

Surface Coatings Based on Water-Soluble Epoxy Allyl Ether Polymer Systems

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Synopsis

Water-soluble polymers based on epoxy esters modified by partial allyl ethers of various polyhydric alcohols were prepared. These have very good hydrolytic and storage stability. The paints prepared from them performed well as primers and also exhibited moderate gloss. The effect of using melamine resin as external cross linker was also studied.

INTRODUCTION

The success of water-thinned emulsion paints which generally give matte finishes has stimulated a great deal of research into producing water-thinnable air-drying and glossy coatings.¹ Many attempts have been made in this direction. The maleinized oils gave glossy but unsatisfactory paint films which were not only sensitive to water but also yellowed on ageing.² High-molecular weight maleinized oils with improved overall properties were prepared by esterifying styrene-allyl alcohol copolymer with maleinized drying oil fatty acids.³ However, none of these polymer systems gave acceptable drying and gloss, and also exhibited poor hydrolytic and storage stability apart from poor alkali resistance due to the presence of many ester linkages.

Polyether esters derived from partial allyl ether alcohols and dicarboxylic acids have been reported to give solvent-soluble air-drying polymers with good resistance to elevated temperatures and discoloration by ultraviolet, as well as giving high gloss to the dried coating.^{4,5} The drying potential is reported to increase with the percentage of allyl ether groups present in the polymer molecule.⁶ The introduction of allyl ether linkages in hydrolytically stable water-soluble polymers to obtain air-drying and glossy paint films has been reported in a few patents.⁷

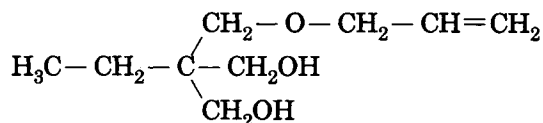
In the present study, the preparation of water-soluble polymers based on epoxy esters modified with partial allyl ethers of various polyhydric alcohols has been carried out and paints based on these polymers have been evaluated as primers and top coats.

EXPERIMENTAL

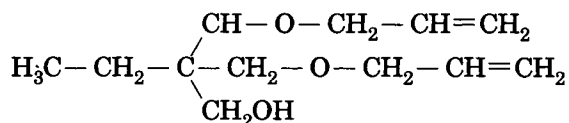
Raw Materials

The partial allyl ethers of polyhydric alcohols, viz.,

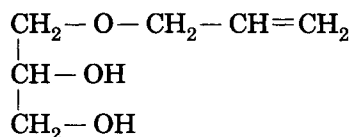
- (a) monoallyl ether of trimethylol propane (MATMP)



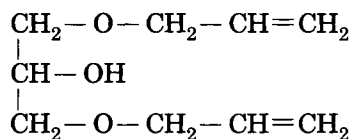
- (b) diallyl ether of trimethylol propane (DATMP)



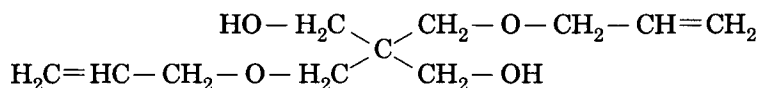
- (c) monoallyl ether of glycerol (MAG)



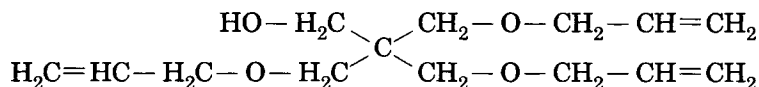
- (d) diallyl ether of glycerol (DAG)



- (e) diallyl ether of pentaerythritol (DAPE)



- (f) triallyl ether of pentaerythritol (TAPE)



were used in the present investigation. We have already reported detailed synthesis of these partial allyl ethers along with their methods of purification and analysis.⁸ In general, partial etherification was carried out by reacting a polyhydric alcohol with allyl bromide in the presence of 60% aqueous sodium hydroxide solution. These partial allyl ethers were characterized by their infrared and proton magnetic resonance spectroscopy in great detail.⁸

The epoxy resin used in the present work was a commercially available Araldite 6084 of M/s. Ciba Geigy, having an epoxy equivalent weight 870–1025, melting point 95–105°C, and viscosity as 40% solution in butyl carbitol at 25°C 4.7–8.9 cps.

Maleinized dehydrated castor oil fatty acid was prepared by reacting dehydrated castor oil fatty acid with maleic anhydride (8 percent on the weight of fatty acid) at 220°C for 5 hours. This product had an acid value of 239.

Preparation of Water-Soluble Epoxy Allyl Ether Polymers

These were prepared essentially by two methods. In the first method the partial allyl ether was esterified with maleinized drying oil fatty acid in appropriate proportions (as shown in Table I) by reacting for 2-3 h at 160°C using sodium carbonate as catalyst along with small amounts of polymerization inhibitor hydroquinone. Then the epoxy resin was added and the reaction continued till the product reached an acid value in the region of 60-90 units. Samples drawn at regular intervals during the reaction were also tested for their solubility in deionized water, after neutralizing with dimethyl ethanolamine, at 10% solids concentration.

In the second method, the epoxy resin was partially esterified with maleinized drying oil fatty acid at 160–180°C until clear beading was obtained. The water formed during the reaction was driven off by continuous flow of nitrogen gas through the reactants. At this stage, partial allyl ether was added and the esterification reaction continued until the acid value of the product reached 60–90 units. The solubility of the product in deionized water at 10% solids concentration was tested after neutralizing the product with dimethyl ethanolamine.

In a few cases, methacrylic acid or acrylic acid was used along with maleinized drying oil fatty acid in the semiesterification reaction with the epoxy resin so as to increase the content of unsaturation in the end polymer product.

The water-soluble polymers prepared by the second method were found to be of better quality than those prepared by the first method. Table I shows the composition of water-soluble epoxy allyl ether polymers prepared by both the above methods. Figure 1 represents the scheme of reaction involved by the second method.

Evaluation of Clear Polymers

The clear polymers were evaluated essentially for their storage stability and hydrolytic stability. The storage stability of the products was assessed by first neutralizing the product with dimethyl ethanolamine and taking out samples of the neutralized product periodically and diluting with deionized water. The product was considered unstable if it gave turbid solution at 10% solids concentration.

Hydrolytic stability test was conducted on aqueous solutions of the product at 25% and 10% solids concentrations. The clarity of the stored solutions was observed periodically. The products were said to have failed if they gave turbid solutions within 12 months of their preparation. This test is of

TABLE I
Composition of Water-Soluble Epoxy Allyl Ethers

Product nos.	Partial allyl ethers									
	Maleinized DCOFA (g)	MATMP (g)	DATMP (g)	MAG (g)	DAG (g)	DAPE (g)	TAPE (g)	Vinyl monomer (g)	Epoxy resin (g)	
1	120	25	—	—	—	—	—	—	25	
2	160	—	27	—	—	—	—	—	25	
3	120	—	—	33	—	—	—	—	20	
4	120	—	—	—	25	—	—	—	25	
5	120	—	—	—	—	30	—	—	25	
6	100	—	—	—	—	—	20	—	20	
7	140	40	—	—	—	—	—	10 ^a	10	
8	100	20	—	—	—	—	—	20 ^b	30	
9	120	—	27	—	—	—	—	—	25	
10	135	13	12	8	—	—	—	—	5	

^a Acrylic acid; DCOFA (dehydrated castor oil fatty acids);

^b methacrylic acid.

Acid values of all the products were in the range of 60–90 units.

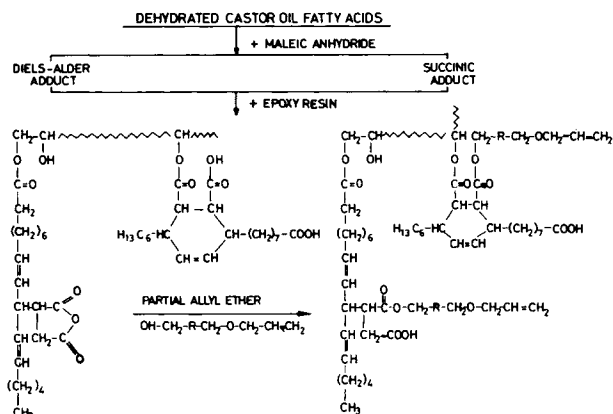


Fig. 1. Scheme of epoxy allyl ether polymer synthesis.

great importance, as the water-soluble polyesters were hydrolytically unstable unless properly designed, due to the hydrolysis of the ester groups catalyzed by the neutralizing amine in the presence of water. This leads to formation of lower molecular weight polymers which can cause pH drift and phase separation.

The ten products reported in Table I were all stable for 20 months to storage and hydrolysis.

Evaluation of Clear Polymers as Coatings

The clear coatings were obtained by neutralizing the polymer with dimethyl ethanolamine, adding requisite amounts of suitable driers, and diluting to 30% solids content with deionized water. The clear coatings were applied on tin-coated mild steel panels (15 × 5 cm) and on test tubes. The coated panels were cured at 100°C for 30 min and tested for adhesion, flexibility, and resistance to 1% aqueous sodium hydroxide solution and different solvents normally used in surface coatings industry. It was found that all 10 products gave flexible (passed in 1/16 inch mandrel) coatings which are resistant to xylene, white spirit, ethyl acetate, and ethyl cellosolve for more than 96 hours. The coated polymer films were also resistant to 1% aqueous sodium hydroxide for more than 12 h.

Preparation of Paints

Paints were prepared based on each of the 10 water-soluble epoxy allyl ether polymers using lead chromate pigment at 10% pigment volume concentration with percent solids being maintained at 40. The viscosity of the paints prepared was in the range of 55–60 s in Ford Cup No. 4 (BSS). These paints were designated as 1200 series (Tables II and III). In the 1300 series of paints, 5% "Sympomine" resin, a 50% aqueous melamine formaldehyde resin manufactured by M/s. Synthetics and Polymers Industries Limited, Ahmedabad, India was added as external crosslinker (Tables IV and V).

TABLE II
Physical Properties of the Baked Paint Films Based on Lead Chromate

Paint code nos.	Prepared from resin (from Table I)	Film thickness (μ)	Scratch hardness IS:101-1961 g	Impact resistance 228 cm.kg (DEF 1053 (17a))		Reflectance Gardner scale	
				Direct	Indirect	45°	85°
1201	1	20-25	1800	NE	NE	2	24
1202	2	25-30	2300	NE	NE	4	9
1203	3	15-20	1500	NE	NE	4	33
1204	4	15-20	2200	NE	NE	10	65
1205	5	20-25	2200	NE	NE	10	65
1206	6	20-25	1500	NE	NE	11	64
1207	7	15-20	2000	NE	NE	6	50
1208	8	15-20	1800	NE	NE	4	22
1209	9	20-25	1800	NE	F	4	41
1210	10	25-30	3000	NE	F	4	55

Abbreviations: IS = Indian Standard Specification; DEF = Defense Specification, London; NE = No effect; F = Failed.

TABLE III
Accelerated Corrosion Test Results of Paints Based on Lead Chromate

Paint code nos.	Corrosion cabinet IS:101-1961. No effect in exposure	Corrosion cabinet after "cross" rust creep (mm)			Salt spray IS:104-1962. No effect in hours of exposure	Salt spray after "cross" rust creep (mm) ASTM B-47-64		
		1200 h	1300 h	1500 h		300 h	400 h	500 h
1201	1400	1.50	2.00	2.50	400	1.00	2.00	—
1202	1500	—	—	1.00	400	2.50	3.00	—
1203	1500	—	—	1.00	300	2.50	3.00	—
1204	1400	1.00	2.00	2.50	300	2.50	3.00	—
1205	1300	—	1.00	2.00	350	2.50	3.00	—
1206	1200	1.00	2.00	3.00	300	2.00	3.00	—
1207	1300	1.50	2.00	2.50	300	2.00	3.00	4.00
1208	1500	—	—	1.00	600	—	—	0.00
1209	1300	—	2.00	2.50	400	—	—	2.00
1210	1500	—	—	0.0	500	—	—	1.00

Abbreviations: IS = Indian Standard Specification; ASTM = American Society for Testing Materials.

TABLE IV
Physical Properties of the Paint Films Based on Lead Chromate and Cross-linked with Melamine Resin

Paint code nos.	Film thickness (μm)	Scratch hardness IS:101-1961 (g)	Impact resistance 288 cm.kg (DEF 1053 (17a))		Reflectance Gardner scale	
			Direct	Indirect	45°	85°
1301	25-30	1000	F	F	8	40
1302	25-30	1600	F	F	6	22
1303	20-25	1900	F	F	12	38
1304	20-25	1600	F	F	15	69
1305	20-25	1800	NE	F	18	72
1306	20-25	1600	F	F	40	90
1307	25-30	1500	NE	F	12	65
1308	25-30	1500	F	F	8	28
1309	30-35	1300	F	F	12	50
1310	25-30	2000	NE	F	10	59

Abbreviations: IS = Indian Standard Specification; DEF = Defense Specification, London; NE = No effect; F = Failed.

TABLE V
Accelerated Corrosion Test Results of Lead Chromate-Based Paints Modified with Melamine Resin

Paint code nos.	Corrosion cabinet IS:101-1961. No effect in hours of exposure		Corrosion cabinet after "cross" rust creep (mm)		Salt spray IS:104-1962. No effect in hours of exposure		Salt spray after "cross" rust creep (mm) ASTM B-47-64	
	300 h	400 h	300 h	500 h	350 h	250 h	300 h	350 h
1301	350	1.0	1.5	2.0	350	1.0	2.0	3.0
1302	350	1.0	1.5	2.0	350	1.0	2.0	3.0
1303	350	—	1.0	1.5	350	—	1.0	2.0
1304	325	—	1.0	1.5	325	—	—	1.5
1305	300	1.0	1.5	2.0	300	1.0	1.5	2.0
1306	300	1.0	1.5	1.5	275	—	1.0	2.0
1307	300	1.0	1.5	1.5	275	1.0	1.5	2.0
1308	350	—	1.0	1.5	300	—	1.0	1.5
1309	300	1.0	1.5	2.0	275	1.0	1.5	2.0
1310	400	—	1.0	1.0	375	—	—	1.0

Abbreviations: IS = Indian Standard Specification; ASTM = American Society for Testing Materials.

Evaluation of Paint Films

The paints were applied on mild steel panels (30 SWG: 15 × 10 cm) by means of spray and baked at 100°C for 30 min. In view of the special interest in primers, the salt spray and corrosion cabinet tests were considered more important in the evaluation of water-soluble vehicles. However, some other tests, viz., adhesion, hardness, flexibility, impact resistance, and gloss were carried out to assess overall worthiness and acceptability of these coatings.

RESULTS AND DISCUSSION

Impact Resistance

Almost all the paints prepared based on lead chromate (1200 series) exhibited very good resistance toward impact (Table II). However, there was marked decline in this property when a melamine resin (up to 5% on the solids) was incorporated into it, except in three formulations [1305, 1307, and 1310 (Table IV)]. All these three formulations were based on higher proportions of diallylic ethers and vinyl monomers.

Scratch Hardness

Scratch hardness of the paints reported in Table II ranged between 1,500 and 3,000 g. The higher the allylic content in the resin, the higher the scratch hardness recorded. When the melamine resin was incorporated, the films became appreciably brittle (Table IV).

Reflectance (Gloss)

Gloss of the paints 1204, 1205, 1206, and 1207 was very satisfactory (i.e., ranged from 50–70 in Gardner scale at 85° incident angle). All these paints contained di- and triallylic ether components. All other paints exhibited a matte finish (Table II). There was a marked increase in gloss when these paints were modified with melamine resin (Table IV).

Accelerated Corrosion Tests

All the 1200 series paints (Table III) showed no effect over 1,300–1,500 h when exposed in a corrosion humidity cabinet. The creep of rust under the paint film was not significant. Similarly, they fared moderately well in salt spray for 400 h. The rust creep under the paint film after 400 h of exposure to salt spray is only 3 mm. There is marked decline in the accelerated corrosion test results of all these paints (1300 series) when modified with melamine resin. These paints failed in corrosion cabinet only in 300–400 h (Table V). In salt spray also, these paints failed in 300–350 h.

CONCLUSIONS

Physical properties such as scratch hardness, impact resistance, and gloss of the paint films improved with the increase in the allylic ether and vinyl monomer content. These paints have also performed well as primers in accelerated corrosion tests.

When melamine resin up to 5% of solids of the paint composition was incorporated in these paints, all the paint film properties deteriorated considerably, except the gloss of the paint films, which improved with the addition of melamine resin.

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