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CONFIDENTIAL

SYNTHESIS AND APPLICATION STUDIES ON HYDROLYZED AROCLORS AND DERIVATIVES

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The alkaline hydrolysis of Aroclor has provided an interesting new family of Monsanto-based chemical intermediates: the polychlorinated bisphenols. These can be used to prepare epoxy-type resins (by reaction with epichlorohydrin). Our interest in these resins was aroused by the possibility they offer for (1) new markets for Aroclors; (2) possible patent protection; and (3) improved flammability, adhesion, and dielectric properties, which might be conferred by the high chlorine content. With this in mind, a detailed study of the hydrolysis, glycidylation reaction and application of the epoxy resins in various outlets was undertaken.

The major current use of epoxies is in the preparation of surface coatings. Because of this, much of our work was directed toward the preparation of drying-oil fatty acid esters and then to the application and evaluation of these esters in coatings.

We hoped that such an epoxy resin might fulfill the requirements of a high temperature, thermosetting and flameproof metal-metal adhesive. This report describes efforts to develop such an adhesive. The scope of study was broadened briefly to include casting, potting, and laminating applications of the unmodified Aroclor epoxies.

Other studies were aimed at using hydrolyzed Aroclors as curing agents in ~~polyesters~~, and the epoxy ethers as vinyl stabilizers and as modifiers for alkyd resins.

Polyepoxies

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Methanolic alkaline hydrolysis of Aroclor 1268 under pressure was investigated. The process studied is similar to the Organic Chemicals Division hydrolysis of tetrachlorobenzene to 2,4,5-trichlorophenol and of hexachlorobenzene to pentachlorophenol (Ref. 1 & 12). Variables studied were time, temperature, excess NaOH and water concentration. The product was isolated as dihydrolyzed Aroclor 1268 (dihydroxypolychlorobiphenyl).

Glycidylation of dihydrolyzed Aroclor 1268 was accomplished most satisfactorily by adaptation of the tetrachlorobisphenol A glycidylation procedure developed by Organic Chemicals Division Research (Ref. 2).

The glycidyl ethers are hard, brittle, amber colored solids, capable of the typical epoxy reactions.

We evaluated these Aroclor epoxy resins as surface coating resins, studying in detail their esterification with drying oil fatty acid. By comparison with conventional epoxies, these new resins react very rapidly. The resulting esters were evaluated both as varnishes and as paints. Particular attention was given to the properties which would make these resins attractive as surface coatings. At the same time, detailed studies were made in efforts to develop suitable formulations for adhesive, potting, and laminating applications. Noteworthy characteristics are the high heat distortion values and adhesion to glass.

The Aroclor epoxies were examined and found promising also as stabilizers for polyvinyl chloride, and curing agents for high acid value alkyds. Exploratory studies on styrene-soluble Aroclor epoxy fumaric acid polyesters were made.

This work was carried out during the period May 25, 1955 to December 1, 1957.

III. CONCLUSIONS

Complete phenolic difunctionality in hydrolyzed Aroclor 1268 can be obtained by the methanolic hydrolysis process. Hydrolyzed Aroclor 1268 having neutral equivalents equal to theory was obtained reproducibly and consistently.

The diglycidyl ether can be prepared reproducibly in good yield and high oxirane oxygen content (91.2% of theory) from this hydrolyzed Aroclor 1268. Epon 828 is 85% theory.

The diglycidyl ether of hydrolyzed Aroclor 1268 reacts very rapidly with drying oil fatty acids to produce esters having good color, low viscosity, and enhanced tolerance for hydrocarbon solvents. Reaction temperatures may be 60°C lower than with conventional epoxies.

These esters, when used as coatings, show satisfactory drying times, excellent adhesion to metal, good water resistance, high flexibility and toughness.

Pigmented samples show excellent weather stability and flame-proofing

The alkali resistance of these coatings is relatively poor and the resistance to weathering in unpigmented films is not as good as conventional epoxy esters.

The Aroclor-epoxies can be readily cured with most conventional epoxy curing agents. Best results property-wise are obtained by using high melting curing agents which can be dry blended with the resin. These cured resins have fair adhesion to glass and ceramics, but very poor adhesion to metal.

The rapid reaction of Aroclor-epoxy resins with dibasic acids could lead to plasticizers, polyester resins and non-drying alkyds. The Aroclor-epoxy can be used to cure high-acid-value alkyds to give interesting new surface coatings.

The dihydroxy material itself can be used to cure regular epoxy resins, yielding hard, brittle, nonflammable castings.

The Aroclor 1268-epoxy is comparable to Paraplex G-60 and Epon 828 as a heat and light stabilizer for plasticized polyvinyl chloride.

IV. RECOMMENDATIONS

We recommend that the Organic Division accept hydrolyzed Aroclor 1268 as a new product and that the application data presented here be used to develop uses within the surface coating industry.

As industry interest develops, it would be advisable to undertake further process studies on the hydrolysis step, aimed at lower costs and better color of the diphenol, since cost and color may be the chief objections to this product.

Application studies aimed at broadening the uses of the diphenol should be instituted. Potential markets exist in polycarbonates, epoxy resin curing agents, and polyesters, in addition to the surface coating uses outlined here.

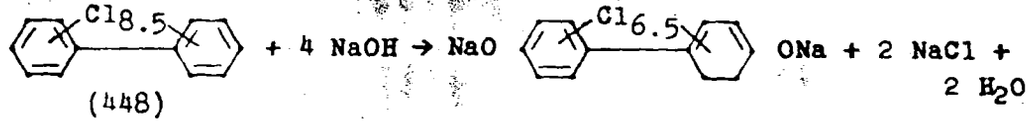
Further applied research is indicated on the Aroclor-epoxy-alkyds, on the glass-glass adhesives, and on flameproof coatings.

The hydrolyzed Aroclors should be promoted as flameproofing epoxy curing agents - comparable to HET anhydride - and as modifiers generally for epoxy resins.

For additional suggestions on the use of hydrolyzed Aroclors please see References 3, 4 and 5.

V. DATA AND DISCUSSION

HYDROLYSIS The chemistry of the hydrolysis reaction appears to be:

1. 

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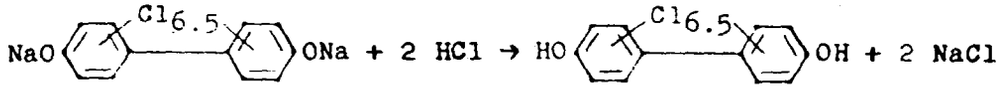
2. 

(411.2)

The molecular weight of the Aroclor was calculated from the chlorine analysis (67.5% Cl) and from this the theoretical neutral equivalent was determined as 205.6.

The initial hydrolysis product was substantially 90% dipnenolic. Application studies particularly in the field of adhesives and potting compounds indicated the desirability of a 100% diphenol. Synthesis work was directed to this goal and by the use of excess NaOH in methanol solution, essentially 100% dihydrolyzed material was obtained. (Ref. 1)

We have shown that increasing the excess NaOH in the hydrolysis of Aroclor 1268 significantly increased the phenolic content of the product (Figure 1).

Increasing the reaction temperature from 190°C to 240°C did not increase the phenolic content as much as anticipated. The effect of increased temperature is summarized below:

EFFECT OF TEMPERATURE ON
HYDROLYSIS OF AROCLOR 1268

	190°*	240°
20% excess NaOH	219 N.E.**	216 N.E.
40% excess NaOH	211	210

*One hour hold period in methanol
**Theory N.E. = 205.6

Increasing the reaction time at 190°C from 1 hour to 3 hours, using 20% excess NaOH (Runs 1 and 4, Table I) decreased the N.E. from 219 to 212. However, since with 40% excess NaOH at 190°C, [illegible] after 3 hours (Run 9) as against 211 after 1 hour (Run 3), longer reaction times do not appear promising.

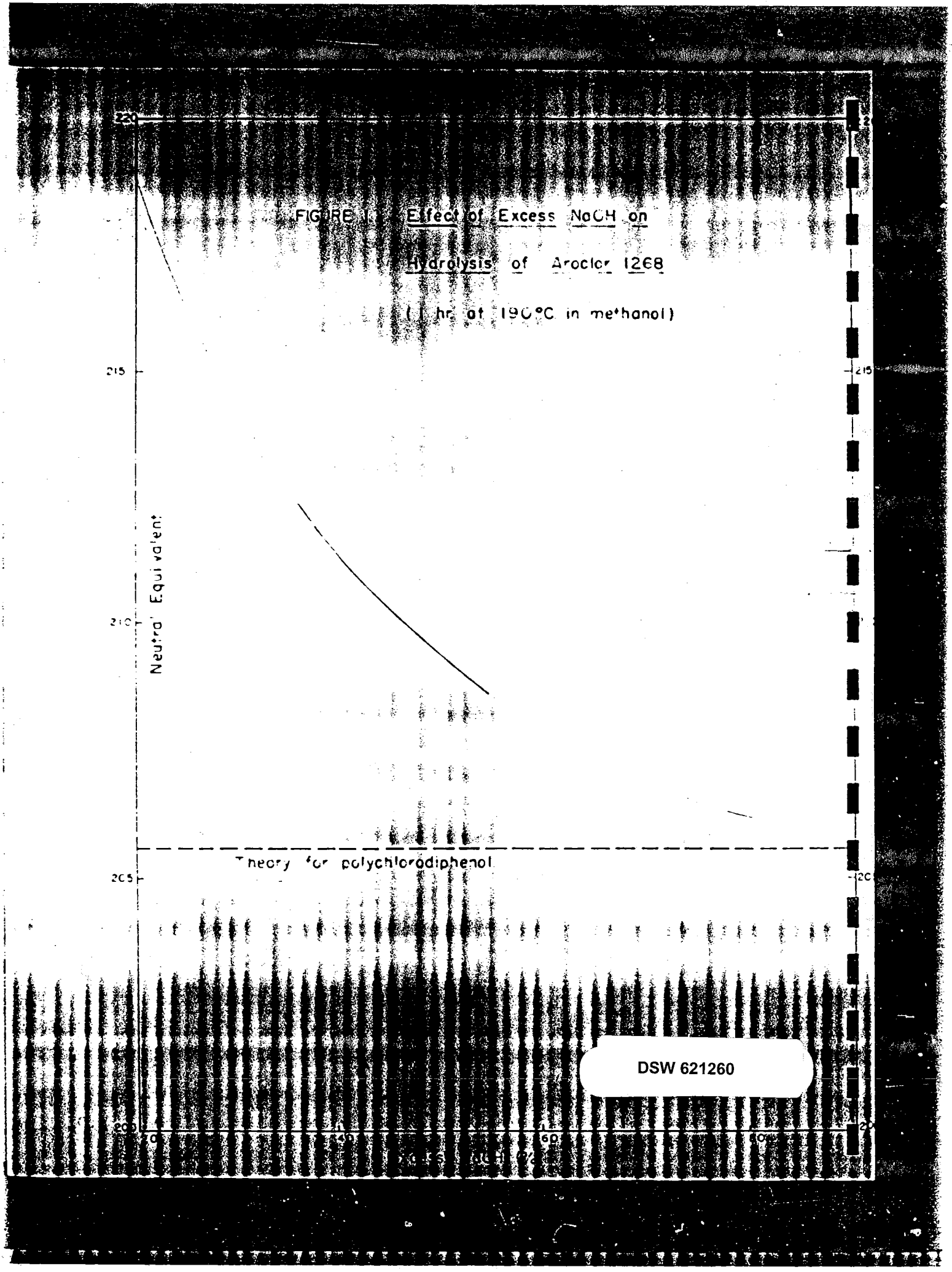


FIGURE 1 Effect of Excess NaOH on Hydrolysis of Aroclor 1268 (1 hr at 190°C in methanol)

TABLE I

HYDROLYSIS OF AROCLOR 1268 IN 1.5-LITER AUTOCLAVE[1]

Run No.	NBP No.	Conditions						Results			
		Temp. °C	Time hr	Excess NaOH, %	Maximum Pressure, psig	MeOH, g	H_2O, g	Yield g	Yield %	N.E.[2]	% OH[2]
1	359388, 9	190	1	20	590	400	-	197.5	95	219	7.65
2	359391, 2	190	1	20	570	400	18	190	92	219	7.67
3	359393	190	1	40	660	400	-	190	92	211	7.63
4	359394	190	3	20	600	400	-	190	92	212	7.70
5	359396, 7	190	1	20	365	200	200	185	89	291	6.29
6	359399	190	3	20	490	200	200	190	92	225	7.42
7	359400	240	1	20	350	-	400	No Hydrolysis			
8	365951	240	1	20	1275	400	-	96.5	46[3]	216	7.95
9	365952	190	3	40	615	400	-	186	90	215	8.00
10	365954	190	1	60	760	400	25	190	92	208	8.12
11	365955	240	1	40	1450	400	25	176	84	210	8.05
13	365959	190	0.5	60	590	400	35	193	94	215	7.87
12[4]	365958	190	1	80	520	400	35	190	92	206[5]	8.19
14[4]	365963	190	1	80	605	400	35	193	94	206[5]	8.12
15[4]	365964	190	1	80	580	400	35	191	93	206[5]	8.18

NOTES

1. All runs were made with 0.5 mole Aroclor 1268.
2. Calc. values based on Cl analysis were 205.6 N.E. and 8.27% OH.
3. Large product loss when batch foamed excessively during acidification.
4. Runs 12, 14 and 15 are identical.
5. Theory difunctionally within limits of accuracy of analytical method.

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Dimethyl ether, identified as a by-product in other methanolic NaOH hydrolysis reactions, appears to be the main by-product. About 30 g of a low boiler was trapped during venting of Run 17 (Experimental Section). Formation of dimethyl ether would account for the pressure build-up during the reaction hold period (see Figure 2). At present, it is assumed that methoxide ion attacks the methanol by an S_{N2} mechanism displacing the hydroxyl group as hydroxyl ion.

$$CH_3O^{\ominus} + CH_3OH \rightarrow CH_3OCH_3 + OH^{\ominus}$$

The methanol recovery for Run 16 (Table II) was 96%, (92% of material containing 83% methanol and 17% water). In Run 14, assuming the same ratio of methanol to water, methanol recovery was 88%. Recycle of methanol was not attempted.

Hydrolysis in water alone failed at 240°C, owing to insolubility of the Aroclor. However, about 94% (about 88% diphenol) hydrolysis took place in 50% methanol-water during 3 hours at 190°C (Run 6) using 20% excess base. These same conditions should be attempted using 80% excess NaOH.

Attempts to hydrolyze Aroclor 1268 in a 5-gallon vibrator-stirred Blaw-Knox autoclave resulted in very little hydrolysis. This is attributed to inadequate agitation resulting from too short a stroke on the vibrating discs.

Scale-up from 1.5-liter to 2-gallon went smoothly except for Run 16 in which too large a batch was attempted. Abnormally high pressures built up due to a small vapor space. Insufficient agitation resulted in incomplete hydrolysis.

The reaction appears to be slightly exothermic when 190°C is first reached. Hence, some cooling is always necessary to keep the reaction at 190°-195°C (see Figure 2).

Acidification was carried out above 90°C since below this temperature the product precipitates as a hydrate (Ref. 2) Acidification was done cautiously since foaming was encountered at the beginning of the acidification in almost all batches

The neutral equivalent was determined by the method of D. K. Lynch, St. Louis Research, and was estimated by E. M. Hubbard to be ± 1% accurate. Based on this figure, material analyzing 206.6 to 207.6 N.E. was assumed to contain theory diphenol (205.6 calculated).

Hydroxyl content determinations were made using acetic anhydride/pyridine, a standard acetylation method. The accuracy of the method is ± 0.3% OH and reported values generally run lower than theory. This may be due to difficulty in completely

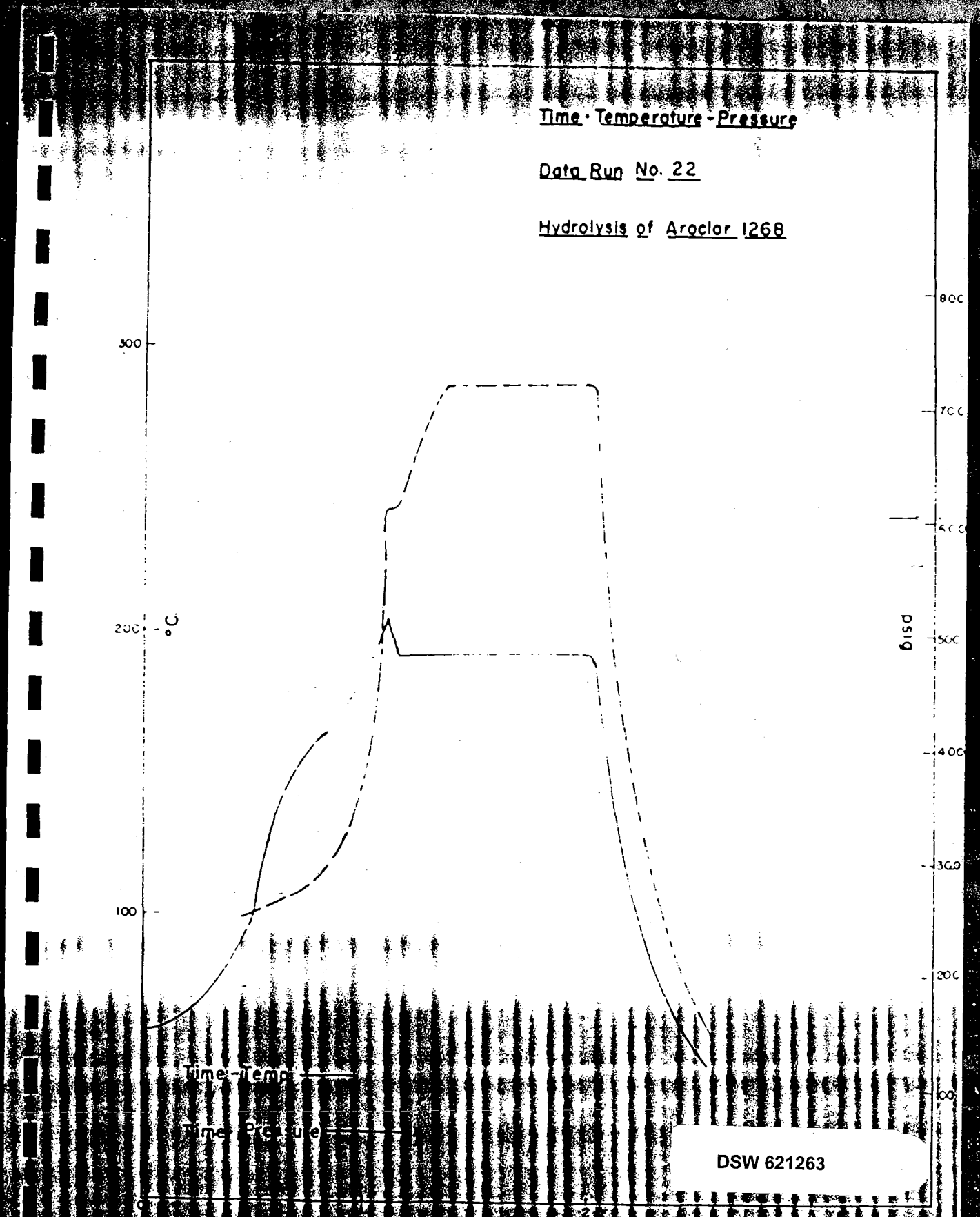


FIGURE 2. Time from Start of Heat-up, Hours

TABLE II

HYDROLYSIS OF AROCLOR 1268 IN 2-GALLON AUTOCLAVE

Run No.	NBP No.	Conditions(1) Temp. Range, °C	Max. Temp, °C	Max. Pressure, psig	Results Yield g	Yield %	N.E.(3)	% OH
16(2)	365969	185-190	196	4400	(4)		257(5)	7.00
17	365970, 1	190-193	193	625	1300	90	204	8.05
20	367259, 60 370312	190-193	205	760	1367	95	207	7.99
21	367262 370313	190-193	200	760	1364	95	207	7.83
22	367263 370314	190-192	203	720	1374	95.5	205	8.06
23	367265 370315	190-194	200	720	1347	93.5	206	7.77
24	367266 370316	189-193	199	700	1348	93.5	206	8.25

NOTES

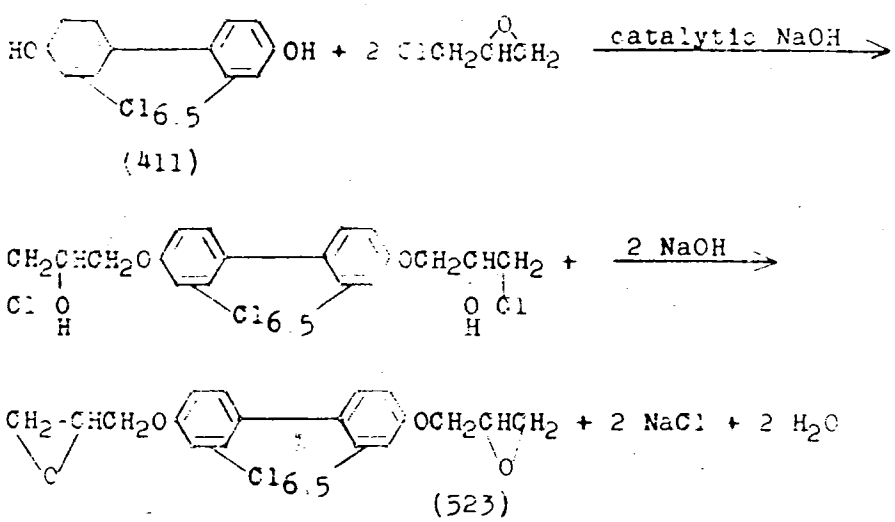
(1) All runs were made using 80% excess NaOH and a 1 hr hold period above 190°.
(2) Run 16 was a 10-fold scale-up of Run 12, Table I; other runs are 7-fold scale-up.
(3) Theory values 205.6 N.E. and 8.27% OH
(4) Aliquot of this run worked up; no yield figures obtained.
(5) Poor result probably due to inadequate agitation caused by overcharge.

acetylating phenolic groups. In view of inherent difficulties of the OH analysis, the N.E. determination was used as the deciding measure of purity.

All products melted at 60-68°C, the range being attributed to the presence of isomers.

BIOLOGICAL EVALUATION Table 5 of the Appendix contains a brief summary on the biological evaluation data on hydrolyzed Aroclors 1242, 1248, 1254, 1262, 1268, 1270 and 1271. Only the last two are difunctional compounds, the others are mixtures of mono- and dihydroxy Aroclors (difunctional hydrolyzed Aroclor 1268 has not been tested as yet) The lower chlorinated Aroclors undergo incomplete dihydrolysis. Biological data failed to show special new leads worthy of further investigation.

GLYCIDYLATION The chemistry of diglycidylation is as follows:



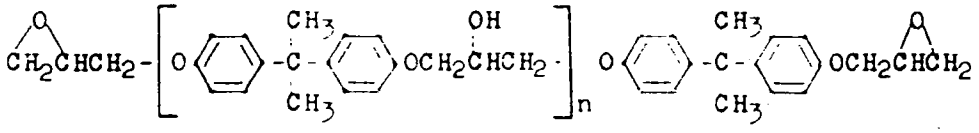
The adaptation of the St. Louis tetrachloro bisphenol A glycidylation procedure (Ref. 2) gives glycidyl ethers of dihydrolyzed Aroclor 1268 which are high in epoxy content and very low in hydrolyzable chlorine. The epoxy content (5.30-5.56% oxirane oxygen) is equivalent to ca. 91% as the diglycidyl ether. This compares well with commercial monomeric diglycidyl ether from bisphenol A (Epon 828 for example with runs 85% diepoxy).

The diglycidyl ether is a light amber resin melting at 46-50°C. Products with lower epoxy content have higher melting points, perhaps due to the presence of "polymeric" units. The potting and encapsulating trade would prefer a liquid glycidyl ether, but this cannot be obtained from dihydrolyzed Aroclor 1268. The lower-chlorinated hydrolyzed Aroclors might yield liquid glycidyl ethers, but these hydrolyzed Aroclors are not completely difunctional. The surface coating applications (which consume the greatest quantity of epoxy resins) on the other hand, prefer the high melting resin such as this.

No measure was made of a shorter dehydrohalogenation step, nor was the use of higher temperature, toluene, or chlorobenzene as reaction solvents tested. At this early stage of investigation our main goal was to prepare reproducibly high epoxy-content diglycidyl ethers, free of alkali, for Applied Research.

APPLICATION STUDIES

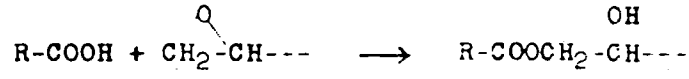
Esterification The structure of conventional epoxy resins is:



Since "n" is an average, it may have fractional values.

This structure can react with carboxylic acids to give esters in two ways (Ref. 6):

1) Reaction of oxirane oxygen

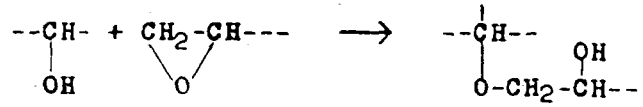


The ester group may be on either the α or β carbon atom. No water is liberated but a hydroxyl group is formed.

2) Reaction of carboxylic acid with hydroxyl. This is a conventional esterification with loss of water. The hydroxyls may be either those originally present or those formed in (1).

In addition, the following may occur in varying degrees depending on reaction conditions:

3) Ether formation



4) Hydration of epoxy by water

It has been shown that in the uncatalyzed reaction at 200° of caprylic acid with an epoxy resin, the first three reactions occur in the approximate order of 2:1:1. Reaction (4) is suppressed by the removal of water by azeotroping with xylene.

Our study of the esterification of the diglycidyl ethers of hydrolyzed Aroclors is divided into several well defined areas:

1) Esterification of oxirane oxygen only of diglycidyl ethers based on 90% dihydrolyzed Aroclors.

2) Esterification of oxirane oxygen only of ethers based on 100% dihydrolyzed Aroclor.

3) The preparation of more completely esterified epoxies, i.e., oxirane oxygen plus some hydroxyl esterification.

Our initial work was on diglycidyl ethers derived from hydrolyzed Aroclor 1268, from the St. Louis pilot plant, which was 90% difunctional. The diglycidyl ethers derived from this phenol were found to be unsatisfactory for casting purposes because of their lack of 100% difunctionality. However, they did make satisfactory coating resins. The presence of 10% monofunctional material apparently does not detract from this material's film forming characteristics.

We used soya fatty acid as a standard unsaturated acid, but made some esters from tall oil to observe color and drying times.

Very early in our work, we noted a marked variance in the rates of esterification of the oxirane oxygen of the several ethers; as shown in the following Table III and graphically in Figure 3.

FIGURE 3.

COOKING SCHEDULE

Glycidyl Ethers of several biphenols plus

Soya FATTY ACIDS

Disappearance of ACID

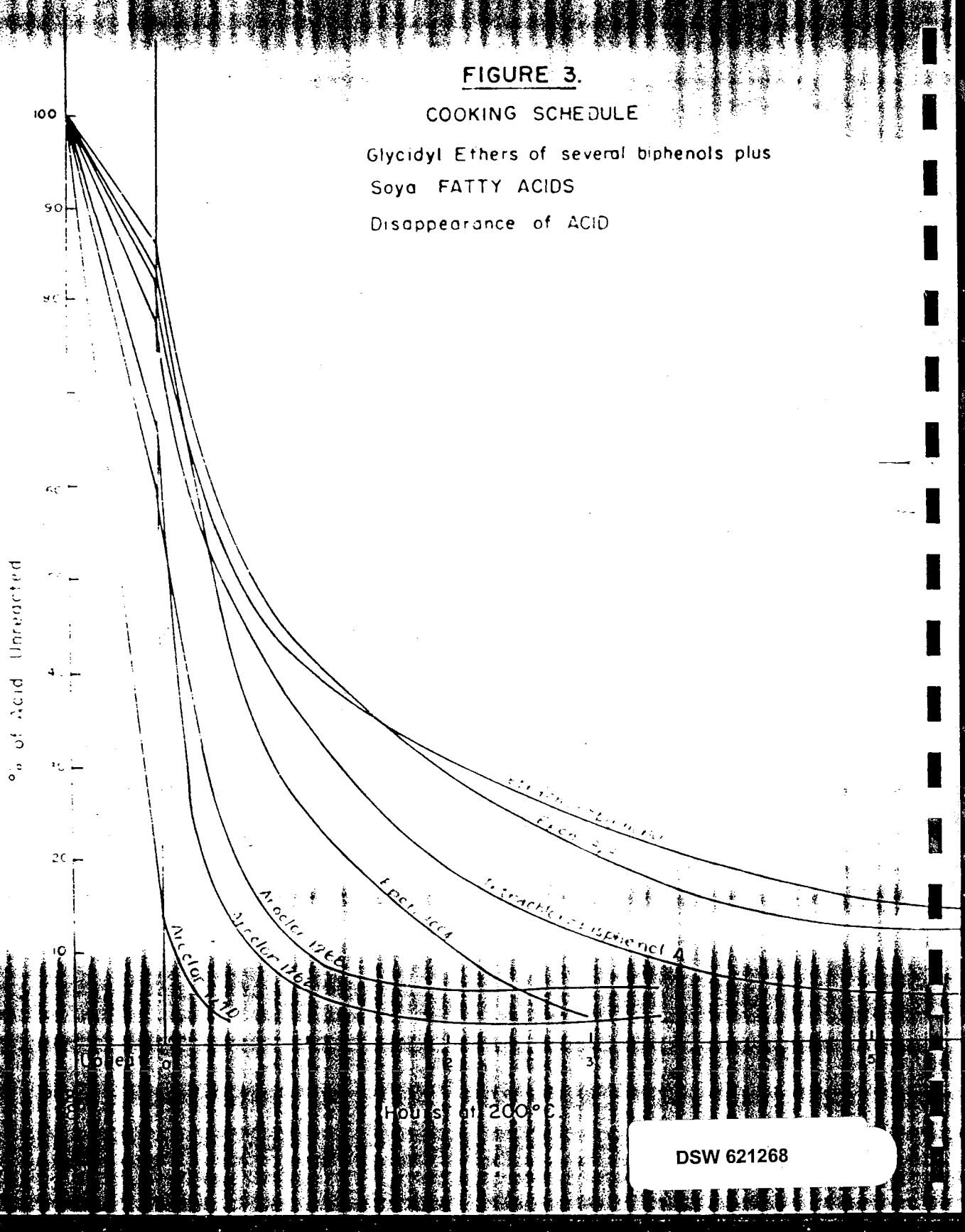


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TABLE III

SOYA FATTY ACID ESTERS OF GLYCIDYL ETHERS
(Oxirane Oxygen Only)

Ester No.	Derivation	% Epoxy	Reaction Time Hrs at 200°C	Reaction Rate
354868-1	Aroclor 1270	3.83	0.5	Rapid
354872	Aroclor 1262	5.39	2.5	Slow
354873	Epon 1004 (Bisphenol A)	1.68	3.5	Slow
354874	Aroclor 1268	5.10	3.5	Slow
354875	Tetrachlorobisphenol A	6.44	6.0	V.Slow
354877	Tetrachlorobiphenol	6.17	11.8	V.Slow
354881	Epon 828 (Bisphenol A)	9.4	8.7	V.Slow

The extremely fast reaction of 354868-1 was very interesting and exciting when compared to the reaction time for Epon 1004. As further data accumulated, it was found that the fast reaction was not limited to derivatives of Aroclor 1270, but also occurred in those of 1268 and 1262. The only significant difference that was found between fast and slow reacting diglycidyl ethers was one related to % epoxy and consequent molecular size or "n" value. This correlation is shown in Table IV and in Figure 4.

TABLE IV

SOYA FATTY ACID ESTERS OF DIGLYCIDYL ETHERS
OF HYDROLYZED AROCLOR 1268 (90% DIFUNCTIONAL)

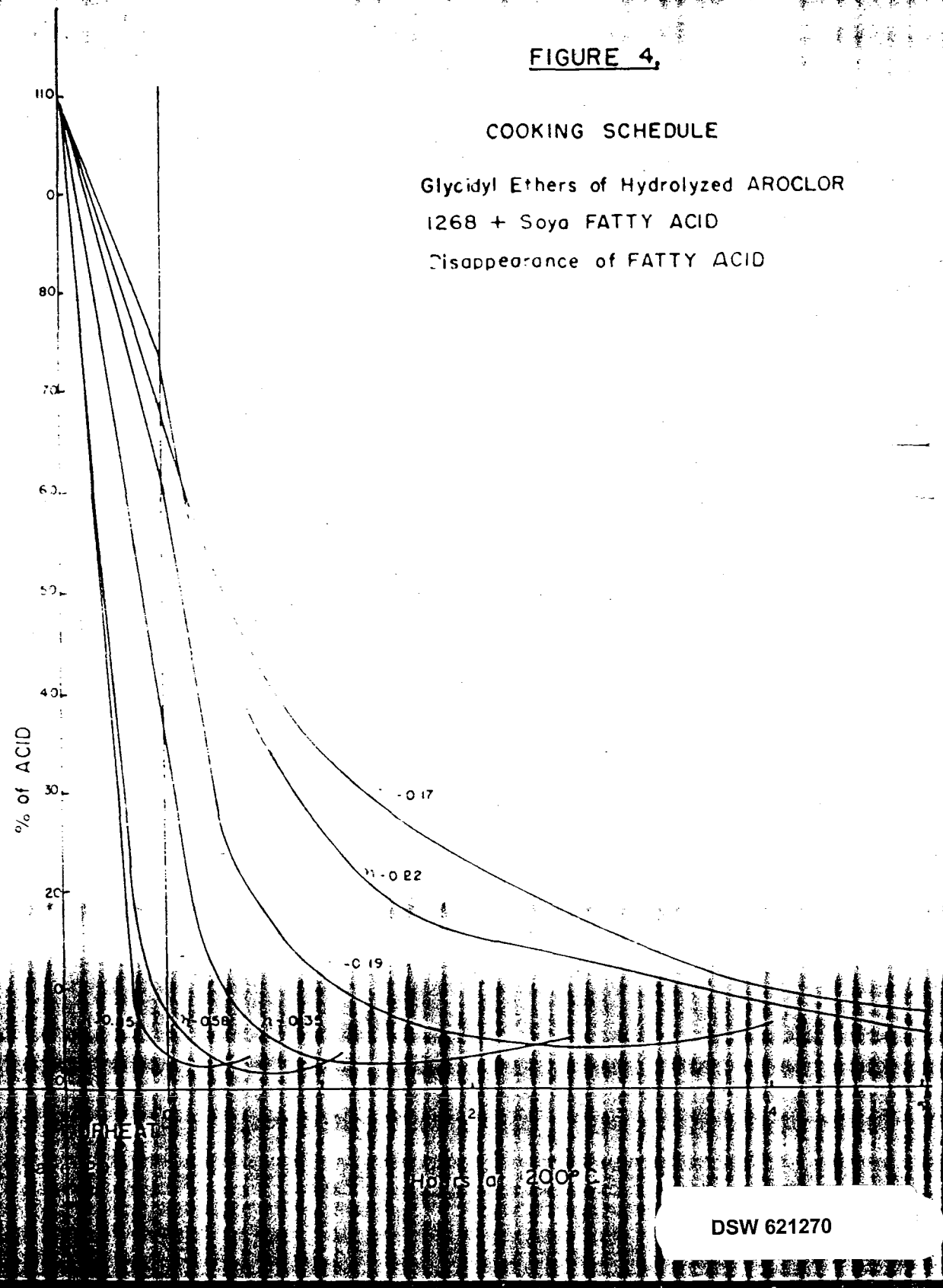
Ester No.	% Epoxy	Mol. Wt. (Based on % Epoxy)	n	Hydrolyzable Chlorine	Reaction Time Hrs at 200°	Reaction Rate
359068	5.16	620	0.17	0.35	7.4	V.Slow
354874	5.10	628	0.19	0.62	3.5	Slow
359060	4.93	648	0.22	0.48	4.75	Slow
359061	4.53	706	0.35	0.015	1.00	Fast
359062	3.90	820	0.58	0.20	0.5	Fast
359094-1	3.37	950	0.85	-	0.0-0.5	V.Fast
359094-2	3.24	988	0.93	-	0.0-0.5	V.Fast
359056	1.52	2100	3.2	0.89	0.0-0.5	V.Fast
359079	0.63	5080	9.4	0.0	Too high melting and insoluble to give useable product.	

FIGURE 4.

COOKING SCHEDULE

Glycidyl Ethers of Hydrolyzed AROCLOR 1268 + Soya FATTY ACID

Disappearance of FATTY ACID



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From this, and other data, it appears the esterification of the oxirane oxygen of the diglycidyl ethers of 90% dihydrolyzed Aroclor is slow when "n" is less than 0.3, rapid when "n" approximates 0.3. The upper limit for "n" has not been well defined, but it appears to be less than 5.4.

The observation of molecular size as a determinant in the rate of esterification is supported by the following series of esters made from the diglycidyl ethers of tetrachlorobisphenol A (Table V and Figures 5 & 6) received from Organic Research (Ref. 7).

TABLE V

SOYA FATTY ACID ESTERS OF OXIRANE OXYGEN OF DIGLYCIDYL ETHERS OF TETRACHLOROBISPHENOL A (Figures 5 & 6)

St. Louis N.B. Reference	% Epoxy	n	Reaction Time Hours at 200°	Reaction Rate
A84890	6.4	0	3.8	Slow
A84980	3.36	1.2	1.4	Fast
A84983	1.98	2.7	1.0	V.Fast
A84982	1.06	6.0	2.0	Fast
A84981	0.61	11.0	6.2	Very slow, incomplete

The commercial epoxy resins further support our concept. Epon 1004 (n = 6) esterifies more rapidly than Epon 828 (n = 0). See Figure 3.

We observed that hydrolyzable chlorine in gross amounts is detrimental to a fast reaction. In preparation No. 359064, "n" was 0.82, and the esterification should have been rapid. However, hydrolyzable chlorine was 3.51% and the reaction was slow. The series of esters reported in Table IV shows that hydrolyzable chlorine content is not too critical as chloride contents range from 0.00 to 0.89% and the distribution of values is random in the series.

At an early stage in our work, it was felt that the analysis for epoxy content was open to question and that our seemingly slow reactions were due to attempts to react more fatty acid than was warranted by the actual oxirane content. Accordingly, two experiments in the Aroclor 1268 series were repeated using smaller amounts of fatty acid to see if the slope of the rate curves would change appreciably. They were not changed. See Figure 7.

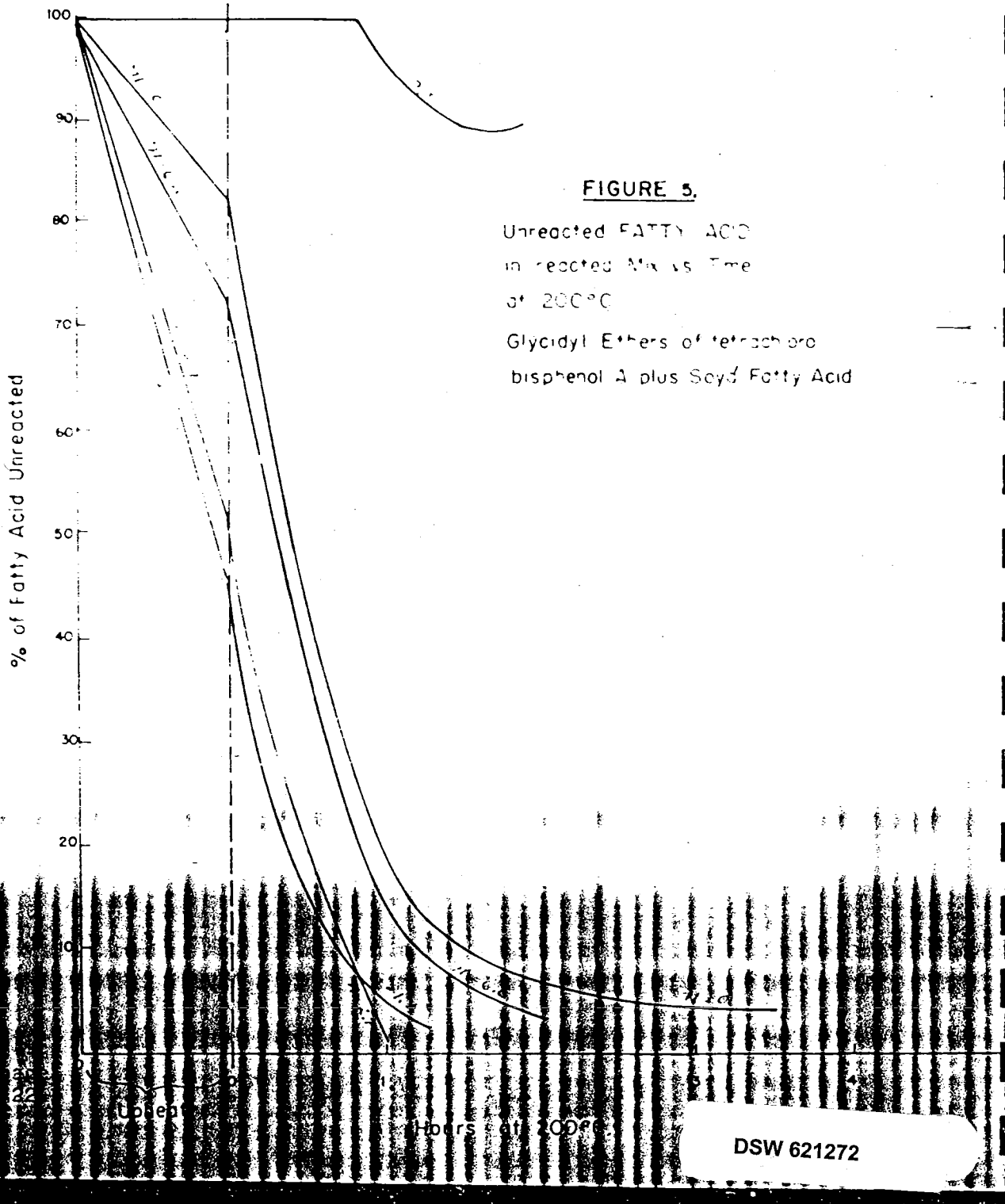

FIGURE 5.

Unreacted FATTY ACID
in reacted Mix vs Time
at 200°C

Glycidyl Ethers of tetrachloro
bisphenol A plus Soyd Fatty Acid

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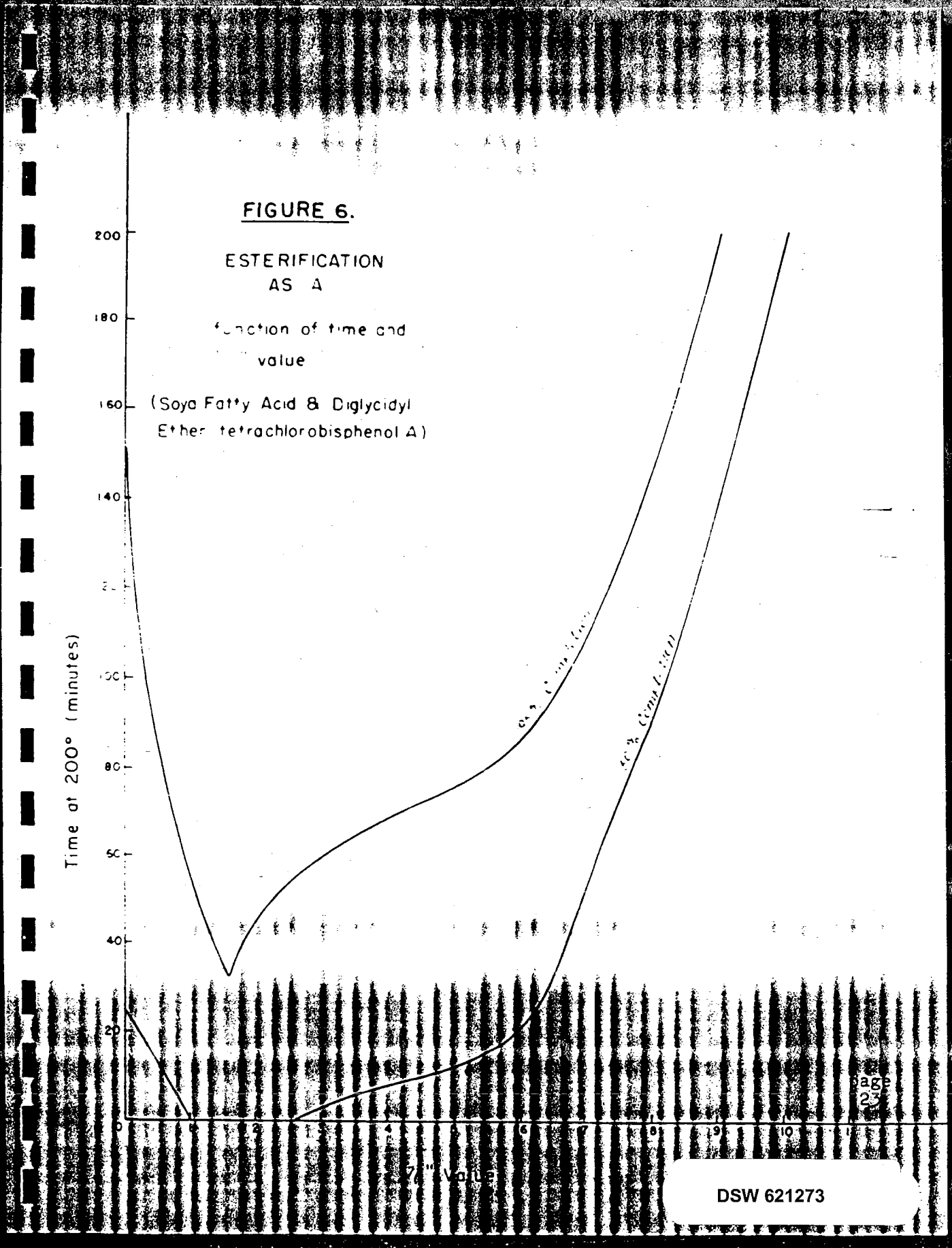

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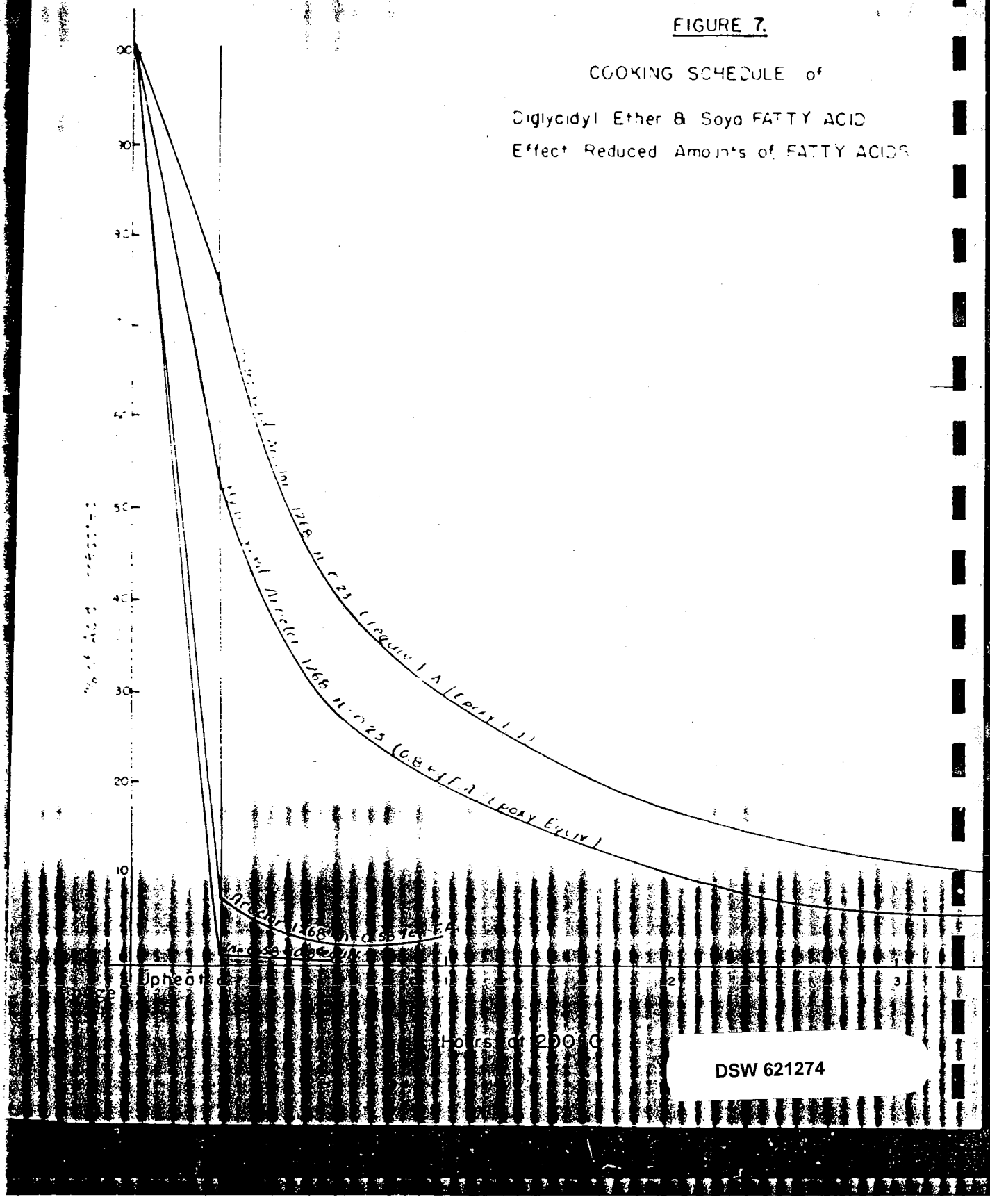
FIGURE 7.

COOKING SCHEDULE of

Diglycidyl Ether & Soya FATTY ACID

Effect Reduced Amounts of FATTY ACIDS



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The fast esterification of the diglycidyl ethers of hydrolyzed Aroclors gives us an unexpected and important advantage over conventional epoxies (or those based on tetrachlorobisphenol A). Reduction of time in the kettle should be of economic importance to the paint vehicle manufacturer, as shown in Appendix B.

As a result of our success with the 90% difunctional compounds, additional successful efforts were made to increase the difunctionality of the hydrolyzed Aroclor. Our later esters were all based on diglycidyl ethers of substantially 100% dihydroxy polychlorinated biphenyls. The bulk of the samples have had an "n" value of ca. 0.09. The reaction rates are rapid, but are significantly slower than when the 90% difunctional material was used. We have no explanation for this. A number of esterifications are tabulated in Table VI.

TABLE VI

NBP	% Epoxy	Mol Wt	n	Reaction Time Hours at 200°	Reaction Rate	Comments
367970	5.65	566	0.06	1.00	Fast	$Ca(OH)_2$ added
366994	5.52	580	0.09	4.42	Slow	
367960	5.52	580	0.09	3.25	Slow	$Ca(OH)_2$ added
367968	4.51	710	0.25	6.25	V Slow	
367955	4.00	800	0.5	0-0.5	V Fast	
367956	3.18	1000	1.0	0-0.5	V Fast	

Thus, the evidence we have on the 100% bifunctional resins tends in general to support our concept - that molecular size influences the rate of reaction. There are some exceptions.

Experiments 367968 and 69, using a resin with an "n" value of 0.25, should have given fast reactions. They were slow even when lime was added to catalyze the reaction. The method of synthesis of this particular resin was different than the method used for other resins. An attempt was made to increase the "n" value by reacting a diglycidyl ether of "n" = 0 value with dihydrolyzed Aroclor 1268. Each molecule of the diphenol should react with two of diglycidyl ether to give a molecule with "n" = 2. The resultant "n" of the resin was raised to 0.35. However, this method of synthesis should not have been the reason for the slow reaction since Experiments 367955 and 56 used resins prepared in a similar manner and the reaction was very fast.

Lime in small amounts, 0.15 to 0.20% based on epoxy, was effective in catalyzing the esterification in some cases. It improved the reaction rate in Run 367970 in which "n" = 0.06. However, lime was not so effective in other cases; for example, Runs 367960, 367968 and 969.

Only the esterification of the oxirane oxygen has been described to this point. Epoxy esters having up to 90% of their functional groups esterified are the usual commercial products.

The preparation of a number of the more completely esterified esters is tabulated in Table VII

TABLE VII

ESTERS OF FATTY ACID w/EPOXY RESINS
(0.5 to 0.9 equivalent)

NBP	Derivation	Fatty Acid	Ester Level	Acid Value	Time At Max Temp.	Temp.	Comment -
359097	Epon 1004	Soya	90%	11	[illegible]	260°C	
354861	" "	"	60%	5.5	[illegible]	260	
354862	" "	"	50%	4.3	[illegible]	260	
359077	Aroclor 1268	"	80%	5.8	[illegible]	200	n = 0.35, % hydroxyl = 7.4%
359080	" "	"	90%	15.8	[illegible]	200	n = 0.35, % hydroxyl = 7.4%
364202	Epon 1004	Tall	90%	12.5	[illegible]	260	
364203	Aroclor 1268	"	90%	9.6	[illegible]	220	n = 0.88
367972	" "	Soya	80%	15.3	[illegible]	240	n = 0.06, $Ca(OH)_2$ present
373945	" "	"	70%	8.8	4 hrs	200	n = 3.2

We found that the 50-90% complete esterification of the Aroclor-epoxies takes place at temperatures 60°C lower than the similar esterification of Epons! This is noteworthy, and could be of considerable economic importance. The examples cited are based on 90% dihydrolyzed Aroclor with the exception of 367972. This was based on 100% dihydrolyzed Aroclor and had the lowest "n" value, 0.06, of the group.

Experiment No. 373945 is noteworthy. The diglycidyl ether has an "n" value of 3.2 and approximates Epon 1001 in chain length.

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and Epon 1004 in molecular weight. The ester is very similar to a commercial product in respect to these two parameters.

The Aroclor-epoxies all show good stability during the esterification reaction. Neither HCl nor Cl_2 was ever detected in the off gases from the reaction. However, the esters do reach a minimum acid value and if held at high temperature for periods beyond this, the acid values increase. No explanation is offered to account for this phenomena.

These esters are quite fluid by comparison with Epon esters. This does not seem to be attributable to molecular size as we at first supposed. Number 373945 is a 0.7 equivalent soya fatty acid ester of an Aroclor 1268-epoxy. Its molecular size is intermediate between Epons 1001 and 1004 and should be similar to an ester of Epon 1004. Its viscosity is only A-3 on the Gardner-Holdt scale compared to a literature (Ref. 8) viscosity of I to K for the Epon ester. This fluidity would be advantageous in spray or dip applications where a high solids loading with low viscosity is desirable.

We attempted to increase the viscosity of these esters by replacing part of the soya fatty acid with dimer acid. The viscosity in Run 367988 was increased from A-3 to G.

Another approach to increasing viscosity by increasing the molecular size was made in experiment 367967 by reacting 0.141 mol of diglycidyl ether of "n" value of 0.06 with 0.023 mol of phthalic anhydride. This "enlarged" diglycidyl ether was esterified with soya fatty acid. Viscosity was not improved, remaining at A-4. However, this reaction demonstrated that phthalic anhydride reacts readily with diglycidyl ethers, at least in limited amounts. This property may be useful in making mixed epoxy-alkyd type resins.

Skinning and gelation of the solutions of the esters of the Aroclor-epoxies takes place to a lesser degree than in Epon esters. No quantitative measure of this was made, but the results were definite.

The Aroclor-epoxy esters are more soluble in hydrocarbon solvents than conventional epoxies, as shown:

TABLE VIII

SOLUBILITY OF EPOXIES IN XYLENE AND ACETONE

Epoxy	n	Mol. Wt.	Wt. (gms)	Xylene (ml)	Ml Acetone to Dissolve
1001	2.3	990	2	5	1.3
1004	5.5	1900	2	5	1.5
Aroclor 1270	0.76	834	2	5	0.5
Aroclor 1268	3.2	2100	2	5	0.8

This tolerance for hydrocarbon solvents by the Aroclor-epoxy could be of considerable economic importance. "Varnolene" may be used instead of xylene, with similar results.

We have shown in Experiment 373946 that the Aroclor 1268-epoxy will cure high-acid-value alkyds. American Cyanamid's Rezyl 1102-5, with an acid value of 48, was used.

TABLE IX

CURE OF ALKYDS

Rezyl 1102-5	Xylene (ml)	Curing Agent	Resistance to Solvents			
			Xylene	Acetone	10% NaOH	5% Alk.
50 gms	35	none	Good	Failed	Failed	Good
50 gms	35	Pb, Co, Mn driers	Good	Failed	Failed	Good
50 gms	35	3.2 gms* 0.63 equiv.	Good	Failed	Improved	Good
50 gms	35	6.4 gms* 1.3 equiv.	Softened	-	Improved	Good
50 gms	35	12.7 gms* 2.5 equiv.	Softened	-	Best- No Attack	Good

*Aroclor 1268-Epoxy

This high acid value alkyd is usually used in conjunction with other alkyds and curing is effected by the use of melamine or urea resins. Such an alkyd system was successfully cured by the Aroclor epoxy to give coatings of high gloss, fair hardness, good detergent resistance, and good flexibility. Resistance to xylene and alkali was only fair.

Coatings The esters prepared from the diglycidyl ethers of 90 and 100% dihydrolyzed Aroclors were evaluated as surface coatings. Cobalt naphthenate drier was added equal to 0.04% cobalt based on the weight of resin. Advance Solvent and Chemical Corporation anti-skinning agent was used at a concentration of 0.25% based on vehicle solids. The vehicles prepared from the 100% dihydrolyzed material were also tested as enamels pigmented with Titanox RA 50. The finishes were coated on steel panels and air dried. They were evaluated as to dry time, physical and protective properties, and exposure in the Weatherometer and on the outdoor test rack.

The following soya esters of the 90% Aroclor-epoxy along with controls based on Epons were evaluated. All are oxirane esters except 354862 which is a 50% equivalent ester.

TABLE X

DRY TIMES FOR VARNISHES MADE FROM EPOXY SOYA ESTERS

Ester No	Derivation	Degree of Ester	Set	Print Free	Tack Free
354873	Epon 1004	Oxirane	10 min	1 hr	2 hrs
354862	Epon 1004	50%	10 min	2 hrs	overnight
354881	Epon 828	Oxirane	2.5 hrs	overnight	not after 4 days
354868-1*	Aroclor 1270	"	10 min	3 hrs	overnight
354868-2*	Aroclor 1270	"	20 min	3 hrs	overnight
354874	Aroclor 1268	"	1 5 hrs	overnight	overnight
354872	Aroclor 1262	"	2 hrs	overnight	overnight
354875	tetrachloro-bisphenol A	"	2.5 hrs	overnight	not after 4 days
354877	tetrachloro-diphenol model compound	"	2.75 hrs	overnight	not after 4 days

*354868-1 & 2, see Experimental Section; No. 1 is ester of low acid number heated to 200°; No. 2 is ester heated to 260° w/acid value of 20

These films have the following properties:

TABLE XI

CHARACTERISTICS OF EPOXY ESTER COATINGS

Ester No.	Derivation	Mar Resistance	Adhesion	Sward Hardness	Alkali Resistance 2% NaOH	Water Resistance
354873	1004	Average	V.Good	15	Good	Excellent
354862	1004	Good	Good	18	Good	Excellent
354881	828	Poor	Fair	4	Poor	Fair
354868-1	1270	Average	V.Good	17	Good	Good
354868-2	1270	Average	V.Good	18	Good	Good
354874	1268	Average	Good	10	Poor	Poor
354872	1262	Average	Good	13	Poor	Fair
354875	TCBPA	Poor	Good	10	Poor	Fair
354877	TCBP	Poor	Fair	6	Poor	Poor

In general, while the esters of Epon 1004 were best, they were closely followed by the derivatives of hydrolyzed Aroclor 1270, 1262 and 1268 in that order. The hydrolyzed Aroclor ester films were much better than those of tetrachlorobisphenol A, tetrachlorodiphenol and Epon 828.

Mar resistance is a qualitative measure of the resistance of the films to fingernail scratching. The ratings reflect the surface toughness of the longer chain Epons as opposed to the shorter chain chlorinated epoxies.

Adhesion was measured in two ways; first by scratching with a knife and attempting to broaden the scratch, and by bending a thin panel around a 1/4" mandrel. The chlorinated epoxies were equivalent to the Epons in this respect.

The hardness of the Aroclor-epoxy esters was as good as that of the esters based on Epon 1004. Epon 828 and TCBP both gave soft films.

The materials rating good in alkali resistance resisted softening for ten minutes in 2% aqueous NaOH. Those listed as poor were dissolved in five minutes or less. The esters based on hydrolyzed Aroclor 1270 were almost as good as those based on the Epon 1004 and much better than Epon 828.

While water resistance of the Epon esters was best, they were closely followed by the esters based on the hydrolyzed Aroclors. All the films were more resistant to water than they had been to alkali.

TABLE XII

PERFORMANCE IN WEATHEROMETER

Ester No.	Derivation	Time to Failure or Completion of Test	Comment (Based on Visual Exam.)
354873	Epon 1004	640 hours	No failure
354862	Epon 1004	640 "	" "
354881	Epon 828	640 "	" "
354868-1	Aroclor 1270	160 "	Failure
354868-2	Aroclor 1270	120 "	"
354874	Aroclor 1268	120 "	"
354872	Aroclor 1262	120 "	"
354875	TCBPA	120 "	"
354877	Model Compound	120 "	"

Failure was accompanied by a complete loss of gloss and the development of a dark brown color, starting at the center of the panel and spreading to the outer edges of the panel as exposure continued.

The esters based on 100% dihydrolyzed Aroclor 1268 and on Epon 1004 were similarly evaluated. Clears and pigmented esters at the oxirane oxygen and 0.7 equivalent level were tested. A commercial epoxy ("Eponal"-Lowe Brothers Paint Co.) was included for comparison. See Table XIII

The pigmented enamels were made up according to the following formulation:

	Parts by Weight
Titanox RA 50	142
Resin Solution (50% soln.)	284

Either xylene or methyl isobutyl ketone (MIBK) was added to give a suitable viscosity for grinding. Grind 24 hours in a pebble mill, adding cobalt drier and anti-skinning agent as needed.

TABLE XIII

ESTERS USED IN EVALUATION OF COATINGS

No.	NBP	Epoxy	Fatty Acid	Degree of Ester	% Fatty Acid	Visc.	Color	lbs/ gal.	Solvent
C-1	367957	Epon 1004	Soya	Oxirane	22.8	D	4	8.19	Xylene + methyl isobutyl ketone
C-2	367959	Epon 1004	Tall	"	23.4	C	7	8.16	Xylene + methyl isobutyl ketone
C-3	367970	Aroclor 1268	Soya	"	49.7	A-4	11+	8.28	Xylene
C-4	367971	Aroclor 1268	Tall	"	50.5	A-4	11	8.28	"
C-5	367975	Epon 1004	Soya	0.7 equiv	53.2	G	11+	7.83	"
C-6	367977	Epon 1004	Tall	"	55.0	F	>18	7.82	"
C-7	367972	Aroclor 1268	Soya	"	60.2	A-3	>18	8 15	"
C-8	Control	LH 1892 - Lowe Brothers - Eponal Clear							

TABLE XIV

CHARACTERISTICS OF ENAMELS MADE FROM EPOXY ESTERS

White No.	NBP	Viscosity No. 4 Ford Cup	lbs/gal.	Solvent (Other than Xylene)
W1	367974	19	9.74	MIBK
W2	367976	52	10.38	MIBK
W3	367978	14	11.08	-
W4	367979	13	11.00	-
W5	367982	77	10.43	-
W6	367983	59	10.48	-
W7	367981	13	10.85	-
W8	C-17238 - Lowe Bros. Eponal Grey			

These varnishes and enamels were coated on steel panels. The dry time, and water resistance was as follows:

TABLE XV

DRY TIMES AND WATER AND ALKALI RESISTANCE

Coating	Epoxy	Dry Time (Hours) Dust Free	Dry Hard	Water Resistance	Alkali Resistance
C-1	1004	0.5	1.5	Excellent	Excellent
C-2	1004	0.5	1.5	"	"
C-3	1268	>2<18	>2<18	Good	Good
C-4	1268	>2<18	>2<18	"	"
C-5	1004	>1<17	>1<17	Excellent	Excellent
C-6	1004	2	2	"	"
C-7	1268	2	2	"	Poor
C-8	Commercial	1	4	"	Excellent
W-1	1004	0.5	1.5	Excellent	Excellent
W-2	1004	0.5	1.5	"	"
W-3	1268	>6<22	>6<22	Good	Good
W-4	1268	>6<22	>6<22	Excellent	Poor
W-5	1004	2	2	"	Excellent
W-6	1004	2	2	"	"
W-7	1268	>4<20	>4<20	"	Poor
W-8	Commercial		4	"	Excellent

The physical properties of the films are given in the following table:

TABLE XVI

PROPERTIES OF COATINGS AS PREPARED

Coating No.	Derivation	Degree of Ester	Sward Hardness	Flexibility	Adhesion
C-1	Epon 1004	Oxirane	41	Good	Failed
C-2	"	"	39	"	"
C-3	Aroclor 1268	"	6	"	Passed
C-4	"	"	8	"	"
C-5	Epon 1004	0.7 equiv.	10	"	"
C-6	"	"	10	"	"
C-7	Aroclor 1268	"	6	"	"
C-8	Commercial	-	4	Fair	"
W-1	Epon 1004	Oxirane	21	Good	Passed
W-2	"	"	24	Fair	"
W-3	Aroclor 1268	"	9	Good	"
W-4	"	"	9	"	"
W-5	Epon 1004	0.7 equiv.	10	"	"
W-6	"	"	8	"	"
W-7	Aroclor 1268	"	6	"	"
W-8	Commercial	-	22	Fair	"

The marked difference between the hardness of the oxirane esters and the Epons is understandable in terms of oil content or "length". The Epon esters are very low in oil content, while the Aroclor-epoxies are medium oil length materials and should be softer because of the increased oil content. Note Table XIII.

The Aroclor-epoxies are excellent with respect to flexibility and adhesion, equal to or better than the Epon esters.

Samples were coated on steel and placed in the Weatherometer for 400 hours.

TABLE XVII

PROPERTIES OF COATINGS AFTER 400 HOURS IN WEATHEROMETER

Coating No.	Derivation	Sward Hardness Hours Exposure 0	200	300	400	After 400 Hours Flexibility	Adhesion
C-1	Epon 1004*	41	50	60	50	Failed	Failed
C-2	" *	37	50	68	40	"	"
C-3	Aroclor 1268*	6	8	6	4	"	"
C-4	" *	7	10	12	4	"	"
C-5	Epon 1004	10	38	50	40	Passed	Passed
C-6	"	10	48	58	50	"	"
C-7	Aroclor 1268	6	22	38	24	Failed	Failed
C-8	Commercial	4	44	62	48	"	"
W-1	Epon 1004*	21	26	34	32	Failed	Failed
W-2	" *	24	36	36	38	"	"
W-3	Aroclor 1268*	9	10	12	10	Passed	Passed
W-4	" *	9	18	18	12	"	"
W-5	Epon 1004	10	26	34	32	"	"
W-6	"	8	36	38	30	"	"
W-7	Aroclor 1268	6	12	18	16	"	"
W-8	Commercial	22	34	36	28	Failed	Failed

*Oxirane esters

The performance of the pigmented Aroclor epoxies with regards to flexibility and adhesion was most gratifying. They are equal to or better than the corresponding Epons or the control.

TABLE XVIII

PERFORMANCE ON OUT-OF-DOOR EXPOSURE (DAYTON, OHIO)

Coating No.	Derivation	Sward Hardness Weeks Exposure 0	2	4	6	8	After 8 Weeks Flexibility	Adhesion
C-1	Epon 1004*	41	58	50	56	50	Poor	Good
C-2	" *	41	58	52	46	42	"	"
C-3	Aroclor 1268*	6	14	14	8	10	"	Poor
C-4	" *	8	22	12	8	12	"	"
C-5	Epon 1004	10	22	24	26	30	Good	Fair
C-6	"	9	24	26	22	26	"	"
C-7	Aroclor 1268	5	20	12	6	8	Poor	Poor
C-8	Commercial	4	16	18	16	24	Good	Fair
W-1	Epon 1004*	20	26	24	32	32	Poor	Good
W-2	" *	22	34	22	30	24	"	"
W-3	Aroclor 1268*	9	12	14	12	14	Good	"
W-4	" *	9	12	14	12	18	"	"
W-5	Epon 1004	10	14	18	16	24	"	"
W-6	"	8	16	18	18	28	"	"
W-7	Aroclor 1268	6	10	12	10	13	"	"
W-8	Commercial	21	30	32	32	28	"	Fair

*Oxirane oxygen

This data parallels that for the Weatherometer very closely. We conclude that the Aroclor-epoxy-esters are as good or better than the corresponding Epon-esters, including the commercial sample, as far as physical durability is concerned.

The appearance of the esters is indicated in the following table:

TABLE XIX

Coating No.	Derivation	Initial Color	Initial Gloss	400 Hours Weatherometer Color	400 Hours Weatherometer Gloss	8 Weeks Out-of-Doors Color	8 Weeks Out-of-Doors Gloss
C-1	Epon 1004	Clear	95	Clear	81	Clear	88
C-2	"	"	100	"	85	"	91
C-3	Aroclor 1268	"	100	Brown	9	Brown	28
C-4	"	"	100	"	6	"	28
C-5	Epon 1004	"	99	Clear	83	Clear	95
C-6	"	"	99	"	85	"	95
C-7	Aroclor 1268	"	98	Brown	21	Brown	23
C-8	Commercial	"	100	Clear	88	Clear	95
W-1	Epon 1004	White	83	White	44	White	75
W-2	"	"	98	"	55	"	94
W-3	Aroclor 1268	"	96	"	13	Sl.Yellow	95
W-4	"	"	95	"	27	"	90
W-5	Epon 1004	"	93	"	83	White	92
W-6	"	"	95	"	82	"	92
W-7	Aroclor 1268	"	94	"	65	Sl.Yellow	93
W-8	Commercial	Grey	77	Grey	5	Grey	50

The clear Aroclor-epoxies developed a grainy type of alligatoring.

The clear Aroclor-epoxy finishes could not be recommended for outdoor service, due to their loss of gloss and darkening. The pigmented finishes, however, stand up quite well out of doors. These results illustrate the problem of correlating Weatherometer data with outdoor performance.

The soya ester of the oxirane oxygen of Aroclor 1268-epoxy has a chlorine content of 53%. This should give a good degree of flameproofing to a paint prepared from it. A paint was made up based on the recommended formula of The Baltimore Paint and Varnish Production Club Technical Committee on Fire-Retardant Paints (Ref. 9). A control was also made containing a conventional non-chlorinated epoxy ester. The formulas are as follows:

	Control	Chlorinated Epoxy
	(Parts by Weight)	
Antimony Oxide	13.5	13.5
Titanox RA-50	9.0	9.0
Magnesium Silicate	13.5	13.5
Vehicle	64.0	64.0
	(No. 367957, oxirane ester Epon 1004, 50% solids) no chlorine	(No. 367970, oxirane ester D.G.E. hyd. Aroclor 1268, 50% solids) 8.6% chlorine

Mill the ingredients in a pebble mill for 24 hours and add driers and solvents as required.

Sticks of pine 3/4" square by 18" long were used in testing the paints. Each stick was given two coats of the test paint The sticks were dried in air for 1 week following the second coat

Tests were run in the hood with an aluminum foil shield around three sides of the test piece. The stick was hung in a vertical position. The procedure was a much simplified version of the ASTM Method D 1361-55T. Ignition was by means of a gauze wick soaked with 4 ml of 95% alcohol. The height of the flame was taken at 10 second intervals for the first 100 seconds after ignition. The weight loss of the sticks was also observed Photographs of the test pieces before and after the test show the results of the fire tests (Figures 8 and 9). The designation of the sticks are as follows: B is an unpainted stick, E the Epon ester, and C the Aroclor epoxy ester. The results are tabulated below:

TABLE XX

	Height of Flame (inches) for -		
	Sample B	Sample E	Sample C
Time:			
10 sec.	2.0	3.0	2.0
20 sec.	2.0	3.0	3.0
30 sec.	3.0	4.0	4.0
40 sec.	3.0	5.0	4.0
50 sec.	3.5	5.0	3.5
60 sec.	4.0	5.0	2.0
70 sec.	5.0	1.0	Flame
80 sec.	5.0	0.0	0.0
90 sec.	5.0	0.0	0.0
100 sec.	2.0	0.0	0.0
Weight loss	2.8 gms	1.1 gms	1.4 gms
Coating	none	Epoxy ester	Aroclor-Epoxy

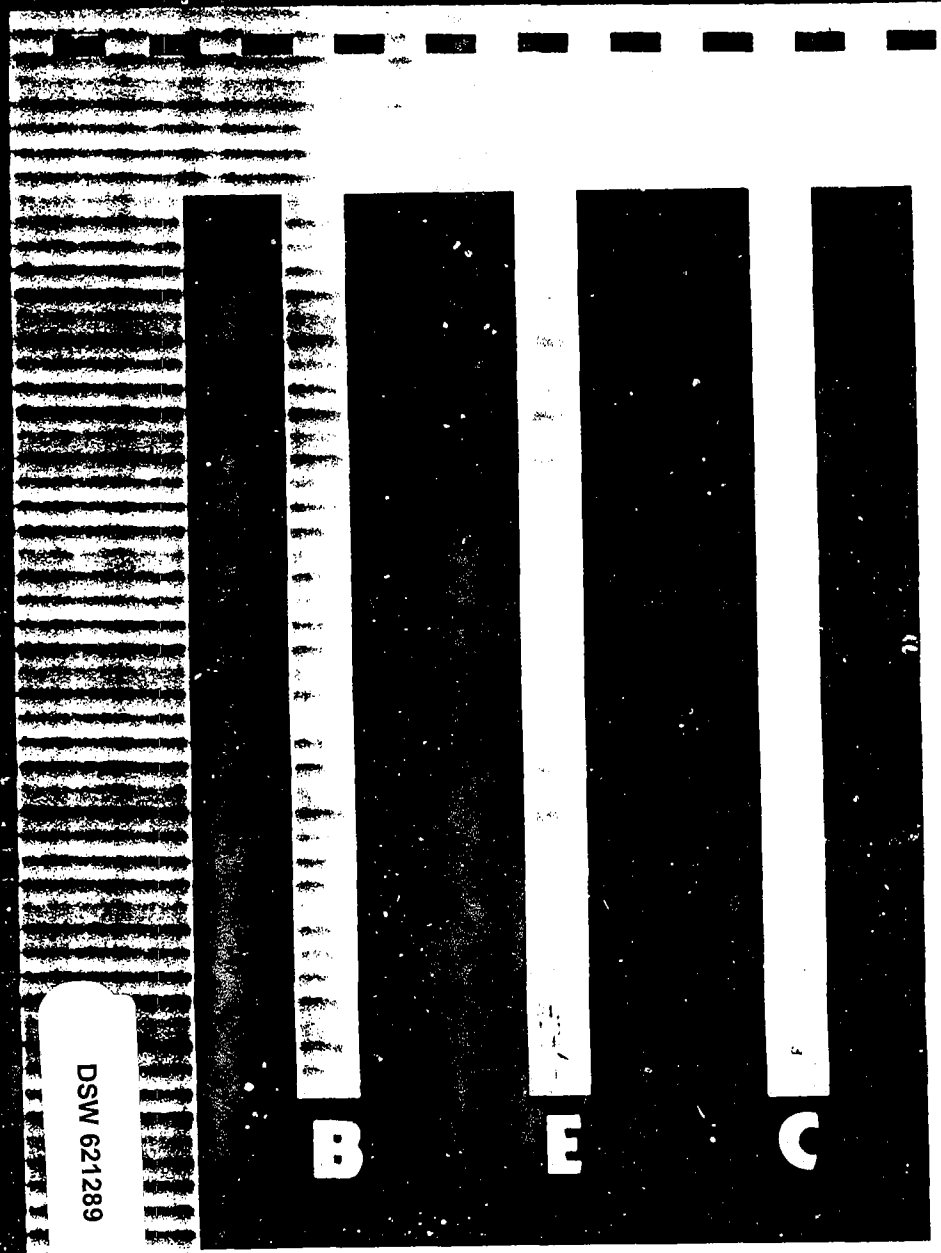

Figure 8. Wood Sticks Before Fire Test

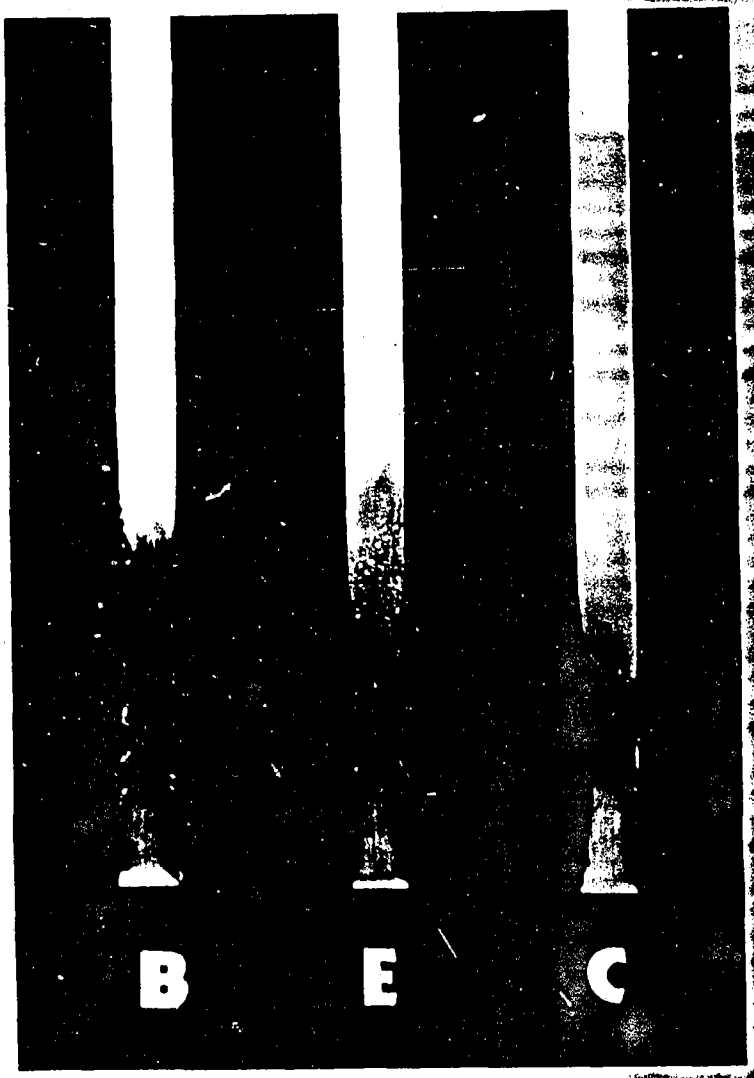

Figure 9. Wood Sticks After Fire Test

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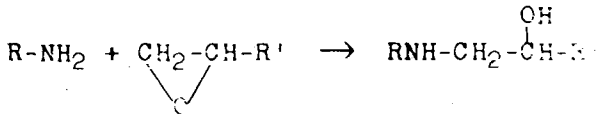
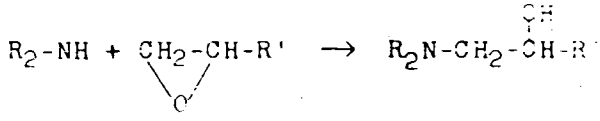
The photographs and the results in Table XX show that the Aroclor-epoxies are superior to conventional epoxies in flame retardancy as measured by flame height, degree of charring and weight loss.

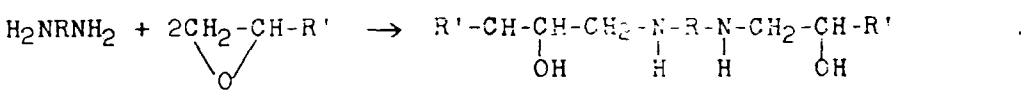
Resin Curing A brief discussion of the mechanism of curing epoxy resins should afford the reader a better insight to the considerations involved in a curing study of epoxy resins.

Amine cures Primary or secondary amines react with the epoxy group giving a secondary or tertiary amine and an α-hydroxy group.





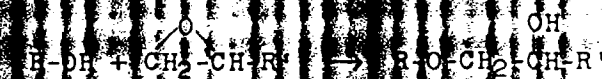
The nitrogen of a tertiary amine can further react with an epoxy ring to form a quaternary ammonium compound followed by chain propagation. Polyfunctional primary and secondary amines can react as above or as cross-linking agents by the following reaction:



If R' groups in the foregoing reaction contain other epoxy groups, a cross-linked, thermosetting polymer is obtained.

From this brief discussion it can be appreciated that a long chain will be formed if the ratio of diamine to epoxy is stoichiometric (ratio of available amino hydrogens to epoxide oxygen is 1:1) and that less than the equivalent quantity of diamine would result in gaps in the chain. Furthermore, if the equivalent amount of diamine is doubled, each epoxy group could react with an amine group without any coupling involved.

Other reactions which can assist in accomplishing cure include opening of an epoxide ring by one of the hydroxyl groups formed in the polymer chain



Here the epoxide group forms another hydroxyl group by gaining hydrogen from the donor and the reaction can repeat itself.

Curing generalizations — The amino group reacts with an epoxide group at room temperature.

Polyfunctional amines by themselves, or those produced in the initial reaction, can couple epoxy resins.

At elevated temperatures and in the presence of certain amines, other coupling reactions such as those involving the hydroxyl groups can occur. Dibasic acids cure epoxy resins by esterification.

Coupling can occur if two hydroxyls are situated on different polymer molecules.

Acids may also react with an epoxy group by donating a hydrogen with the formation of an ester linkage.

The total cure with an acid anhydride probably involves both of the above mechanisms. In general, acid curing requires higher temperatures than amine cures.

A study of the variables in the curing of epoxy resins involves many unknowns. Anhydride-type equivalency (per epoxy equivalent) is about 85% of theory, due to epoxy hydroxyls which, as they form, serve as reactive centers and account for about 15% of the reaction. Amine equivalency appears near normal generally, but equivalencies can deviate from 65 to 125%, depending primarily on steric factors. BF_3 adducts, t-amines, polymeric curing agents, etc., all require detailed study.

In general, in regards to the variables mentioned, Aroclor-epoxy resins resemble commercial epoxies. Experience gained in curing studies of commercial epoxies can be applied to the Aroclor-epoxies within reasonable limits. The presence of the chlorine in the Aroclor-epoxy resins apparently does not greatly alter its general reactivity with a wide variety of common curing agents for epoxy resins. However, in some instances the curing agents for Aroclor-epoxy resins are too reactive, so that insolubility occurs before cross-linking can occur.

Aroclor-epoxies containing some monofunctional species

A large number of curing agents were studied using a variety of Aroclor-epoxy resins derived from Aroclor 1262, 1268 and 1270 (Appendix C, Tables [illegible]). To obtain mixing of the curing agent and resin [illegible]

(methyl ethyl ketone) was added to the solid Aroclor-epoxy along with the curing agent, and then evaporated prior to curing. This always led to superior cured products compared to that obtained from a dry blend of the reactants.

A low melting epoxy resin (92°C) prepared from hydrolyzed Aroclor 1268 (90% difunctional) was cured with 6-15% by weight of various polyfunctional amines. Optimum cure times were dependent on the size of the mass, the rate of development of exothermic heat, and the dissipation of this heat. Best results in terms of "high softening temperature products" were obtained when using 6% triethylene tetramine, dimethylaminopropylamine or diethylaminopropyl amine. As the concentration of the amine was increased to 10%, the softening temperature of the cured product was significantly lowered. This was probably due to a high amine/epoxy equivalence, leading to a lower degree of cure.

With the development of a reliable oxirane-oxygen analysis for Aroclor epoxies, curing studies could be performed on a quantitative basis. The primary variable for study was then reduced to the effect of epoxy content on the properties of the cured product.

Our early work had indicated that with maleic anhydride curing systems, the best results were obtained with Aroclor-epoxies of fairly low epoxy content and high hydroxyl content. (Such materials contain considerable amounts of the Di-α-glycerol-monochlorohydrin derivative (GMH)). From the stoichiometry, it appeared some additional reaction must be occurring since a large excess of anhydride was required for curing. If stoichiometric equivalence of anhydride to epoxide oxygen was used, abnormally long curing cycles were required and lower heat resistance was exhibited by the cured product.

It was concluded that in these low epoxy resins the excess anhydride must be reacting with the hydroxyl present and that the products resulting from excess anhydride was not some phenomenon unique with the Aroclor-epoxy system.

Duplication of earlier Aroclor/polyfunctional amine curing studies indicated several problems with Aroclor-epoxies. As resins of increasing epoxy content became available, the expected improvement in properties of the cured product did not materialize. Aroclor-epoxies with epoxy contents approaching those of commercial resins behaved quite differently in the sense that extremely brittle products were always obtained. No variations in curing agent and curing time appeared to alter the brittle behavior of Aroclor-epoxy resins.

[illegible] this and other considerations, we [illegible] judged that the presence of monofunctional derivatives in the hydrolyzed Aroclor were contributing to the poor properties of the epoxy by acting as [illegible] chain terminators.

Difunctional Aroclor-epoxies In order to verify the predicted importance of complete difunctionality in Aroclor-epoxy resins, an evaluation was made on the bisglycidyl ether of 4,4'-bi-(2,6-dichlorophenol). This model compound (made via chlorination of dihydroxy biphenyl) should be free of the monofunctional, chain-terminating epoxides known to be present in the early Aroclor-epoxies.

A model-compound epoxy, containing 91.5% of the calculated epoxy content and very low (0.41%) hydrolyzable chlorine, exhibited excellent resin-forming properties with several curing agents (phthalic anhydride, p-phenylene diamine and HET anhydride). Best results, in terms of high heat resistance and strength, were obtained with epoxy compound cured with HET annydride at 85% stoichiometric equivalence of anhydride.

It was noted that as the epoxy content of the model compound increases the melting point rises, probably a consequence of the increased molecular symmetry; a melting point of 183°C was found for 6.7% epoxy material. It should be recognized that this high melting point imposes some limitation as to the type of curing agents one may use. Many polyfunctional amines used in conventional curing formulations are volatile at temperatures considerably lower than this (183°C). For this reason, the curing agents used in this study were restricted to higher melting solids - particularly anhydrides - which could be dry blended or formulated with the resin in the melt.

Curing studies on an epoxy resin derived from completely dihydric Aroclor 1268 containing 88.5% of the calculated epoxy content and very low hydrolyzable chlorine (0.17%) were encouraging. This difunctional epoxy exhibited excellent resin forming properties with several curing agents, particularly phthalic anhydride at 85 to 100% stoichiometric equivalence of anhydride to epoxide oxygen.

With the preparation of a larger size batch (3.5 lb.) of completely dihydric Aroclor 1268 (5.42% oxirane oxygen and 0.18% hyd. Cl.) curing studies on larger size castings, suitable for physical measurements, could be made. This Aroclor-epoxy exhibited excellent resin-forming properties with phthalic anhydride, bisaniline A, or methylene dianiline. Comparison with Shell Epon 828 cured with methylene dianiline and bisaniline A indicates the two cured systems were comparable in

stability, the volatile loss after 7 days at 150°C was negligible in both instances. Heat distortion temperature of the Aroclor-epoxy was 171°C when cured with bisaniline A. This is ca. 25°C higher than the distortion temperature for the Shell epoxy cured in similar fashion.

Adhesive Studies

Aroclor-epoxies containing monofunctional species Early experiments indicated that the Aroclor epoxy resins did not possess the inherent adhesive characteristics normally associated with conventional epoxy resins (Appendix C, Table 4).

Our initial study on metal-to-metal epoxy-adhesives was directed largely toward obtaining good aluminum to aluminum bonds with the Aroclor epoxies. Efforts to obtain the necessary shear strengths to meet military standards were unsuccessful. The highest shear strengths obtained with the Aroclor-epoxy were ca. 400 psi as compared with 2000-5000 psi for commercial epoxy resins (Gov't minimum is 2500 psi).

Several experiments were made, designed to "build-in" additional adhesiveness into Aroclor epoxy resins. A formulation containing Aroclor epoxy (ca. 40% by wt.), plus liquid phenolic resin and hexamethylene tetramine did exhibit adhesion to wood, paper, and aluminum. However, the shear strengths obtained of aluminum/-aluminum bonds (200-400 psi) were far below target values. Fifty parts by weight of Aroclor epoxy resin (FD-4) was blended with commercial Epon 834. The two components are compatible in all proportions. We hoped that by using mixtures of Aroclor epoxies with commercial epoxies that synergistic effects of adhesion to metal, high heat resistance and flame-proofness might be realized with the cured product. It was found that the shear strength of an aluminum/aluminum bond of Shell Epoxy/Aroclor epoxy mixture decreases (almost linearly) with the amount of Aroclor-epoxy present. (Appendix C, Table 4).

To an epoxy Aroclor (218392) was added 33% by weight of finely divided aluminum powder. This was done by melting the epoxy and stirring in aluminum powder until a paste-like consistency was obtained. To this mixture was added dimethylaminopropyl amine as a curing agent. The mixture was then used as a bonding agent for aluminum. Very poor bond strengths were obtained (Appendix C, Table 4). Slight improvements were obtained in blends of Aroclor epoxy with polyamides (Versamids). However, here again the shear strengths measured were very low.

Difunctional Aroclor-epoxy The adhesive character of the model epoxy compound was investigated. This completely difunctional epoxy (derived from 4,4'-bi-(2,6-dichlorophenol) contained 91.5% of the calculated epoxy content and very low (0.41%) hydrolyzable chlorine and exhibited good resin-forming properties with several different curing agents. However, no improvement in metal adhesion was obtained.

Difunctional epoxy resin derived from Aroclor 1271 and Aroclor 1268, like the model compound, exhibited poor adhesion to aluminum. However, the epoxy resin derived from Aroclor 1268 (5.42% oxirane oxygen and 0.18% hydrolyzable chlorine) appeared to have fair adhesion to glass and porcelain. Equipment limitations precluded actual measurement of these values. The shear strengths of the aluminum to aluminum bonds were ca. 110 psi with phthalic anhydride cures. Some improvement was obtained with bisaniline A cures in which values of 550-600 psi were measured. These values are still far below the 2500 psi target strengths.

These results cast a pessimistic outlook to the use of Aroclor epoxy resins in an unmodified form in any adhesive applications. Because of the limited time available for our study of completely difunctional Aroclor-epoxy resins, no study was made on formulation variations that might be expected to lead to improved adhesion. However, on the basis of data obtained to date, the use of Aroclor epoxy resins as metal adhesives does not appear promising.

Casting and Potting Applications

Aroclor epoxies containing monofunctional species
Attempts were made to translate findings from curing studies to development or casting and potting applications.

Miniature electronic components were encapsulated using a variety of Aroclor/curing agent systems. In most instances the residual stresses developed during curing were sufficient to crack and rupture the castings. Variations in curing conditions did not change the inherent brittleness of the final products. Similar effects were noted in thin films and glass laminates prepared from these Aroclor-epoxy resins; the cured products exhibited very poor strength and were too brittle for testing.

Difunctional Aroclor-epoxy The scouting results obtained with the cured model epoxy resin were encouraging. Epoxy formulations cured with HET anhydride were successfully used

[illegible] cracking or shrinkage was observed. This was similarly true with the Aroclor-epoxy resins derived from 1268 and 1270.

Metal inserts, incorporated into cured Aroclor 1268 epoxies, were firmly anchored with no visual voids noted at metal/resin contacts. However, metal adhesion in addition to strength is a necessary prerequisite. The earlier results indicated poor adhesion of Aroclor epoxy to metal might restrict its use in this type application. This is particularly true in electrical applications where incomplete adhesion of the resin to the potted component results in minute "free spaces" in the casting which can lead to electrical break-downs or performance variations.

This area of application would require considerable additional study before the potential of Aroclor-epoxy resins could be fully evaluated for potting use.

Hydrolyzed Aroclor as an epoxy curing agent — Curing studies have shown that the hydrolyzed Aroclors themselves effectively cure Epon 828 to give hard castings. These castings have improved flame resistance similar to that obtained when HET-anhydride is used as a curing agent. Our data are listed in Table XXI.

TABLE XXI

(NBP - 342792)

Epoxy	Curing Agent	% Curing Agent	Soluble	Comment -
Epon 828	Hydrolyzed Aroclor 1268	20	Yes-70°	slowly at 190-200° - dark red, brittle.
"	"	33	-	rapid, 190-200° - dark red brittle, non-flammable.
"	"	37	Yes	cures slowly at 140-160°C.
"	Tetrachloro-bisphenol A	33	Yes-70°	no cure at 200° for 18 hrs.
"	Resinox 760	33	Yes-70°	cures slowly at 200°C thermoplastic.
"	Bisphenol A	37	Yes	no cure at 200°C

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The difference between hydrolyzed Aroclor 1268 and the other polyfunctional phenols is noteworthy. We attribute its higher activity to its markedly more acidic nature. The pH values of the three biphenols tested are as follows:

Bisphenol A	3.58
Tetrachlorobisphenol A	3.49
Hydrolyzed Aroclor 1270	3.37

The values were determined in 1-1 dioxane-water solution, using a glass electrode.

Less than stoichiometric amounts of hydrolyzed Aroclor 1268 could be caused to react with and modify conventional Epons.

Aroclor-Epoxy Resin as a Stabilizer The epoxy resins have been used as HCl acceptors and stabilizers for chlorine containing resins, particularly polyvinyl chloride. The diglycidyl ethers of tetrachlorobisphenol A and hydrolyzed Aroclor 1268 were equal to Paraplex G 60 and Epon 828 in stabilizing polyvinyl chloride plasticized with tricresyl phosphate against the effect of heat and light.

TABLE XXII

PVC - 70 parts
Tricresyl Phosphate - 30 parts
Stabilizer - 2 parts

No.	Stabilizer	Heat Stability 5 Hrs at 150°C	Weather-Ometer 100 Hrs.	Outdoor 2 Weeks
1	Paraplex G-60	clear-reddish brown	clear-water white	very slight bleach
2	Epon 828	equals 1	equals 1	not as good as 1.
3	Tetrachlorobisphenol A diglycidyl ether	"	"	"
4	Hydrolyzed Aroclor Epoxy 1268	"	"	equals 1

VI. EXPERIMENTAL DETAILS

HYDROLYSIS The experimental details on hydrolysis have been previously reported (Ref. 1) and are repeated here for the sake of completeness.

1.5-Liter Batch (Run No. 14, Table I) Into a 1-liter Erlenmeyer flask was placed 144 g reagent grade NaOH pellets (3.6 moles, 80% excess) and 400 g methanol (C.P., Carbide & Carbon). The temperature rose on shaking, due to heat of solution. After a short boiling period on the steam bath, some makeup methanol was added and the methanolic NaOH was decanted into a 1.5-liter, 316 stainless steel bottom-stirred Aminco autoclave. The residual NaOH was dissolved in about 35 g distilled water and this solution was charged to the autoclave. Monsanto production grade (Lot 86) Aroclor 1268 (224 g or 0.5 mole) was charged to the autoclave which was then sealed, flushed out thrice with N_2 (to 300 psig) and heated with stirring as follows:

Time	Temp. °C	Pressure psig	Remarks -
0845	35	0	Both heaters on
0945	173	345	
0951	181	420	Fixed heat off, 97 volts on variac
1001	190	510	Slight cooling required
1016	192	550	
1101	193	605	Cooling water on
1308	25	40	

The bomb was vented slowly without agitation, opened and the dark solution poured out, and the bomb was rinsed out with water (ca. 200 ml), which dissolved the solid NaCl. Distillation to a head temperature of 98°C yielded 423 g of methanol plus water. The thick residue was diluted with distilled water to 450 ml and filtered on coarse filter paper at about 50-60°C, to remove the small amount of solid. The solution was heated to boiling and acidified at reflux (Ref. 3) with 190 ml conc. HCl (reagent grade) then 10 ml extra HCl was added and stirring continued at reflux for about 30 min. The still acid mixture was allowed to stand overnight and decanted. The lower layer was washed with 5 x 300 ml portions of hot (90°C) distilled water. After the fourth wash a silver nitrate test for chloride in the wash water was negative. To the organic layer [illegible]

benzene was added, the water azeotroped off and the benzene distilled to a pot temperature of 145°C/2 mm which was maintained for about 30 minutes. Residue weighed 193 g, a 94% conversion and yield.

2-Gallon Batch (Run No. 17, Table II) Into two 4-liter Erlenmeyer flasks were divided 1008 g (25.2 moles or 80% excess) NaOH and 2800 g methanol. The mixtures were shaken, heated gently on steam baths and, after addition of some makeup methanol, combined. Most of the remaining NaOH was dissolved in about 250 ml distilled water and all the solutions plus undissolved NaOH were charged to a 2-gallon, top-stirred Autoclave Engineers autoclave. Aroclor 1268 (1568 g, 3.5 moles) was then charged and the autoclave sealed, flushed with 3 x 300 psig N_2 and then heated with stirring as follows:

Time	Temp. °C	Pressure psig	Remarks -
1130	35	atmos	95 Volts on both heaters
1205	116	50	
1212	144	100	Cut back to 90 volts
1225	166	200	
1227			Fixed heat off, exothermic reaction to 186°C
1228	178	400	Intermittent heat on
1235	181	425	
1245	187	500	
1248:30	190	525	Cracked cooling water inlet valve for a few seconds to control temp.
1255	193	600	
1300	192	600	
1338:30	192	625	Cooling water on

The bomb was vented through a dry ice-acetone trap in which 30 g of a low boiling material, probably dimethyl ether, collected. The bomb was opened, the batch was siphoned out and the reactor was washed out with one liter of distilled water. The methanol was distilled to a head temperature of 94°C and 2565 g of methanol and water (17% water by Karl Fisher titration) recovered. The batch was diluted with water to a final volume of about 5 liters and filtered hot on coarse filter paper. A very small amount of solid material was removed. The filtrate was acidified carefully at about 95-100°C with about 1320 ml conc. HCl, then 25 ml excess acid was added, the batch stirred for another 1.2 hours to make sure it would remain acid, then allowed to separate. The water was decanted and the batch washed with [illegible] ml water (90°).

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distilled water, separating by decantation, after [illegible] tive halide test was obtained on the last water wash. About 100 ml benzene was added, the water was azeotroped off, and the benzene distilled to a pot temperature of 150°C/2 mm, at which the residue was maintained for about 30 minutes. The conversion yield was 1300 g or 90%.

GLYCIDYLATION

Expt. NBP 367489 Dihydrolyzed Aroclor 1268 (0.5 mole, 206 g, N.E. 204, made by J. R. LeBlanc NBP 365970) and Shell epichlorohydrin (6.0 moles, 556 g) were placed in a 1-liter, 4-necked flask equipped with a mechanical stirrer, dropping funnel, condenser and thermometer. The mixture was heated to 90°C, then 0.5 mole of NaOH as a 50% aqueous solution was added over a 14 minute period. A mildly exothermic reaction took place and brought the mixture to reflux. In 35 minutes, the solution became neutral. Excess epichlorohydrin and water were distilled at 20 mm pressure, and at a maximum pot temperature of 100°C. The hot residue was diluted with 250 g of benzene and one mole of NaOH as a 50% aqueous solution (a 50% molar excess) was added. The mixture was refluxed with stirring for 7.5 hours and water was removed azeotropically. The solution was diluted with benzene and washed to neutrality with ~8-liters of water, at which point the neutral water wash remains clear on acidification. The benzene solution was dried by distillation, then the solvent was removed. Final traces of benzene were removed at 120-30°C at 2-4 mm, or at 150°C at 20 mm for 20 minutes. The product (221 g) is a light amber resin, m.p. 46-7°C. The yield is 84.5% based on dihydrolyzed Aroclor 1268 charged.

Anal. Found: % Epoxy - 5.47; 5.65
% Hydrolyzable Cl - 0.11; 0.12
% Total Cl - 42.94; 43.16

Expt. NBP 367491 This is a three-fold scale up experiment from the previous with the difference that a lower (1:6) hydrolyzed Aroclor 1268 to epichlorohydrin molar ratio was used. In this run, the sodium chloride formed was extracted with water before the excess epichlorohydrin used was distilled off. Layer separation was rapid. The residue was diluted with benzene, treated with the excess sodium hydroxide as in previous experiment then was washed to neutrality with water (emulsion) to give a resin containing 5.52% epoxy and 0.09% hydrolyzable Cl, m.p. 46-47°C. The yield is 79.6%. This is the general procedure used (by J. R. LeBlanc) to prepare the large size samples submitted to Applied Research.

Expt. NBP 367467 This experiment is a duplication of the St. Louis process given in Ref. 2. Dihydrolyzed Aroclor 1268 (1 mole, 411 g, N.E. 204, made by J. R. LeBlanc, NBP 365970) and Shell epichlorohydrin (6 moles, 556 g) were stirred at 90°C. To this was added 1 mole of NaOH as a 50% aqueous solution over a 17 minute period. A mildly exothermic reaction took place after 7 minutes when 45 ml NaOH had been added, and the mixture refluxed. In 40 minutes the solution became neutral. Excess epichlorohydrin and water were distilled off at 20 mm pressure at a maximum of 100°C. The hot solution was diluted with benzene (4.4 moles, 340 g) refluxed, and 2 moles of NaOH was added as a 50% aqueous solution (a 50% molar excess). This was refluxed for 6.5 hours as given in experiment 367489. The solution was diluted with 400 g of benzene, and the residue washed with more benzene. The filtration was slow and the washing was incomplete since the filtration residue contained 57 g of water-insoluble material (glycidyl ether). The filtrate was dried by distillation, then the solvent was removed. Final traces of benzene were removed at 1-2 mm at 100°C. The product (442 g) is a light amber resin, m.p. 49-50°C. The yield is 84.5% based on dihydrolyzed Aroclor charged. The material is slightly alkaline.

Anal. Found: % Epoxy - 5.33; 5.47
% Hydrolyzable Cl - 0.07; 0.09
Alkalinity - 0.013 Milliequivalent NaOH/gm resin

The identical experiment (NBP 367467) made at a 0.25 mole scale gave a 92.8% yield due to more complete washing of the filter cake; this cake contained 4.4 g of water insoluble material. The final product analyzed 5.44% epoxy oxygen and 0.10% hydrolyzable Cl.

ESTERIFICATION Our esterifications follow the method recommended in Reference 8.

Expt. NBP 354873 Esterification of oxirane oxygen of Epon 1004

The reaction was carried out in a four-necked flask, fitted with a stirrer, gas inlet tube, vent tube, and thermometer. Nitrogen at approximately 1 to 2 bubbles/second was passed through the reaction mixture.

150 gms Epon 1004 (Shell Chemical Co.)
44.1 gms Soya Fatty Acid (Armour Neo Fat 127)

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The reactants were heated to 200°C and held at this temperature until a low acid value was reached. This required 4 hours, 5 minutes to reach an acid value of 1.16. This was 3 hours, 5 minutes after reaching 200°C. The ester was then cooled and dissolved in an equal weight of xylene. Viscosity = 1005 centipoises (Z_5 - Gardner-Holdt), Color = 7.

Expt. NBP 354868 Esterification of oxirane oxygen of diglycidyl ether of hydrolyzed Aroclor 1270.

125 gms Diglycidyl ether of hydrolyzed Aroclor 1270, 3.83% Epoxy "n" value 0.76
84 gms Soya Fatty Acid (Armour Neo-Fat 127). Initial acid value = 81

The resin and fatty acid were heated to 200°C. After a total time of 1 hr, 55 min, and 30 min after reaching 200°, the acid value was 1.47. After this the acid value started to rise. At a value of 2.25, the ester was divided, one-half was dissolved in an equal weight of xylene and the other half heated for a total of 5 hrs, 15 min at 200°, and 8 hrs, 5 min at 260°. The acid value finally rose to 20.0. The off gases were scrubbed to remove HCl during this experiment; no indication of chloride ion was found in the gas scrubber. The viscosity of the portion heated to 200°C was 35 centipoises, Gardner-Holdt N. The color was 7.

Expt. NBP 359094 Esterification of oxirane oxygen of diglycidyl ether of hydrolyzed Aroclor 1268.

50 gms Diglycidyl ether of hydrolyzed Aroclor 1268, 3.37% Epoxy oxygen, "n" value = 0.85
29.5 gms Soya Fatty Acid (Armour Neo-Fat 127). Initial acid value = 37.0

The previously described cycle was followed. After 1 hr, 10 min total, and only 15 min at 200°C, the acid value was 2.13. During the next 30 minutes the acid value started to rise. The ester was cooled and dissolved in an equal weight of xylene.

Expt. NBP 364202 Tall fatty ester of Shell Epon 1004, 0.9 equivalent.

150 gms Epon 1004 (Shell Chemical Co.)
220.2 gms Tall Fatty Acid (Arizona Chemical Co. Actinol FA No. 2). Initial acid value = 119

The reaction was carried out at 280°C. After 6 hrs, 45 min at 280°C), the acid value was 12.5. The reaction was stopped at this point and the ester dissolved in an equal weight of xylene.

Expt. NBP 364203 Esterification of diglycidyl ether of hydrolyzed Aroclor 1268 with Tall Fatty Acid 0.91 ester.

150 gms Diglycidyl ether of hydrolyzed Aroclor 1268, 3.3% Epoxy "n" 0.88
143.8 gms Tall Fatty Acid (Arizona Chemical Acintol FA 2) Initial acid value = 98

The usual procedure was followed. The temperature was held at 220°C. The total time to an acid value of 9.6 was 10 hrs, 10 min, of which 7 hrs, 50 min was at 220°C. If the reaction had been stopped at an acid value of 13.8 comparable to the 12.5 of the preceding ester of Epon 1004, the time would have been 6 hrs, 25 min at 220°C. The ester was dissolved in an equal weight of xylene.

Expt. NBP 354899-4 Preparation of polyester.

4.2 gms Hydrolyzed Aroclor 1270 diglycidyl ether 353864
1.3 gms Benthal
0.5 gms Fumaric acid

The ingredients were heated on a hot plate 15 minutes at 400°F. The product was cooled and ground in a mortar. 2.1 gms of above resin was dissolved in 0.9 gms of Styrene. One drop of cobalt naphthenate and a trace of benzoyl peroxide was added. The material was heated in a hot water bath to yield a rubbery resin which became hard on standing overnight. This material would burn in a flame, but would not support combustion.

Expt. NBP 359094 Preparation of polyester.

4.17 gms Diglycidyl ether of hydrolyzed Aroclor 1270
1.29 gms Benthal
0.25 gms Maleic anhydride
0.30 gms Phthalic anhydride

Heated on hot-plate 10 minutes and dissolved in 2.4 gms of styrene to give a viscous solution. With cobalt naphthenate and Lupersol DDM, a hard block of polyester was obtained on standing overnight.

Expt. NBR 367988 -- Ester of diglycidyl ether of hydrolyzed Aroclor with Soya Fatty Acid and Dimer Acid.

55 gms Diglycidyl ether of hydrolyzed Aroclor 1268
40 gms Soya Fatty Acid (Armour Neo-Fat 127)
5 gms Dimer Acid (Emery - M461-R)

Materials were heated at 260°C for one hour to obtain an acid value of 13.24. The acid value did not fall any lower but began to rise. The final viscosity of this material was a Gardner-Holdt G.

CURING STUDIES

Melt Mixing — Curing studies on Aroclor-epoxy resins were performed on a 5 g scale by several different techniques, dictated largely by the solid state of the resin. In the melt technique, five grams of resin were added to a test tube (which had been well lubricated with silicone), melted and the curing agent added. This method imposed several limitations; one, if the melting point of the Aroclor was higher than that of the boiling point of the curing agent (which is often the case with liquid amines), the curing agent would be partially flashed, and the stoichiometry of the curing reaction would be unknown; two, at the temperature required for melting the Aroclor epoxy, addition of the curing agent often led to violently exothermic reaction.

In addition, at the high mixing temperatures, the curing agents are often so reactive that insolubility occurred before sufficient reaction time ensued. For these reasons, melt mixing was restricted to slower-reacting, solid curing agents such as acid anhydrides.

Dry Blending with Liquid Curing Agents — In instances where a low-boiling, liquid curing agent was to be used, it was dry-blended with the Aroclor-epoxy, at room temperature. Although this method leaves a lot to be desired in terms of dispersion of the curing agent, it did lead to fairly satisfactory results.

An alternate procedure was to dissolve the Aroclor-epoxy and the curing agent in a mutual solvent, evaporate the solvent, and recover the mixture. One difficulty encountered in this method is finding a sufficiently low-boiling solvent which can be evaporated under conditions in which no pre-cure of the resin is obtained (Ref. 10).

Dry Blending of Solid Curing Agents — This method of combining the curing agent was physically the most desirable for Aroclor epoxies. The resin and the curing agent are first ground through 60-mesh screens and then dry-blended via tumbling. Solution mixing was also investigated with solid curing agents; however, the difficulties mentioned above in solution blending are similarly troublesome.

The Use of Reactive Diluents — The use of reactive diluents as both solvent and curing agent, such as allyl glycidyl ether, etc., was not extensively studied. Such reactive diluents are known to lead to lower heat distortion products. Since heat resistance was one of the expected "plus" values of Aroclor epoxies, use of such diluents could effectively mask this important property.

Curing Conditions — Optimum curing temperatures and times must be determined empirically for each curing agent. In general, acid and anhydride cures require longer times and higher temperatures than amine cures. The addition of catalytic amounts (<1.0%) of amine will sometimes accelerate anhydride cures

Evaluation of Cured Products — Our criterion for cure, adapted to a micro-scale, was the behavior of the cured product on a melting point bar and its solubility characteristics in a series of selected solvents. In general, a product which exhibited no visual change in appearance at temperatures up to 300°C, and remained unaffected by the selected solvents, was considered fully cured. Most of the early Aroclor epoxies (found later to contain monofunctional derivatives) led to cured products which were very brittle in nature and "soluble in" or "attacked by" a variety of solvents. Such behavior is not associated with high molecular weight, highly cross-linked epoxy resins.

In the evaluation of the completely difunctional Aroclor-epoxy, larger size castings were made, from which test specimens for heat-distortion temperatures were cut. The measurements were made in accordance with A.S.T.M. procedure.

Adhesive Studies — Our method consisted of lap-bonding aluminum strips (4" x 1" x 1/16") which have first been degreased in trichloroethylene and then etched in a sulfuric acid/dichromate solution. The strips are lapped 1-inch to give a 1-inch square test area. The shear strength of the bonded aluminum is measured on the Instron machine.

Potting Experiments — Potting and encapsulation experiments were performed by embedding miniature electronic parts with various Aroclor-epoxy formulations. Silicone-coated aluminum weighing dishes were used for molds.

Glass Laminating — Both wet and dry lay-up procedures were employed in preparation of glass laminates.

In one instance glass cloth was covered with a dry blend of Aroclor-epoxy and curing agent, and a sandwich structure built up by adding alternate layers of glass cloth and epoxy mixture. The "sandwich" was contained in a mold and cured.

Another method consisted of dipping glass cloth into a solution of Aroclor-epoxy and curing agent, evaporating the solvent, and repeating the operation until a sufficient thickness of resin on glass was obtained.

In both of these instances, the cured products were too brittle to be of any interest. There was no opportunity to evaluate the completely difunctional Aroclor epoxies in this application.

PATENT STATUS

A patent disclosure has been submitted covering the use of at least 80% excess NaOH in the hydrolysis of Aroclor 1268, polychlorinated polyphenyls, to give complete phenolic difunctionality. (D2472)

Patent disclosures have also been submitted for the following uses of hydrolyzed Aroclor:

1. The reaction of hydrolyzed Aroclor with compounds containing an epoxy group, e.g. epichlorohydrin. (D1869)
2. Hydrolyzed Aroclor as industrial preservatives. (D2078)
3. Glycidyl ethers derived from hydrolyzed Aroclor as stabilizers for polyvinyl chloride and as plasticizers. (D2320, D2321)
4. The preparation of fatty acid esters of diglycidyl ether of hydrolyzed Aroclor. (D2335)
5. The preparation of casting resins by the reaction of equimolecular quantities of diglycidyl ether of hydrolyzed Aroclor, benzoic acid, and fumaric acid and cross-linking with styrene. (D2355)
6. The preparation of a thermosetting resin by the reaction of diglycidyl ether of hydrolyzed Aroclor with a dicarboxylic acid. (D2356)
7. Diglycidyl ethers of hydrolyzed Aroclor as a curing agent for epoxy resins. (D2477, D2506)
8. The use of catalytic amounts of lime in epoxy reactions. (D2567)
9. The use of diglycidyl ethers of hydrolyzed Aroclors to cure high acid value alkyds. (D2568)

VIII. REFERENCES

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APPENDIX

A. Epoxy Constants

B. Calculations for Preparation of 300 Gallons of Epoxy Ester (0.8 equivalent)

C. Key to Abbreviations Used in Tables

Curing Studies - Tables 1, 2, and 3

Shear Strength of Epoxy Aluminum/Aluminum Bonds - Table 4

D. Biological Toxicant Evaluation

E. Esterification Tables 6, 7 and 8

F. Notebook Pages

G. List of Raw Materials

H. List of Tables

I. List of Figures

J. Table of Contents

APPENDIX A

Epoxy Constants. Epoxy resins have a number of values that serve to characterize the resin.

1. Percent epoxy - determined by analysis, reported as per cent oxirane oxygen.

2. Epoxy value = $\frac{\text{Epoxide oxygen content (\% Epoxy)}}{16}$

3. Epoxy equivalent weight = $\frac{1}{\text{Epoxy value}} = \frac{16}{\text{\% Epoxy}} \times 100$
(grams of resin containing one gram equivalent of epoxide)

4. Equivalent weight = grams of resin required to esterify completely, one gram mol. of a monobasic acid, e.g., 60 gms acetic acid.

5. Calculated molecular weight = 2 x Epoxy equivalent.

"n" number = Mols bisphenol-1, or
Mols epichlorohydrin-2, or
Number of hydroxyl groups, or

$$\frac{\text{Calculated M.W. - Wt. outside bracket in formula}}{\text{Weight inside bracket in formula}}$$

Functionality = Mols eipchlorohydrin + 2, or
Mols biphenol + 3, or
n + 4.

Percent hydroxyl = determined by analysis.

Percent hydrolyzable chlorine = amount of chlorine, other than that attached to the aromatic nuclei, left in the resin.

Calculations for Epoxy Esters Ref. 1) For preparation of the oxirane ester of the diglycidyl ethers, the calculation is as follows:

$$\frac{16}{\text{\% Epoxy}} \times 100 = \text{Epoxy Eq. Wt.}$$

$$\frac{\text{Wt. diglycidyl ether}}{\text{Epoxy Eq. Wt.}} \times \text{Eq. Wt. of Fatty Acid} = \text{Wt. of Acid.}$$

In calculating the amount of fatty acid for the more completely esterified diglycidyl ethers, two possible methods can be followed:

If the equivalent weight is known:

$$\text{Required Fatty Acid} = \frac{\text{Weight diglycidyl ether}}{\text{Eq. Wt.}} \times \text{Eq. Wt. of Fatty Acid}$$

If the equivalent weight is not known, the following course may be followed:

Functionality = n + 4 by definition

$$\frac{\text{Calculated Molecular Wt.}}{n + 4} = \text{Eq. Wt. (calculated)}$$

$$\left[\frac{\text{Wt. of diglycidyl ether}}{\text{Eq. Wt. (calculated)}} \times \text{Eq. Wt. of Fatty Acid}\right] \times \text{Fractional amount of complete esterification}$$

APPENDIX B

Calculations* for Preparation of 300 Gallons of Epoxy Ester (.5 equivalent)

Charge to kettle -
483 lb Epon 1004
627 lb Soya Fatty Acid

Sparge with CO_2 and heat. As soon as melting is complete, start agitation. Bring to required temperature and hold for desired acid value.

260°C (500°F)

Time for up heat - 2.5 hours
Acid value - 6-9
Time to acid value - 9 hours
Cool - 1 hour (to 350°)
Thin with mineral spirits - 0.5 hr

Total time - 13 hrs (9 hrs at 260°C)

Charge to kettle -
627 lb diglycidyl ether
630 lb Soya Fatty Acid

200°C (392°F)

Time for up heat - 2 hours
Acid value - 5.8
Time to acid value - 4.3 hrs
Cool - 1 hour
Thin with mineral spirits - 0.5 hr

Total time - 7.8 hrs (4.3 hrs at 200°C)

*Based on 1-liter laboratory batches

APPENDIX A

Key to Abbreviations Used in Tables

MA	Maleic Anhydride
TETA	Triethylene Tetramine
DMAP	Dimethylaminopropyl Amine
DEAP	Diethylaminopropyl Amine
P	Phthalic Anhydride
PA	Pyromelletic Dianhydride
DD	Durene Diamine
DET	Diethylene Triamine
PD	Phenylene Diamine
M	Maleic Acid
DADPS	Diaminodiphenylsulfone
DA	Dimethyl Aniline

TABLE 1.

CURING STUDIES ON AROCLOR EPOXIES

Sample Identification	Analysis % Oxirane Oxygen	Analysis % Aliphatic Chlorine	% GMH[1] Derivative in Epoxy	Mol Ratio of Curing Agent	Curing Agent	Curing Conditions Hrs	Curing Conditions °C	Behavior at 300°C ("S" Denotes Softening)
[illegible][2]	5.03	1.14	10	0.5	MA	24	130	<150 (S)
				0.75	MA	24	130	No Change
				0.85	MA	24	130	" "
				1.0	MA	24	130	" "
				1.25	MA	24	130	" "
				1.50	MA	24	130	<210 (S)
				1.75	MA	24	130	<150 (S)
				2.0	MA	24	130	<150 (S)
				1.0	TETA	2	130	<250 (S)
				0.5	TETA	2	130	<150 (S)
				0.25	TETA	2	130	<150 (S)
				0.75	TETA	2	130	<150 (S)
				1.0	DMAP	2	130	<230 (S)
				0.5	DMAP	2	130	<150 (S)
				0.25	DMAP	2	130	<150 (S)
				0.75	DMAP	2	130	<150 (S)
[illegible][3] FD-3A	2.51	[illegible]	[illegible]3	[illegible]50	MA	24	130	<150 (S)
				[illegible]75	MA	24	130	No Change
				[illegible]	MA	24	130	" "
				1.[illegible]	MA	24	130	" "
				1.25	MA	24	130	" "
				1.[illegible]	MA	24	130	" "
				1.[illegible]	MA	24	130	" "
				2.[illegible]	MA	24	130	" "
				2.5	MA	24	130	" "
				3.0	MA	24	130	<215 (S)
				[illegible]5	MA	24	130	<200 (S)
				[illegible]	MA	[illegible]	130	Liquid

[illegible]-glycerol monochlorhydrin

= Aroclor 1262

= Aroclor 1271

DSW 621313

STLCOPCB4095343

TABLE 1. (Cont'd)

Sample Identification	Analysis % Oxirane Oxygen	Analysis % Aliphatic Chlorine	% GMH[1] Derivative in Epoxy	Mol Ratio of Curing Agent	Curing Agent	Curing Conditions Hrs	Curing Conditions °C	Behavior at 300°C ("S" Denotes Softening)
XD-67	1.51	8.27	73	1.0	TETA	2	130	Very low cure
				0.50	TETA	2	130	" " "
				0.25	TETA	2	130	" " "
				0.75	TETA	2	130	" " "
				1.0	DMAP	2	130	" " "
				0.50	DMAP	2	130	" " "
				0.25	DMAP	2	130	" " "
				0.75	DMAP	2	130	" " "
XD-68[2]	5.37	0.53		0.50	MA	24	130	<150 (S)
				0.75	MA	24	130	No Change
				0.85	MA	24	130	" "
				1.0	MA	24	130	" "
				1.25	MA	24	130	" "
				1.50	MA	24	130	<170 (S)
				1.75	MA	24	130	<145 (S)
				2.0	MA	24	130	<150 (S)
				1.0	TETA	2	130	<200 (S)
				0.50	TETA	2	130	<150 (S)
				0.25	TETA	2	130	<150 (S)
				0.75	TETA	2	130	<170 (S)
				1.0	DMAP	2	130	No Change
				0.50	DMAP	2	130	<150 (S)
				0.25	DMAP	2	130	<150 (S)
				0.75	DMAP	2	130	<150 (S)
Monet Compound 346678	6.17	1.05		1.0	P	24	130	No Change
				2.0	P	24	130	<150 (S)
				0.85	P	24	130	No Change
				1.0	DD	24	130	" "
				2.0	DD	24	130	<150 (S)
				3.0	DD	24	130	<150 (S)

1 - Di-α-glycerol monochlorohydrin
2 - Aroclor 1262
3 - Aroclor 1271

DSW 621314

TABLE 1. (Cont'd)

Analysis					Curing Conditions		Behavior at 300°C ("S" Denotes Softening)
% Epoxy Oxygen	% Aliphatic Chlorine	% GMH[1] Derivative in Epoxy	Mol Ratio of Curing Agent	Curing Agent	Hrs	°C	
6.17	1.05		1.0	HET	24	130	No Change
			1.0	MA	24	130	" "
			0.5	MA	24	130	<150 (S)
			0.85	MA	24	130	No Change
			1.0	PA	24	130	" "
			2.0	PA	24	130	" "
			0.85	PA	24	130	" "
			1.0	PD	24	130	" "
			1.0	DA	24	130	" "
			1.0	TETA	2	130	" "
			1.0	DET	2	130	" "
4.9	2.87		2.0	PD	12	150	200 (S)
			3.0	PD	12	150	200 (S)
			4.0	PD	12	150	<200 (S)
			0.5	PD	12	150	<200 (S)
			1.0	P	12	150	No Change
			2.0	P	12	150	" "
			0.5	P	12	150	" "
5.33	0.32		1.0	TETA	2	130	250 (S)
			1.0	DD	2	130	250 (S)
			1.0	P	24	130	No Change
			1.0	HET	24	130	" "
			1.0	PD	24	130	" "
			1.0	DET	2	130	Decomposed
			1.0	MA	24	130	>250 (S)
			0.85	MA	24	130	>250 (S)
			1.0	PA	24	130	No Change
			1.0	DA	24	130	" "

[1] Di-α-glycerol monochlorohydrin

[2] Aroclor 1262

[3] Aroclor 1271

DSW 621315

TABLE 2.

CURING STUDIES ON AROCLOR EPOXY

Epoxy Content	Analysis % Oxirane Oxygen	Analysis % Aliphatic Chlorine	% GMH[1] Derivative in Epoxy	Mol Ratio of Curing Agent	Curing Agent	Curing Conditions Hrs	Curing Conditions °C	Behavior at 300°C ("S" Denotes Softening)
[illegible]	7.05	-	-	1.18	PD	2	150	157 (S)
				1.23	DMAP	2	150	204 (S)
				2.38	TETA	2	150	186 (S)
				1.29	MA	2	150	No Change
[illegible][2]	2.55	-	-	0.81	MA	2	150	Very little cure
				1.62	MA	2	150	" " "
				3.24	MA	2	150	" " "
				6.48	MA	2	150	" " "
				0.71	PD	2	150	No Change
				1.42	PD	2	150	" "
				2.84	PD	2	150	" "
				5.68	PD	2	150	" "
	5.38	0.56	6.5	0.38	MA	2	150	<150 (S)
				0.76	MA	2	150	<150 (S)
				1.52	MA	2	150	<150 (S)
				0.74	PD	2	150	<150 (S)
				0.68	PD	2	150	<150 (S)
				1.36	PD	2	150	<150 (S)
				0.68	TETA	2	150	No Change
				1.36	TETA	2	150	148 (S)
				0.35	DMAP	2	150	-
				1.68	DC	2	150	<150 (S)

[illegible] glycerol monochlorohydrin

[illegible] 1270

[illegible] 1262

TABLE 2. (Cont'd)

Sample Identification	Analysis % Oxirane Oxygen	Analysis % Aliphatic Chlorine	% GMH[1] Derivative in Epoxy	Mol Ratio of Curing Agent	Curing Agent	Curing Conditions Hrs	Curing Conditions °C	Behav... at 3... ("S" Denot... Softening
PD-3[2]	3.39	4.98	41.0	0.61	MA	2	150	No Change
				1.22	MA	2	150	"
				2.44	MA	2	150	"
				1.07	TETA	2	150	"
				2.14	TETA	2	150	"
PD-4[3]	3.52	4.53	39.0	0.28	MA	2	150	<125 (S)
				0.56	MA	2	150	No Change
				1.16	MA	2	150	"
				2.32	MA	2	150	"
				0.25	PA	2	150	<125 (S)
				0.50	PA	2	150	<125 (S)
				1.16	PA	2	150	No Change
				2.32	PA	2	150	<125 (S)
				0.47	M	2	150	<125 (S)
				0.94	M	2	150	<125 (S)
				0.56	MA+10% M	2	150	<125 (S)
				1.16	MA+10% M	2	150	<125 (S)
				0.28	MA+20% M	2	150	<125 (S)
				1.16	MA+20% M	2	150	<125 (S)
				2.32	MA+20% M	2	150	No Change
PD-4[3]	3.52	4.53	39.0	0.56	MA	21	150	<125
				1.16	MA	21	150	No Change
				1.53	MA	21	150	"
				1.85	MA	21	150	"
				2.32	MA	21	150	"
				2.78	MA	21	150	"
				3.46	MA	21	150	"
				4.65	MA	21	150	"

[1] Di-α-glycerol monochlorohydrin

[2] Aroclor 1270

[3] Aroclor 1262

DSW 621317

TABLE 2 (Cont'd)

Sample Identification	Analysis % Oxirane Oxygen	Analysis % Aliphatic Chlorine	% GMH[1] Derivative in Epoxy	Mol Ratio of Curing Agent	Curing Agent	Curing Conditions Hrs	Curing Conditions °C	Behavior at 300°C ("S" Denotes Softening)
Shell Epon 562	ca. 10.4	-	-	0.19	MA	21	125	Discolored
				0.39	MA	21	125	"
				0.52	MA	21	125	"
				0.63	MA	21	125	No Change
				0.79	MA	21	125	"
				0.95	MA	21	125	"
				1.18	MA	21	125	"
				0.18	TETA	Room	Temp.	<75 (S)
				0.36	TETA	"	"	<75 (S)
				0.54	TETA	"	"	<75 (S)
				0.72	TETA	"	"	<150 (S)
				0.18	DMAP	"	"	Discolored
				0.36	DMAP	"	"	"
Shell Epon 834	ca. 6.4	-	-	0.33	MA	21	125	<125 (S)
				0.64	MA	21	125	No Change
				0.84	MA	21	125	"
				1.02	MA	21	125	"
				1.27	MA	21	125	"
				1.53	MA	21	125	"
				1.92	MA	21	125	"
				0.29	TETA	Room	Temp.	Discolored
				0.58	TETA	"	"	No Change
				0.87	TETA	"	"	"
				1.16	TETA	"	"	"
				0.29	DMAP	"	"	<75 (S)

[1] Di-α-glycerol monochlorohydrin

[2] Aroclor 1270

[2] Aroclor 1262

DSW 621318

TABLE 2. (Cont'd)

Sample Identification	Analysis % Oxirane Oxygen	Analysis % Aliphatic Chlorine	% GMH[1] Derivative in Epoxy	Mol Ratio of Curing Agent	Curing Agent	Curing Conditions Hrs	Curing Conditions °C	Behavior at 300°C ("S" Denotes Softening)
DER 332	8.0	-	-	0.24	MA	21	125	No Change
				0.51	MA	21	125	" "
				0.68	MA	21	125	" "
				0.82	MA	21	125	" "
				1.22	MA	21	125	" "
				1.52	MA	21	125	" "
				0.23	TETA	Room	Temp.	" "
				0.46	TETA	"	"	" "
				0.69	TETA	"	"	" "
				0.92	TETA	"	"	" "
				0 24	DMAP	"	"	<75 (S)
				0.48	DMAP	"	"	No Change
FD 1 2	3.52	4 53	39.0	0 19	P	21	125	<75 (S)
				0.37	P	21	125	<75 (S)
				0.77	P	21	125	No Change
				1.0	P	21	125	" "
				1 5	P	21	125	<75

1 = DL-a-glycerol monochlorohydrin

2 = Aroclor 1270

3 = Aroclor 1262

DSW 621319

TABLE

EFFECT OF CURING VARIATIONS ON AROCLOR EPOXIES

Sample Identification	PPH of Curing Agent	Curing Agent	Curing Conditions Hrs	Curing Conditions °C	Softening Temperature °C
Aroclor 310448	12	1-Cyanoguanidine	0.5	115	92
			1.0	115	96
			1.5	115	100
			2.0	115	94
			2.5	115	93
	12	1-Cyanoguanidine	0.5	150	109
			1.0	150	136
			1.5	150	145
			2.0	150	144
			2.5	150	144
	12	1-Cyanoguanidine	0.5	175	150
			1.0	175	151
			1.5	175	151
			2.0	175	150
			2.5	175	150
	20	1-Cyanoguanidine	0.5	150	123
			1.0	150	144
			1.5	150	146
			2.0	150	140
			2.5	150	134
	6	1-Cyanoguanidine	16	150	150
	12	"	16	150	155
	6	p-Phenylene Diamine	0.5	150	120
			1.0	150	124
			1.5	150	128
			2.0	150	127
			2.5	150	126
	12	p-Phenylene Diamine	0.5	150	120
			1.0	150	114
			1.5	150	114
			2.0	150	113
			[illegible]	150	[illegible]

TABLE 3 (Cont'd)

Sample Identification	PPH of Curing Agent	Curing Agent	Curing Conditions Hrs	Curing Conditions °C	Softening Temperature °C
Aroclor 310448	12	o-Phenylene Diamine	0.5	150	104
			1.0	150	105
			1.5	150	105
			2.0	150	110
			2.5	150	110
	12	Glutaric Acid	0.5	150	95
			1.0	150	110
			1.5	150	110
			2.0	150	113
			2.5	150	109
Aroclor 310448 (1268)	20	Ethylene Maleic Anhydride	2.5	150	103
	6	Triethylene Tetramine	2.0	150	234
	10		2.0	150	192
	20		2.0	150	159
	6	Diethylaminopropyl Amine	2.0	150	214
	10		2.0	150	196
	20		2.0	150	158
	6	Dimethylaminopropyl Amine	2.0	150	220
	10		2.0	150	203
	20		2.0	150	150
Aroclor 316097	10	Maleic Anhydride	0.5	150	105
			1.0	150	105
			1.5	150	106
			2.0	150	107
			2.5	150	110
	10	Ethylene Maleimide	0.5	150	101
			1.0	150	103
			1.5	150	105
			2.0	150	106
			2.5	150	108

TABLE 5. (Cont'd)

Sample Identification	PPH of Curing Agent	Curing Agent	Curing Conditions Hrs	Curing Conditions °C	Softening Temperature °C
Aroclor 323108	10	Diaminodiphenyl-sulfone	2.0	150	157
	20		2.0	150	146
	50		2.0	150	124
	10	Polyamide Resin 93	2.0	150	102
	20		2.0	150	101
	50		2.0	150	98
	100		2.0	150	96
	3	Triethylene Tetramine	2.0	150	140
	3	Diethylaminopropyl Amine	2.0	150	116
Aroclor 32310	6	Diethylaminopropyl Amine	2.0	150	142
	6	Triethylene Tetramine	2.0	150	143
	12	Diethylaminopropyl Amine	2.0	150	126
	12	Triethylene Tetramine	2.0	150	118

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TABLE 4.

SHEAR STRENGTH OF EPOXY ALUMINUM/ALUMINUM BONDS

Sample Identification	Aroclor Type	Curing Agent	Curing Conditions Time	Curing Conditions °C	Bond Thickness (Mils)	Shear Strength (psi)
	1262 + 33% Al. Powder	Diethylaminopropyl Amine	90 min	100	0.026	50
Shell Adhesive (VIII)	-	Diethylaminopropyl Amine	90 "	100	0.017	2100-3200
Shell Adhesive (VI)	-	Diethylaminopropyl Amine	4 hrs	100		1700-2100
FD-2A	1262	Triethylene Tetramine	12 "	150	0.020	145
FD-1	1262	Maleic Anhydride	24 "	150	0.019	98
FD-2	1262	Triethylene Tetramine	2 "	130	0.022	115
018930-A	1262 + Liquid Phenolic (60%)	Hexamethylene Tetramine	8 "	130	0.025	200
[illegible]	1262	Maleic Anhydride	24 "	130	0.015	140
Epon 834	-	Diethylaminopropyl Amine	90 min	100	0.16	3100
75% Epon 25% Aroclor	1262 (FD-4)	" "	90 "	100	0.20	1620
50% Epon 50% Aroclor	"	" "	90 "	100	0.19	900
25% Epon 75% Aroclor	"	" "	90 "	100	0.21	420
365999	1262	Methylene Dianiline	18 hrs	150	0.010	105
365999	1262	Bisaniline-A	18 "	150	0.10	510

NOTE: The majority of Aroclor adhesive test specimens were too poor to clamp into the testing device without breaking.

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TABLE 5.

BIOLOGICAL TOXICANT EVALUATIONS OF HYDROLYZED AROCLORS

Hydrolyzed Aroclor	1271	1270	1268	1262	1252	1248	1242	
C.P. No.	11682	12702	11683	3689	11685	11686	11687	Notes
Evaluation								
A. Microbiological								
1. Industrial Preservative	0	+	+	+	+	+	+	mod.act.[c]
2. Agricultural Fungicide	+	0	+	+	+	+	+	sl.act.
3. Soap Bacteriostat	0	0	+	0	+	+	+	some act.
4. Bacteriostat for Secondary Oil Recovery Waters [a]	0	+	0	0	0	0	+	mod.act.
[b]	0	0	0	0	0	0	+	mod.act.
B. Herbicide	+		+	+	+	+	+	sl.act.
C. Insecticide	0	0	0	0	+	+	+	inact.after II test
D. Nematocide	0	-	0	0	0	0	0	inact.

NOTE: Nitro reacted CP 3689 and 11685 with P_2S_5 and had screened as CP 13688-9.

Rating Key: 0 = not tested
+ = activity as shown in notes
- = inactive

[a] Against sulfate reducing strain A.

[b] Against sulfate reducing strain B and C; see D. P. Roman Report No. 1746.

[c] Only as bacteriostats, similar to CP 11683.

Only CP 12702 was tested in wooden block, activity half that of C_6Cl_5OH.

ESTERIFICATION [illegible] BIDI[illegible] DY[illegible] S[illegible] BY FATTY ACIDS

Oxirane Oxygen Only [illegible] Unhydrolyzed Aroclor.

[illegible]	Derivative (1)	[illegible]	[illegible]	[illegible]	[illegible]	Reaction Time at Max. Temp. (Hrs)	Reaction Rate (4)	Resin Synthesis Reference	Viscosity Fluid	Viscosity Gardner	[illegible]	Comment
354868-1	1270	3.93	[illegible]	[illegible]	[illegible]	[illegible]	Rapid	[illegible]	[illegible]	[illegible]		
[illegible]	1262	[illegible]	[illegible]92	0.31	[illegible]	2.5	Fast	Spfld.	[illegible]	[illegible]		
[illegible]	Epon 1004	[illegible]	[illegible]	[illegible]	-	[illegible]	Slow	-	[illegible]	[illegible]		
[illegible]	1268	5.10	[illegible]	[illegible]	[illegible]	[illegible]	Slow	[illegible]	1.	[illegible]		
354975	TCBPA (2)	[illegible]	496	[illegible]	[illegible]	[illegible]	Slow	Spfld.	[illegible]	[illegible]		
354977	Model (3) Compound	[illegible].17	519	[illegible]	[illegible]	11.[illegible]	Slow	[illegible]	[illegible]	[illegible]		
[illegible]	Epon 828	ca. [illegible].2	386	[illegible]	-	[illegible]	Slow	-	[illegible]	G		
354891	1262	3.93	816	[illegible]	[illegible]	[illegible]	Rapid	Spfld.	[illegible]	F		
359053	1270	0.95	[illegible]	[illegible]	[illegible]	-	-	[illegible]16056	-	-		Too high melting and insol. to give useable product.
359056	1268	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		
359057	1270	[illegible]	[illegible]	[illegible]	[illegible]		-	353864-[illegible]	-	-		Too high melting and insol. to give useable product.
359060	1268	[illegible]	[illegible]	[illegible]	[illegible]	4.75	Slow	[illegible]	[illegible]	[illegible]	7.57	
359061	1268	[illegible]	706	[illegible]	[illegible]	1.00	Rapid	353548	[illegible]	H	7.4[illegible]	
359062	1268	3.99	[illegible]	0.58	[illegible]	0.5	Rapid	[illegible]	[illegible]	K		
[illegible]	1268	[illegible]	[illegible]	0.92	[illegible]		Slow	[illegible]	[illegible]	[illegible]		
359065	1270	4.16	[illegible]	0.77	0.11		Rapid	353896	[illegible]	L		
[illegible]	1268	5.16	620	0.17	0.35	[illegible]	Slow	[illegible]	-			
359070	1270	4.43	720	0.24	0.06		Rapid	[illegible]	-			
[illegible]	1268	0.63	5060	[illegible]	0.00		-	[illegible]	-	-	-	Too high melting and insol. to give useable product.
359094-1	1268	3.37	950	0.35	-	0.0	Rapid	359373-1	-	-	-	
[illegible]	1268	3.24	[illegible]	[illegible]	-	0.0	Rapid	359373-2	-	-	-	
[illegible]	Epon 1004	1.68	1900	5.5	-	1.58	Fast	-	-	-	-	
[illegible]	1268	3.31	966	0.88	0.03	0.25	Rapid	359373	-	-	6.4	
[illegible]	1268	3.31	966	0.88	0.03	0.5	Rapid	359373	-	-	6.4	Tall Oil Fatty Acid.
[illegible]	Epon 1004	1.68	[illegible]	[illegible]	-	[illegible]	Slow	[illegible]	[illegible]	[illegible]	[illegible]	Tall Oil Fatty Acid.
[illegible]	Epon 1004	1.68	[illegible]	[illegible]	-	[illegible]	Slow	[illegible]	[illegible]	[illegible]	[illegible]	Dehydrated Castor Oil Fatty Acid.
[illegible]	TCBPA	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	TCBPA	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Rapid	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	TCBPA	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Fast	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	TCBPA	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	

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STLCOPCB4095355

NBP	Derivation (1)	% Epoxy	[illegible] Based on Epoxy	n	[illegible] Gl.	[illegible] Temp. (hrs)	Rate (2)	Resin Synthesis	Comment -
366994	1268	5.52	580	0.09	0.09	4.42	Slow	365988	End Av. 11.
367951	1268	-	-	ca. 0.13		2.75	Slow	367167	
367955	1268	ca. 4.0	800	0.5		[illegible]	Rapid	[illegible]-1&2	Very small amount of material; blend of two different lots of resin; values for resin approximate.
367956	1268	ca. 3.18	1000	1.0	-	[illegible]	Rapid	[illegible]-3&4	
367957	Epon 1004	1.68	1900	5.5	-	[illegible]	Slow		
367959	Epon 1004	1.68	1900	5.5	-	2.08	Slow	-	
367960	1268	5.52	580	0.09	0.09	3.25	Slow	365988	0.15% $Ca(OH)_2$ present as catalyst.
367961	1268	5.52	580	0.09	0.09	6.58	Slow	365988	0.2% Triphenyl Phosphite.
367964	1268	5.52	580	0.09	0.09	2.08	Slow	365988	End Av. 21.[illegible].
367965	1268	5.52	580	0.09	0.09	5.09	Slow	365988	End Av. 5.3[illegible].
3679[illegible]	1268	4.51	710	0.35	-	6.25	Slow	365997	End Av. 11.2[illegible]. - [illegible] added 3/4 through.
367969	1268	4.51	710	0.35	-	5.00	Slow	365997	End Av. 9.9[illegible] - $Ca(OH)_2$ at begin 0.15% [illegible]
367970	1268	5.65	566	0.06	-	1.00	Fast	365991	End Av. 4.72 - $Ca(OH)_2$
367971	1268	5.65	566	0.06	-	2.83	Slow	365991	End Av. 6.23 - $Ca(OH)_2$

(1) Numbers designate Aroclor, unless otherwise noted.
(2) Slow > 2 hrs, Fast > 1 hr < 2 hrs, Rapid < 1 hr.

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APPENDIX F

List of Notebook Pages

Gabbert - 370312-7

LeBlanc - 359388-9, 91-4, 96-99, 356400; 365951, -2, -4, -5, -8, -9, -63, -69; 365970, -1, -3, -4, -5, -6.

Sharp - 367259, -60, -2, -3, -5, -7.

Schwendeman - 354851 to 354881 incl., 354884 to 354900 incl., 359051 to 359054 incl., 359056 to 359083 incl., 359094 to 359100 incl., 364201 to 364207 incl., 364245 to 364247 incl., 366951 to 366952 incl., 366955, 366972 to 366974 incl., 366977-78, 366991 to 366995 incl., 373940, 373945.

Grant - 367951 to 52 incl., 367955 to 367994 incl., 379803, 379080.

Craver - 342751, 342752, 342792, 342797, 342798.

Herbig - 322801-07, 10-13, 23-27, -32, -34, -43; 330501, -04, -07, -08, -12, -15, 19-21, 23-44, 46; 336401-05, 09-14, -18, -48; 346552, -78, -89; 375801-04; 380715-16.

Koch - 342583, 92-93

Dazzi - 218932; 310448; 316057, 098; 323108, 131; 328956; 330507; 341300; 346529, 52, 78; 353864, 865, 889, 896, 897, 900; 353546, 547, 548; 367467, 367775.

APPENDIX C

List of Raw Materials

Aroclor 1270, 1268 and 1262	Monsanto
Tetrachlorobisphenol A	Monsanto
Bisphenol A	Monsanto
Diglycidyl ether tetrachlorobisphenol A	Experimental
Epon 1004 and 828	Shell
Epichlorohydrin	Shell
Soya Fatty Acid	Armour
Tall Fatty Acid	Arizona Chemical
Methanol	Carbide
Dimer Acid M-461-R	Emery
Allyl Glycidyl Ether	Shell
Maleic Anhydride	Monsanto
Triethylene tetramine	Carbide
Dimethylaminopropyl Amine	Carbide
Diethylaminopropyl Amine	Carbide
Phthalic Anhydride	Monsanto
Benthal	Monsanto
Fumaric Acid	Monsanto
Styrene	Monsanto
Pyromellitic Anhydride	DuPont
Durene diamine	Experimental
Diethylene triamine	Carbide
Phenylene Diamine	Mallinckrodt
Maleic Acid	Tennessee-Eastman
Diamino diphenyl sulfone	Experimental
Dimethyl Aniline	Eastman
Rezyl 1105	American Cyanamid

APPENDIX — LIST OF TABLES

APPENDIX I List of figures.

APPENDIX

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