### DION® 9480NP

A non-promoted (NP) epoxy novolac containing vinyl ester. It is unique in providing outstanding resistance to many organic chemicals including aliphatics and aromatics, esters, ketones, and alcohols in addition to resistance to degradation from high temperature exposure.

High temperature epoxy novolac vinyl ester display improved performance in aggressive solvents and organic vapors. They are not recommended for aggressive alkaline environments, especially at high temperatures.

## ***Rubber Modified Vinyl Ester Group***

### DION® 9500

DION® 9500 is a non-accelerated, rubber modified epoxy based vinyl ester resin. This resin possesses a unique combination of properties such as high tensile elongation, good toughness, low shrinkage and low exotherm. It also demonstrates excellent adhesion properties and good chemical resistance. These properties make this vinyl ester well suited as a primer and for applications subjected to dynamic loads.

## ***Bisphenol Fumarate Group***

Bisphenol fumarates, such as DION<sup>®</sup> 6694 and DION<sup>®</sup> 382, provide excellent corrosion performance in strong acids and have the highest resistance to alkali at elevated temperatures. They are derived from alkoxyated bisphenol-A with fumarate reactive groups.

Bisphenol fumarate polyesters are characteristically rigid and have very high glass transition temperatures. This facilitates high structural performance retention, even at temperatures over 300°F. They are used predominantly in hand lay-up applications utilizing mat or chopper spray for complex process equipment typically having high cross sectional thickness.

### **DION<sup>®</sup> 6694**

Premium corrosion grade modified bisphenol fumarate resin providing superior performance in high temperature and alkaline applications. Widely used for contact molded pulp and paper mill components and chlor-alkali applications, especially cell covers and auxiliary chlorine handling equipment.

### **DION<sup>®</sup> 382**

Bisphenol fumarate resin provides a wide range of chemical resistance. They are particularly well regarded for alkaline environments and formulated for contact molding applications requiring FDA and USDA approvals. DION<sup>®</sup> 382-05A is pre-accelerated with dimethylaniline.

### **DION<sup>®</sup> 4010A**

Resilient bisphenol fumarate resin formulated for filament winding applications or cases where more flexibility is required. They are recommended for tanks and piping used in caustic, sodium hypochlorite, and in food and pharmaceutical processes. DION<sup>®</sup> 4010A is pre-accelerated with dimethylaniline and meets FDA and USDA requirements.

## ***Terephthalic Group***

These resins are very similar to their isophthalic counterparts but do provide higher temperature performance and somewhat higher tensile elongation. They are derived from terephthalic acid, which imparts enhanced thermal and corrosion properties to the products.

### **DION<sup>®</sup> 490**

High molecular weight terephthalic polyester resins offer excellent structural properties and are resistant to a wide variety of chemicals at moderate temperatures. Resins with the highest corrosion performance are rigid. Flexible isophthalics generally have poor corrosion resistance and should be used only for non-aggressive materials at ambient temperature.

Resins in this class perform very well in acidic conditions and are qualified under FDA Title 21, CFR 177.2420. They are not recommended for use in alkaline environments.

## DION® 495

Terephthalic polyester resin offers similar structural and corrosion properties to DION® 490 with the added benefit of low styrene content.

## DION® ISO 6631

Rigid, thixotropic, prepromoted resin suitable for chopper spray-up and filament winding. High molecular weight isophthalic resin with good corrosion resistance and excellent physical strength properties, meets FDA and USDA requirements.

## DION® ISO 6334

Resilient isophthalic resin developed for filament winding and centrifugal cast pipe intended for ambient sewage and wastewater, meets FDA requirements.

## ***Chlorendic Group***

### DION® 797

Premium chlorendic-based polyester resin engineered to provide exceptional corrosion resistance, particularly to mixed, concentrated acids, and other oxidizing environments at high temperatures. Heat resistance to gases and vapors up to 350°F results in excellent mechanical strength retention characteristics at these elevated temperatures. This chlorendic polymer provides fire retardant features for applications requiring ASTM E-84 Class II ratings, when used with the addition of 5% antimony trioxide. Chlorendic resins are rigid and should never be used in alkali environments.

## ***Flame Retardant Group***

DION® FR 7767 and DION® FR 7704 are prepromoted resins formulated from brominated intermediates to meet a range of fire performance requirements. Brominated derivatives of vinyl esters (DION® FR 9300) provide superior thermal and corrosion performance. Brominated polyester resins provide excellent fire protection at lower cost and are usually selected for moderate temperature requirements in ducts, hoods, fans, and other fume handling applications. The addition of antimony trioxide in DION® FR 7704 is required in all resins to meet a flame spread rating of 25 by ASTM E-84. DION® FR 7767 is Class 1 (< 25 flame spread) without antimony.

### DION® FR 9300

DION® FR 9300 series are brominated, bisphenol-epoxy vinyl ester that provide corrosion-resistance in a wide variety of acidic and mildly alkaline environments. These tough, high-strength resins can be used to produce glass-reinforced laminates with excellent impact and stress-fatigue resistance, making them ideal for filament winding operations and applications that require resistance to corrosive environments and thermal cycling. An ASTM E-84 Class 1 flame-spread rating (<25 flame spread) can be achieved by incorporating 1.5% antimony trioxide into the resin.

## **DION® FR 9310**

The DION® FR 9310 Series are non-promoted, premium flame retardant resins designed to meet ASTM E84 Class I flame spread properties without the addition of antimony based synergists. DION® FR 9310 series resins also have low VOC content (<35%) and provide corrosion resistance equal to, or in some cases superior to, well-recognized DION® FR 9300 resin. The DION® FR 9310 Series has a typical heat deflection temperature (ASTM D-638) of 125°C (257°F)

## **DION® FR 9315**

The DION® FR 9315 Series are non-promoted, premium flame retardant resins designed to meet ASTM E84 Class I flame spread properties without the addition of antimony based synergists. DION® FR 9315 series resins also have low VOC content (<30%) and provide corrosion resistance equal to, or in some cases superior to, well-recognized DION® FR 9300 resin. The DION® FR 9315 Series has a typical heat deflection temperature (ASTM D-638) of 136°C (276°F)

## **DION® FR 7704**

DION® FR 7704 series are low-viscosity, high-solids, general-purpose flame-retardant\* polyester resins. These resins provide smooth gelcoat surfaces, excellent fiberglass wet-out and positive curing performance, making them well-suited for a variety of general-purpose flame-retardant and moderately corrosive vapor FRP applications. In addition, incorporation of aluminum trihydrate allows DION® FR 7704 resins to meet certain smoke emission and smoke toxicity specifications.

## **DION® FR 7709**

DION® FR 7709 is a low-viscosity, high-solid, general-purpose flame-retardant polyester resin. These resins have been formulated to offer excellent fiberglass wet-out while maintaining a low HAP monomer content and offer superior curing performance. The good mechanical properties make these resins well suited for a variety of fabricating applications.

## **DION® FR 7767**

DION® FR 7767 is a specialty flame-retardant isophthalic polyester resin that features an ASTM E-84 Class 1 flame spread without antimony trioxide. DION® FR 7767 provides excellent fiberglass wet-out and positive resin curing performance, making it ideal for demanding flame-retardant FRP applications.

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