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FINAL REPORT

ON

HYDROLYZED AROCLORS 1262 and 1268

SAMPLE PREPARATION

Job No. 2-02-750.01-3038

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INTRODUCTION

Preliminary work at Dayton and Springfield indicated that hydrolyzed Aroclors (containing approximately two hydroxy groups per molecule of polychlorobiphenyl) were of interest in the field of epoxy and other type resins. The high halogen content of such polyhalogenated dihydroxy biphenyls could give flame retardent and other desirable properties to resins.

The Plastics Division at Springfield requested that the Organic Division prepare larger samples of hydrolyzed Aroclor 1262 and 1268 for further evaluation in their research and evaluation program.

SUMMARY

Suggested Procedures for the Preparation of Hydrolyzed Aroclors 1262 and 1268 (References 4 and 5) were prepared, based on the ethylene glycol-lye hydrolysis procedure supplied by J. Dazzi at Dayton. One batch each of Hydrolyzed Aroclor 1262 and 1268 were prepared in the pilot plant. Samples of these Hydrolyzed Aroclors were sent to Springfield and Dayton for use in their research and development programs. Hydrolyzed Aroclor 1262 was supplied both as the crude and distilled material and Hydrolyzed Aroclor 1268 as the crude material.

No extensive process development work was carried out and none is currently planned. Further work will depend on development of uses for these materials.

The Pilot Plant preparation of these materials has been reported (Ref. 6 and 7). A cost estimate for the production of the Hydrolyzed Aroclors has been prepared (Ref. 8).

CONCLUSIONS

Hydrolyzed Aroclors 1262 and 1268 can be prepared by the ethylene glycol-lye hydrolysis of Aroclors 1262 and 1268. However, minor process variations such as heat up time and temperature control apparently may cause some variation in the degree of hydrolysis and thus affect the uniformity of the finished product from batch to batch, as indicated by differences between laboratory and pilot plant prepared material. A certain degree of non-uniformity is to be expected when using mixtures such as Aroclors 1262 and 1268 as raw materials.

Ethylene glycol losses of approximately 25% may be expected, based on the evaluation of the water [illegible] from the pilot plant run of hydrolyzed Aroclor 1262. A considerable quantity of what appears to be diethylene glycol is formed.

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RECOMMENDATIONS

If further work is undertaken, process development for the preparation of Hydrolyzed Aroclors should include the study of the methanol-lye hydrolysis procedure which has been found successful on similar products at Nitro.

Various process controls that would assure as uniform a product as possible should also be investigated.

PATENT STATUS

The patent situation with regard to the hydrolysis of Aroclors using ethylene glycol as the solvent has been reviewed by the patent department. The following are their comments, quoted from a memo from A. J. Green to H. L. Hubbard dated February 2, 1956:

In view of the Organic Division's interest in manufacturing hydrolyzed Aroclors with sodium hydroxide in the presence of ethylene glycol, concern was expressed with respect to U.S. 2,509,245 and U. S. 2,692,899, which patents, respectively, relate to the hydrolysis of 1,2,4,5-tetrachlorobenzene to 2,4,5-trichlorophenol and to the hydrolysis of hexachlorobenzene to pentachlorophenol employing sodium hydroxide in the presence of ethylene glycol. It is our opinion that the proposed process for hydrolyzing Aroclors infringes neither U.S. 2,509,245 nor U. S. 2,692,899. While we feel there is no infringement problem with respect to the said patents, we wish to advise that we are further looking into this matter in order to determine whether there are any patents which would present an infringement problem.

REFERENCES

1. Procedure for Sample Preparation, Phosphate Division Research Dept. (1) Octochloro biphenoquinone, (2) Polychlorometaterpheno-quinone, October 20, 1947, Rueckert and Hartzog.

2. Procedures for the Hydrolysis of Aroclo[illegible]268, 1262, 1254, 1248 and 1242. See Appendix for procedures for Aroclors 1268 and 1262.

3. Minutes of Trip to Springfield to discuss Epoxy Resins and Intermediates Derived from Aroclors. March 12-15, 1956, J. Dazzi.

4. Suggested Procedure, St. Louis Research Report No. P-663, Preparation of Hydrolyzed Aroclor 1262, Job No. 2-02-750.01-3638, October 3, 1955, D. K. Lynch.

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5. Suggested Procedure, St. Louis Research Report No. P-664, Preparation of Hydrolyzed Aroclor 1268, Job No. 2-02-750.01-3038, December 16, 1955, D. K. Lynch.

Final Report, St. Louis Research Report No. 1335, Pilot Plant Preparation of Hydrolyzed Aroclor 1262 November 14, 1955, J. C. Goss.

6. Final Report, St. Louis Research Report No. 1528, Pilot Plant Preparation of Hydrolyzed Aroclor 1268, Job No. 2-02-750.01-3093, May 29, 1956., J. C. Goss.

EXPERIMENTAL

The experimental work on the hydrolysis of Aroclors 1262 and 1268 was based on the procedures supplied by J. Dazzi at Dayton (Reference 2). and included in the appendix.

The initial laboratory preparation of a sample of Hydrolyzed Aroclor 1268 for Springfield was carried out as follows:

A three liter three necked flask equipped with an agitator, thermometer, and twelve-inch punched column and still head was charged with 908 g. (2.0 moles) Aroclor 1268, 704 g. (8.8 moles) 50% lye and 1680 g. (27 moles ethylene glycol. The mixture was heated with agitation, distilling off water as necessary to attain and maintain a batch temperature of 190-200°C. for one hour. The reaction mixture was cooled to 80-100°C., transferred to a five liter three necked flask equipped with an agitator, and diluted to four to four-and-a half liters with hot water. Sufficient 60° Be sulfuric acid was added with agitation to neutralize the excess lye, liberate the hydrolyzed Aroclor and adjust the pH to 1-2 (approximately 300 g. of acid was required). The layers were allowed to separate and the water layer decanted.

The oil (hydrolyzed Aroclor) was washed by decantation, stirring each wash 10-15 minutes at 85-95°C. until the pH of the batch was in the range of 5-5.5. These washes removed the excess sulfuric acid and ethylene glycol. Four to six washes were required.

The oil layer was then dried by distilling off the water under reduced pressure to a final temperature of 140-150°C. and a pressure of 25-30 mm Hg Abs.

The product was cooled to 110-150°C., poured into pans to solidify and finally milled in a blender, using dry ice as a coolant.

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770-790 grams of milled material was obtained per batch, which represents a yield of 92-94% of theory based on the Aroclor 1268 charged. The product, a composit of three batches, has a total chlorine content of 53.2% and an equivalent weight of 232.5. Theory values are 52.7% and 217 respectively. The values for lot no. L-1044 hydrolyzed Aroclor 1268 obtained from J. Dazzi are 53.05% and 245.2 respectively.

The procedure used for Hydrolyzed Aroclor 1262 was essentially the same as that for Hydrolyzed Aroclor 1268 except that the product was refined by a high vacuum distillation.

Charges for a typical laboratory batch were:

Material	Wt. in Grams	Moles
Aroclor 1262	585	1.5
50% lye	528	6.6
Ethylene glycol	490	11.25
Sulfuric acid (approx.)	190	1.9

The ethylene glycol (solvent) concentration in the laboratory was varied from 6.67 to 10 moles per mole of Aroclor 1262 with no apparent change in the quality of product. The sulfuric acid used in the laboratory was 96% acid diluted to about 60° Be strength. 530 g of Crude Hydrolyzed Aroclor 1262 was obtained from the typical run. 95% recovery of the crude was obtained on the flash distillation of the crude at 190-200°C. at 2-5 mm. Hg. abs. pressure.

Typical material prepared in the laboratory had a total chlorine content of 48-50% (theory 48.1%) and an equivalent weight of 220-230.

Methods other than distillation were tried, either independently or in combination, to obtain a light colored hydrolyzed Aroclor 1262. These were: (1) hydrolysis under an atmosphere of nitrogen with and without a reducing agent (Na_2SO_3), (2) coal treatment of the reaction, filtering before or after partial neutralization, (3) coal treatment of the dehydrated crude in a solvent followed by solvent removal. Lighter colored materials were produced, but none approached the quality of the distilled material.

DISCUSSION

An equivalent quantity of flake or 70% caustic could be substituted for the 50% lye. In this case the flake caustic is completely dissolved in the ethylene glycol before addition of the Aroclor

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As the hydrolysis reaction reaches 190-200°C. a considerable quantity of heat is liberated. The batch will foam badly if allowed to boil too vigorously at this point. On larger scale runs, consideration should be given to the addition of 50 or 70% lye over a period of time to the Aroclor in ethylene glycol at reaction temperature.

No practical controls for the completion of the hydrolysis have been worked out.

The oil layer holds up a considerable quantity of water, possibly due to the formation of a hydrate.

Hydrochloric acid may be substituted for sulfuric acid in the acidification step.

A flash type distillation, in the case of Hydrolyzed Aroclor 1262, is preferable since better recoveries are obtained and the material is exposed to heat for a shorter period of time.

The distillation step was included, in the case of Hydrolyzed Aroclor 1262 in order to supply a material equivalent to that originally submitted to the Plastics division from Dayton. It is possible that the crude material may find some application in the plastics field.

The difference between the OH and Cl content of the hydrolyzed Aroclors prepared and the calculated values may be due to one or more of the following. (1) incomplete hydrolysis, (2) condensation of two moles of the hydrolyzed aroclor to form a bis diphenyl ether (3) analytical errors due to the difficulty of converting all of the organic chlorine to ionic chlorine by standard analytical procedures.

Recovery of ethylene glycol was not studied in detail, however laboratory recovery of ethylene glycol from samples from the pilot plant preparation of Aroclor 1262 showed a possible loss of 25% of the glycol charged. Some of the ethylene glycol appears to be converted to a high boiling product which appears to be diethylene glycol.

DESCRIPTION OF RECOMMENDED PROCESS

The descriptions of the recommended processes for Hydrolyzed Aroclors 1262 and 1268 are embodied in the respective Suggested Procedures, references 4 and 5. Additional discussion concerning these procedures will be found in this report and in the Final Reports for the Pilot Plant Preparation of Hydrolyzed Aroclors 1262 and 1268, References 6 and 7.

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COST ESTIMATES

A cost estimate, grade 1, on Hydrolyzed Aroclors has been prepared by J. F. Adams of the Chemical Engineering Section, designated Evaluation Report No. 56-3-11, Job No. 2-02-750.01-3156 dated March 6, 1956.

MATERIAL SPECIFICATIONS AND ANALYTICAL METHODS

These items will be found in the appropriate sections of the Suggested Procedures for Hydrolyzed Aroclors 1262 and 1268, References 4 and 5.

TOXICITY AND HAZARDS

For discussion of these items see the appropriate sections of the Suggested Procedures for Hydrolyzed Aroclors 1262 and 1268, References 4 and 5 and the Final Reports on the Pilot Plant Preparation of Hydrloyzed Aroclors 1262 and 1268, References 6 and 7.

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APPENDIX

The following procedures were supplied by J. Dazzi at Dayton for the preparation of Hydrolyzed Aroclors 1262 and 1268

Notebook pages covering the work reported herein are as follows:

A 69705-69710, A69715-69725
A 69727-69729, A69743, A74421

PROCEDURE FOR THE HYDROLYSIS OF AROCLOR 1268

Apparatus:

a 5-l., 4-neck Pyrex flask equipped with a good agitator, thermometer, 17 inch Vigreaux column bearing a distillation head, and Glas-col heater was used for the hydrolysis step.

Charge:

1.5 moles (681 g.) Aroclor 1268 ($C_{12}H_{1.3}Cl_{8.7}$, m.w. 454).

6.6 moles (264 g.) NaOH flakes (10% excess)

20 moles (1240 g.) ethylene glycol (techn.)

Procedure:

The following is a sample procedure:

The ethylene glycol is placed in the flask and the NaOH is added at once; the heat of solution brings the mixture temperature up to 70-75°C. The mixture is heated further, if necessary, to complete the solution of the NaOH. (85-90°C). At this point the Aroclor 1258 is added in one portion. The mixture is heated, with continuous removal of water to 190°C. and the temperature is maintained at 190-200°C. for one hour. The mixture is allowed to cool to 100-120°C. 2.1 of hot water are added and the mixture filtered while hot. The residue represents 1-5 g. of unreacted Aroclor 1268. The filtrate is stirred at 70-80°C. (heat if necessary) and concentrated HCl is added until the mixture is strongly acid (about 3.6 moles necessary). This yields a brown viscous oil which is only slightly soluble in water. The material is separated in a pre-heated separatory funnel and is then washed twice by stirring vigorously for 10-15 minutes at 70-80°C. with 1500 ml. portions of hot water; the washes being separated in the same manner. The material is dried by heating to 150°C. at 20-25 mm. pressure.

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Yield 90-95% conversion and yield of dihydroxypolychlorodiphenyl (not counting ~~few~~ grams of dihydroxy compound which precipitates from the wash water on standing at room temperature.

Comments

Hydrolyses of other Aroclors has indicated that the amount of ethylene glycol necessary may be reduced, but no experiments have been made with Aroclor 1268 using less ethylene glycol as yet.

PROCEDURE FOR THE HYDROLYSIS OF AROCLOR 1262

Apparatus:

The apparatus used was the same as that used in the hydrolysis of Aroclor 1268 except that the column and distillation head were replaced by a reflux condenser.

Charge:

1 mol (390 g.) Aroclor 1262 ($C_{12}H_{9.25}Cl_{6.75}$, M.W. 390).

15 moles (930 g.) ethylene glycol (techn.)

4.4 moles (176 g.) NaOH flakes (10% excess).

Procedure:

The procedure is that used for Aroclor 1268 except that the material is kept at reflux (about 160°C) for 12 hours during the hydrolysis.

The yield is 90-95%.

Comments:

This work was done before later work with Aroclor 1268 showed that higher temperatures, and resultant shorter hydrolysis time, could be obtained by removal of water from the reaction mixture.

Analysis:

Found	C - 39.71%	
	H - 2.03%	
	Cl - 51.53%	
Calc'd for $C_{12}H_{5.25}Cl_{4.75}O_2$:	C - 41.20%	
	H - 1.51%	
	Cl - 48.14%	
(Calc'd for $C_{12}H_{3.25}Cl_{5.75}O_2$:	C - 39.59%	
	H - 1.00%	
	Cl - 59.23%	

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