SOME USEFUL PRODUCTS BASED ON EPOXY RESINS

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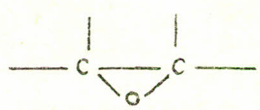
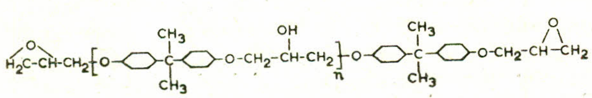
Some useful industrial and engineering materials like high temperature anticorrosion linings, universal flooring for chemical plants, grinding stones and fire resistant coatings on wood have been made from epoxy resins. Steel and iron have been metallized with Zn, Tin and Al using new technique based on these resins.

An epoxy resin is generally a product of the reaction between epichlorohydrin and bisphenol-A. The product is called an epoxide or epoxy resin because of the existance in the polymer of a carbon-oxygen chemical arrangement known as an epoxide group or an oxirane ring[1] shown in the following manner:—



Most of the epoxide resins at present available have the following general structure.[2]



These resins are liquid or solid, depending upon the degree of polymerisation, indicated by refractive index.

Epoxy resins, as such, are useless thermoplastic materials. To convert them into useful products, they are hardened or cured by condensing with anhydrides of polybasic acids, like phthalic anhydride, alkaline curing agents such as polyamines or compounds containing active hydrogen atoms.

Unlike[3] the condensations leading to polyesters and polyamides, in which one water molecule is split out of the product, the expoxide condensation proceeds by opening cyclic structures which then combine to form chains. Since end groups[4] are not lost, there is little volume change on condensation; furthermore, no water removal is involved. These two inherent properties are primarily responsible for the rapid growth in the use of these resins in recent years. They find application in many fields of industry and technology on account of their high strength, excellent adhesion, outstanding insulating properties and chemical resistance.

Uptil now, no work appears to have been done in Pakistan on epoxy resins. In view of the versatility of these resins and the multifarious uses to which they can be put with success, no country can ignore their development for long. Because of the availability of glycerine and acetone in the country now, it was considered desirable to start work on these useful resins.

Epoxy resins of different properties have been prepared by changing the proportion of the reactants. The low molecular wt. epoxies can be prepared by taking epochlorohydrin in large excess. Some of the epichlorohydrin reacts with bis-phenol-A while the rest provides the medium for the condensation of the reactants. After the completion of condensation, the excess epichlorohydrin is recovered by distillation in vacuum. In case of high molecular wt. and solid resins, only the calculated quantity of epichlorohydrin is taken for condensation. Thus, solid resins with melting point upto 150°C. have been prepared. Resins of low viscosities have been used without expensive solvents in high temperature coatings, fire-proof coatings and in metallizing steel. High viscosity resins were found to be satisfactory for their high chemical resistance. These resins in combination with phenol-formaldehyde and some suitable fillers have been used in the production of lining material which can be applied within the factory by an ordinary operator. High viscosity resins have also proved useful for the production of universal flooring for chemical industry.

Experimental

Epoxy Resin.—In a 2 lit. four-necked flask equipped with thermometer, reflux condenser and mechanical stirrer were placed 228 g.[5] of 2,2-bis (4-hydroxy phenyl propane) and 925 g. of epichlorohydrin. The flask was heated in a water bath. 82 g. of NaOH (10% solution) were added in ten equal instalments. After the addition of NaOH, the reaction flask was heated for another hour at a temperature of 95°C. with constant stirring. The reaction being exothermic, the temperature during condensation should not be allowed to exceed 100°C. After the completion of condensation, the solution was filtered by suction and the filtrate distilled in vacuum to remove excess of epichlorohydrin when a light yellow viscous resin was left behind.

Epoxy resin of high viscosity was prepared in the same way, taking 228 g. of bisphenol, 145 g. of epichlorohydrin and 75 g. of NaOH.

Resins thus prepared were utilized in a number of useful products which are described below.

New Lining Material for Chemical Plants.—12 g. of graphite and 27 g. of specially compounded hard rubber powder (200 mesh) were mixed in a pebble mill with 45 g. of liquid epoxy resin and 11.5 g. of phenol-formaldehyde resin (Resol form). After the addition of diethylene triamine (4.5 g.) and thorough mixing, the mass was applied on glass plates and was allowed to set for 24 hours at room temperature. The composition was tested for its chemical resistivity by dipping the coated glass pieces in different chemicals. The results are recorded in Table 1.

TABLE 1.—CHEMICAL RESISTANCE OF NEW LINING MATERIALS.

Chemicals	Permissible concentrations for which the material is excellent.
Alum	All concentrations
NH_4Cl	,, ,,
$(NH_4)_2SO_4$	,, ,,
$CuSO_4$	,, ,,
NaCl	,, ,,
$NaNO_3$	,, ,,
Na_2SO_4	,, ,,
NaOH	,, ,,
H_2SO_4	Upto 85%
HCl	,, 35%
HNO_3	,, 20%
Phosphoric acid	,, 85%
HF	,, 60%
BaS	,, 10%
Na_2CO_3	,, 10%
Na_2S	,, 10%

Epoxy Flooring.—A composition of suitable consistancy was prepared by blending 15 parts of high viscosity resin with 50 parts of inert and cheap material like barytes. 1.3-1.5 parts of diethylenetriamine were then incorporated and the mass applied on glass plates and concrete slabs with a spatula approximately to a thickness of 1/10″. It set to a hard stone-like mass in 24 hrs. The chemical resistance of coated glass plates was tested with a number of chemicals. The results are given in Table 2.

TABLE 2.—CHEMICAL RESISTANCE OF EPOXY FLOORING.

Test Fluid	Condition of flooring material	
	after one week	after two weeks
Ammonium hydroxide 10%	Excellent	Excellent
Ammonium hydroxide concn	Good	Good
Citric acid 5%	Excellent	Excellent
Carbon tetrachloride	,,	,,
Calcium hypochlorite 8%	,,	,,
Hydrochloric acid 37%	,,	,,
Nitric acid 10%	Good	Good
Phosphoric acid 10%	,,	,,
Sulphuric acid 50%	,,	,,
Sodium hydroxide 50%	Excellent	Excellent
Sodium chloride 25%	,,	,,
Ammonium sulphate 25%	,,	,,
Sodium sulphate 5%	,,	,,
Potash alum	,,	,,
Kerosene	,,	,,
Soap solution	,,	,,
Petrol	,,	,,

Epoxy flooring has been found indestructable, stronger than concrete and non-skid. It was prepared in different beautiful colours. Zinc oxide hinders the curing mechanism of epoxy resins. It should not, therefore, be used to get a white shade flooring. Attractive white shades were produced by the addition of 10% TiO_2 to the above flooring composition.

Water-proof Coating to Prevent Efflorescence on Concrete.—It was observed that epoxy resins without filler absorb more water as compared with those containing fillers. Different cheap fillers were studied and the percentage of water absorbed plotted against time as in Fig. 1.

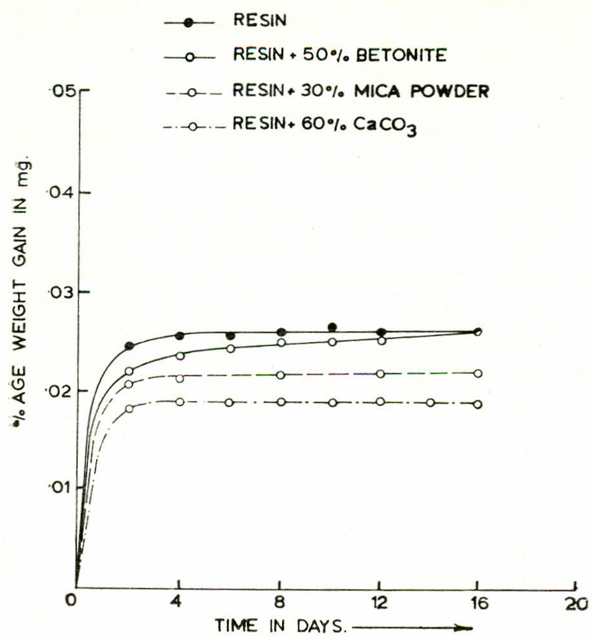


Fig. 1. — Effects of Fillers on Properties of Epoxy Resins. Water absorption at room temperature).

Coatings containing 62% $CaCO_3$ were immersed in salt solutions and other reagents to examine their chemical resistance. The results are tabulated in Table 3.

The strong seal of the composition produced on the concrete prevents efflorscence and stops the oozing out of the alkaline salts extracted from the concrete by moisture.

High Temperature Coatings.—Coatings which can stand high temperatures were made by thoroughly mixing 100 parts of low molecular weight epoxy resin, 1.5 parts (100 mesh) mica powder and 35 parts aluminium powder. Just before the application of this mixture, 10 parts of ethylenediamine were incorporated in it. These coatings have excellent service characteristics at 300—350 °C.

Decorative Coatings.—Formica like sheets produced from these resins were quite stable and strong. Various attractive finishes on bakelite backing, wood, steel, and Al-alloys have been made. These sheets have vast field of application in furniture, table tops, trays, doors, windows and inner linings of railway coaches and buses etc.

TABLE 3.—CHEMICAL RESISTANCE OF 62% $CaCO_3$ PIGMENTED RESIN PAINT USED FOR THE PROTECTION OF CONCRETE.

Reagent	Time in days	Condition of films
1. Tap water	60	Excellent
2. Tap water + 5% NaCl	90	,,
3. Tap water + 5% NaCl, 3% KCl, 3% $MgCl_2$.	90	,,
4. Tap water + 3% $CaCl_2$ and 2% $MgCl_2$	90	,,
5. Vegetable oils	10	,,
6. Animal fat	10	,,
7. 10% soap solution	7	,,

Fire-proof Coatings for Wood.—The wooden article was impregnated with a solution containing 12 parts ammonium chloride, 15 parts ammonium carbonate and 10 parts each of boric acid and sodium hydroxide per 100 parts of water. After complete drying of the wood, it was coated with a paint consisting of 100 parts low molecular weight epoxy resin, 12 parts ammonium phosphate, 8 parts borax, 40 parts asbestos powder, (200 mesh) and 25 parts mica powder (200 mesh). Just before the application of the paint it was activated by 10 parts diethylene triamine. After overnight cure, it was tested by pasting a patch of cotton wool soaked in acetone on the painted wood and burning it. It was observed that there was no crack on the surface and the paint protected the wood from burning.

New Technique of Metallizing Steel.—This process depends upon the application of a special composition consisting of metal powders and a low molecular weight epoxy resin. This composition is applied to the well-cleaned article of steel which is then heated gradually, first at 60°C. and then at a temperature approaching the melting points of the respective metal powders. Different metal powders like aluminium, copper, zinc, tin, Cr and Ni were studied for metallising steel. Good results were achieved only with Al, Tin and Zn.

Grinding Stones and Grinding Pins.—50 parts of epoxy resin and 45 parts of phenolic resin (resol form) were heated together in a china dish for 1-2 minute at 100°C. 1000 parts abrasive material was then mixed with it thoroughly and the whole mass put into a steel die and pressed under a pressure of 5000 lb./sq. inch. The stone so formed was taken out of the mould and was baked, first at 80°C. for 4 hours and then at 150°C. for another 8 hours.

In case of grinding pins, a layer of epoxy resin containing suitable filler was applied on the specific portion of the steel pin which was to be covered with the same abrasive composition as is used for grinding stones.

Results and Discussion

It is evident from Table 1, 2 and 3 that the different compositions evolved are useful materials of construction for the chemical industry. There are a number of other materials which can be used for coating and lining the concrete storage tanks. But they fail in one respect or the other. Materials such as concrete, abestos cement, brick work and plaster work are alkaline which affect adversely the setting of phenol and urea resin coatings. Oil-based paints are readily saponified when applied to concrete. The vinyls and chlorinated rubber paints, no doubt, possess good alkali resistance but their adhesion to concrete is not very satisfactory. Epoxy-based compositions have proved very successful on every type of material. It is, therefore, more economical to construct tanks of big capacity lined with epoxy resin for the handling and storing of corrosive chemicals.

The nature of fillers affects the water absorption properties of epoxy resins. The compositions with $CaCO_3$ as the filler were successful in overcoming the corrosion of outgoing drainage from the chemical industry and laboratories. Moreover, due to the smooth surface of these paints the cleaning becomes easy.

Epoxy resins, when mixed with suitable chemicals give coatings which can stand high temperatures, rendering the coated material even fire-resistant. Ordinary paint coatings are not stable above 100°C. At this temperature,[6] the film ages rapidly with the consequent loss of elasticity, adhesion and corrosion resistance. In the range of 100-200°C., the film starts breaking down and in some cases this break-down is accompanied by the evolution of gases such as HCl in the case of P.V.C. and other chlorinated polymers. At temperatures above 300°C., the majority of organic film-forming materials are carbonized. All these difficulties are eliminated by a coating based on epoxy resins.

The technique of aluminizing iron and steel with the help of epoxy resins is more advantageous as compared with the conventional method of hot dipping because the resinous material protects the aluminium from oxidation, especially during the time the temperature is raised and when the resin burns away, the metal particles sinter on to the steel surface.

As an adhesive, epoxy resins along with phenolic resins have proved good binding materials for abrasives. The grinding stones produced have got better service characteristics.

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