ADVANCED POLYMER COATINGS

A Technical Whitepaper
Polymer Technology in the Coating Industry

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INTRODUCTION
Polymer Technology in the Coating Industry

To properly understand many of the phenomena that apply to coating chemistry it is essential to have a working appreciation of the chemical and physio-chemical forces that hold the coating together.

The more we understand how polymers work the better the choice can be made to solve corrosion problems.

It is the Aerospace Composite requirements for high strength, light weight, corrosion resistance, cost effective materials that led to the choice of Polymers for their composites.

In order to meet the performance specifications set by the aerospace industry in the early stages of missile development, which led to the Boeing 787 and AirBus 350, the following Polymers were extensively investigated.

- **Phenolics**
- **Epoxies**
- **Polyester**
- **Vinylester**

Polyester and Vinylester were eliminated early in the investigation due to low physical properties and poor bonding to the reinforcing fibers used in various composite structures.

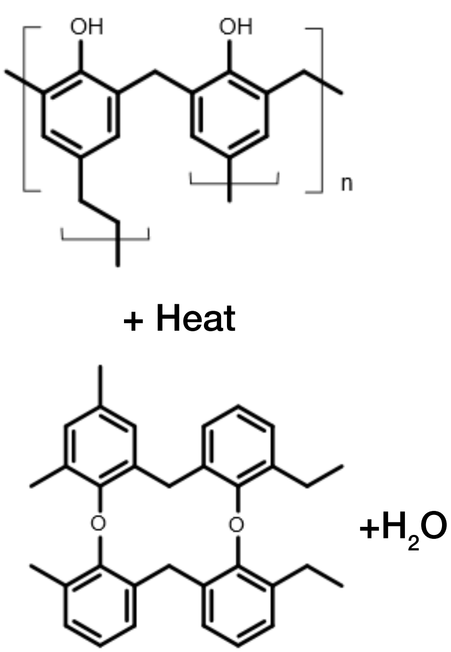
Phenolics are in limited use due to lack of toughness and processing limitations.

Epoxy polymers became the major choice for aerospace structures due to their variable formulation capabilities, high strength, high bond strength and low surface energy.

PHENOLIC
A 70 Year Old Technology

Phenolic was the first Thermoset developed (called Bakelite) was originally used to replace Ivory in Billiard Balls in the beginning of the twentieth century. Phenolic Coatings have been around for over 70 years.

Generalized Diagram of (High Bake) Phenolic



Crosslinking by condensation reaction giving off H_2O

Advantages

Chemical Resistance:

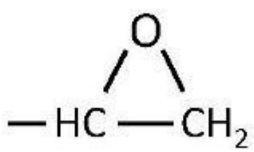
- Sulfuric Acid - Good from 78% to 98%
- Solvent Resistance - Fair
- Caustic Resistance - Poor
- Chlorite/Chloride - Poor

Disadvantages

- Very Brittle
- Porous to Sulfuric Acid and water vapors causing “Hydrogen Groving”
- 3 or more coats with heat curing @ 250°F required after each coat with final cure @ 400°F due to condensation reaction
- Non-repairable
- Very high solvent content
- Can not be applied to large field tanks

EPOXY
A Wide Range of Choices

The term “Epoxy” is basically a generic term meaning any Organic Structure having Epoxide or Oxirane end caps.



OXIRANE

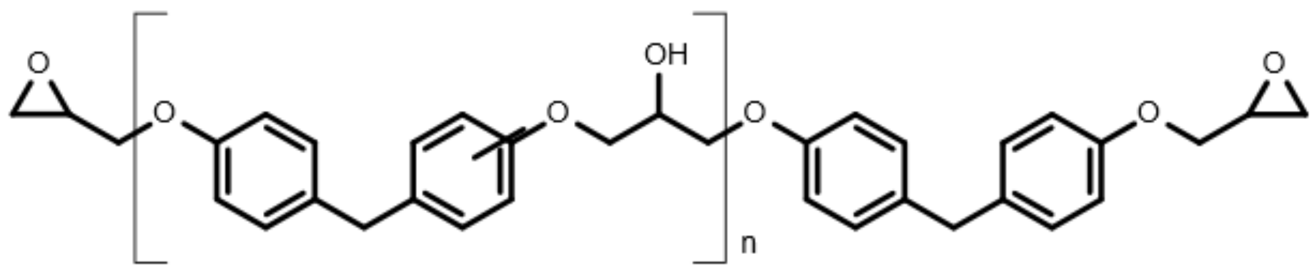
Epoxies come in a large number (+50) of structures ranging from the simple Di-Functional resins to Multi-Functional and include Aromatic and Aliphatic backbones. Epoxy polymers are reactive with themselves with heat or with curing agents. Curing Agents used in Chemical Resistance Coatings:

- Aromatic Amines
- Cyclo-aliphatic
- Aliphatic Amines
- Lewis Acid Catalyst

During cure, epoxy and curing agent molecules chemically crosslink to form larger molecules that form three dimensional ladder like networks. Generally to increase a polymer’s temperature and chemical resistance cross-linked density (Number of cross-links per unit of volume) of the polymer must be increased. The result of higher cross-link density is reduced flexibility and toughness. All competitive Epoxies use flexibilizers or diluents to overcome this problem. This inclusion reduces chemical and temperature resistance.

EPOXY
Various Epoxies Used In Coatings

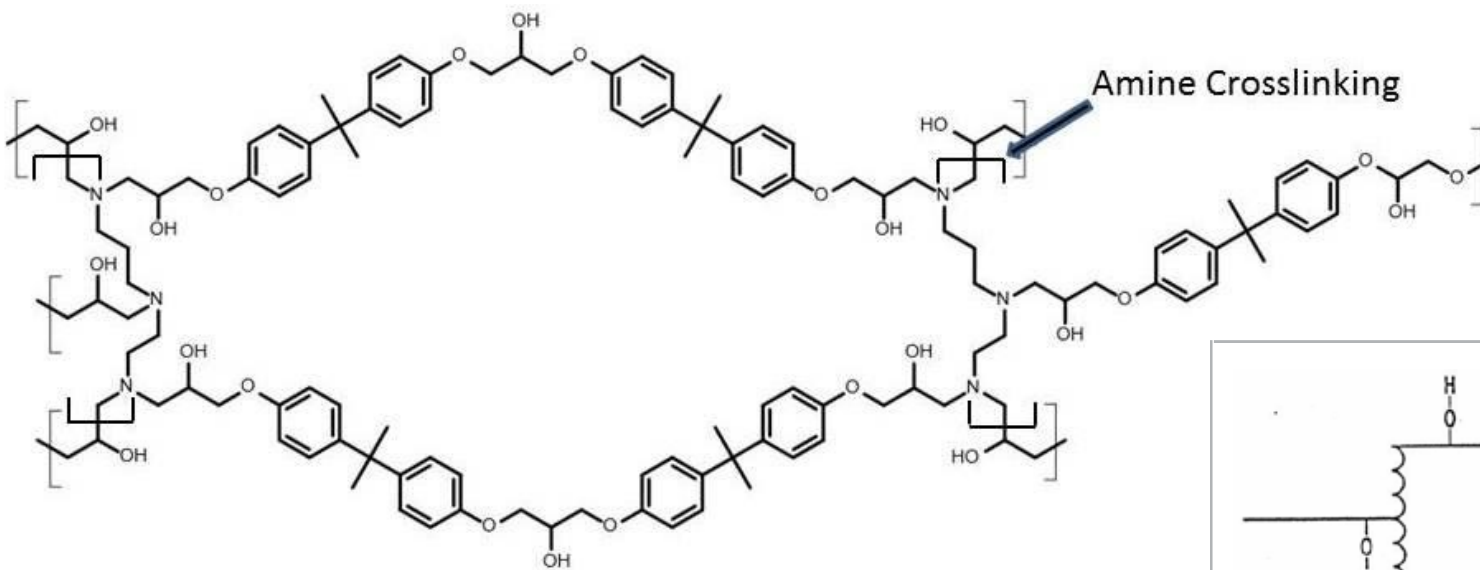
Generalized Diagram of Glycidyl Ether of Bis-Phenol "A"



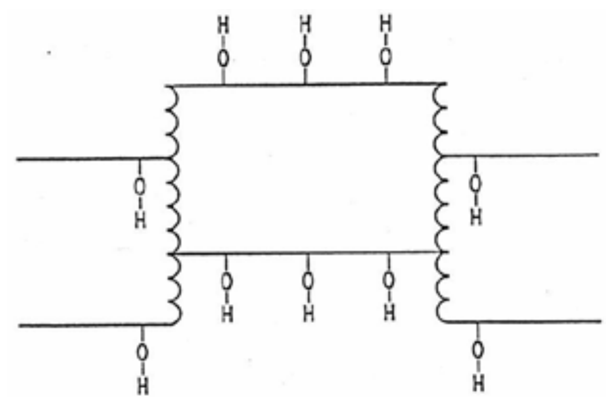
- DGEBA First Epoxy manufactured in large quantities
- Still used in low cost Epoxy Coatings
- Low Chemical Resistance
- High viscosity need diluent or solvent to lower viscosity for coatings

EPOXY RESIN
Diglycidyl Ether of Bisphenol A Cured with an Aliphatic Amine

Amine curing agents crosslink by forming Hydroxyl groups (OH) which are Hydrolizable. Hydrolysis is a chemical decomposition in which a molecular structure is broken down and changed into other structures by taking up the elements of water (Oxygen or Hydrogen).



All Epoxies cured with Amines form
Hydroxyl molecules in the ladder like structure



Simplified Epoxy's crosslinked ladder like structure

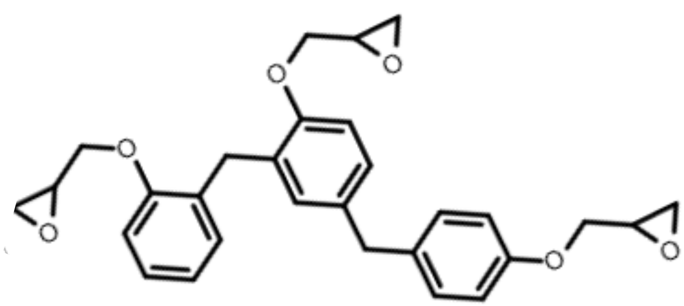
EPOXY
Normal Novolac Epoxies

Normal Novolac Epoxies are linear structures and range from semi-solid to solid depending on number of functional endcaps.

The higher the functionality the higher the crosslink density, the higher chemical and temperature resistance.

So called Novolac Epoxy coatings contain only 10 to 20% Novolac Resin. Most are called Phenol-Epoxy.

Generalized Diagram of Glycidyl Ether of Novolac



Advantages

- Acid Resistance - Limited
- Caustic Resistance - Good
- Solvent Resistance - Limited

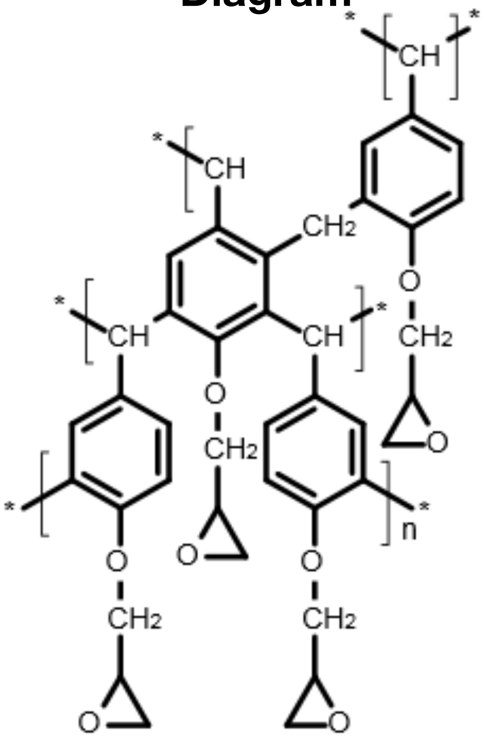
Disadvantages

- Need full Heat Curing to reach maximum chemical resistance
- Need Diluents or Solvents to lower viscosity for coatings decreasing Chemical and Temperature Resistance

EPOXY
A Patented Bridged Novolac Polymer

A Patented Bridged Novolac Polymer used in Advanced Polymer Coatings ChemLine® and MarineLine® coatings provides higher functionality than any other Novolac.

Chemline's/MarineLine's Bridged Pb5 Novolac Epoxy Generalized Diagram



When Pb5 Novolac Epoxy is catalyzed epoxy groups bond together thru ether linkages (C-O-C) one of the strongest bonds in chemistry. ChemLine's/MarineLine's high crosslink density delivers high corrosion and temperature resistance.

Advantages

Chemical Resistance

- Acids – Excellent
- Caustics – Excellent
- Solvents – Excellent
- Oxidizing Agents – Good

Disadvantages

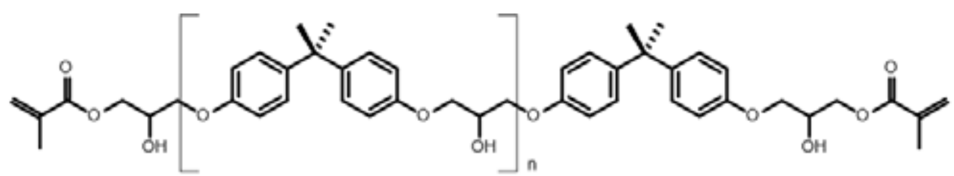
- Needs to be heat cured

VINYLESTERS
Vinylesters Have Different Backbone Structures

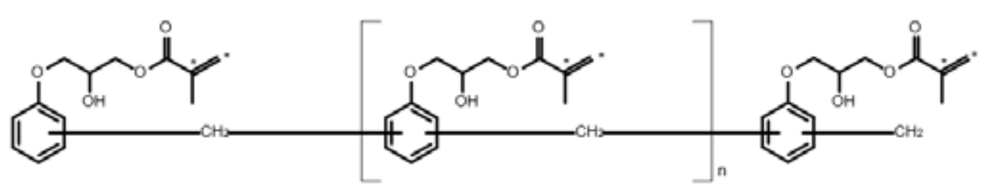
In order to improve Polyester's chemical resistance one ester group was removed and Vinyl Groups were added as end caps on to the Bisphenol A molecular structure.

The two Vinylesters are: (Generalized Diagrams)

Bisphenol "A" based Vinylester.



Novolac Epoxy based Vinylester.



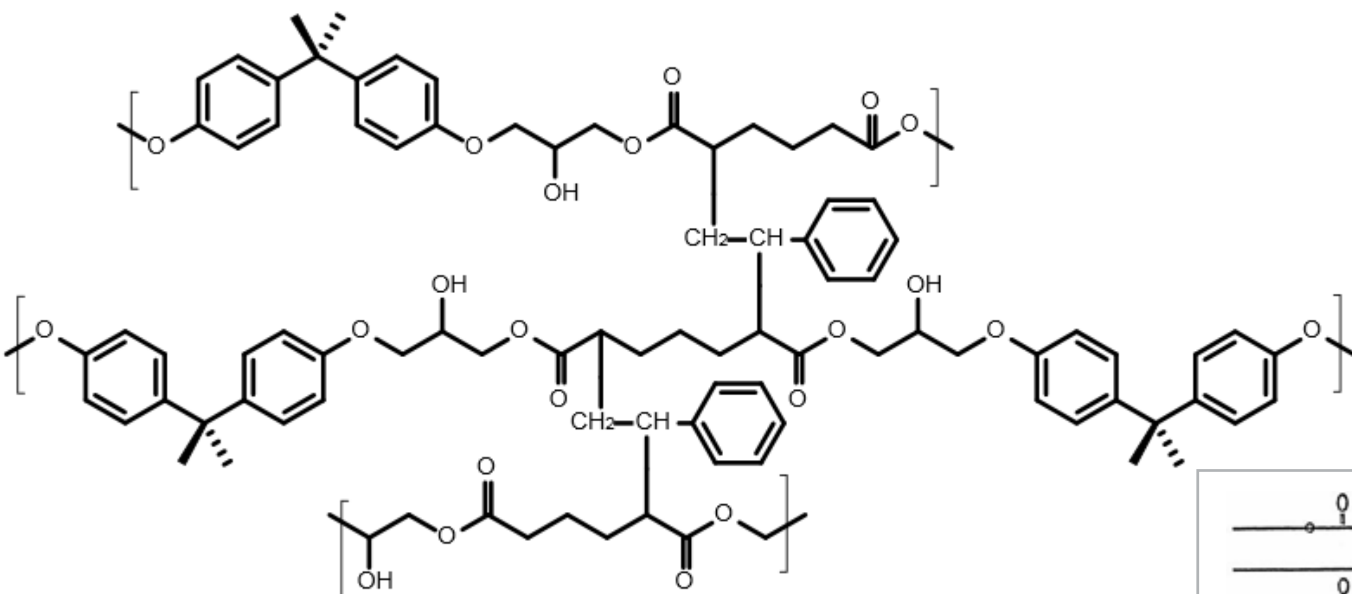
There are two types of Vinylesters with different backbone structures. Vinylesters are limited to modification or improvement after being manufactured and removed from the chemical reactor (unlike Epoxies which can be modified through the crosslinking agent). Vinylesters, like Epoxies, form 3 dimensional ladder like structure.

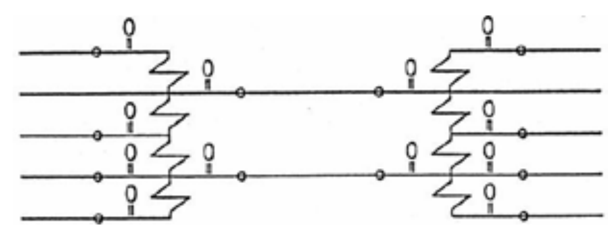
Both Vinylesters require a co-reactant (Styrene Monomer), a catalyst (Cobalt Naphthenate) and a Free Radical initiator (Peroxide).

POLYMERIZED BISPHENOL A VINYLESTER
Open Ladder Structure

Vinylesters have very open ladder like structure.To slow down permeation of chemicals, decrease shrinkage and brittleness Flake Glass is added to the resin.

Hydroxyl (OH) and Ester ($\overset{O}{\|}$) Groups are Hydrolyzable.

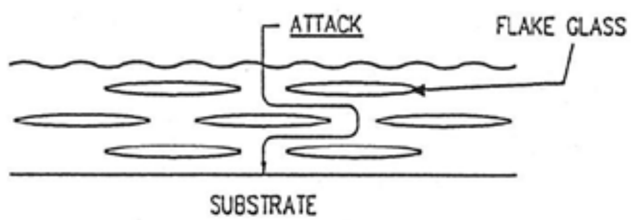




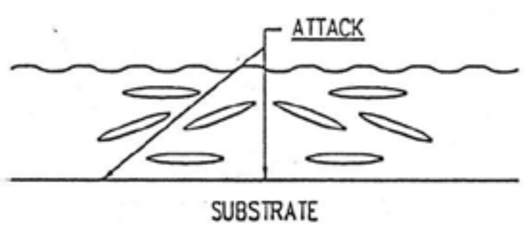
Simplified Vinylester's crosslinked ladder like structure

VINYLESTER
Flake Glass Theory

Flake Glass Theory



NORMAL FLAKE GLASS FORMATION IN RESINS



Advantages

- 1 to 70% Sulfuric Acid – Good
- Chlorite and Chloride containing Chemicals – Good
- Temperature Resistance to 300°F

Disadvantages

- Caustics - Poor
- Absorbs Water
- Solvents – Limited
- High Styrene content and strong Odor
- High Cure Shrinkage
- Brittle
- Bond Strength - Poor
- To Achieve Good Chemical resistance Need Heat Curing
- Non-Repairable

FOR MORE INFORMATION

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