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PROGRESS REPORT

ORGANIC CHEMICALS DIVISION

ST. LOUIS RESEARCH DEPT.

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REPORT BY	JOB NO.	REPORT NO.	CODE
* B. Katlafsky * W. E. Koerner * E. M. Emery * R. E. Keller	2-02-6-50.01-4285	1	UNCL-5
	FOR: March 1962		

SPECIAL INSTRUCTIONS

1.* R. A. Geisman/J.F. Caldwell - JFQ	9.
2.* W. J. Gresham/R. F. Schubert - WGK	10.
3.* H. L. Hubbard - Res 1	11.
4.* R. W. Wise - Nitro	12.
5.* P. Benignus - G-O-B-2-S	13.
6.* MCL (2) via J. F. Stickley-B-3-N	14.
7.* K. McHugh - Res. 2	15.
8.	16.

*COPY INCLUDES DETAILS

TITLE

ANALYTICAL CHEMISTRY AND SPECTROSCOPY INVESTIGATIONS

PROBLEM

Aroclor 1242 Production Variations - Evaluation of Infrared and Gas Chromatography Methods.

SUMMARY

An infrared and GLPC (gas-liquid partition chromatography) study of five normal production samples of Aroclor 1242 from Anniston showed that most of the variations in isomer content were small and random. However, one pronounced periodic variation was observed in the infrared spectra in the region of 14.3-14.4 microns which was shown by a combination of infrared and GLPC analysis to be the result of variations in the lower chlorination level isomers, namely the 2-chloro, 2,2¹-dichloro and the 2,4¹-dichlorobiphenyls.

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DETAILS Yes

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DETAILS

Infrared absorption spectroscopy and GLPC (gas-liquid partition chromatography) methods were used to study compositional variations in production lots of Aroclor 1242 shipped to General Electric over the past six months. The study was initiated to determine if more than normal variations were present and, if so, what is the cause of these differences.

Reserve samples of lots D-122, D-145 and D-185 were obtained from Anniston to represent normal production material. Since no sample of lot D-153, the subject of a recent General Electric complaint, was available samples of lots D-152 and D-154 were substituted. Infrared spectra were run under conditions such that the gross infrared spectra could be compared rather than under special conditions to study a particular isomer. The GLPC analysis was carried out using a 150' x 0.020" stainless steel capillary column coated with silicone gum rubber and a flame ionization detector.

A critical comparison of the IR spectra showed primarly the minor random variations expected for small differences in isomer distribution. However, in the region of 14.3 to 14.4 microns two weak absorption bands were observed whose intensities varied periodically with lot number. The attached IR spectrum shows the superimposition of the spectra of the five lots of Aroclor 1242 studied run under conditions to amplify the difference. Examination of the spectra in the region of 14.3-14.4 microns shows that the intensity of the absorption bands at these wavelengths increases sharply from lot D-122 to D-145. The absorption reaches a maximum in lot D-152 then tapers off in lots D-154 and D-185. The maximum variance observed between lots D-122 and D-152 was 30% in terms of optical absorption units.

The GLPC data for the five samples shows the random variations of isomers also detected by IR. No variations in a single component was observed that could explain the difference found in the IR spectra. The GLPC data is tabulated in Table I. Where possible the GLPC fraction has been identified as a particular isomer on the basis of retention time.

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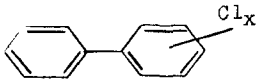
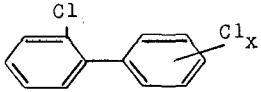
Despite the fact that the positive identification of the components involved in the observed periodic variation in the IR spectra could not be made structural characteristics of the materials contributing to this variation could be assigned based on infrared interprepation of aromatic absorption patterns.

The chlorine distribution patterns in Aroclor 1242 fit the following general classes:

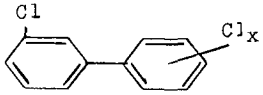
Type I



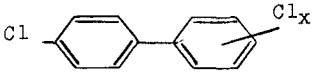
Type II



Type III



Type IV



Of these four general classes of chlorine distribution patterns only Types I and II (the monosubstituted aromatics and the ortho disubstituted aromatics) produce absorption bands in the 14.3-14.4 micron region. Although it is possible to detect and differentiate the Types I and II materials in other regions of the IR spectra, interferences and overlapping of bands prevents this in the bulk sample.

In order to resolve this problem and identify the components causing the observed variance in the IR spectra, lot D-152 was fractionally distilled by Mr. George Ashworth under reduced pressure and four top fractions representing a total of 8.4% of the charge were isolated for subsequent analysis. The GLPC analytical data which was confirmed by IR analysis shows that the mono and dichlorobiphenyls having the type I and II structures postutated by IR interprepation of the bulk sample were the major contributors to the variation observed in the IR spectra of the bulk sample. The GLPC data is tabulated in Table II.

A combination of IR and GLPC analysis has demonstrated that the periodic variation observed in Aroclor 1242 lots D-122, D-145, D-152, D-154 and D-185 are the cumulative effects of variations primarily of the 2-chloro, 2,2'-dichloro and the 2,4'-dichloro-biphenyls.

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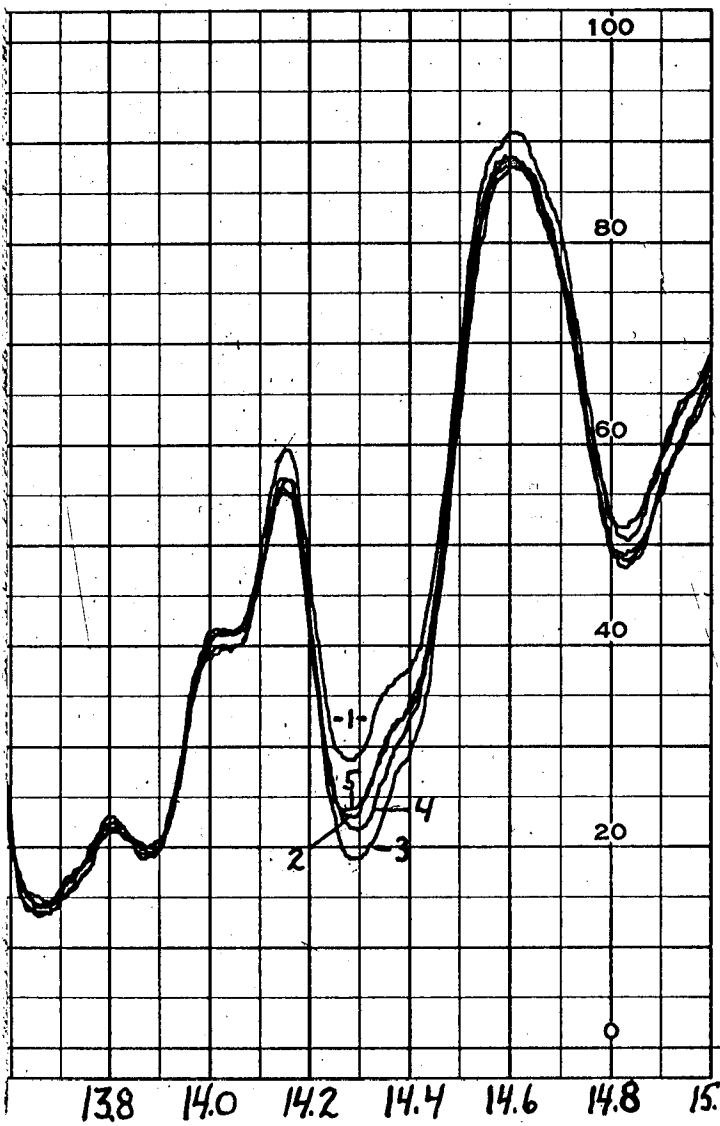

SPECTRUM NO. _____

SAMPLE AROCLOR 1242

ORIGIN _____

PURITY PRODUCTION SAMPLES

PHASE LIQUID

THICKNESS 0.05 mm.

1 LOT D-122	4. LOT D-154
2 LOT D-145	5. LOT D-185
3 LOT D-152	

DATE 1/15/62

OPERATOR BK

REMARKS 78% TRANS. SCREEN REFERENCE

PRISM NaCl

RESOLUTION 927

RESPONSE _____

GAIN 4.2

SPEED 32

SUPPRESSION 4

SCALE 10 cm./μ

TECHNICAL
CHARTS INC. BUFFALO, N.Y.
PR-1108
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Table I

AROCLOR 1242

Fraction/Component	Lot D-122	Lot D-145	Lot D-152	Lot D-154	Lot D-185
1 Biphenyl	0.04	0.03	0.3	0.2	0.03
2 Ortho	0.8	1.0	1.9	1.8	0.9
3) Meta	0.2	0.3	0.6	0.5	0.2
4) Para					
5 2,2[1]	4.5	4.9	5.2	4.8	4.6
6 2.5	0.8	0.8	1.0	1.0	0.8
7 (2,4 or 2,3 or 2,3[1])	1.4	1.8	1.9	1.8	1.6
8 2,4[1]	9.1	9.6	10.3	9.6	9.5
9 (3,5 or 3,3[1])	0.7	0.8	0.6	0.7	0.7
10 (3,4 or 2,5,2[1])	10.2	10.0	9.4	9.5	10.1
11 4-4[1]	5.3	5.7	5.2	5.3	5.4
12	0.2	0.5	0.3	0.4	0.5
13 2,3,2[1]	4.8	5.8	5.1	5.2	5.7
14) 15)	1.5	1.8	1.5	1.4	1.6
16) 2,5,4[1] 17)	15.3	14.9	13.7	14.1	15.0
18 3,4,2[1]	6.7	6.6	6.0	6.1	6.6
19 2,3,4	3.0	3.0	2.7	2.7	3.0
20	0.7	0.7	0.6	0.7	0.7
21	0.2		0.2		0.2
22	3.6	3.4	3.4	3.9	3.5
23	2.7	2.4	2.4	2.6	2.6
24	1.9	1.5	1.7	1.8	1.8
25	3.5	3.3	3.3	3.4	3.3
26 3,4,4[1]	3.3	3.2	3.1	3.0	3.2
27	3.4	3.2	3.1	3.3	3.4
28	0.6	0.7	0.6	0.6	0.8
29	0.1	0.1	0.1	0.1	0.1
30	0.1	0.05	0.05	0.05	0.1
31) 32)	5.1	4.6	4.9	5.1	4.9
33	3.9	3.5	3.7	4.0	3.8

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Table I (cont'd)

Fraction/Component	Lot D-122	Lot D-145	Lot D-152	Lot D-154	Lot D-185
34	0.2	0.1	0.2	0.2	0.2
35	2.7	2.4	2.6	2.6	2.6
36	0.3	0.3	0.3	0.3	0.3
37	0.5	0.5	0.7	0.7	0.5
38	0.2	0.2	0.5	0.3	0.2
39	0.03	0.05	0.1	0.05	0.02
40	0.2	0.2	0.3	0.2	0.2
41	0.4	0.3	0.5	0.4	0.3
42	0.2	0.2	0.3	0.2	0.1
43	0.8	0.8	1.1	0.9	0.7
44	0.1	0.2	0.1	0.2	0.1
48	0.6	0.4	0.3	0.5	0.4
52	0.3	0.4	0.3	0.3	0.2

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Table II

ARCOCLOR 1242 LOT D-152 TOPPING EXPERIMENT

Fraction/Component	Starting Mat'l	F#1 1.9%	F#2 1.7%	F#3 2.3%	F#4 2.5%	Residue 91.6%
1 Biphenyl	0.3%	8.6%	0.8%	trace	trace	0
2 ortho	1.9	29.7	26.0	7.1%	1.3%	0
3) meta	0.6	6.5	7.3	5.9	4.1	trace
4) para						
5 2,2'	5.2	36.8	43.0	41.3	36.0	0.2
6 2,5	1.0	2.8	3.4	5.6	6.6	0.2
7(2,4 or 2,3 or 2,3')	1.9	2.9	4.2	6.9	9.2	0.9
8 2,4'	10.3	11.5	14.1	27.4	35.0	5.7
9 (3,5 or 3,3')	0.6	0.3	0.3	1.1	1.5	0.5
10(3,4 or 2,5,2')	9.4	0.8	1.0	3.5	4.7	9.9
11 4,4'	5.2			0.8	1.2	6.6
12	0.3	0	0	0.1	0.1	0.5
13 2,3,2'	5.1	trace	trace	0.3	0.4	6.1
14)	1.5			0	0	2.1
15)						
16) 2,5,4'	13.7			trace	trace	17.6
17)						
18 3,4,2'	6.0					7.7
19 2,3,4	2.7					2.1
20	0.6					0.7
21)	3.6					4.5
22)						
23	2.4					3.1
24	1.7					2.0
25	3.3					4.1
26 3,4,4'	3.1					3.8
27	3.1					3.8
28	0.6					0.7
29	0.1					0.1
30	0.1					
31)	4.9					6.1
32)						
33	3.7					4.5

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Table II (cont'd)

Fraction/Component	Starting Material	F#1	F#2	F#3	F#4	Residue
34	0.2					0.2
35	2.6					3.1
36	0.3					0.2
37	0.7					0.6
38	0.5					0.3
39	0.1					trace
40	0.3					0.3
41	0.5					0.4
42	0.3					0.2
43	1.1					1.0
44	0.1					0.1
48	0.3					0.5
52	0.3					*

* instrument shut down before this peak was eluted from the column.

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