HYDROLYSIS OF AROCLOR 1268 IN METHANOLIC SODIUM HYDROXIDE

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I PURPOSE

Hydrolyzed Aroclors offer Monsanto potentially cheap diphenols, possibly valuable as monomers and other chemical intermediates. Hydrolysis of Aroclor 1268 in ethylene glycol has previously been demonstrated in Pilot Plant quantities (Refs. 1-5).

However, epoxy resins derived from this material had poor properties traceable to the presence of appreciable (10%) monofunctional epoxy compound which acted as a chain stopper. This arose from precursor monophenol, formed during incomplete di-hydrolysis of the Aroclor.

Therefore, a hydrolysis study of Aroclor 1268 in methanolic NaOH under pressure was initiated, directed toward increasing the phenolic difunctionality of hydrolyzed Aroclor 1268 and reducing process costs.

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II SUMMARY

Methanolic alkaline hydrolysis of Aroclor 1268 under pressure was investigated. The process studied is similar to the Organic Chemical Division hydrolysis of tetrachlorobenzene to 2,4,5-trichlorophenol, and of hexachlorobenzene to pentachlorophenol (Ref. 6, 7). The product was isolated as dihydroxy Aroclor 1268.

Variables studied were time, temperature, excess NaOH and water concentration.

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III. CONCLUSIONS

Complete phenolic difunctionality in hydrolyzed Aroclor 1268 can be obtained by hydrolysis for 1 hr at 190°C in methanol using 80% excess NaOH. Hydrolyzed Aroclor 1268 having a neutral equivalent (N.E.) of 204 to 207 (theory N.E. = 205.6) was obtained reproducibly in nine runs under the above conditions.

Excess NaOH is the critical factor: if less than 80% excess was used, complete phenolic difunctionality was not achieved, even at longer reaction times and higher temperatures. Up to 10% water was not harmful.

Diglycidyl ether with good curing properties can now be prepared reproducibly in good yield and high oxirane oxygen content (91.2% of theory) from this hydrolyzed Aroclor 1268.

Raw material costs for the hydrolysis of Aroclor 1268 in methanol under pressure are calculated to be $0.13-0.16/lb compared with $0.18-0.25/lb for the ethylene glycol process (Ref. 8).

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IV RECOMMENDATIONS

PROCESS It is recommended that the 2-gallon process (Experimental Details Section) be scaled up to pilot plant quantities. The process provides a source of polychlorodiphenol from Aroclors.

Further process studies should be directed at establishing minimum hold period at 190°C with a continuous process as the ultimate objective. Other factors which should be established are optimum methanol-water ratio, recycle of the methanol, possible omission of the filtration step, and improvement in methanol recovery.

Hydrolysis of other Aroclors (1262, 1254, 1248, etc.) using 80% (or more) excess NaOH should be attempted. It seems probable that the 75% diphenol content of hydrolyzed Aroclor 1262 (St. Louis ethylene glycol run, Refs. 2, 3) could be increased significantly.

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V. DATA AND DISCUSSION

Increasing the excess NaOH on the hydrolysis of Aroclor 1268, as shown in Fig. 1, following, significantly increased the phenolic content of the product.

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 hr to 3 hr 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, N.E. was 215 after 3 hr (Run 9) as against 211 after 1 hr (Run 3), longer reaction times did not appear promising.

The reactions for the process appear to be:

1. $C_{12}H_{8.5}Cl_{3.5}$ + 4 NaOH → $NaO\,C_{12}H_{6.5}Cl_{3.5}\,ONa$ + 2 NaCl + $2H_2O$

(448)

2. $NaO\,C_{12}H_{6.5}Cl_{3.5}\,ONa$ + 2 HCl → $HO\,C_{12}H_{6.5}Cl_{3.5}\,OH$ + 2NaCl

(411.2)

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

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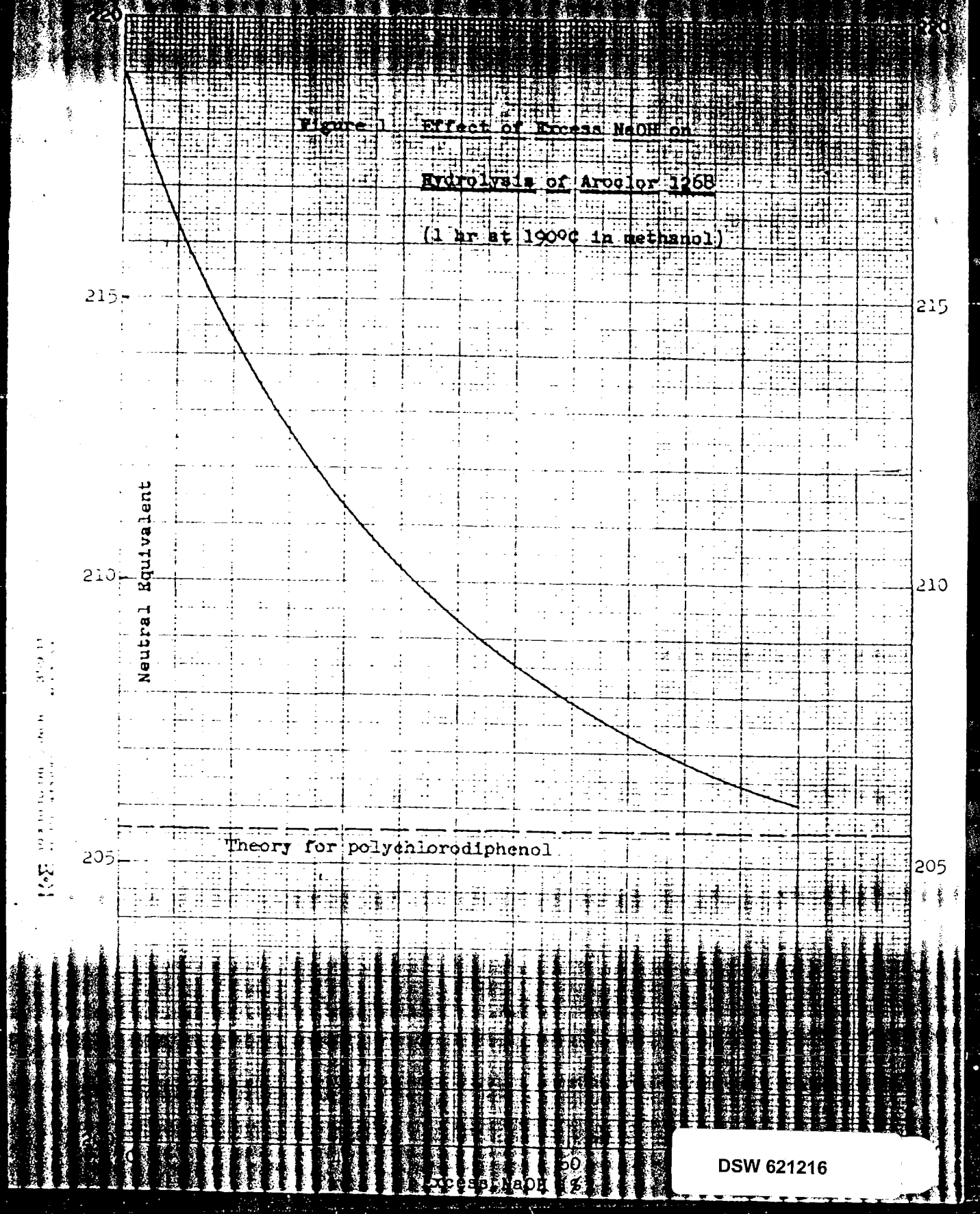

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Dimethyl ether, identified as a byproduct in other methanolic NaOH hydrolysis reactions, appears to be the main byproduct. About 30 g of a low boiler was trapped during venting of Run 17 (Experimental Section). Formation of dimethyl ether would account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

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

This will be checked.

The methanol recovery for Run 16 was 76%, (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 hr 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, Appendix for time-temperature-pressure plot).

Acidification was carried out above 90°C since below this temperature the product precipitates as a hydrate (Ref. 4). 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 203.6 to 207.6 N.E. was assumed to contain theory diphenol (205.6 calculated).

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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 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.

USES The Applied Ingenuity Research Group at Dayton (J. K. Craver, J. Schwendeman) has demonstrated epoxy ethers derived from hydrolyzed Aroclors when cooked with fatty acids are useful in surface coatings. This work is being continued, since surface coatings at present are the largest potential market.

Curing studies of these epoxy ethers as resins per se by the Plastics Evaluation Group (J. A. Herbig) have been carried out. It is recommended that general physical and chemical properties of these cured resins be determined.

Initially, Dr. J. Dazzi (Ref. 10) has recommended that hydrolyzed Aroclors should be useful in the following applications:

Epoxy resins
Polyethers
Polyesters
Polyurethanes
Polycarbonates
Industrial preservatives
Biological toxicants
Diethers (dielectrics and functional fluids)

*Anal. of St. Louis Tetrachlorobisphenol A
Lot No. Z-2046

	Calc.	Found
N.E.	183	182
% Cl	38.74	38.81
% OH	9.29	8.95

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VI PATENT STATUS

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

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VII. RECOMMENDED PROCESS

The 2-gallon process described in detail on p.11-12 of this report is recommended for scale-up to Pilot Plant batches. It is recommended that H_2SO_4 be used for acidification in the plant instead of conc. HCl.

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VIII COST ESTIMATES

A raw material cost estimate based on Run No. 14, Table I, and using figures of 60% and 80% methanol recovery follows:

60% Methanol Recovery

	Aroclor 1268	Methanol	100% NaOH	100% H_2SO_4	Total Costs per 100 lbs
lb/100 lb product	116.1	86	74.6	61.8	
Cost/lb	$ 0.07894	$ 0.0422	$ 0.025	$ 0.007	
Cost/100 lb product	$ 9.16	3.63	1.87	0.43	$15.09

80% Methanol Recovery

$15.09
-1.81

$13.28

The cost/lb figures were taken from pp. 8-9 of a report by T. F. Adams (Ref. 4) estimating cost of hydrolyzed Aroclors.

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IX EXPERIMENTAL DETAILS

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	Mixed heat off, 97 volts on variac
1001	190	510	
1016	192	550	
1101	193	605	Cooling water on
1108	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 [illegible] 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, 25 ml 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 2-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 to dissolve, most of the remaining NaOH was dissolved in

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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 hr to make sure it would remain acid and then allowed to separate. The water was decanted and the batch washed hot with 5 x 800 ml hot (90°C) distilled water, separating by decantation, after which a negative 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 and yield was 1300 g or 90%.

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X REFERENCES

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3. Lynch, D. K. Organic Research, St. Louis, Report No. 1706, "Hydrolyzed Aroclors 1262 and 1268 Sample Preparation", January 8, 1957.

4. Dazzi, J., R&E Dayton, memo to F. B. Zienty, "Hydrolysis of Aroclors", June 28, 1955.

5. Dazzi, J., R&E Dayton, memo to H. L. Hubbard, "Hydrolysis of Various Aroclors", August 19, 1955.

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8. Adams, J. F., Chem. Eng. Section, Organic Research, St. Louis, Report No. 56-3-11, "Cost Estimate (Grade 1) on Hydrolyzed Aroclor", March 6, 1956.

9. Wade, W. W., Research Dept. - Phosphate Division, Report No. 2317, Job No. 171-518, "The Preparation of Hexachlorodihydrozybiphenyl", February 4, 1949.

10. Dazzi, J., R&E Dayton, "The Aroclors and Other Halogenated Aromatics as Chemical Intermediates", January 16, 1956.

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XI APPENDIX

LIST OF NOTEBOOK PAGES

Dazzi - 360228-9
Gabbert - 370312-7
LeBlanc - 359388-9; 91-4, 96-99, 359400; 365951, -2, -4, -5, -8, -9, -63, -69; 365970, -1, -3, -4, -5, -6.
Sharp - 367259, -60, -2, -3, -5, -7.

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TABLE I

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

Run No.	NBP No.	Conditions: Temp. °C	Time hr	Excess NaOH, %	Maximum Pressure, psig	MeOH, g	H_2O, g	Results: Yield g	Yield %	N.E.[2]	% OH[2]
1	359388, 9	190	1	20	590	400	-	197.5	95	219	7.7
2	359391, 2	190	1	20	570	400	18	190	92	219	7.8
3	359393	190	1	40	660	400	-	190	92	211	7.7
4	359394	190	3	20	600	400	-	190	92	212	7.8
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
	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
12	365959	190	0.5	60	590	400	35	193	94	215	7.87
13	365958	190	1	80	520	400	35	190	92	206[5]	8.19
14	365963	190	1	80	605	400	35	193	94	206[5]	8.12
15	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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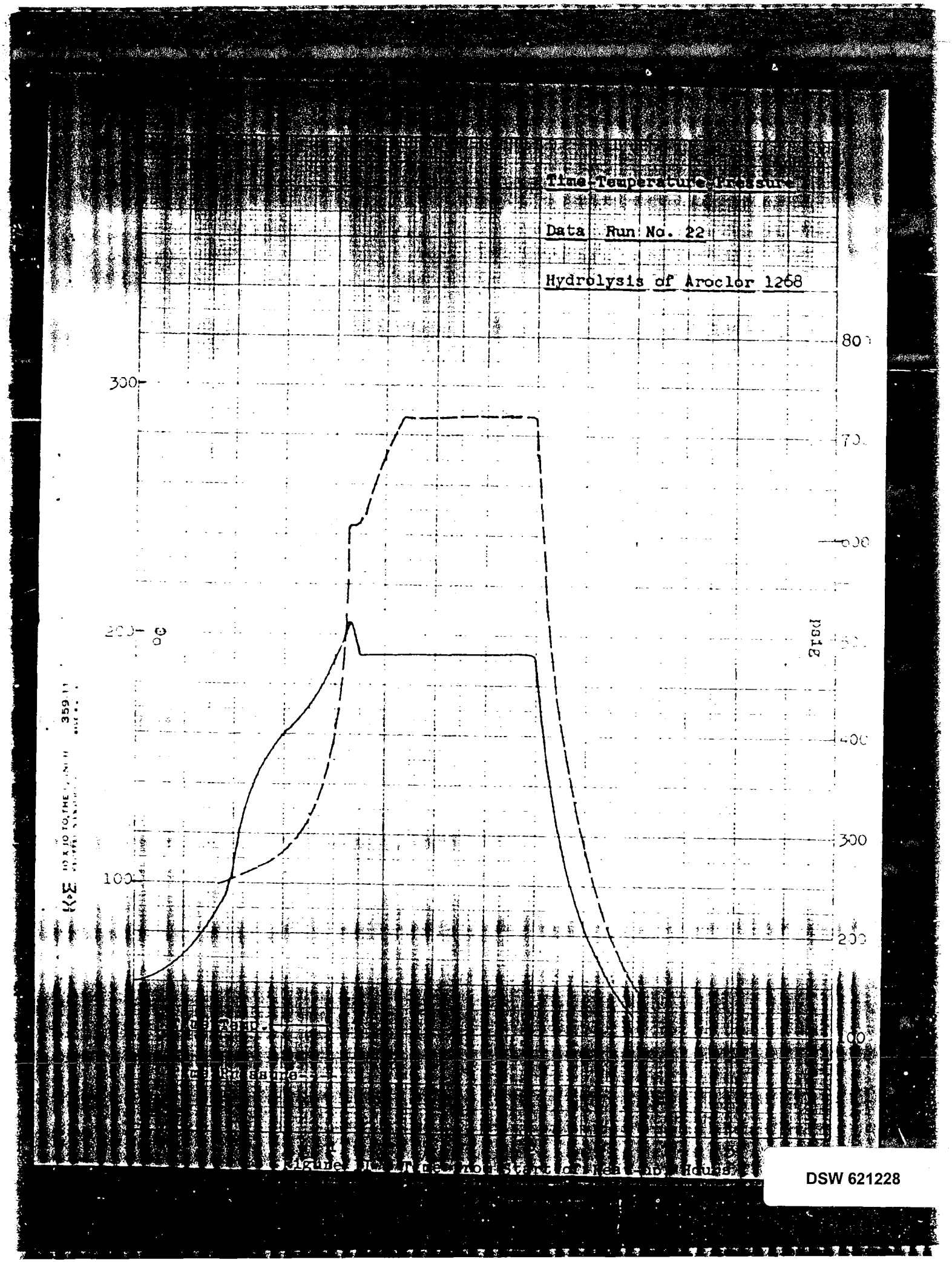
TABLE II

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 II; 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 over charge.



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