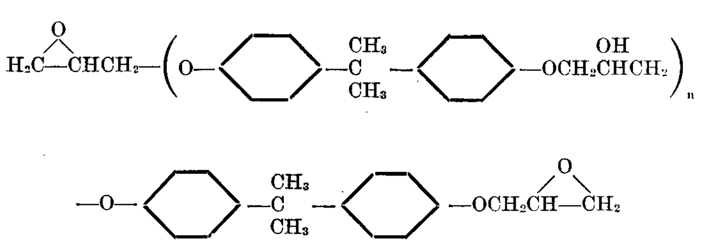
Oleoresinous Varnishes from Epoxy Resins and Drying Oils[1]

ROY W. TESS, Shell Development Company, Emeryville, California

THE RESINS (1) formed by the condensation of epichlorohydrin with 2,2-bis(p-hydroxyphenyl) propane (Bisphenol A) comprise the bulk of commercially available epoxy resins. The theoretical structure is as follows, but the actual structure appears to be somewhat different, mainly insofar as the epoxy groups are partially hydrolyzed:



The molecular weight of the resins, which range from viscous liquids to hard solids, depends upon the ratio of reactants. These resins may be cured in a variety of ways: by diamines (5), by polyamide resins (4), by phenolic or amino-formaldehyde resins (6), or by other chemical agents. Air-drying vehicles, which represent a major use of epoxy resins, are made by esterifying the resins with a variety of unsaturated acids, such as drying oil acids (6, 7), tall oil (8), and rosin.

The present paper deals with the use of the hard epoxy resins as varnish resins for cooking with the oils themselves rather than for cooking with fatty acids in the conventional way. These oleoresinous varnishes have properties which are distinctly different from the conventional epoxy resin esters. On the other hand, these varnishes are similar in most respects to conventional soft oil varnishes, but they differ from the conventional varnishes in some noteworthy respects, as will be shown. To a lesser extent this paper deals with the simple alcoholysis of glyceride oils by the hydroxyl groups in epoxy resins and the subsequent conversion of an alcoholyzed mixture to an oil-modified alkyd resin by means of phthalic anhydride.

Experimental

Materials Used. Commercial epoxy resins used in this investigation were as follows:

Epoxy Resin A[2]: molecular weight, approximately 860 (ebullioscopic in ethylene dichloride); melting point, 68°C., by Durrans' mercury method; epoxide value, 0.191 moles per 100 g. by the hydrochloric acid-dioxane method described by Jungnickel, Peters, Polgar, and Weiss (3).

Epoxy Resin B[2]: molecular weight, approximately 1,400; melting point, 96°C.; epoxide value, 0.103 moles per 100 g.

Epoxy Resin C[2]: molecular weight, approximately 2,900; melting point, 129°C.; epoxide value, 0.056 moles per 100 g.

Linseed oil: alkali-refined; Wolburn iodine value, 180 by method of Von Mikusch and Frazier (9).

Mineral spirits: b.p. 310-390°F.; Kauri-Butanol value, 44.

Varnish Cooking Procedure. Varnishes were cooked in open, stainless steel kettles equipped with mechanical stirrer but no inert gas sparge. Although resin and oil were charged all at once before the application of the direct gas heat, it is sometimes desirable, in order to avoid local overheating of resin, to heat the oil alone and add the resin to the hot oil on the upheat. The top heat (usually 580°F.) was reached in about 45 min. A clear pill usually was obtained at about 510°F. on the upheat. The end-point was taken as the time when a three-foot string could be drawn from a few drops of varnish on a cold tin plate. In order better to simulate larger-scale practice wherein the cooling time is slower than that obtained in small laboratory cooks, the varnish was usually cooked at top temperature for from 2 to 5 min. beyond the end-point described. The partially cooled varnish was diluted with mineral spirits and finally adjusted to 50% nonvolatile content.

Discussion of Varnish Preparation

A summary of the preparation and solution properties of the epoxy resin varnishes is given in Table I. Moderate differences in viscosity of varnish solutions have little significance because viscosities could be changed easily by slight changes in cooking times. At 50% nonvolatile content the viscosities ranged from about J to Y on the Gardner scale.

The effect of molecular weight of the epoxy resin upon cooking properties of 25-gal. linseed oil varnishes at 580°F. is shown by comparing varnishes 2, 6, and 7 in Table I. Using the epoxy resin of highest molecular weight (Epoxy Resin C, MW 2,900, Varnish 7), reactivity with linseed oil was too great to provide desirable control over the reaction; also compatibility was achieved at a slower rate than with resins of lower molecular weight. Resins of lower molecular weight (Epoxy Resin A, MW 860, and Epoxy Resin B, MW 1,400) were similar in cooking properties, but Epoxy Resin B was preferred because of somewhat better film properties.

A comparison of varnishes made at different cooking temperatures is shown in varnishes 2, 8, and 9. The cooking times at top temperatures were 190, 60, and 36 min., respectively, at 500, 550, and 580°F. A temperature of 500°F. was not regarded as practical because of unduly slow reaction and somewhat inferior film properties. Although a temperature of 580°F. was favored because of marginally superior film properties, 550°F. may be preferred if better control of bodying is desired.

Inspection of the cooking logs of varnishes 1, 2, and 3 in Table I shows that as the oil length of linseed varnishes was increased, the rate of bodying was retarded. The cooking times for 15-, 25-, and 35-gal. varnishes were 18, 36, and 55 min., respectively.

When tung oil was heated to 575°F. with epoxy resin (Epoxy Resin B), in most cases the varnish gelled by the time 575°F. was reached. On one occasion the varnish gelled after addition of bodied linseed oil as a chillback. Epoxy Resin B could be

---

[1] Presented at the Minneapolis meeting of the American Oil Chemists' Society, October 11-13, 1954.

[2] Epoxy Resins A, B, and C are, respectively, Epon® Resins 1001, 1004, and 1007 and are manufactured by the Shell Chemical Corporation.

TABLE I

Preparation of Varnishes from Epoxy Resins

Code No. of Varnish	1	2	3	4	5	6	7	8	9
Gallons oil length	15	25	35	25	25	25	25	25	25
Type of oil	Linseed	Linseed	Linseed	Soya	Tung + lin.	Linseed	Linseed	Linseed	Linseed
Type epoxy resin	B	B	B	B	B	A	C	B	B
Top cooking temp., °F	580	580	580	580	500	580	580	500	550
Reactants									
Epoxy resin, grams	454	454	454	454	454	454	454	454	454
Oil, grams	530	881	1234	877	712 + 185	881	881	881	881
Cooking data									
Time to top temp., minutes	42	44	40	44	41	47	44	44	45
Time at top temp., minutes	18	36	55	33	2[a]	37	7	190	60
Additional minutes to gel	....	15	....	....	....	....	5	....	25
Properties of Varnish									
% Nonvolatile	49.6	50.3	49.8	50.0	50.3	49.4	50.0	50.0	50.0
Viscosity, Gardner-Holdt	X–Y	V–W	N–O	J	W–X	S–T	L–M	J–K	V–W
Viscosity, poises	15.2	9.8	3.6	2.5	11.8	5.2	3.1	2.6	9.8
Color, Gardner	9–10	10–11	9–10	9–10	9–10	11–12	7–8	10	11
Solvent	Mineral spirits[c]	Mineral spirits	Mineral spirits	Mineral spirits	Partly aromatic[b]	Mineral spirits	Mineral spirits	Mineral spirits	Mineral spirits
Acid No. on solids, mg. KOH/g	0.4	2.0	1.6	0.5	0.1	0.6	0.4	0.2	0.6

[a] Bodied (Z2) linseed oil was used as a chill-back.

[b] Shell solvent TS28 was used as solvent. This is a hydrocarbon mixture of boiling range 318°F. to 390°F. and Kauri Butanol value of 70.

[c] For adequate stability a solvent containing about 50% aromatics should be used.

conveniently cooked with tung oil at the low temperature of 500°F.; in these cases bodied linseed oil was used as a chillback (varnish 5 in Table I). This varnish however was not gas-proof and had a tendency to wrinkle, particularly upon glass. Although a lower molecular weight grade of epoxy resin would seem to offer greater promise for cooking with tung oil at gas-proofing temperatures, this was not tried.

It is particularly interesting to note that a 25-gal. epoxy resin varnish (No. 4) made from soya oil bodied just as rapidly as the corresponding varnish (No. 2) made from linseed oil.

The rapid attainment of high viscosity in the varnish cooking process is one of the distinguishing characteristics of the epoxy resins. With most conventional varnish resins the cooking time was found to be at least twice that required when the epoxy resins were employed. For example, the cooking time at 580°F. of a 25-gal. Epoxy Resin B-linseed varnish was about 35 min. When other resins were used under similar circumstances, the cooking times were as follows: ester gum, 97 min.; pentaerythritol rosin ester, 115 min.; rosin modified phenolic resin, 85 min.; maleic modified ester gum, 74 min.

The ability of the epoxy resins to contribute to rapid cooking of oleoresinous varnishes suggested its use in small quantities to accelerate the heat-bodying of oils. Alkali-refined soya oil required 14.3 hrs. of heating at 580°F. in order to achieve a viscosity of Z4 (63 poises) on the Gardner scale. When only 5 parts of Epoxy Resin B were added to 95 parts of soya oil, the same viscosity was achieved after only 6.5 hrs. at the same temperature. Moreover the acid number of the latter oil was much lower (13.9 *vs.* 51.8 mg. KOH/g.), and the color was lighter (9 *vs.* 16-17 Gardner). The oil modified with epoxy resin dried dust-free in 4.5 hrs. in the presence of 0.05% cobalt, whereas the straight bodied soya dried in 5 days. In fact, the epoxy resin-oil product dried more rapidly than soya oil bodied to equal viscosity by means of 0.5% anthraquinone; this latter product dried dust-free in 32 hrs. under identical conditions.

Dilution of the epoxy resin varnishes usually could be accomplished with regular mineral spirits. However, to avoid opalescence, and especially when short oil length varnishes were concerned or when tung oil was present, it was found advantageous to include a portion of aromatic solvent. The change of viscosity with concentration of a typical varnish, a 25-gal. Epoxy Resin B-linseed varnish, is shown in Table II.

Film Properties. Film properties of selected epoxy

TABLE II

Viscosity of a 25-Gallon Linseed-Epoxy Resin B Varnish Upon Reduction with Mineral Spirits[a]

% Nonvolatile	Viscosity, Gardner-Holdt	Viscosity, Poises
50	T–U	5.9
47.5	Q–R	4.5
45	M	3.2
42.5	J–K	2.6
40	G–H	1.8
37.5	E–F	1.3
35	D	1.0
32.5	B–C	0.75
30	A1–A	0.4

[a] The mineral spirits was a regular commercial product; Kauri-Butanol value 44, boiling range 310–390°F.

TABLE III

Properties of Clear Films of Varnishes

Description of Varnish	15-Gallon Linseed Oil-Epoxy Resin B	25-Gallon Linseed Oil-Epoxy Resin B	25-Gallon Soya Oil-Epoxy Resin B	25-Gallon Linseed Oil-Rosin Modified Phenolic	25-Gallon Linseed Oil-Ester Gum
Solution Properties					
% Nonvolatile	41.2	37.8	43.0	50	50
Color, Gardner	8	9	8	12	14
Viscosity, Gardner-Holdt	E–F	E–F	E–F	C	B
Drying Time, 1 Mil Dry Films					
Set Touch	1.3 hrs.	1.3 hrs.	1.3 hrs.	1.3 hrs.	2 hrs.
Dried Hard	2 days	5–12 hrs.	5–12 hrs.	2–3 days	2–3 days
Cotton-Free	6–10 hrs.	1–3 days	3 days	1 day	16 hrs.
Sward Hardness, 1 Week Old	8	8	2	18	15
Cold Water, 18 Hours[a]					
Degree of Haze	heavy	slight	slight	slight	sl.-mod.
Recovery Time	10 min.	5 min.	10 min.	12 min.	11 min.
Boiling Water, 15 Minutes[a]					
Degree of Whitening	heavy	slight	mod.	slight	slight
Recovery Time	overnight	1 min.	5 min.	18 min.	4 min.
Acid No., mg. KOH/g., Solids	0.4	2.0	0.5	12.2	7.6

[a] Films 48 hrs. old on tin plate panels.

TABLE IV

Outdoor Durability of Clear Varnishes on Wood [a]

Description of Varnish	No. Weeks to First Crack or Check	Appearance After 7 Months	Appearance After 9 Months
Oleoresinous Varnishes from Epoxy Resin B			
25-Gallon Linseed Oil	42–48	10 crack, E glass	10 crack
35-Gallon Linseed Oil	42	10 crack, G-E gloss	10 crack
25-Gallon Soya Oil	42	10 Crack, G gloss	10 crack
Other Oleoresinous Varnishes			
25-Gallon Ester Gum-Linseed Oil	17	2 crack, F-P gloss	2 crack
25-Gallon Ester Gum-Tung Oil	23	4 crack, P gloss	2 crack
25-Gallon Pentaerythritol Rosinate-Linseed Oil	18	2 crack, P gloss	1 check
25-Gallon Penta Rosinate-Penta Linseedate	18	2 crack, F-P gloss	1 crack
25-Gallon Rosin Modified Phenolic-Linseed Oil	22	2 crack, P gloss	2 crack
25-Gallon Rosin Modified Phenolic-Tung Oil	26	7 crack, F-P gloss	2 crack
25-Gallon Rosin Modified Phenolic-Penta Linseedate	26	8-9 crack, F-G gloss	5 crack
25-Gallon Straight Phenolic-Tung Oil	34	10 crack, F-G gloss	9 crack
12.5-Gallon Straight Phenolic-Tung Oil	26	8 crack, VP gloss	9 crack
25-Gallon Maleic Resin-Linseed Oil	18	6 crack & lift, F-P gloss	0 crack
18-Gallon Hydrocarbon Resin-Linseed Oil	17	2 check, P gloss	2 check, 2 crack
6-Gallon Kopal Ester-Linseed Oil	2	0 crack, no gloss	85% bare wood
33-Gallon Straight Phenolic-Tung-Linseed Oil	43	10 crack, E gloss	10 crack
Styrenated Vehicles			
Commercial Styrenated Alkyd A (34% Styrene)	23	8 crack and lift	6 crack and lift
Commercial Styrenated Alkyd B (44% Styrene)	17	2 crack and lift	2 crack and lift
Commercial Styrenated Alkyd C (35% Styrene)	17	3 crack and lift	....
Styrenated Soya-Dehydrated (80-20) Ester of Epoxy Resin B (33% Styrene)	47	10 crack	10 crack
Styrenated Linseed Ester of Epoxy Resin B (33% Styrene)	23	8 crack and lift	top coat peeling
Commercial Styrenated Soya Oil A	4	5-6 crack and lift, G gloss	0 crack
Commercial Styrenated Soya Oil B	8	0 crack	0 crack
Oil Modified Alkyd Resins			
Commercial Alkyd A (37% Linseed Acids)	29	9 crack, E gloss	9 crack
Commercial Alkyd B (40% Dehydrated Castor Acids)	22	6 lift, G-E gloss	6 lift
Commercial Alkyd C (41% Soya Acids)	27	9 lift, E gloss	8 lift
Commercial Alkyd D (49% Linseed Acids)	33	10 crack, E gloss	8 crack
Commercial Alkyd E (60% Linseed Acids)	22	6 lift, G-E gloss	6 lift
Laboratory Alkyd (60% Linseed Acids)	37	10 crack, G-E gloss	9 crack
Commercial Alkyd F (73% Soya Acids)	58	10 crack, G gloss	10 crack
Straight Epoxy Resin Esters			
Dehydrated Castor Ester of Epoxy Resin B (30% Acids)	18	8 crack & lift, F gloss	3 crack & lift
Dehydrated Castor Ester of Epoxy Resin B (40% Acids)	52	10 crack, G gloss	10 crack
Dehydrated Castor Ester of Epoxy Resin B (50% Acids)	45	10 crack, G-E gloss	10 crack
Dehydrated Castor Ester of Epoxy Resin B (55% Acids)	31	9 crack & lift, G-E gloss	7 crack
Dehydrated Castor Ester of Epoxy Resin B (60% Acids)	27	9 crack & lift, G gloss	8-9 crack
Soya Ester of Epoxy Resin B (55% Acids)	40	10 crack, G-E gloss	10 crack
Upgraded Soya of Epoxy Resin B (50% Acids)	45	10 crack, G-E gloss	10 crack
Linseed Ester of Epoxy Resin B (50% Acids)	38	9-10 crack	9 crack

[a] Panels for outdoor exposure were made by brushing 3 coats (occasionally 4 coats) on Western red cedar and exposing at 45° facing south at Oakland, Calif., on Oct. 14-17. Failure was rated on a scale of 10 where 10 means perfect (no failure of type indicated) and 0 means complete failure.

Abbreviations: E = excellent, G = good, F = fair, P = poor.

resin varnishes which are representative of various types and which could be prepared without difficulty are shown in Table III. Also shown in Table III are film properties of two typical soft oil varnishes.

Compared to conventional oleoresinous varnishes, the epoxy resin varnishes had very low acid numbers. They dried slowly at a rate similar to many other soft oil varnishes, had similar fair water-resistance but were softer than most oleoresinous varnishes. On the other hand, the epoxy resin varnishes were more viscous and consequently were lower in solids content at application viscosity.

The outstanding feature of the epoxy varnishes was the remarkably better durability and gloss retention of clear films when exposed outdoors upon wood. Exposure tests were carried out on a great variety of clear varnishes on western red cedar panels at Oakland, Calif., as shown in Table IV. Panels were mounted at a 45° angle facing south and first exposed on October 15. It is obvious that the first few months of weather were relatively mild but, after about 6 months' exposure the sunshine became quite intense. Durability therefore is not proportional to the number of weeks before failure because of the ever-changing degree of severity of weather. All the varnishes were first exposed on the same date, but a few were exposed in a subsequent year. Although severity of weather does differ from year to year, it has been observed, by repeated exposure of some controls, that fairly reliable comparisons could be made among panels exposed during different years. Although typical oleoresinous varnishes started to fail by cracking at 18 to 22 weeks, the 25-gal. linseed oil-Epoxy Resin B varnish did not start to develop cracks until 42 to 48 weeks after first exposure. Moreover the gloss during this period was excellent. It is noteworthy that the durability of the epoxy varnish exceeded that of the clear alkyds, which failed by a combination of cracking and then lifting in the area around the crack. This typical failure of alkyds leaves a film which has excellent gloss in many portions but is marred by the unsightly grayish-appearing areas. Several clear esters of epoxy resins also had very good durability.

The film properties of epoxy varnishes were determined by use of 0.05% cobalt as the naphthenate on total solids. The use of 0.10% cobalt or of a combination of 0.05% cobalt and 0.50% Pb led to only slight changes in properties such as drying rate, hardness, and water-resistance. Increasing the oil length of the varnishes resulted in slower surface drying rate, faster through-drying rate, improved water-resistance, and softer films.

To avoid possible confusion it may be desirable to emphasize the differences between the epoxy resin varnishes and the more commonly used esters of epoxy resins. In the first place, the epoxy resin content of the esters is usually greater; for example, although the 25-gallon epoxy varnish contains only 34% resin, the esters usually contain from about 43 to 60% resin. Also, although the esters can be made in open kettles, they are ordinarily made in closed kettle equipment. On the other hand, the varnishes can easily be cooked in open kettles because no water is liberated. The epoxy varnishes do not have the outstanding all-around properties of straight esters, but they are cheaper. The esters dry more rapidly and yield films with greater hardness, abrasion-resistance, and chemical resistance.

A further favorable property of the epoxy varnishes was discovered in artificial weathering tests of pigmented gray enamels sprayed upon steel. After exposure in the Atlas Weatherometer for 500 hrs., the chalk resistance of the enamels derived from the epoxy varnishes was decidedly better than enamels based on a 25-gal. tung-phenolic varnish or upon epoxy resin esters. Moreover the chalk resistance was slightly superior to that of alkyd enamels in the tests carried out thus far (see Table V). Enamels of this nature are suitable for exterior coatings on steel storage tanks and similar objects.

TABLE V

Artificial Weathering Tests on Gray Enamels [a]

Vehicle	Gloss[b]	Chalking[b]
35-Gallon linseed-epoxy resin[c]	7	10
25-Gallon linseed-epoxy resin[c]	6	9
25-Gallon soya-epoxy resin[c]	7	10
25-Gallon tung-phenolic	5	6
Commercial alkyd enamel	6	9
Laboratory medium soya alkyd enamel	8	8
Commercial epoxy ester enamel	8	2

[a] Coatings on steel were exposed for 500 hrs. in the Atlas Weatherometer. The composition of the enamels was as follows:
45% Pigment
Rutile chalk resistant titanium dioxide....................99.5%
Lampblack...0.5%
55% Vehicle solids

[b] Ratings on a scale of 0 to 10 where 0 = no gloss or very severe chalking and 10 = perfect gloss or no chalking.

[c] The epoxy resin was Epoxy Resin B.

Chemical Nature of the Reactions in Varnish Cooking. In an effort to obtain some clue to the nature of the chemical reactions involved in the cooking of glyceride oils with epoxy resins, the total epoxy (3) and hydroxyl (2) content of some varnishes were obtained. These values were compared with the original values of the mixtures as calculated from the quantity of epoxy resin present. In the case of 25-gal. linseed or soya varnishes cooked at 580°F., it was found that the total hydroxyl content remained unchanged during the cooking process. It was also found that the great bulk of the epoxy groups were destroyed at varnish cooking temperatures of 580°F. The actual figures for a 25-gal. linseed oil-Epoxy Resin B varnish were as follows:

Original epoxide value of Epoxy Resin B = 0.103 mole/100 g.

Theoretical epoxide value of epoxy varnish if no destruction of epoxy groups occurred = 0.035 mole/100 g.

Found: epoxide value of varnish = 0.004 mole/100 g. (11% of epoxide groups remained).

Original hydroxyl value of Epoxy Resin B = 0.328 mole/100 g.

Theoretical hydroxyl value of varnish if no net change in total number of hydroxyl groups occurred = 0.111 mole/100 g.

Found: hydroxyl value of varnish = 0.118 mole/100 g.

In the case of the 25-gal. soya varnish the theoretical values for epoxy and hydroxyl values are the same as above. The values actually found were as follows:

Found: epoxide value of varnish = 0.008 (23% of epoxide groups remained).

Found: hydroxyl value of varnish = 0.12 mole/100 g.

When the varnish cooking was carried out at lower temperatures of 550° and 500°F., the final epoxide values of the linseed varnishes were larger, being 0.014 and 0.020 mole/100 g., respectively. This indicates that the higher the temperature, the greater is the destruction of epoxy groups.

The alcoholysis of glycerides by epoxy resins has been carried out readily in the presence of catalysts at lower temperatures (250°C., 482°F.), and under these conditions the total quantity of hydroxyl and epoxy groups remained essentially unchanged, as demonstrated by the following experiment utilizing an especially prolonged time of reaction. In a Pyrex flask equipped with stainless steel stirrer and carbon dioxide atmosphere, a mixture of 278 g. of Epoxy Resin B, 884 g. of alkali-refined soya oil, and 6 g. of calcium oxide was heated to 250°C. over a period of 2 hrs. and held at 250°C. for 2.5 hrs. Analysis of the product showed that the epoxy groups were unaffected and no significant change in total hydroxyl content occurred in the alcoholysis treatment.

Theoretical epoxide value of product if no destruction of epoxy groups occurred = 0.0245 mole/100 g.

Found: epoxide value of product = 0.026 mole/100 g.

Theoretical hydroxyl value of product if no net change in total hydroxyl groups occurred = 0.079 mole/100 g.

Found: hydroxyl value of product = 0.083 mole/100 g.

The alcoholysis reaction was utilized in the preparation of an alkyd resin by reaction of the alcoholyzed mixture with phthalic anhydride. An example of this type of reaction is described in the next section.

The analytical data are in agreement with an alcoholysis reaction between the free hydroxyl groups in the epoxy resin and the ester groups of the oil. This reaction could account for the attainment of compatibility upon heating oils and epoxy resin. As the temperature is increased, the epoxy groups are destroyed; this could be accounted for by polymerization of epoxy groups with each other or by addition of hydroxyl groups to epoxy groups whereby an ether linkage and a new hydroxyl group are formed. It is not possible to say which of these reactions (or others) may occur, but both are compatible with the analytical data.

Alcoholysis of a Glyceride Oil by an Epoxy Resin and Preparation of an Alkyd Resin. This preparation of an alkyd resin is offered as an example of a distinctive method of use of an epoxy resin. The product is not intended to represent the best epoxy resin alkyd that may be made.

The formula used was as follows:

	%	Actual charge, grams
Epoxy Resin B	30.6	915
Linseed oil	59.2	1,768
Phthalic anhydride	10.2	306
Calcium oxide	....	6

According to functional groups present the charge can be represented as follows:

Epoxy Resin, epoxide content	0.94 mole
Epoxy Resin, hydroxyl content	3.00 equivs.
Epoxy Resin, total esterifiable content	4.88 equivs.
Phthalic anhydride	4.13 equivs.

The oil, epoxy resin, and calcium oxide were charged to a Pyrex flask equipped with stainless steel stirrer and inert gas atmosphere. The charge was heated to 250°C. in 1.4 hrs. and held for 1 hr. After cooling to 175°C., the phthalic anhydride was added, mixture was heated to 250°C. over a period of 2 hrs., and maintained at 250°C. for 1.25 hrs. After cooling and dilution with xylene, the alkyd had the following properties: nonvolatile, 58.3%; Gardner-Holdt viscosity, W, Gardner color, 10-11; acid number on solids, 20.2 mg. KOH/g. Upon further reduction with xylene the solution had viscosity E-F, color 8-9, and 44.2% solids.

In the presence of 0.05% cobalt, this alkyd had a good balance of surface- and through-drying properties; it was dried hard in 7 hrs. and cotton-free in 8 hrs. in films of 1 mil dry thickness. It had better ultimate resistance to alkali than conventional glycerol alkyds.

Summary

Epoxy resins derived from epichlorohydrin and Bisphenol-A have been converted into air-drying varnishes by cooking with vegetable oils. Compared to varnishes derived from ordinary varnish resins, the epoxy resin-oil varnishes have faster bodying rate, higher viscosity, lighter color, and lower acid number. Although the epoxy resin-oil varnishes dry slowly and yield soft films like many other soft oil varnishes, they have remarkably good exterior durability in clear films upon wood, and in pigmented films have good chalk resistance. The varnishes are quite different from epoxy esters derived from epoxy resins and fatty acids. These latter products dry rapidly and yield hard, flexible films possessing good abrasion and chemical resistance.

In cooking the varnishes at the high temperatures (580°F.) employed, epoxy groups are destroyed and the total hydroxyl content remains essentially unchanged. At lower temperatures (480°F.) the alcoholysis of oils by the hydroxyl groups in the epoxy resin proceeds readily while the epoxy groups remain essentially intact. Such alcoholyzed products may be used for further cooking with acids of various types. Phthalic anhydride, for example, was used to convert the product to an alkyd having good drying properties.

Acknowledgment

Thanks are due to J. R. Scheibli for data on the chalk resistance of the gray enamels, and to C. A. May and R. D. Schmitz for aid in preparation and evaluation of the varnishes.

REFERENCES

1. Greenlee, S. O., U. S. Patents 2,456,408 (1948), 2,493,486 (1950).
2. Hochstein, F. A., J. Am. Chem. Soc., *71*, 305 (1949).
3. Jungnickel, J., Peters, E., Polgar, A., and Weiss, F., "Organic Analysis," vol. I, p. 127, Interscience Publishers, New York, 1953.
4. Renfrew, M. M., Wittcoff, H., Floyd, D. E., and Glaser, D. W., ACS Division of Paint, Plastics, and Printing Ink Chemistry Preprint Booklet, vol. 14, p. 171, Kansas City, March 1954).
5. Scheibli, J. R., and Dannenberg, H., Offic. Dig. Federation Paint and Varnish Production Clubs, No. 330, 491 (1952).
6. Shell Chemical Corporation, Brochure "Epon Resins for Surface Coatings," 1952; Paint, Oil, Chem. Rev., *113*, No. 23, 15 (1950).
7. Tess, R. W., Jakob, R. H., and Bradley, T. F., Ind. Eng. Chem., *46*, 385 (1954).
8. Tess, R. W., and May, C. A., Offic. Dig. Federation Paint and Varnish Production Clubs, No. 311, 1114 (1950).
9. Von Mikusch, J. D., and Frazier, C., Ind. Eng. Chem., Anal. Ed., *13*, 782 (1941).

[Received November 12, 1954]

Determination of Free Gossypol In Chemically Treated Cottonseed Meals Containing Dianilinogossypol

WALTER A. PONS JR. and CARROLL L. HOFFPAUIR, Southern Regional Research Laboratory,[1]
New Orleans, Louisiana

COMMERCIAL PRODUCTION of solvent-extracted cottonseed meal in which free gossypol has been reduced to low levels by means of chemical treatment (1) is one of the more recent developments in the cottonseed processing industry. As a result of the chemical treatment employed, a portion of the gossypol originally present in the seed is converted to dianilinogossypol, in contrast to conventional meals where the major portion of the gossypol is bound to constituents of the meal. The determination of free or unreacted gossypol in such meals is of considerable importance, particularly when these meals are used as protein supplements in poultry feeds (2). Present analytical methods (3, 4, 5) for the estimation of free gossypol have been designed primarily for application to conventional cottonseed meals. These methods utilize aqueous acetone for extraction of free gossypol, followed by colorimetric determination based on the difference in the optical density of duplicate aliquots of the extracts before and after reaction with p-anisidine (3, 4) or aniline (5) under specified conditions. Such a system requires that the aqueous acetone extract and subsequent dilutions be stable for reasonable periods of time and that no substances in the extract other than gossypol pigments react with p-anisidine or aniline to produce colored products. For conventional meals these requirements are satisfied, and the system has been shown to be valid (3, 5). In the case of chemically treated meals containing dianilinogossypol these methods cannot be assumed to be applicable, and it was therefore deemed advisable to investigate the factors involved in the extraction and analysis of free gossypol in the presence of dianilinogossypol. A method is proposed for the determination of free gossypol in chemically treated cottonseed meals. Since the procedure is not recommended for use with conventional meals, a rapid qualitative test has been developed for detecting the pres-

---

[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.