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St. Louis Research Report No. 1184

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FINAL REPORT

ALKYLATION OF AROCLORS FOR EVALUATION AS EXTENDER PLASTICIZERS

Job No. 2-02-750.01-2682

(Work done by Phosphate
Research under Anniston
Job No. 171-1042)

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Date: January 17, 1955

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D I S T R I B U T I O N S H E E T

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TABLE OF CONTENTS

		Page No.
I.	INTRODUCTION.	1
II.	SUMMARY	1
III.	CONCLUSIONS	1
IV.	RECOMMENDATIONS	2
V.	REFERENCES TO PREVIOUS WORK	2
VI.	EXPERIMENTAL DATA	3
VII.	DISCUSSION OF RESULTS	4

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I. INTRODUCTION

It was desired to develop an inexpensive plasticizer for use as a plasticizer extender with polyvinyl chloride. HB-40 is presently used as plasticizer extender, however, it has a rather high volatility, it discolors on exposure to ultraviolet light and the supply at a low price is limited. Aroclors could be made available in almost unlimited quantities, but have an objectionable odor when used as plasticizers.

It was intended to attempt to develop a plasticizer by the alkylation of a low molecular weight Aroclor which would be competitive in price with HB-40 but with lower volatility, of good color stability and without an objectionable odor.

II. SUMMARY

Aroclors 1232, 1242 and 1248 were successfully alkylated, as described in Table I, with n-butyl chloride, isopropyl chloride and propylene, using aluminum chloride as the catalyst. A yield of 73.5% was obtained when Aroclor 1232 was alkylated with n-butyl chloride whereas yields of 86.0% and 74.5%, respectively, were obtained when Aroclors 1242 and 1248 were alkylated with isopropyl chloride. Respective yields of 81.5% and 83.0% were obtained when Aroclors 1242 and 1248 were alkylated with propylene. Yields of less than 20% were obtained when the alkylation was attempted with various amyl chlorides; a large amount of the amyl chloride was recovered as amylene. Attempts to alkylate various Aroclors with tripropylene and with isobutylene failed when aluminum chloride and various boron trifluoride complexes were used as catalysts.

The alkylated Aroclor was compared with HB-40 as a plasticizer extender at the Organic Division Research Department. The alkylated Aroclor was slightly less volatile than HB-40 but also less flexibilizing. The balance of properties made them quite similar in plasticizer value; however, the high specific gravity of the alkylated Aroclor made it less valuable than HB-40 on a volume basis. Surprisingly, the light stability of the alkylated Aroclor was inferior to HB-40, both in stabilized and unstabilized polyvinyl chloride compositions and by direct exposure of the alkylated Aroclor to ultraviolet light.

III. CONCLUSIONS

From this experimental work it is concluded that Aroclors 1221, 1232, 1242 and 1248 can be alkylated with propylene, isopropyl chloride and n-butyl chloride in yields of over 70%. Further study would probably permit definition of conditions to give maximum yields; however, this work would not be justified on the basis of product evaluation.

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It is also concluded that Aroclor 1242 cannot be alkylated with amyl chloride under the conditions used as the amyl chloride decomposes to amylene. (Yields of alkylated product were less than 20%)

Aroclors could not be alkylated with isobutylene or tripropylene as these compounds tended to polymerize under the conditions used.

The alkylated Aroclors which were prepared were not sufficiently light stable to be used as an extender plasticier in polyvinyl chloride compositions. In addition, these compounds tended to bleed from the plasticized polyvinyl chloride.

The specific gravity of the alkylated Aroclor was sufficiently high so as to make them less valuable on a volume basis than HB-40 when used as plasticizers.

IV. RECOMMENDATIONS

No further work toward developing alkylated Aroclors as substitutes for HB-40 is indicated.

V. REFERENCES TO PREVIOUS WORK

1. Phosphate Research Report No. 2042, "Alkylated Biphenyls", Dec. 31, 1945, D. W. Cheape, Jr.

2. Procedure for Sample Preparation for Alkylated Biphenyls, Phosphate Division, July 11, 1946, D. W. Cheape, Jr.

3. Phosphate Research Report No. 2129, "Pilot Plant Production of Alkylated Biphenyls", Sept. 12, 1947, C. D. Wood, Jr.

4. Phosphate Research Report No. 2281, "Preparation of Alkylchlorobiphenyls", Dec. 1948, R. L. Wolf.

5. Central Research Report (Job No. 4015), June 21, 1943, J. S. Butler

6. Phosphate Division Report No. 2809, "Color Stability of HB-40", Oct. 24, 1952, J. K. Sears.

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VI. EXPERIMENTAL DATA:

NB 81151-81200
84851-84859

Into a three-necked flask equipped with thermometer, stirrer, and dry ice condenser was charged 1034.0 g. (4 moles) Aroclor 1242 and 30.0 g. (0.225 moles) of aluminum chloride and the mixture was heated to 80° C. while 377 g. (48 moles) of isopropyl chloride was added over a period of two hours. The temperature was held at 80° C. for one hour after the addition was completed. The reaction product while hot was poured into 2 liters of cold water, separated, and then washed with one-liter portions of water until the washes were neutral. The crude product was then heated to 120° C. to remove water and then treated with dry Attapulgus earth and filtered while still hot. The crude was then vacuum distilled and the fraction distilling at 150-185° C. at 1.5 mm Hg was taken as the product. By total chlorine analysis it was determined that this product was essentially monoalkylated Aroclor 1242. (See Table I).

In cases where gaseous alkylating agents such as isobutylene and propyylene were used, the gas was introduced below the surface of the reaction mixture by means of a sparger. Treatment of the reaction mixture was essentially the same as described above. Reaction conditions, yields, etc. are tabulated in Table I.

The alkylated Aroclor 1242 prepared in Run No. 23 was compared with HB-40 as a coplasticizer for polyvinyl chloride by Mr. J. R. Darby of the Organic Division Research Department at St. Louis. Both plasticizers are incompatible when used alone, and therefore were evaluated as coplasticizers with dioctyl phthalate. The alkylated Aroclor was slightly less volatile than HB-40 but also less flexibilizing. The balance of properties made them quite similar in plasticizer value; however, the high specific gravity of the alkylated Aroclor makes it less valuable than HB-40 on a volume basis. Surprisingly, the light stability of the alkylated Aroclor in a polyvinyl chloride composition was inferior to HB-40 in both stabilized and unstabilized compositions. Plasticizer evaluation data are given in Table II. Bleeding of the alkylated Aroclor from the polyvinyl chloride composition was noted after several months; this did not occur in the HB-40 coplasticized samples.

DSW 620792

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Light stability tests on some alkylated Aroclors as compared to HB-40 were run by J. K. Sears, as described in reference 6:

Substance	Gardner Color after exposure to G.E. sun lamp for ___ hours				
	0	42	84	126	168
HB-40	Water White	6	7	8	9
isopropylated 1248 (Run 20)	1	5	9	11	-
isopropylated 1242 (Run 23)	-	7	9	-	-
mono butylated 1232 (Run 17)	3	6	9	9+	-
di butylated 1232 (Run 17)	7	10	11	12	-

From this data it appears that the alkylated Aroclors are somewhat less light stable than HB-40.

An interesting observation on the alkylated Aroclors which were stored in indirect light in the laboratory was that after several weeks alkylated Aroclors prepared using olefin alkylating agents darkened considerably, whereas those prepared using alkyl chloride alkylating agents did not appear to change color. This discoloration was probably due to a trace of olefinic impurities in the products, which easily oxidize in the presence of ultra-violet light to give highly-colored products.

VII. DISCUSSION OF RESULTS

It was found that Aroclors 1232 and 1242 could be readily alkylated with alkyl chlorides. The resulting yields of alkylated Aroclors decreased, however, as the length of the alkyl chloride chain increased. This was probably due to the fact that Aroclors are difficult to alkylate and in the case of amyl chlorides the amyl chloride was more readily decomposed to amylene during the reaction, which did not readily react with the Aroclor.

Aroclors 1242 and 1248 were easily alkylated in good yields with propylene, whereas low yields were obtained when isobutylene and tripropylene were used. This was probably due to the ease with which isobutylene and tripropylene are polymerized by acid catalysts of the aluminum chloride type. Anhydrous hydrogen chloride was used as a promoter with olefin alkylating agents, but was not determined that it improved the yields.

DSW 620793

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Further study would probably permit definition of conditions to give higher yields as indicated by comparison of Runs 27 and 29, Table I, however this work is not justified on the basis of product evaluation.

The alkylated Aroclors made from olefins became highly colored on prolonged exposure to subdued light whereas the alkylated Aroclors prepared with alkyl chlorides did not show this tendency. This is probably due to traces of olefins in the alkylated product which are easily oxidized to form highly-colored products.

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Run No.	Aroclor No.	Catalyst	Alkylating Agent	Promotor	Aroclor, Moles	Catalyst, Moles	Alkylating Agent Moles	Ave. Pot Temp. °C.	Gauge Pressure in. Hg.	Product Distillation Temp. Range, °C.	Pressure mm Hg	Yield, based on Aroclor Charged: Conversion*	Aroclor Recovered, %	Loss Total, %	Product Analysis - Total Cl, %	Remarks
1	1242	$AlCl_3$	Tripropylene	-	1.0	0.037	1.0	120	Atm.	-	-	0.0	-	-		No alkylation. Alkylating agent reacted with itself under these conditions.
2	1221	BF_3 - Phenol	"	-	1.0	0.105	1.0	80	"	-	-	0.0	-	-		" " " "
3	1221	BF_3 - Ether	"	-	1.0	0.070	1.0	95	"	-	-	0.0	-	-		" " " "
4	1221	$AlCl_3$	"	-	1.0	0.50	1.0	150	"	-	-	0.0	-	-		An undistillable tarry material was obtained a small amount of alkylated material obtained; most of isobutylene reacted with itself polymerized.
5	1221	$AlCl_3$	Isobutylene	-	2.0	0.075	2.6	95	"	-	-	16.0	-	-		
6	1221	$AlCl_3$	"	-	2.0	0.075	4.0	70	"	-	-	0.0	-	-		Reaction temp. too low - no alkylation.
7	1221	$AlCl_3$	"	-	2.0	0.075	3.6	95	+1.0	-	-	16.4	-	-		Low yields of highly colored material - probably due to polymerization of the olefin
8	1232	$AlCl_3$	"	-	2.0	0.075	4.7	120	+1.0	-	-	17.3	-	-		
9	1232(pp')	"	"	-	2.0	0.075	1.6	145	+1.0	-	-	-	-	-		Discontinued. Lines plugged due to sublimed Aroclor.
10	1232	"	"	HCl	2.0	0.075	2.4	130	Atm.	-	-	-	-	-		
11	1232	"	"	"	2.0	0.075	4.0	130	"	-	-	-	-	-		Low yields of highly colored material - probably due to polymerization of olefin.
12	1232	"	"	"	2.0	0.075	4.0	115	"	-	-	17.0	-	-		
13	1242	"	"	"	2.0	0.075	4.6	135	"				[illegible]	[illegible]		
15	1232	"	"	CH_3Cl	2.0	0.075	2.6	120	"			220	-	-		
17	1232	"	n-butylchloride	-	2.0	0.225	3.0	90	"	160-185 185-227	2.0	73.6	17.2	9.2	25.75 21.25	Mono and di alkylated Aroclors were obtained.
8	1232	H_3PO_4 - BF_3	Isobutylene	-	2.0	0.15	3.0	95	"	-	-	6.0	75.4	24.6	-	
9	1242	$AlCl_3$	Isopropyl Chloride	-	2.0	0.225	4.0	81	"	170-186	2.0	79.5	0.3	12.4	37.82	
10	1248	"	"	-	2.0	0.225	4.0	90	"	170-208	1.3	74.5	2.6	22.9	39.0	
11	1232	"	Tripropylene	-	2.0	0.225	1.1	130	"	155-191	1.4	-	-	-	-	
3	1242	"	Isopropyl chloride	-	4.0	0.225	4.8	80	"	151-184	1.6	56.0	[illegible]	[illegible]	35.93	Essentially monoalkylated Aroclor obtained
4	1242	"	Mixed amyl Chlorides	-	4.0	0.225	4.8	82	"	140-186	0.9	12.1	76.0	11.9	38.15	25-40% of the amyl chloride was recovered as amylene. Apparently most of the amyl chloride was dehydrohalogenated to form amylene.
5	1242	"	Primary Amyl Chloride	-	2.0	0.110	2.4	90	"	142-192	0.9	14.4	70.0	15.6	-	
6	1242	"	"	-	2.0	0.180	2.4	70	"	142-184	0.9	13.7	75.6	11.7	-	
7	1242	"	Propylene	HCl	2.0	0.180	3.2	170	"	143-180	0.9	67.5	12.0	20.5	35.65	
9	1242	"	[illegible]	[illegible]	2.0	0.180	3.6	155	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	35.68	
0	1242	"	[illegible]	[illegible]	2.0	0.180	3.6	150	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	24.92	
1	1242	"	[illegible]	[illegible]	2.0	0.180	3.6	150	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	40.39	
[illegible]	Santovar A	Isobutylene	[illegible]	2.0	0.180	3.6	150	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	2.0	0.180	3.6	120	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	2.0	0.180	3.6	150	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	

	40% HB40	HB40 20% DOP 20%	HB40 13.4% DOP 26.6%	Isopropyl Aroclor 1242	Isopropyl Aroclor 1242 (20%) DOP (20%)	Isopropyl Aroclor 1242 (13.4%) DOP (26.6%)
Milling Results	Incompatible Serious Exudation			Incompatible Serious Exudation	Moderate	
Fuming	Heavy	Heavy	Heavy	Moderate	Moderate	Moderate
Odor	Strong	Moderate	Moderate	Moderate	Moderate	Moderate
Color	Sl.discolored	Sl. Discolored	Sl. Discolored	Lt. Yellow	Sl. Discolored	Sl. Discolored
Molded Sheet						
Transparency	Clear	Clear	Clear	Sl. Opaque	Clear	Clear
Odor	Very slight	Very slight	Very slight	Very slight	Very slight	Very slight
Color	Lt. Yellow	Sl. Discolored	Sl. Discolored	Lt. Yellow	Sl. Discolored	Sl. Discolored
Low Temp. Flex.	-2.5°	-24.3°	-30.6°	+12.9°	-20.4°	-25.8°
Volatility % Plast. Lost	23.77%	28.20%	23.58%	15.16%	21.21%	17.48%
Hardness						
Before Volatility	98	84.2	79.3	97	88	83.6
After Volatility	98	89.7	85	97.3	91	85
Heat Stability						
Color after 30 min. at 325°F.	Lt. Amber	Amber	Amber	Lt. Amber	Amber	Amber
Rating	Good	Fair	Fair	Good	Fair	Fair
Water Absorption						
% sol. matter lost	0.96%	0.13%	0.13%	0.23%	0.09%	0.06%
% Absorption	0.45%	0.40%	0.44%	0.29%	0.31%	0.30%
Kerosene Extraction	55.71%	65.37%	79.02%	53.90%	90.30%	82.42%

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