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BIS PHENOL EPICHLOROHYDRIN CONDENSATE
MODIFICATION OF ALKYD RESINS

BY

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NEWARK, NEW JERSEY

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ABSTRACT

A method is given for the modification of alkyd resin systems with Bis-Phenol Epichlorohydrin Condensates.

The properties of the modified alkyd resins are evaluated using similar unmodified alkyd resins as reference.

A theory of linear esterification is postulated.

STATEMENT OF THE PROBLEM

The object of this paper is to prepare Bis-Phenol Epichlorohydrin Condensate modified alkyd resins.

A further object of this paper is to determine the physical properties of these resins and explain these properties as a function of the resin structure.

INTRODUCTION

A search of the literature indicated that the possibility of modification of an alkyd resin system with a Bis-Phenol Epichlorohydrin condensate was considered impossible (1). The primary purpose of this paper is to show that such modification is possible and to explain the resins produced by the structure envisioned.

It will be shown that by linear esterification, prevention of the formation of three dimensional molecules, it is possible to modify alkyd resins with Bis-Phenol Epichlorohydrin condensates. It will be further shown that the physical properties of these resins are explainable as linear polyesters.

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DISCUSSION

An alkyd resin may be defined as the polymeric ester of a polyhydric alcohol and a polybasic acid Figure 1. The usual types used by the paint and varnish industry are phthalic anhydride esters of such alcohols as ethylene glycol, glycerol, pentaerythritol, tri-methylol ethane and sorbitol. These esters are hard brittle resins and rarely used as such for film forming materials. Modification with vegetable oil fatty acids ranging from 6 to 22 carbon atoms and contains from 0 to 3 olefinic linkages of the conjugated and non conjugated type, is common practice.

The alkyd resin film is profoundly affected by the type of polybasic acid poly alcohol ester incorporated with the vegetable oil. The viscosity of an alkyd resin system varies directly with the molecular weight of the phthalate ester, while the cure or drying time varies inversely. It is therefore usually desirable to form the highest molecular weight phthalate ester possible at any given oil percent. The limit to the molecular weight of the phthalate ester is that point at which the molecule becomes three dimensional or cured. This condition is known as gelation.

The conditions for the gelation of such condensation polymers have been treated mathematically by Carothers (2).

f = Degree of functionality (avg. no. of functional groups per molecule)

No = Number of molecules at beginning of reaction

N = Number of molecules at end of reaction

$No(f)$ = Number of functional groups at the beginning

$No-N$ = Number of molecules having disappeared

$2(No-N)$ Number of functional groups lost

Extent of Reaction $P = \frac{2(No-N)}{No(f)}$

Degree of polymerization X

$$X = \frac{No}{N}$$

$$P = 2/f - \frac{2}{Xf}$$

As the reaction proceeds to completion $2/Xf$ approaches zero as a limit. Therefore: $P = 2/f$.

It can readily be seen that as the value of f is increased the extent of reaction possible before gelation is sharply reduced. To incorporate high phthalate ester into an alkyd system requires the addition of excess poly alcohol to lower the value of f to a point possible to condense the polymer. In this case the functionality of glycerol would be calculated as follows: $f = \frac{3}{1+N}$, N = number of moles of excess glycerol. The excess poly alcohol in such an alkyd film would effect its quality deleteriously. A balance of viscosity, extent of reaction and excess alcohol must be reached in such a system.

The purpose of this research was to devise a practical method of incorporating Bis-Phenol Epichlorohydrin condensate resins Figure 2 into an alkyd structure. These condensate resins, commercially available as grades of Epon from the Shell Chemical Corporation, are resinous poly alcohols of molecular weight ranging from 870 to 4000 and having 10 to 20 hydroxyl groups. Extremely small amounts of these resins, as predicted by the Carothers equation, will result in the gelation of alkyd resin systems. The expected results of this introduction would be a faster drying rate, for two reasons; (1) the molecular weight increase would be very large and (2) the olefinic functionalities per molecule would be greatly increased. Additional expected results were improved adhesion due to the epoxy structure and greater viscosity due to the insolubility of Epon.

Alkyd resin synthesis involves many competing reactions. The esterification of phthalic anhydride with the poly alcohol is the most rapid reaction occurring at temperatures in the range 265-300°F (4). The phthalic half ester is formed before the batch reaches processing temperature. The half ester reacts at a less rapid rate with the remaining primary hydroxyls and then at a considerably slower rate with the secondary hydroxyl groups.

The ethoxyline resin modified and standard alkyds proceed initially by the same reaction; formation of the phthalic half ester. The remaining primary hydroxyls are then esterified by the half ester with minor esterification of the secondary hydroxyls jointly occurring. When the primary hydroxyls are completely esterified the slow esterification of the secondary hydroxyls is the main reaction. In the Epon modification, the secondary hydroxyls of the epoxy structure compete with those of the poly alcohol for esterification. Esterification of the secondary hydroxyls of the epoxy resin is probably favored over that of the polyol since they are less sterically hindered.

Contrary to normal alkyd formulation, the addition of extra hydroxyl groups via the Epon ester did not decrease the functionality of the alkyd. The main factor causing the deviation is probably due to a reduction of phthalic anhydride cyclic inter ester formation as postulated by Kienle Etal (3). Cyclic structures of the type given Figure 3 were probably reduced by the esterification of the secondary hydroxyls of the epoxy resin with the phthalic half ester. The reduction of this type of inter-ester would greatly increase the functionality of the phthalic anhydride.

To incorporate ethoxyline resins in an alkyd system prevention of cross linking, formation of a three dimensional structure, is accomplished by a method of linear esterification. Two methods of accomplishing this reaction were developed. The first method was to form the half ester of the di-basic acid Figure 4 with the lower molecular weight poly alcohol before the introduction of the epoxy resin. This was accomplished with iso and tere phthalic acid but not with phthalic anhydride. Phthalic anhydride could not be used because of the reversal of its esterification yielding free phthalic acid during all stages of the reaction. This unesterified phthalic acid results in the cross linking and gelation of the reaction mass. This method was abandoned after completion of a few alkyds because the isomers of ortho phthalic acid were not commercially available at that time. The second approach to the problem was to reduce the average functionality of the epoxy resin by esterification with a mono functional fatty acid before combining it into the alkyd structure.

The alkyd resins prepared for this research were of the vegetable oil type. In this type of alkyd the oil fatty acid tri glyceride undergoes a trans esterification reaction Figure 5 with glycerol or other poly alcohol to form mixed glycerides before the phthalic anhydride is introduced. The phthalic anhydride esterifies the free hydroxyl groups of the mixed glycerides forming a resinous material. The reaction progress is followed by reduction in acid value, grams of KOH required to neutralize 1000 grams of resin, and viscosity increase, stopping the reaction before reaching the point of gelation.

As previously mentioned gelation of alkyd resins when modified with Bis Phenol Epichlorohydrin condensates is a result of phthalic anhydride cross linking. Esterification of sixty percent of the hydroxyl and epoxy groups available from the epoxy resin with a mono functional fatty acid reduces its functionality to a point where linear molecule formation is possible. At this esterification level most of the remaining hydroxyls must be condensed with phthalic anhydride to cross link the structure. Steric hinderence prevents a stochiometric esterification and cross linking is probably very minor.

Supporting evidence is given by the effect of varying the alcoholysis procedure. When the partially esterified Epon resin was added to the oil during the trans esterification reaction an increase in functionality was noted. Alcoholysis of the epoxy ester increased the number of hydroxyl groups available from the epoxy resin. In the case of the linseed oil alkyd gelation resulted. The other alkyds had greater viscosities, indicating a greater amount of phthalic Epon ester.

The structure envisioned for the Epon modified alkyd is given in Figure 6.

FIGURE I

FIGURE II

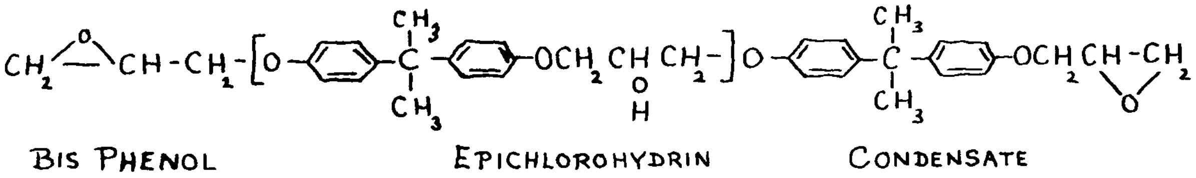
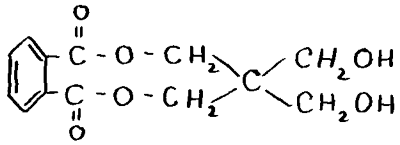


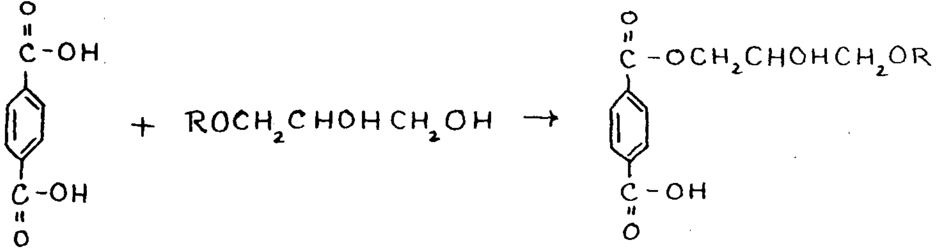
FIGURE III

CYCLIC GLYCERYL PHTHALATES



CYCLIC PENTAERYTHRITOL PHTHALATE

FIGURE IV



P-PHTHALIC ACID

HALF ESTER
(MONO FUNCTIONAL ACID)

FIGURE V

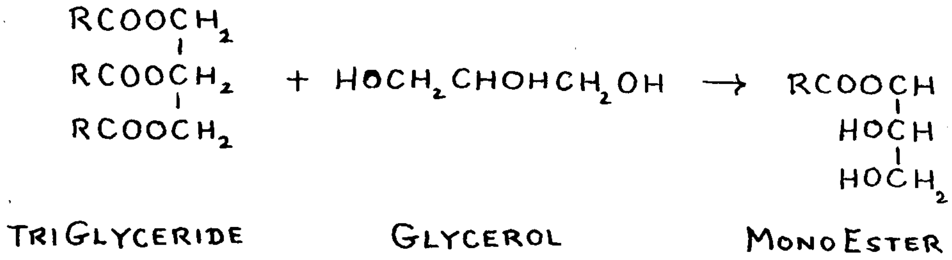
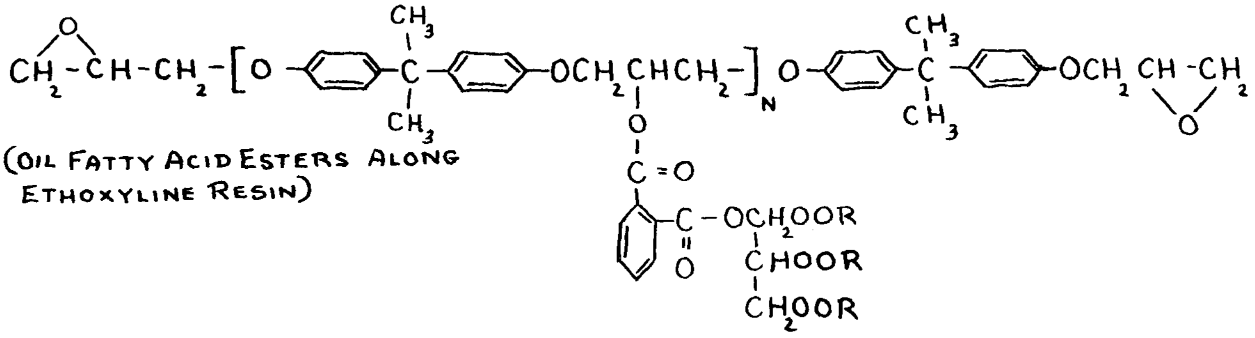


FIGURE VI



(OIL FATTY ACID ESTERS ALONG ETHOXYLINE RESIN)

EPON - PHTHALIC LINEAR POLY ESTER

EXPERIMENTAL

The alkyd resins described were prepared by the simultaneous esterification of alcoholized oils and partially esterified Epon esters with phthalic anhydride, according to the formulations given in the following tables.

Epon Ester Formulation

Material	Equivalent Weight	Weight
Epon 1004	175	175
Soya Fatty Acid	280	168

Base Alkyd Formulation

Resin	(1)	(2)	(3)	(4)
% Oil	62.0	53.3	53	38.4
Type Oil	Soya	Soya	Linseed	Soya
% Phthalic Anhydride	24	34	28	42

Three neck, 5 liter, glass reaction flasks were employed using an automatic on-off controller to maintain the desired temperature. The reaction flask was equipped with a thermocouple, a stirrer and a condenser lead for reflux. Carbon Dioxide was bubbled through the reaction mass to prevent darkening. Xylene was used as reflux solvent to maintain temperature and remove the water of esterification.

In the preparation of the epoxy ester the bis phenol-epichlorohydrin condensate resin and soya fatty acid were charged to the reaction flask and held at 525°F under xylene reflux. The reaction progress was followed by the reduction in acid value, grams of KOH required to neutralize 1000 grams of resin. When the acid value was under 10 the reaction mass was cooled to room temperature.

In the preparation of the alkyd, the oil portion was heated in the reaction flask to 400°F in the presence of the glycerine necessary to form the phthalic ester. At this point litharge was added to catalize the trans esterification reaction Figure 5. The temperature was then increased to 450°F and held until one part of reaction mass was completely soluble in 4 parts of methyl alcohol. Phthalic anhydride, Epon ester and xylene were then added, the temperature increased and the batch held under reflux until the acid value was below 10.

Exposure Procedure

Enamels were prepared from the Epon modified and standard alkyd resins vehicles by grinding the following formula for twelve hours in a laboratory pebble mill.

Enamel Formula

Material	Weight (grams)
Vehicle (40% Non Volatile)	700
Rutile TiO_2	200
Carbon Black	4
	904

Cobalt and lead naphthenate driers were added to the finished enamels. (0.05% of cobalt metal and 0.5% lead metal based on the resin content).

Exposure panels were then prepared by spray coating a 16 gauge hot rolled steel panel with a uniform film thickness of enamel. In each case the panels were primed with a standard alkyd red lead primer.

Panels were exposed at 45° facing south at Metuchen, New Jersey and Miami, Florida.

Viscosity

The viscosities recorded in the various tables were determined by comparison with oils of standard viscosity in a Gardner Bubble Tube Viscosimeter. The rate of travel of a standard size bubble through a tube of 10.50 mm inside diameter is matched with a standard and recorded as a Gardner number.

Drying Time

The measurement of drying time is a rather empirical method common to the protective coating industry. Metal salts of naphthenic acids are added to the resin solution in the required amount, in the case of the alkyd resins under study 0.05% Co and 0.5% Pb. Metal calculated on the resin were added.

A film of the resin solution, plus driers, was cast at a standard film thickness of .0015 inch on a glass plate using a Bird film applicator. The set to touch time was recorded as that time lapse that produced a film that left no material on a finger lightly touching it. The tack free time was recorded as that time lapse which produced a film that had no tack when touched. Print free time was recorded as that time lapse that prevented a film from being marred by thumb pressure. Twist free time was that time lapse that prevented any material from being removed upon a twisting thumb pressure.

Alkali Resistance

The alkali resistance of the resins described was measured as the time lapse required to cause various film defects when immersed in a aqueous 5% NaOH solution at 68°F.

The resin solutions plus driers were flowed over clean inverted test tubes and allowed to air dry for 3 days before immersion.

Impact Testing

Impact tests were performed by use of a Gardner Reverse Impact Tester. Enamels prepared from each of the resins were sprayed to a uniform film thickness over 16 gauge hot rolled steel panels. After aging the panel was reversed and a standard weight was droped from increasing measured heights until a fracture of the film was noted. Impact was measured in inch-pound units.

Weatherometer Exposure

An Atlas Twin Arc Weatherometer was used to subject panels of enamel prepared from the resins described to alternate cycles of ultra violet radiation and water spray.

The gloss readings were measured as a percentage of reflection of a standard beam of light intensity using a vitreous panel as 100%.

TABLE #1 PROPERTIES OF OIL MODIFIED ALKYD RESINS AND EPON OIL MODIFIED ALKYD RESINS

CODE NO.	1		2		3		4		
% P.A.	24.2	24.2	34.2	34.2	28	28	42.4	42.4	42.4
% Oil	62.0	62.0	53.3	53.3	53	53	38.4	38.4	38.4
Type Oil	Soya	Soya	Soya	Soya	[a]Linseed	Linseed	Soya	Soya	Soya
Epon	-	10	-	10	-	10	-	5.2	10[d]
Temp.	450°F	450°F	450°F	450°F	450°F	450°F	400°F	400°F	400°F
Visc.[b]	U-W	Z_4-Z_5	Z-	Z_1+	V+	X-Y	Z_3	Z_6	X-Y
Acid No.	<10	7.5	9.0	5.1	9.0	4.9	4.7	5.6	9.4
Color[c]	6	6	6	6	7	5	5	5	7
Solvent[e]	M.S.	M.S.	M.S.	M.S.	M.S.	15% Xylene 85% M.S.	66% Xylene 34% M.S.	66% Xylene 34% M.S.	Xylene
Time	-	5hrs. 35min.	5hrs. 10min.	6hrs. 15min.	8 hrs	3hrs. 57min	7hrs. 20min.	7hrs. 55min.	7 hrs.
N.V.[f]	60	60	50	50	50	50	50	50	50

a 5% modification phenolic resin
b Gardner viscosity scale
c Gardner (1933) Color Scale
d Epon 1009
e M.S. = Mineral Spirits
f Non Volatile content expressed as a percent of total

TABLE #2 VISCOSITY REDUCTION PATTERNS OF EPON MODIFIED AND STANDARD ALKYDS

	Solvent	Viscosity (Gardner Scale)				
ALKYD	**K.B.**	**60 N.V.**	**50 N.V.**	**40N.V.**	**30 N.V.**	**20 N.V.**
Std 62% Oil	25	U	E-F	A_2-A_1	A_4-A_3	-
Epon 62% Oil	25	Z_6-Z_7	Z_2	R+	A_3-A_4	-
Std 62% Oil	40	R+	C-D	A_3-A_4	-	-
Epon 62% Oil	40	Z_4-Z_5	W-X	F+	A_3-A_4	-
Std 62% Oil	100	E+	A+	A_3-A_4	-	-
Epon 62% Oil	100	V-	I-J	A-B	-	-
SOYA						
Std 53.3% Oil	25	Semi Solid	Z_5-	X-Y	F+	
Epon 53.3% Oil	25	Semi Solid	Z_5+	Z_2+	U-V	-
Std 53.3% Oil	40	Z_2-Z_3	G-R	A_2-A_1		
Epon 53.3% Oil	40	Z_4	X-Y	I-J	-	-
Std 53.3% Oil	100	I-J	A_1-A	A_3-A_4		
Epon 53.3% Oil	100	Q-R	D-E	A_2-A_1		
LINSEED						
Std 53.3% Oil	25	Semi Solid	Z_4-Z_5	V-	C-D	
Epon 53.3% Oil	25	Semi Solid	Z_6-Z_7	Z_2-Z_3	T-	
Std 53.3% Oil	40	Z_4-Z_5	V-	C-D	A_3-A_4	
Epon 53.3% Oil	40	Semi Solid	Z_4	U-	A-B	

TABLE #3 [a]DRYING TIME OF EPON MODIFIED VS STANDARD ALKYDS

ALKYD TYPE	SET TO TOUCH	TACK FREE	PRINT FREE	TWIST FREE
62% Oil Std	14 mins.	12hrs.	24 hrs.	-
62% Oil Epon Mod.	4 mins.	6hrs.14min.	6hrs.14mins.	6hrs.34min.
SOYA				
53.3% Oil Std	4 mins.	2hrs.54min.	2hrs.54mins.	2hrs. 54mins
53.3% Oil Epon Mod.	4 mins.	1hr. 41mins.	1hr.41mins.	1hr. 41 mins
LINSEED				
53% Oil Std.	3 mins.	5hrs.3mins.	4hrs.12mins.	5 hrs.
53% Oil Epon Mod.	3 mins.	2hrs.54mins.	2hrs.54mins.	2hrs. 54mins
38.4% Oil Std	6 min.	49 mins.	1hr. 7 mins.	1hr. 7 mins.
38.4% Oil 10% Epon 1009	3 mins.	11 mins.	22 mins.	22 mins.
38.4% Oil 5% Epon 1004	3 mins.	11 mins.	49 mins.	49 mins.

Drying speeds of the Epon modified alkyds were improved over the standard products. The through cure of the Epon modified alkyds was far superior, especially during the early stages of dry, and a noticeable improvement in adhesion was evident.

[a] .0015 wet film; .0500 + 5Pb calculated as percent metal on the non volatile of the resin solution.

TABLE #4 WEATHEROMETER EXPOSURE RESULTS

ALKYD TYPE	GLOSS READINGS INITIAL	50 Hrs.	90 Hrs.	200 Hrs.	300 Hrs.
62% Oil Std	95	75	65	36	20
62% Oil Epon Mod.	91	76	69	36	15
SOYA					
53.3% Oil Std	90	70	55	29	15
53.3% Oil Epon Mod.	92	66	62	38	19
LINSEED					
53% Oil Std	95	72	56	29	14
53% Oil Epon Mod.	92	70	64	36	18
38.4% Oil Std	95	68	60	41	18
38.4% Oil Epon Mod.	87	75	63	40	19

Exposure was continued for 500 hours with the result that standard and Epon modified alkyds appear to be equal in gloss, chalking and clean up.

TABLE #5 ALKALI RESISTANCE 3% NaOH 68°F

TYPE RESIN	TIME TO DISCOLOR	TIME TO FIRST FILM DEFECT	TIME TO BLISTER	FINAL FAILURE
SOYA				
62% Oil Std	4 min.	22 min.	49 min.	61 min.
62% Oil Epon Mod.	9 min.	52 min.	127 min.	180 min.
SOYA				
53.3% Oil Std	7 min.	22 min.	50 min.	180 min.
53.3% Oil Epon Mod.	19 min.	52 min.	180 min.	Discontinued at 300 min.
LINSEED				
*53% Oil Std	24 min.	66 min.	)	Discontinued at 300 min.
53% Oil Epon Mod.	19 min.	81 min.	)	
SOYA				
38.4% Oil Std	9 min.	31 min.	54 min.	60 min.
38.4% Oil Epon	25 min.	54 min.	-	180 min.

*5% Mod. phenolic resin

TABLE #6 IMPACT TESTING OF EPON MODIFIED VS STANDARD ALKYDS

ALKYD TYPE	FAILURE IMPACT	FILM THICKNESS MILLS
SOYA		
62% Oil Std.	80 in/lbs (Passes)	0.6
62% Oil Epon Mod.	80 in/lbs (Passes)	0.8
SOYA		
53.3% Oil Std.	80 in/lbs (Passes)	0.8
53.3% Oil Epon Mod.	80 in/lbs (Passes)	0.8
LINSEED		
*53% Oil Std.	15 in/lbs	0.8
53% Oil Epon Mod.	80 in/lbs (Passes)	1.0
SOYA		
38.4% Oil Std.	17 in/lbs	0.6
38.4% Oil 10% Epon 1009	12 in/lbs	0.6
38.4% Oil 5% Epon 1004	15 in/lbs	0.8

* 5% Modification phenolic resin

RESULTS

Viscosity

The Epon modified alkyds exhibited uniformly higher viscosities than the standard resins from which they were prepared (Table I). This viscosity pattern is a function (Table 2) of the solubility of the poly ester structure in the solvent selected. A practical result of this reduction pattern is a greater degree of formulation flexibility. Enamel and flat paint vehicles have been prepared from the long and medium oil base alkyds by using solvents of kauri butanol values ranging from 90 to 25. When reduced to 35% non volatile with mineral spirits varnishes suitable for wood finishing were obtained.

Drying Time (Table 3)

The melting point of the Epon modified alkyd is higher than that of the standard due to its greater molecular weight. Since the Epon resin enables a greater percentage of drying acids to be incorporated into any given molecule, an increase in olefinic functionality is experienced. Cross linking by formation of peroxide structures upon exposure to air is thereby enhanced yielding a three dimensional or cured film. The practical result of these properties is a faster set of touch and tack free time. A contributing factor to the early through cure noted with the epoxy alkyds is probably due to the polar nature of the hydroxyl and epoxy groups, which results in greater adhesion during all stages of cure.

Impact Resistance

The impact limitations of the Gardner instrument was insufficient to rupture cured films of standard and Epon modified alkyds in the

24 to 34 percent phthalic anhydride range. (80 in-lbs maximum). It was interesting to note that 5% of a hard phenolic resin reduced the flexibility of a 28% phthalic anhydride alkyd to that obtained with a 42% phthalic resin. Modification of this same alkyd with twice the hard resin content as Epon did not reduce its impact resistance at all. A more sensitive testing device might show an increase in flexibility, perhaps as a function of adhesion, as compared with the standard alkyd.

Exposure

Exposures of enamels prepared from the standard and Epon modified alkyds were run at Metuchen, New Jersey and Miami, Florida on exterior test fences and compared with accelerated test results obtained by the use of an Atlas Twin Arc Weatherometer (Table 4). The purpose of these exposures was to determine if the incorporation of Epon would result in the early chalking and loss of gloss experienced with Epon fatty acid esters. After 500 hours of accelerated exposure, one year exterior exposure at Metuchen, N. J., and six months at Miami, Florida, no difference in gloss, chalking or clean up was noted.

Alkali Resistance

The Epon modified alkyd resins exhibited greater resistance to alkali than their standard counter parts. In relating this property to the linear poly ester structure postulated two factors are important: (1) Molecular weight (2) nature of ester bonds.

In the case of the Epon modified alkyd both of these properties tend to give the polymer greater alkali resistance. If the Carothers equation, previously mentioned, is rewritten as follows:

$$\text{MWn} = \frac{\text{Weight of Resin}}{\text{Mf (alc.)} - } \; (f-1)\,(\text{Mf acid} + A)$$

MWn = Molecular Weight Number

Mf(alc) = Moles of alcohol of f functionality

Mf acid = Moles of acid of f functionality

it can be calculated that the molecular weight of such an alkyd is infinite at the gelation point. Therefore greater alkali saponification is necessary before film defects become obvious. It has also been previously proven that the Epon ester bond is much more resistant to saponification than the normal fatty acid or phthalic ester bond.(5)

CONCLUSIONS

Bis-Phenol Epi Chlorohydrin condensate modification of alkyd resins is possible by prevention of three dimensional molecular formation. This is accomplished by reducing the functionality of the condensate by esterification with a mono functional fatty acid in the case of the ortho phthalic anhydride alkyds. Para or meta phthalic acid may be used by this method or by reducing their functionality to the half ester using a simple polyol before the epoxy resin is introduced. These methods enable the synthesis of high molecular weight linear poly esters of high olefinic functionality per molecule.

The properties of these resins, speed of dry, viscosity reduction pattern, alkali resistance, flexibility and adhesion have been related to the high molecular weight linear poly ester described.

Formulation of flat, gloss and non pigmented base coatings from the same resin indicates a greater degree of end product flexibility than possible with a standard oil modified alkyd.

LITERATURE CITED

1. Hopper, T.R., Shell Chemical Corporation, presented to the New York Paint and Varnish Production Club, March 4, 1954.

2. Carothers, Trans. Far. Soc. 32, 39 (1936)

3. Kienle, R.H., Van Der Meulen, P.A. and Petke, J. Am. Chem. Soc., 61, 2258 (1939)

4. Spitzer, N.C., Lecture Series, Illinois Institute of Technology, 1950.

5. Epon Resin for Surface Coating, Shell Chemical Corporation, Tech. Publication SC:52-31.