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INTERDIVISIONAL TRANSFER OF TECHNOLOGICAL DEVELOPMENTS

cc: H. K. Nason
R. M. Morris
E. W. Gluesenkamp
F. B. Zienty
D. T. Mowry
M. C. Throdahl
J. S. Hayes

To: Dr. J. H. Lum
Director, R&D
Organic Chemicals Division

AROCLOR 1242 WITH IMPROVED DIELECTRIC PROPERTIES

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DESCRIPTION OF PROJECT

A study of a market survey report by John S. Harris of Organic Division Development (Ref. 1) and our own preliminary investigations led us to the conclusion that an attempt should be made to improve the following properties of Aroclor 1242:

(a) Dielectric constant (Dk) ($5.8_{25°}$)
(b) Pour point (-19°C)
(c) High temperature stability

We have had gratifying success in improving property (a) and our results constitute the subject of this report.

Result:

A dielectric material, Aroclor 1242' with a Dk of 6.7-7.2, and a practical procedure for its preparation believed subject to patent coverage.

HISTORICAL BACKGROUND

"We have very few products of which we are the only manufacturer, and the Aroclor family is a prime example. It has had a long and profitable history and last year (1955) some 33 million pounds were sold for over $5 million - two-thirds of this for electrical use. Notwithstanding its low price, it gives us a very good return on investment. But with our protective patents gone, and a half-dozen other chemical manufacturers looking at the Aroclors, we stand a good chance of losing our hold on these products at any time. With the electrical sales alone estimated in 1965 from 30 to 55 million pounds, this would be quite a loss."

This quote from Ref. 1 explains why we are carrying out a research program in this area.

*This report was written by Harold Weingarten; Van R. Gaertner, Group Leader.

The process described in this report was developed as a direct result of a three-phase fundamental study carried out during the last two years.

Phase one, the study of the Gomberg reaction, permitted the laboratory preparation of high Dk chlorinated biphenyls leading to the discovery that an increase of one or two units in the Dk of chlorinated biphenyl mixtures did not adversely influence the power factor or resistivity. Phase two, the study of biphenyl chlorination, revealed 2,4'-dichlorobiphenyl as the precursor of most of the high Dk trichlorobiphenyls. A summary of this work is given in Table I. And Phase three, the study of the distribution of isomers in Aroclors, revealed Aroclor 1232 to be an excellent source of 2,4'-dichlorobiphenyl (see Table III). Figure 1 summarizes the isomer distribution study made on Aroclor 1242. The vapor phase chromatogram of Aroclor 1242' is included for comparison. Also included in Figure 1 are the estimated Dk's of the trichlorobiphenyls arising from the 2,4'-isomer.

This project was begun in February of 1957 and the total expense through June, 1959, was $89,965.

CHARACTERIZATION

Process

Method (a)

1. Aroclor 1232, made by direct chlorination of biphenyl (not by blending 1221 and 1242), is fractionally distilled* (see Figure 2) and the fraction rich in 2,4'-dichlorobiphenyl (85 to 100%)** is used in the next step.

2. The fraction rich in 2,4'-dichlorobiphenyl is chlorinated to the trichloro level according to the standard Aroclor processing conditions. Purification is also carried out by the standard Aroclor method.

3. The low boiling fractions can be recycled through the chlorinators or used as Aroclor 1221.

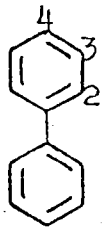
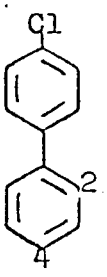
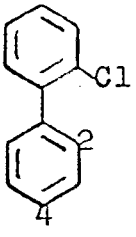
4. The high boilers are chlorinated to higher levels for non-capacitor uses. A sample of Aroclor 1260' was prepared in this way and sent to Organic Division for comparison with standard Aroclor 1260. Its physical properties and Dk were found to be essentially identical to the standard Aroclor 1260. Table II described the comparison (Ref. 4). Minor instability was apparent but can presumably be corrected by proper treatment.

*For details see references 2 and 3.

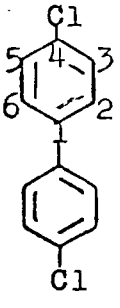
**Vapor phase chromatography is used to follow the distillation and determine the purity of the desired fractions.

TABLE I

BIPHENYL CHLORINATION STUDY

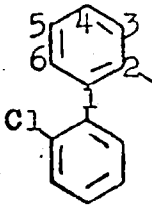
2	4			2	4
26%	74%	$\xleftarrow[Cl_2\ R.T.]{HoAC:CCl_4}$		$\xrightarrow[Cl_2\ 40^o]{FeCl_3}$ Benzene or CCl_4	43%	57%
32	68	←		→	45	55
22	78	←		→	46	54

No reaction in 40 days

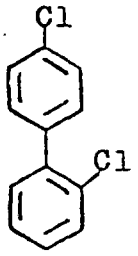


→ Orthene solvent

2	3
80%	20%



3	4	5	6
24%	10%	60%	5%



Must give all six isomers in about the same order of magnitude

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Figure 1. Aroclor Component Study

MATERIAL FLOW FOR PRODUCING 15 M LB/YR OF MODIFIED AROCLOR 1242 FROM AROCLOR 1232

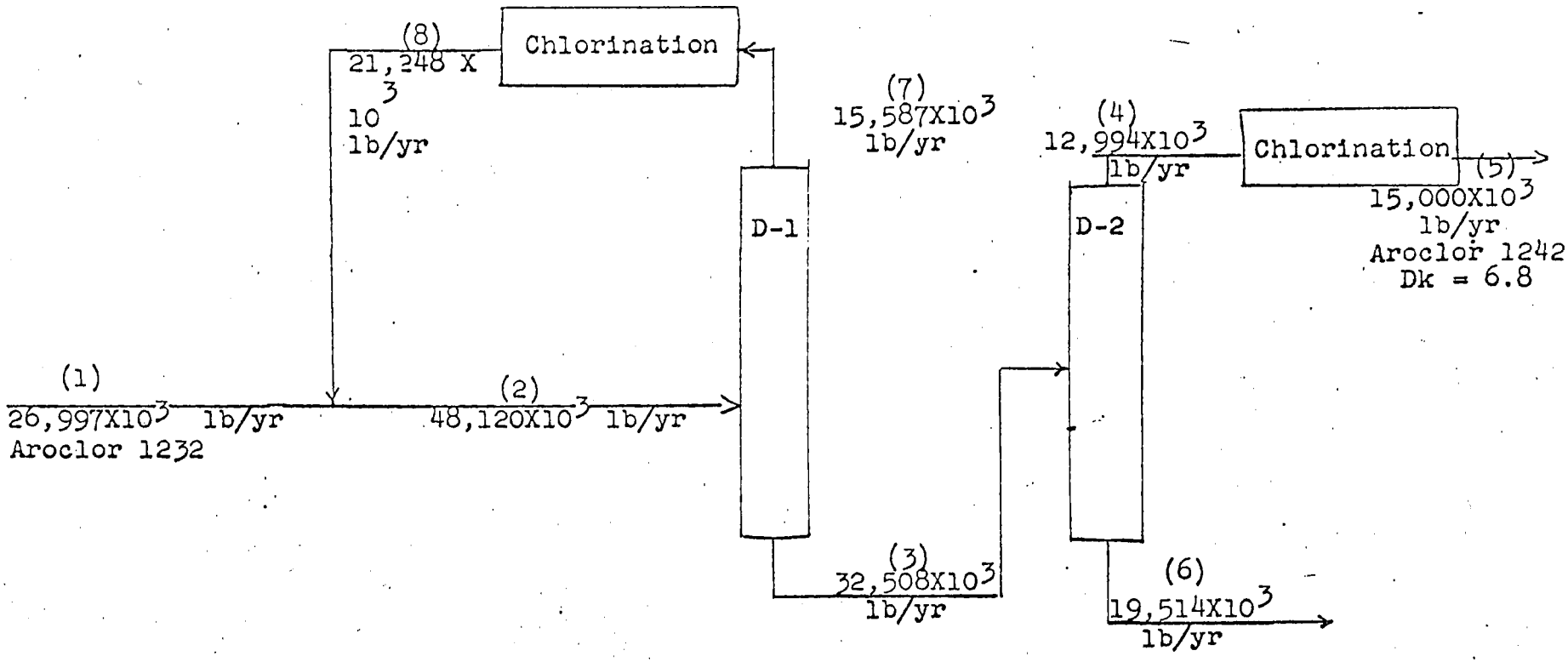

Figure 2

TABLE II

Property	Aroclor 1260 Dayton Lot T-656	Aroclor 1260 Specifications
Color, APHA	45	150, max.
Condition	Clear	Clear
Sp. Gr. at 90/15.5°C	1.555	1.555-1.566
Acidity, mg ROH/gm.	0.002	0.014, max.
Moisture, ppm	20	35, max.
Viscosity at 210°C, SUS	72.4	72 - 78
Refractive Index at 25°C	1.6459	1.6455 - 1.6470
Inorganic Chlorides	NDA	No detectable amount
Pour Point, °C	28	25 - 34
Distillation Range		
ASTM D-20		
10% Distilled by wt.	392°C	385-398°C
50% Distilled by wt.	395	390-404
90% Distilled by wt.	411	400-420
Corrosion Test (6 hrs. at 210°C with bright Aluminum foil)		
Change in wt. of Al.	None	None
Color	45	150, max.
Condition	Clear	Clear
Acidity	0.003	0.014, max.
Inorganic Chlorides	0.1 ppm	NDA
Dielectric Constant, 100°C, 1kc	3.8	3.6 - 3.8
Power Factor, 100°C, 1kc	0.21%	----
Resistivity, 100°C	825×10^9	500, min.
Dielectric Strength at 25°C	35 KV	30 KV, min.
Monsanto Stability Test (16 hrs. at 210°C)	0.8 ppm	0.7 ppm, max.

Method (b)

1. Aroclor 1232-S is prepared by chlorinating biphenyl in the presence of $FeCl_3$ and sulfur as catalyst.

   Typical experimental conditions: Melt 4 kg of biphenyl in convenient size 4-neck flask fitted with stirrer, thermometer, gas inlet and outlet apparatus. Add 20 g $FeCl_3$ (anhyd. sublimed)* and 11 g of sulfur (flowers)*.

*A ten-fold excess of catalyst was used here as a precaution against losses due to atmospheric moisture.

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Pass in chlorine gas as rapidly as possible maintaining temperature at 100°C. Continue chlorination until liquid density reaches 1.280 (25°C).

Pass dry nitrogen through the crude maintaining temperature at 80 to 90°C until HCl is removed. Add 30 g $Ca(OH)_2$ (powdered) and distill through a 6 to 8" distilling head, taking all that comes over. The boiling range is about 130 to 215°/10 mm.

2. The Aroclor 1232-S is then put through a fractional distillation exactly as described in method (a).

Method (b) provides us with three advantages as a result of the difference in isomer distribution (Table III).

TABLE III

TYPICAL ISOMER DISTRIBUTION: AROCLOR 1232 STANDARD

2-Chloro	4-Chloro	2,2'-	2,4-	2,4'-	4,4'-	Trichloro
18%	8%	14%	6%	32%	13%	9%

TYPICAL ISOMER DISTRIBUTION: AROCLOR 1232-S

1%	0	12%	1%	44%	31%	13%

The first advantage is flexibility. For example, we can remove essentially all monochlors without greatly increasing trichlors thus eliminating the recycle process. The second advantage is an increase in 2,4'-isomer concentration. And third, the 2,4-isomer is greatly reduced thus simplifying the fractionation since the 2,4-isomer is the most difficult contaminant to remove.

ESTIMATED COST

Based on a production volume for Aroclor 1242' of 15 million lbs. per year R. C. Binning has estimated the new distillation facilities would cost $600,000. He has further estimated that for an incremental sales price of 4.0¢ per lb. for Aroclor 1242' a 35% return on this investment (after taxes) could be realized. J. O. Bright of Organic Division Research Dept. has also prepared an economic evaluation of the Aroclor 1242' process (Ref. 5).

The estimate above does not cover the use of $FeCl_3$ + S catalyst, which should be more favorable.

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RELATIONSHIP TO EXISTING PROCESS

One of the most favorable aspects of the process under discussion is the relatively small change it will cause in the existing process, requiring little more than the installation of the fractional distillation equipment (see Figure 2). Since the new process involves a fractionation the fate of the chlorinated biphenyl byproduct (low Dk dichlors) is of great importance. We feel certain this problem can be handled by the chlorination of the byproducts to higher Aroclors such as 1248, 1254, 1260 etc. These higher Aroclors are expected to have essentially the same physical properties as the corresponding standard Aroclors. This is borne out by the properties of Aroclor 1260 prepared from the low Dk dichloro byproduct (see Table II).

Also important is the ratio of high Dk dichlors (to be converted to Aroclor 1242') versus the low Dk dichlor byproduct. Assuming optimistically that all of the Aroclor 1242 to be replaced by Aroclor 1242' and all of the low Dk dichloro byproduct to be converted to higher Aroclors, Table IV was constructed to show that a reasonable product balance is possible.

TABLE IV

Aroclor	Yearly Production $\overline{M}$ Lbs. [based on Aug. 1958 to Apr. 1959 (Ref. 6)]	Amount of Dichloro Required $\overline{M}$ Lbs.
1242	12.6	11.0
1248	4.05	
1254	6.3	
1260	7.45	12.4
1262	0.42	
1268	0.15	

Product Balance

	Aroclor 1242'	High Dk Dichlor	Low Dk Dichlor
Example (A)	12.6 $\overline{M}$ lbs.	11.0 $\overline{M}$ lbs.	16.4 $\overline{M}$ lbs.
Example (B)	12.6	11.0	14.0
Example (C)	12.6	11.0	11.0

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The yearly production data (Ref. 6) is based on monthly averages from August 1958 to April 1959 for both the Anniston and W.G.K. plants. 12.6 $\overline{M}$ lbs. of Aroclor 1242' requires 11.0 $\overline{M}$ lbs. of dichloro precursor while all of the remaining higher Aroclors require 12.4 $\overline{M}$ lbs. Three examples are given under product balance (Table IV) to describe the limits of high Dk dichlor versus low Dk dichlor distribution. Example (A) was actually calculated by R. C. Binning (see Refs. 1 and 2) based on the composition of current Aroclor 1232 and shows a surplus of low Dk dichlor byproducts. Example (B) was estimated based on the composition of Aroclor 1232-S (see Table III) and the low Dk dichlors are found to be much closer to the 'ideal' 12.4 $\overline{M}$ lbs. Example (C) is an estimated lower limit for the production of dichloro byproducts, assuming a lower degree of chlorination to give negligible trichlors. Both (A) and (B) can then be made to approach (C) more closely by a judicious selection of the degree of chlorination and the conditions of recycle of monochlors to recover more of the 2,4' values.

PRODUCT

Specifications

Aroclor 1242' -

Dk_{25°	6.7 to 7.2
ASTM pour point	-19°C

The other properties should be identical to those of standard Aroclor 1242 which are listed here for reference.

Density 25°	1.380
Distillation range	325-360°
Refractive index D-line 20°	1.627-1.629

Outstanding Features

Aroclor 1242' has a Dk between 6.7 and 7.2 compared to a Dk of 5.8 for standard Aroclor 1242.

MARKETS

(This section supplied by J. K. Craver, R&E Development)

Based on estimates made by the Organic Development Department, there appears to be a market of from 5-15 million pounds per year for a high dielectric constant fluid to be used in low voltage power-factor correction capacitors. This is in addition to those markets now served by the regular Aroclors and would have to be developed over the next 5-10 years. In addition to satisfactory physical and electrical properties, Organic feel that any new product should be patentable and that the selling price should not be higher than 30¢/lb.

The R&E Patent Department believe that we will have patent coverage on the processes for producing the high Dk Aroclor.

A sales price in the range of 19-20¢/lb. would yield 40% pre-tax return according to calculations made by Organic Research (Ref. 5). This estimate assumes the fractional sparation of a pure 2,4'-dichlorodiphenyl isomer which is then chlorinated to a trichlorodiphenyl of high Dk. The lower-boiling chlorinated diphenyls are recycled and the higher-boiling materials are used to produce the conventional Aroclors. Production rates of 5-15 million pounds per year are assumed. At this price level, we feel the improved Aroclors described in this report should be of considerable interest to the electrical industry, particularly in low voltage devices.

We are aware that there are a number of other new dielectrics being considered by the trade; tolyl xylyl sulfone, 2,2'-dichlorodiphenyl ether and hexachlorobutadiene to name three that seem especially promising. However, the already established position of the Aroclors and their history of reliability at low cost should make the job of introducing an improved grade much simpler than that of bringing out an entirely new product such as tolyl xylyl sulfone or hexachlorobutadiene. The picture on 2,2'-dichlorodiphenyl ether is somewhat more enigmatic since much depends upon the relative costs of the raw materials.

REFERENCES

1. J. S. Harris, "Liquid Dielectrics and Aroclor: A Market Survey", Development Department Report O.D. 1134, August 15, 1956.

2. R. C. Binning, Report to R. W. Schuler on Relative Volatility of Aroclor 1232 Components, Dayton, April 8, 1959.

3. R. C. Binning, Report to R. W. Schuler on Fractionation Requirements for Separation of 2,4'-Dichlorobiphenyl from Aroclor 1232, Dayton, June 5, 1959.

4. A. M. Ellenburg, memo to Harold Weingarten on Aroclor 1260 from Special Process, St. Louis, September 8, 1959.

5. J. O. Bright, memo to F. B. Zienty, August 5, 1959, Economic Evaluation of High Dk Aroclors.

6. A. M. Ellenburg, memo to M. Kosmin on Aroclor Process, St. Louis, June 8, 1959.

7. H. Weingarten, memo to G. F. Deebel on Preparation of Aroclor 1242' and 1260', Dayton, July 28, 1959.

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8 . H. Weingarten, memo to A. M. Ellenburg, on Compositions of Aroclor 1232 by Catalytic Variations, August 13, 1959.

9 . H. Weingarten, Progress Report on Dielectrics, Issue 23, June, 1959.

RECOMMENDATIONS FOR FUTURE WORK

At Organic Division

We recommend that a study be carried out to determine the optimum level of 'dichlorination' and recycle chlorination. The optimum level will, of course, be related to the desired product balance between high Dk dichlors and low Dk dichloro byproduct. We further recommend that the process details be firmed up and moved into the pilot plant stage as soon as possible since there is likely to be a two-year lag between the time we present our customers with samples and the time they complete their evaluations for acceptance.

At R&E Division

The pour point of Aroclor 1242 is another property we are anxious to improve while retaining a high Dk. A study of the viscosity of a series of chlorinated biphenyl isomers and the three lower Aroclors (Ref. 9) convinced us that the viscosity and pour point are related to the degree of chlorination and not related to isomeric structure. We are, therefore, in the process of testing high Dk Aroclors intermediate between 1232 and 1242. Estimated completion time - 3 months.

We also plan to finish our chlorination and component studies and examine the possibilities of improving the Aroclors (pour point and Dk) with ether type additives. Estimated completion time - 12 months.

PATENT SITUATION

We have filed a patent application (C2167) directed to the dielectric composition of matter, the process of preparing same described above as methods (a) and (b), and electrical capacitors employing the new dielectric composition. To date we have not received the first Office action from the Patent Office.

Additionally we have filed a patent application (C2088) directed to high Dk Gomberg chlorinated biphenyls as dielectric compositions of matter, the method of preparing same, and electrical capacitors utilizing these Gomberg mixtures. The first Office action has been received from the Patent Office and five claims directed to the electrical capacitors have been held to be allowable.

ACKNOWLEDGMENTS

The acknowledged items listed below are to be given by the Organic Chemicals Division via memoranda between General Managers to be attached as addenda to each copy of this report.

A. Acceptance, reason and data.
B. Requirements for and availability of manpower to initiate and carry on the project.
C. Program and time schedule for further development of the project.

F. C. Meyer
Associate Director

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