[illegible] LIQUIDS: FORMATION, COMPOSITION AND IMPROVEMENT OF AROCLOR 1242

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I. PURPOSE

A market survey report (Ref. 1) by John S. Harris of Organic Division Development very clearly underlined the need for expanding our research efforts on the subject of dielectric liquids. The following quote from this report will obviate further discussion of motives for undertaking the research.

> "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."

In the initial phases of the research carried out at Dayton the objectives were necessarily vague and generalized. They were stated as follows:

1. Study stability, electrical properties and methods of purification of highly polar liquids.

2. Develop patentable compositions and processes for dielectric properties, thermal stabilities, and pour points superior to those of presently available dielectric liquids.

Although these objectives are still valid, they have been greatly altered and refined during the course of research.

The period covered by this report extends from March, 1957 to January, 1960.

II. SUMMARY AND CONCLUSIONS

Although the literature abounds in dielectric constant (Dk) values for the more common organic liquids, resistivity (R) and power factor (PF) data are quite sparse. Aside from the published electrical properties (Dk, R and PF) for the commercial dielectric liquids, the only other available data was in Monsanto reports (Ref. 2) or PB reports. Therefore,

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We felt necessary to begin our program by measuring the electrical properties of a number of representative organic liquids. To this end a series of amides, ketones, ethers, nitriles, alcohols, esters, sulfonamides and halogenated aromatics were subjected to preliminary electrical screening. These materials, ranging in Dk from 3 to 116, were compared to commercial dielectric liquids. We were convinced as a result of this comparison that the next marketable improvement over the Aroclors would be small, occurring in the range of Dk = 6 to 10. This conclusion is not new but it was necessary for us to verify it independently and it has since served as the foundation for subsequent research.

The principal outcome of the above conclusion was our decision to subject the Aroclors themselves to a more detailed scrutiny. We know the Aroclors to be good - they have maintained a firm market position for more than twenty years. We, therefore, set out to answer two questions. What are the Aroclors? How are they formed? Hopefully in the process of getting answers we would discover what made them good, how they might be improved and what the prospects are for finding new type dielectric liquids.

The component study and chlorination study herein reported depend heavily on each other but are presented independently in the interest of clarity.

With vapor phase chromatography as the principal tool, our component study has been able to answer, to a large extent, the question of what the Aroclors are. Aroclors 1221 and 1232 have been more or less completely characterized (see Figure II). Aroclors 1242 and 1248 have been shown to be mixtures containing over twenty chlorinated biphenyls, most of which have been identified (see Figure III). Furthermore, it was demonstrated that a number of these components (mostly trichlorobiphenyls) have Dk's between 6 and 12.

Simultaneous with the component study, a chlorination study was carried out to determine how the Aroclors are formed. Biphenyl, 2-chlorobiphenyl, 4-chlorobiphenyl, 2,2'-trichlorobiphenyl and 4,4'-dichlorobiphenyl were each monochlorinated. The result of this study (see Figures V, VI, and VII) allowed the course of the chlorination reaction to be outlined in stepwise fashion. The most important piece of information gleaned in this study is the fact that the 2,4'-dichlorobiphenyl is the precursor of most of the high Dk trichlorobiphenyls in Aroclor 1242.

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The knowledge that Aroclor 1242 contains components having Dk's between 6 and 12 and that the precursor of these components is 2,4'-dichlorobiphenyl has provided the foundation for a promising process modification (Ref. 3). The previous discovery that Aroclor 1232 is rich in 2,4'-dichlorobiphenyl (30-40%) (see Figure II) narrowed the problem down to separating the 2,4'-isomer from Aroclor 1232. Below is a self-explanatory outline of the process as it has been currently evolved.

1. Aroclor 1232 is fractionally distilled.

2. The fraction, rich in 2,4'-isomer (82-100%), is chlorinated to the trichloro level yielding an Aroclor 1242' having a Dk between 6.7 and 7.2.

3. The low boiling fractions, which cannot be efficiently recycled, and high boiling fractions are combined and chlorinated to higher levels for non-capacitor uses.

Research is continuing toward improvement of the above process particularly with respect to the effects of catalyst changes on the Aroclor 1232 isomer distribution.

III. R E C O M M E N D A T I O N S

SHORT RANGE It is recommended that necessary research to define the Aroclor 1242' process be completed during the projected two-year life test period. This will insure an optimum product and process. It is further recommended that Organic Division research investigate the advantages of catalysts other than $FeCl_3$ in the preparation of Aroclor 1232 and determine the extent of interest in an Aroclor 1237 with $Dk_{25°}$ 6.5 and a pour point of -26°C.

LONG RANGE It is very unlikely that Aroclor 1242 or even 1242' will not be challenged by alternative or more advanced dielectric liquids in the next ten years. We, therefore, must continue our research efforts toward new dielectric materials with particular emphasis on lower pour points and greater high temperature stability.

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IV. DATA AND DISCUSSION

PRELIMINARY STUDY The relative silence of the literature on the subject of organic liquid electrical properties (except for Dk and relaxation times) prompted us to carry out a study of our own. Although a study of the electrical properties of various organic liquids is not unique within the company (Ref. 2), we felt it necessary to perform this independently. We hoped, in so doing, to educate and orient ourselves and possibly to uncover useful relationships which would allow us to proceed by design rather than chance.

The various candidates were first purified in the usual chemical sense, depending on their structure and origin (acid or base wash, distillation, chromatography, etc.). This was followed by the standard treatment with attapulgus earth at elevated temperature. Attasorb LVM gave us the best results. The apparatus with which the purified liquids were to come in contact was cleansed as described in Ref. 2. Table I summarizes the data collected in the preliminary study.

The most important conclusion drawn from this tabulation is the relationship between Dk and R (Dk, R and PF are related to a first approximation by the formula

$$PF = \frac{1.8 \times 10^{14}}{\text{freq.} \times Dk \times R}\ ).$$

Aside from differences in purity and viscosity which prevent complete correlation it is clear that as the Dk increases R decreases exponentially. Table II summarizes this relationship.

Examination of several mixtures of Aroclors and higher Dk additives reveals a tendency for R to resemble that of the high Dk component rather than the Aroclor. While this does not appear to be important when one adds high Dk chlorinated biphenyls to Aroclors (see page 8), it does appear to be harmful if the additive has a high Dk by virtue of a very polar unsaturated functional group; i.e., amide, ketone. These observations caused us to consider the probability of finding a dielectric liquid with a Dk above 10 and R above 10^{12} to be remote. This led us to conclude that the next marketable improvement in Dk over Aroclor 1242 would be small and in the range between Dk 6 to 10.

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TABLE I (Dk vs. R)

Compound	$Dk_{25°}$	$R_{25°}$
N-(1,4-dimethylcyclohexylmethyl)acetamide	82($116_{100°}$)	10^{9}
N-(t-dodecyl)acetamide	75	10^{8}
N-(t-dodecyl)lauramide	40	7×10^{9}
N-methylpyrolidone	40	10^{7}
N-(n-butyl)sulfonamide	34	10^{7}
Benzonitrile	25	10^{8}
Acetophenone	18	7×10^{8}
N-isobutyl urethane	18	5×10^{8}
2-Ethyl-1,3-hexanediol	18	10^{7}
Cyclohexanol	16	10^{8}
4-Methylbenzophenone	11.5 (60°)	5×10^{9}
N-(t-dodecyl)C_{13} kochamide	11.5	10^{10}
N,N-(di-isopropyl)lauramide	11	10^{8}
4-Ethylbenxophenone	11	10^{10}
2,5-Dimethylbenzophenone	10.8	10^{10}
Mixed dimethylbenzophenone	10.6	10^{10}
Trifluoromethyl-2'-chlorobiphenyl	10.3	10^{10}
2,4,6-Trimethylbenzophenone	10.1	10^{11}
Dimethylphthalate	8.7	10^{9}
N,N-(t-dodecyl)C_{13} kochamide	8.4	10^{11}
o-Chlorophenoxy-2-butoxyethane	7.4	10^{11}
2,6(2,3)-Dichlorophenyl cyclohexyl ether	6.8	5×10^{11}
Dibutylphthalate	6.6	10^{11}
Aroclor 1248 (control)	2.5	4×10^{13}
2,3(and 2,6)-Dichlorophenyl-2-ethylhexyl ether	5.4	8×10^{11}
Tridecanol	4.5	10^{11}
2,4-Dichloro-2-ethylhexyl ether	4.1	10^{11}
Tetra(2-ethylhexyl)orthosilicate	2.5	10^{14}
Mixtures with Aroclors		
Aroclor 1248/N-(t-dodecyl)lauramide, (1:1)	11.7	10^{10}
Aroclor 1242/N-(t-dodecyl)acetamide, (10:1)	9.1	6×10^{9}
Aroclor 1242/trimethylbenxophenone, (5:1)	7.0	10^{11}
Aroclor 1242/o-dichlorobenzene	6.5	10^{12}

TABLE II

$Dk_{25°}$	$R_{25°}$	Type of Material
2 to 3	10^{16} to 10^{14}	Hydrocarbon oils, silicones, fluoro-chemicals
4 to 6	10^{14} to 10^{12}	Aroclors, caston oil (above are commercial dielectric liquids)
7 to 10	10^{12} to 10^{10}	
10 to 20	10^{11} to 10^{8}	Exploratory liquids
above 20	below 10^{10}	

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AROCLOR COMPONENT STUDY The first indication that the Aroclors could be resolved into their various components came when Aroclor 1242 was subjected to vapor phase chromatography on a silicone impregnated firebrick column. The chromatogram showed ten component peaks (see Figure I).

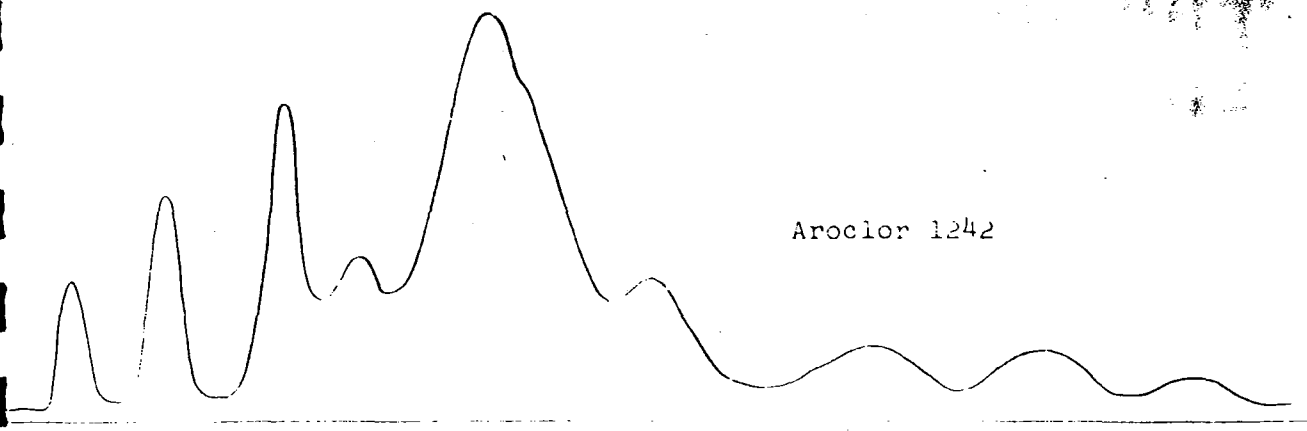

FIGURE I

This analysis was followed up by a fractional distillation on a Todd glass helices packed column. Most of the fractions, enriched in one component or another, yielded crystalline material. These crystalline components were purified, analyzed and either oxidized to the corresponding chlorinated benzoic acids or independently synthesized to establish their structure. A few were previously reported in the literature and were identified by comparison of physical properties. Aroclors 1221 and 1232 have been almost completely characterized in the above ways and the results are described in Figure II.

The method of independent synthesis was the Gomberg biaryl coupling reaction. This reaction was studied in detail and the work is recorded in the Appendix.

As it gradually became obvious the above chromatogram (Figure I, showing 10 peaks) did not represent the total number of components, independent synthesis through the Gomberg reaction was intensified to prepare possible alternative components. Several isomers were shown to be hidden under peaks hitherto believed to represent one component. (The chlorination study described in the subsequent section finally proved the three major dichlorobiphenyls gave all possible trichlors, 10 in number, on further chlorination.) At the same time our spectroscopy group installed a Pye Argon

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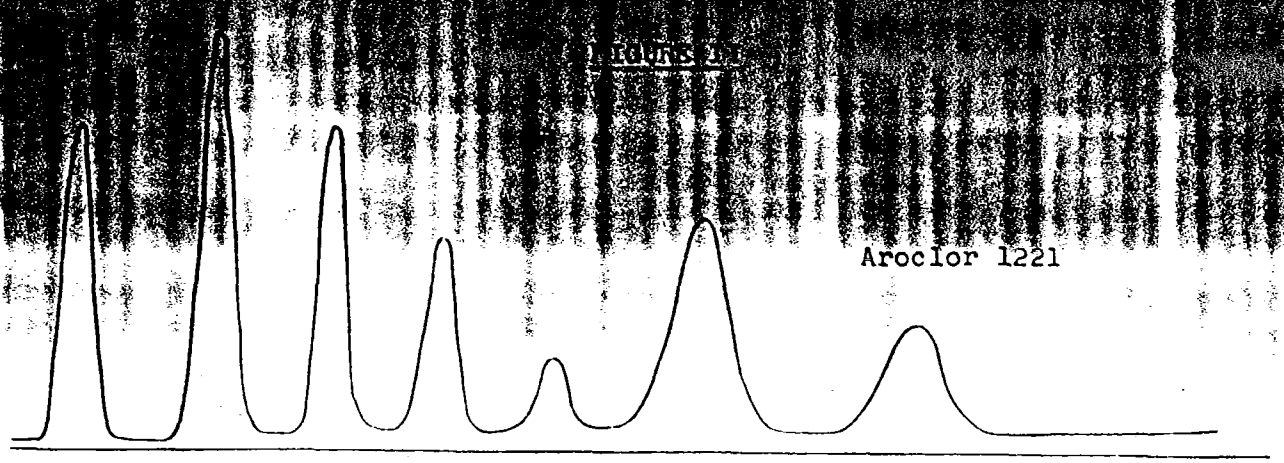

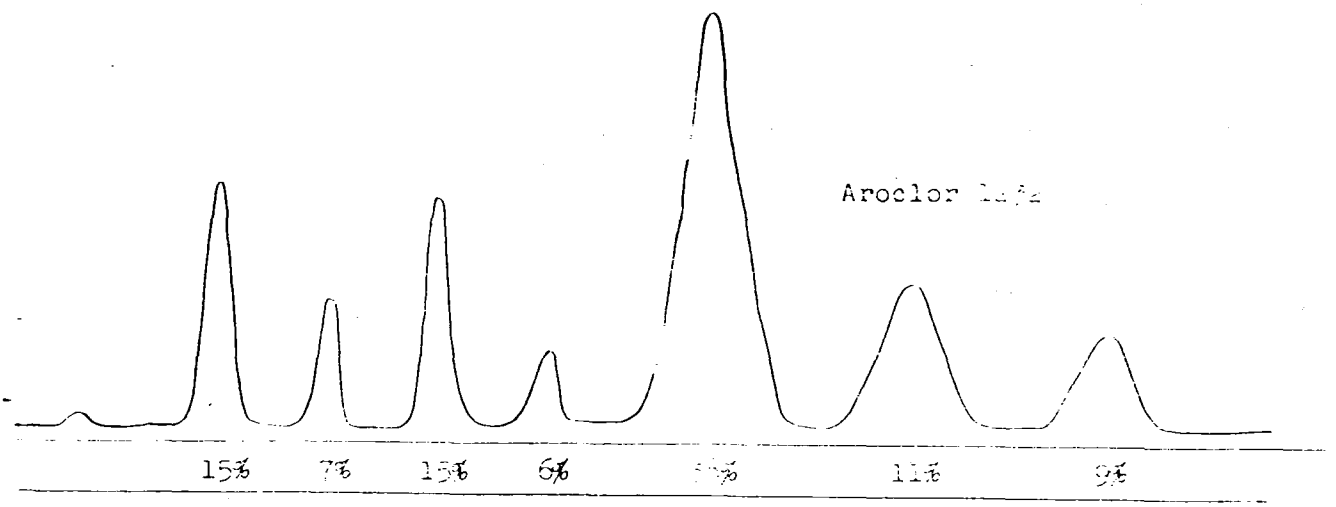

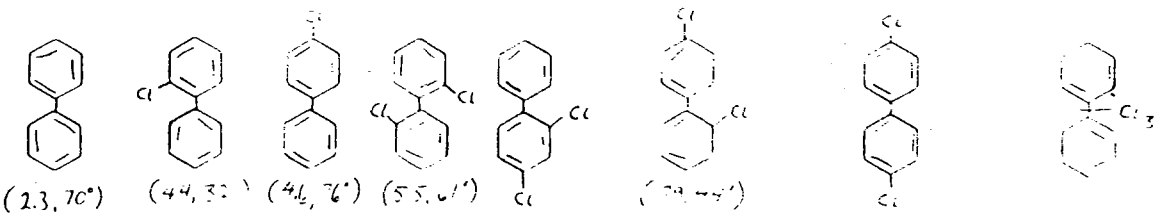

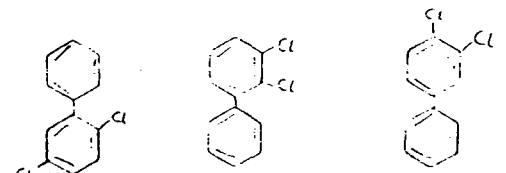

Estimated dielectric constants and melting points are in parentheses (Dk, 5°, m.p.)

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