RESEARCH DEPARTMENT - PHOSPHATE DIVISION

SHORT FORM REPORT

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			R. L. Jenkins - St. Louis
Work Started:	October 15, 1951		H. V. Moss
Work Completed:	May 15, 1952		C. A. Hochwalt - St. Louis
Date Reported:	July 3, 1952		N. N. T. Samaras - Dayton
			Edgar E. Hardy
Job No.:	171-1028		H. F. Weaver - St. Louis
File No.:	141-27-3		A. M. Ellenburg
			W. T. Durrett
Investigators:	A. M. Ellenburg		R. P. Loewen
	H. B. Richards, Jr.		H. O. Tittel
	J. E. Feltham		C. Barbre - Monsanto, Ill.
			T. W. Dalton - Monsanto, Ill.
			Jack Clegorn
			Extra (2)

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TITLE: Increased Production of Aroclor by More Rapid Rate of Chlorination.

INTRODUCTION:

In view of the desired eight-million pound per year increase in distilled Aroclor production, plant experiments were made increasing the rate of chlorination of biphenyl to crude liquid Aroclors to determine if the Aroclors so produced would meet the present specifications.

SUMMARY:

Several experimental chlorinations in chlorinators 5 and 6, which have been modified for more rapid chlorination rates, were carried out on batches of 1142 and 1154 at increased chlorination rates. These fast chlorinations (up to 770 pounds chlorine per hour) were compared to normal operations (550 pounds chlorine feed) in these modified chlorinators and to normal operations (400 pounds chlorine feed) in chlorinators 3 and 4, which have not been modified for rapid chlorination.

In all cases the Aroclors produced at the increased rates were within specifications.

CONCLUSIONS:

1. Production of crude Aroclors with existing equipment has been increased about 30% in modified chlorinators 5 and 6.
2. An additional increase of up to 40%, over this 30% increase, is within possibility by closer control of the chlorine feed rate on Aroclor 1142.
3. The additional increase in feed rate on Aroclor 1154 is only 15%, and on Aroclor 1160 it would be less. The inability to continue the increase in chlorine pressure accounts for the reduced improvement.
4. Better dispersion of chlorine is not needed in the chlorination at high feed rates to obtain specification grade Aroclor.

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RECOMMENDATIONS:

It is recommended that the four unmodified chlorinators be equipped with individual cyclone entrainment separators so that they may be operated at more rapid rates of chlorination, if the proposed increase in Aroclor production is to be carried out.

Henry B. Richards, Jr.
Henry B. Richards, Jr.

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EXPERIMENTAL DATA:

Notebook References - 74867-8, 74870-1, 74873, 74875-6, 74881, 74894-5, 77351-7, 77364-71, 80514-16, 82604-6.

CHLORINATION DATA:

TABLE I

REGULAR AROCLOR 1142 CHLORINATIONS

NO. 5 CHLORINATOR AT INCREASED RATE, NOS. 3 AND 4 CHLORINATORS AT NORMAL RATE

Run No.	Date	Chlorinator No.	Avg. Rate, Lbs. Cl_2 per Hr.	Chlor. Time, Hrs.	Equivalent* Chlor. Time, Hrs.	Charge to Chlor., Lbs.	Product Pounds	Chlor. Time Before Circulating, Hrs.
455	4/21/51	4	437	13.0	---	4000	7400	4.3
307	10/24/51	5	574	9.9	---	4000	7100	3.8
389	1/11/52	3	378	13.5	15.0	3600	5900	---
377**	5/14/52	5	537	9.5	10.6	3600	7100	3.5
383**	5/15/52	5	521	9.8	10.8	3600	7100	4.0

* The calculated time that would have been required for the chlorination of a full charge of 4000 lbs. of biphenyl.

** These two runs are 1154 chlorinations on which the data are given through the 1142 stage as a basis of comparison for the experimental chlorinations in this chlorinator. See Table II.

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TABLE II

EXPERIMENTAL 1142 CHLORINATIONS IN NO. 5 CHLORINATOR

Run No.	Date	Avg. Rate, Lbs. Cl_2 Per Hr.	Chlor. Time, Hrs.	Equivalent Chlor. Time, Hrs.	Charge to Chlor., Lbs.	Product, Lbs.	Chlor. Time Before Circulating, Hrs.
278	10/16/51	756	7.5	—	4000	—	—
303	10/25/51	515	11.0	—	4000	6500	—
341	11/20/51	568	10.0	—	4000	5900	—
293 *	3/25/52	639	8.0	8.9	3600	—	1.42
381 *	5/15/52	786	6.5	7.2	3600	—	1.5

* 1154 Chlorinations, data taken only through 1142 stage.

NOTE: Runs 278, 303, and 341 were carried out by the plant and data given to Research. Runs 293 and 381 were carried out in the plant by research personnel.

TABLE III

REGULAR 1154 CHLORINATIONS AT INCREASED RATES

Run No.	Date	Chlor. No.	Avg. Rate, Lbs. Cl_2 Per Hr.	Chlor. Time, Hrs.	Charge to Chlor., Lbs.	Product, Lbs.	Chlor. Time Before Circulating, Hrs.
799	10/25/51	5	671	12.2	3600	7400	3.2
819	10/30/51	5	505	16.2	3600	—	3.8
977	12/20/51	6	545	15.0	3600	—	3.2

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TABLE IV

EXPERIMENTAL 1154 CHLORINATIONS

Run No.	Date	Chlor. No.	Avg. Rate, Lbs. Cl_2 Per Hr.	Chlor. Time, Hrs.	Equivalent Chlor. Time, Hrs.	Charge to Chlor., Lbs.	Product, Lbs.	Chlor. Time Before Circulating, Hrs.
292	10/22/51	5	618	14.7	13.3	4000	7700	——
66	1/15/52	6	671	12.2	——	3600	7330	1.0
86	1/18/52	6	693	11.8	——	3600	7440	1.0

TABLE V

AROCLOR CHLORINATION RATES

Aroclor	Operating Conditions	Avg. Rate, Lbs. Cl_2 Per Hr.	% Increase Over Condition 1	% Increase Over Condition 2
1142	1. Regular plant operation	410	——	——
	2. Increased plant operation	545	33	——
	3. Experimental operation	770	88	41
1154	1. Regular plant operation	415	——	——
	2. Increased plant operation	575	39	——
	3. Experimental operation	660	59	15

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Data on Laboratory Distilled Aroclors from Rapid Chlorinations:

TABLE VI

AROCLOR 1242 ANALYSES

Property	Run Number 278	303	341	293	381	Control Specification
% Recovery on Distillation	96.7	98.4	95.0	98.8	98.4	------
Color, APHA	20+	-----	25	----	35	100 max.
Condition	Clear	Clear	Clear	Clear	Clear	Clear
Sp. Gr. at 25°C.	1.384	1.380	1.378	1.388	1.390	1.378-1.388
Acidity $\frac{mg.NaOH}{g.}$	0.001	-----	-----	-----	0.001	0.014 max.
Inorg. Cl., ppm.	0.05	-----	-----	-----	0.05	0.1 max.
Viscosity, S.U.S. at 100°F.	85.4	----	----	----	89.8	83 ± 5
D. K. at 100°C.	4.68	4.80	4.82	4.86	4.89	4.7-4.9
Resistivity, ohm-cm X 10^{-9} at 100°C.	11,000	5,700	1,400	4,500	6,400	500 min.
Ref. Index at 25°C.	1.6263	1.6245	1.6243	----	1.6253	1.6245-1.6265
Pour Point, °C.	-18	-----	-----	-----	-18	-14 max.
Water, ppm.	86	----	----	----	90	35 max.
Dist. Range, °C. Corrected						
10%	317	331	329	332	332	
50%	350	337	337	339	339	
90%	366	352	353	357	354	
Corrosion Test	passes	-----	-----	-----	passes	

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TABLE VII

AROCLOR 1254 ANALYSES

Property	Run Number 292	66	86	Control Specifications
% Recovery in Distillation	97.6	96.3*	95	----
Color, APHA	45	65	35	100 max.
Condition	Clear	Clear	Clear	Clear
Sp. Gr. at 65°C.	1.498	----	1.498	1.495-1.505
Acidity, $\frac{mg.NaOH}{g.}$	0.001	----	0.001	0.01 max.
Inorg. Cl., ppm.	0.05	----	0.05	0.10 max.
Viscosity, S.U.S. at 98.9°C.	45.2	----	45.4	44-47
D. K. at 100°C.	4.23	----	4.15	4.15-4.35
Resistivity, ohm-cm X 10^{-9} at 100°C.	12,000	3,400	7,300	>500
Refractive Index at 25°C.	1.6379	1.6380	1.6387	1.6370-1.6390
Pour Point, °C.	8	----	8	8-12
Water, ppm.	33	----	35	35 max.
Evap. Loss at 100°C., %	0.024	----	0.032	0.4 max.
Distillation Range °C., observed				
10%	354	355	354	350-355
50%	360	360	359	355-362
90%	370	371	368	362-379
Corrosion Test	passes	----	passes	

* No lime in distillation

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Graphs: Data for the curves, Graphs I, II, and III are tabulated as follows:

GRAPH I

SPECIFIC GRAVITY OF CHLORINATED BIPHENYL VS. % CHLORINE

at 25°C.		at 65°C.	
Sp. Gr.	% Cl.	Sp. Gr.	% Cl.
1.182	21	1.155	21
1.267	32	1.243	32
1.383	42	1.348	42
1.452	48	1.414	48
1.543	54	1.505	54
1.623	60	1.587*	60
1.807	68	1.773*	68
1.033**	0	1.000**	0

* Estimated from 25°C. curve
** Extrapolated values for biphenyl

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GRAPH II

SPECIFIC GRAVITY VS. TOTAL CHLORINE FEED

FOR 3600 LB. CHARGE OF BIPHENYL

It can be shown that for chlorination of biphenyl -

$$\frac{X}{0.972\,X + 2\,Y} = Z$$

where X = total weight of chlorine feed, pounds

Y = weight of biphenyl charged, pounds

Z = decimal fraction of chlorine in the product (i.e. for Aroclor 1254, Z = 0.54)

Using this equation, and reading the % chlorine vs. specific gravity curve, Graph I, the following data are obtained for a 3600 lb. charge of biphenyl:

% Chlorine	Sp. Gr. at 65°C.	Total Weight of Chlorine Feed, Lbs.
10	1.067	797
20	1.144	1,788
30	1.229	3,050
40	1.325	4,710
50	1.445	7,010
60	1.600	10,360
70	1.825	15,740

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GRAPH III

RATE OF CHLORINATION VS. TIME

CHLORINATOR NO. 6

AROCLOR 1154

REGULAR RUN 977

Time Elapsed, Hr.	Specific Gravity at 65°C.	Cumulative Wt. of Cl_2 Feed, Lbs.	Increase in Cl_2, Lbs.	Avg. Rate per Interval, Lbs. Cl_2 Feed Per Hr.	Cl_2 Back Pressure Psig.
0	1.000	----	----	----	14
1.58	1.068	800	800	506	15
2.58	1.092	1,100	300	300	15
3.58	1.129	1,600	500	500	20
4.58	1.172	2,200	600	600	20
5.58	1.202	2,650	450	450	20
7.08	1.272	3,750	1,100	734	25
8.08	1.312	4,430	680	680	25
9.08	1.333	4,800	370	370	25
10.08	1.368	5,450	650	650	25
11.08	1.416	6,360	910	910	25
12.08	1.430	6,650	290	290	25
13.08	1.475	7,630	980	980	28
14.33	1.485	7,840	210	168	28
15.00	1.506	8,300	460	687	28
Average Rate				553	

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AROCLOR 1154

EXPERIMENTAL RUN 66

Time Elapsed, Hrs.	Specific Gravity at 65°C.	Cumulative Wt. of Cl_2 Feed, Lbs.	Increase in Cl_2, Lbs.	Avg. Rate Per Interval, Lbs. Cl_2 Feed Per Hr.	Cl_2 Back Pressure, Psig.
0	1.000	---	---	---	16
1.5	1.060	700	700	466	18
2.0	1.078	930	230	460	20
3.0	1.120	1,470	540	540	20
4.0	1.160	2,030	560	560	24
5.0	1.209	2,760	730	730	24
6.0	1.246	3,340	580	580	28
7.0	1.285	3,980	640	640	28
8.0	1.316	4,500	520	520	32
9.0	1.361	5,300	800	800	32
10.0	1.403	6,120	820	820	32
11.0	1.445	6,980	860	860	35
12.0	1.490	7,950	970	970	35
12.17	1.498	8,150	200	1,177	35
Average Rate				670	

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AROCLOR 1154

EXPERIMENTAL RUN 86

Time Elapsed, Hrs.	Specific Gravity at 65°C.	Cumulative Wt. of Cl_2 Feed, Lbs.	Increase in Cl_2, Lbs.	Avg. Rate Per Interval Lbs. Cl_2 Feed Per Hr.	Cl_2 Back Pressure, Psig.
0	1.000	----	----	----	16
1.5	1.070	830	830	553	18
2.0	1.087	1,030	200	400	18
3.0	1.130	1,600	570	570	20
4.0	1.168	2,150	550	550	22
5.0	1.215	2,850	700	700	24
6.0	1.255	3,490	640	640	26
7.0	1.296	4,150	660	660	28
8.0	1.333	4,810	660	660	30
9.0	1.378	5,630	820	820	32
10.0	1.420	6,470	840	840	34
11.0	1.467	7,650	1,180	1,180	34
11.75	1.500	8,180	530	707	34
Average Rate				696	

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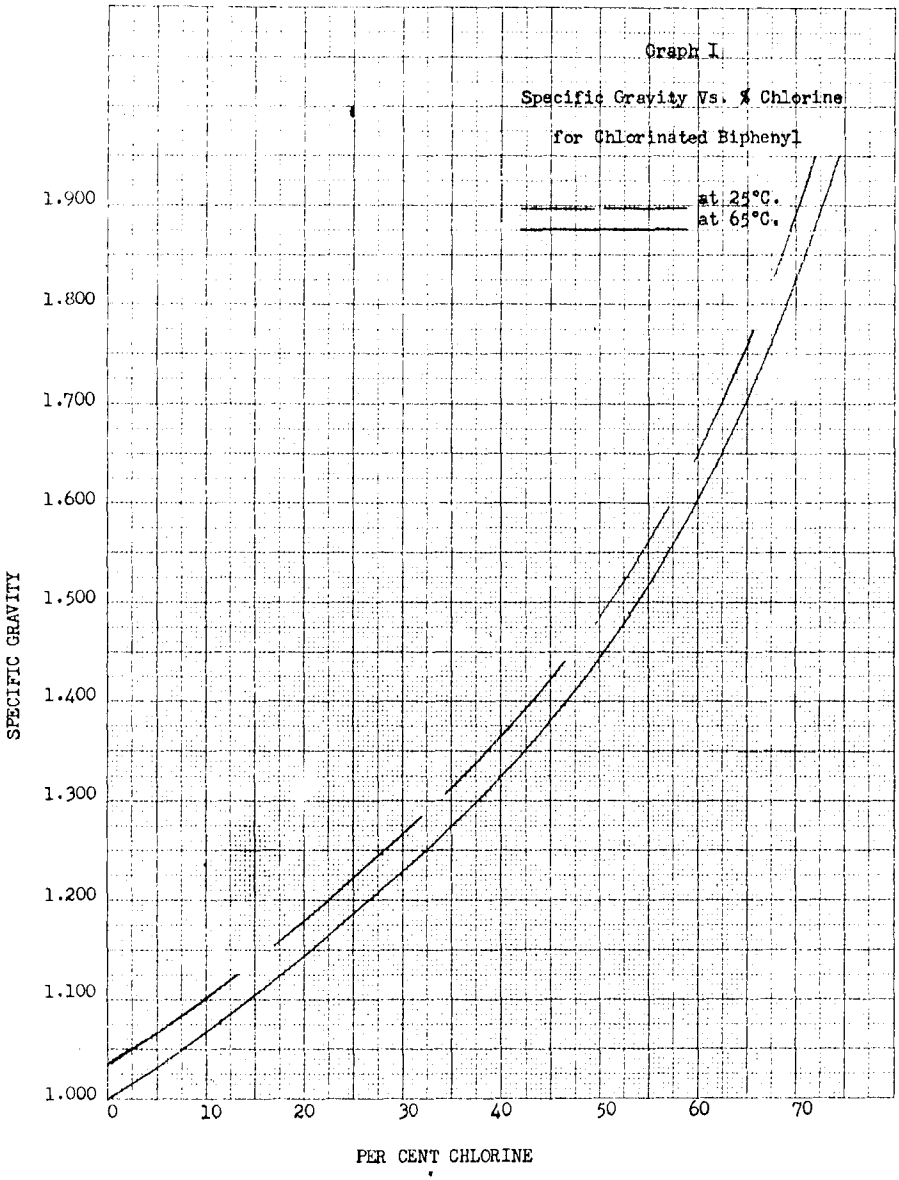

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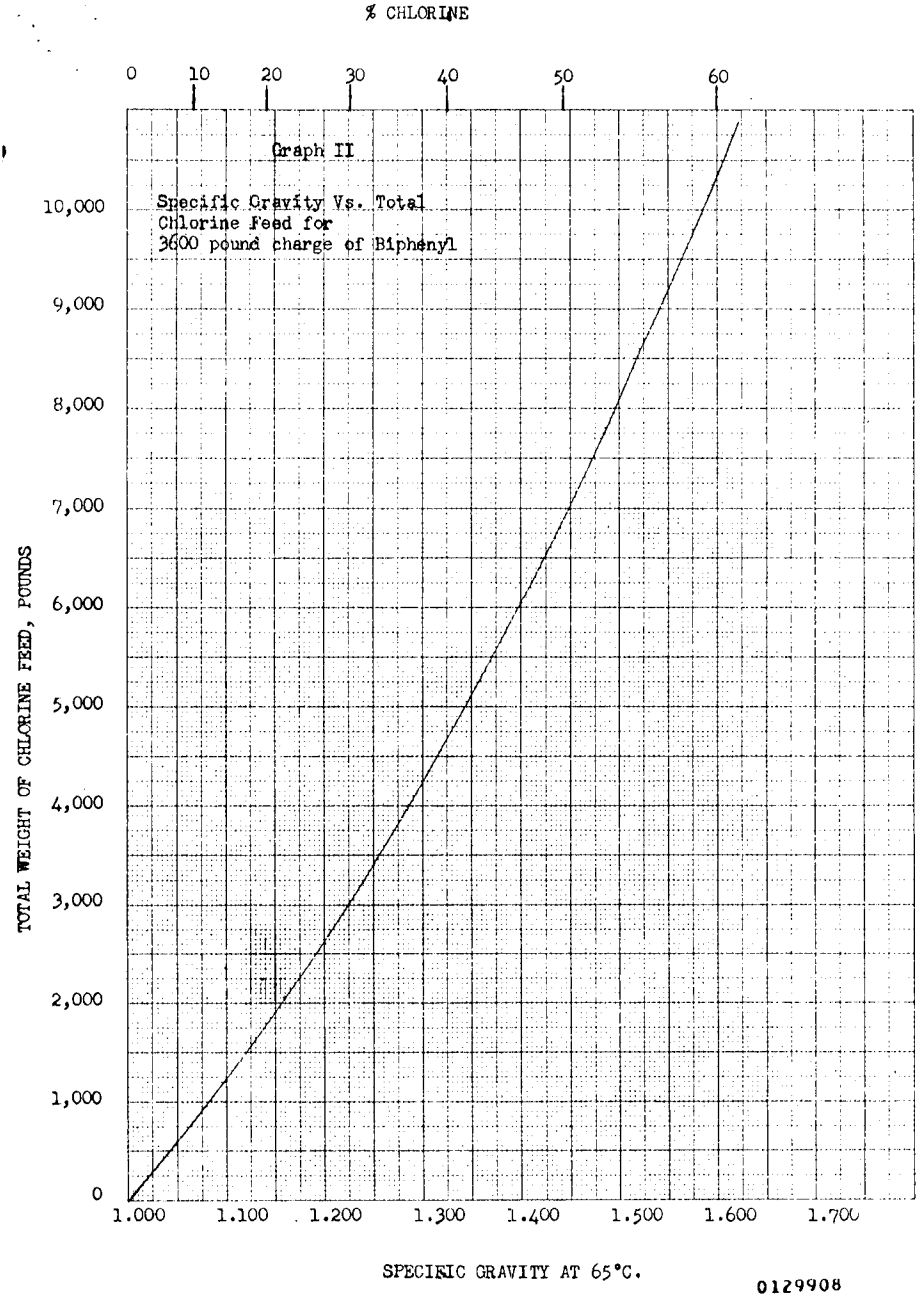

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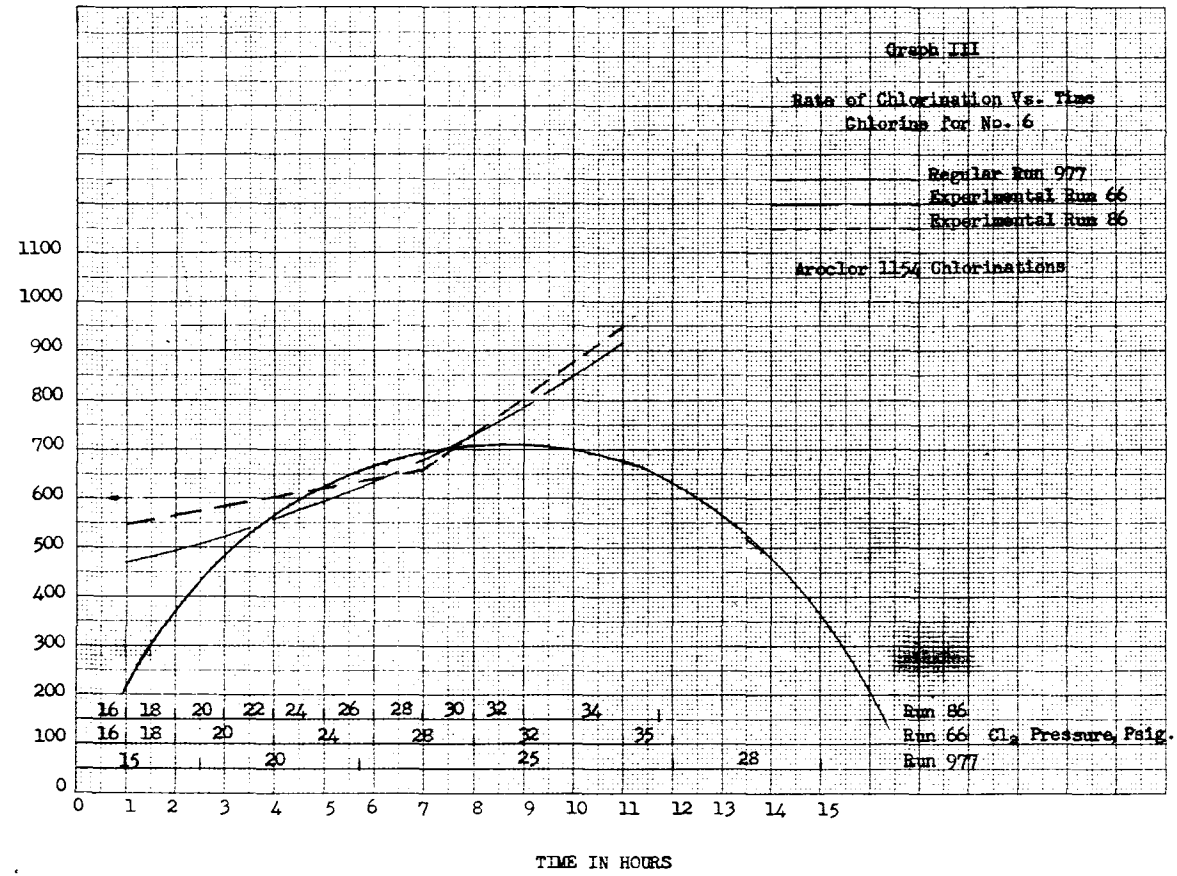

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DISCUSSION:

Chlorinators 5 and 6 have been modified for rapid chlorination by installation of small individual cyclone entrainment separators with return lines to the chlorinators. Normal plant operation in these two chlorinators is faster than in the unmodified chlorinators, but observation of the plant operations indicated that the time of chlorination might be even further reduced by better control of chlorination rates throughout the chlorination.

Graph III of this report shows the rate curve for a normal plant chlorination, Run 977, which is typical of the rate curve for usual plant operation. The rate of chlorination starts low, builds up in excess of 700 to 800 pounds per hour toward the middle stage, sometimes greater than 1000, and then decreases toward the end. This behavior results from inadequate control of the chlorine pressure being supplied to the chlorinator. It seemed apparent that by controlling the chlorination more closely to give more uniform rates, considerable time might be saved during a chlorination.

Two experimental plant runs were made during which the chlorine was admitted at a faster rate throughout the run. Chlorinator 6 was chosen for these tests because it is one of two chlorinators equipped with small individual entrainment separators as well as the large cyclone separators. Chlorinators 1, 2, 3, and 4 are equipped with the large separators only.

The first test run, No. 66, required twelve hours and ten minutes to complete the chlorination. The chlorine was admitted at an initial back pressure of sixteen pounds and after gradual increases for the first several hours, the pressure was increased four pounds every two hours until a final pressure of thirty-five pounds was reached. This pressure was maintained at thirty-five pounds for one hour and ten minutes with no apparent difficulty.

The second test run, No. 86, required eleven hours and forty-five minutes. This run was started at an initial chlorine pressure of sixteen pounds; however, during this test, the pressure was increased two pounds every hour until a maximum pressure of thirty-four pounds was attained.

At the beginning of Run No. 66, the chlorine tank car was practically full, and during the run the pressure of the car decreased from 80 to 76 p.s.i.g. The only unusual observation was that the chlorine vapor line coming out of the vaporizer turned cool when a back pressure of thirty-five pounds was reached.

At the beginning of Run No. 86, the chlorine tank car was about half full, and while the pressure of the car remained constant throughout the run, the pressure was only 63 p.s.i.g. The maximum back pressure of thirty-four pounds could not be increased at the conclusion of the run.

Circulation of the material in the chlorinator was started only one hour after chlorination was started. The usual plant procedure is to wait three or four hours; however, because chlorine was going in at a faster rate, circulation was starter earlier.

The temperature of the chlorinator was easily maintained within the required operating temperatures of 105°C. to 150°C.

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At the conclusion of each run, the trappings, or material collected by the cyclone separator, were drained. Material from chlorinators 3, 4, 5, and 6 totalled approximately one-half of a 55-gallon drum. This was considered normal by the operator.

Graph III also shows the rate curves for these two experimental chlorinations. There appears to be little difference in raising the pressure four p.s.i.g. every two hours, and in raising it two p.s.i.g. every hour. Both of these runs started at about 500 pounds of chlorine per hour, gradually increasing toward the middle of the run, and then entered a somewhat greater upward trend toward the end of the run. These curves of course show only the general trends in the rates. There is still considerable variation, but not as wide as in the regular runs. The reduced time of chlorination is adequate proof of the effectiveness of the method.

Table III and Table IV show the detailed data for the 1154 chlorinations, both regular and experimental operation. Table V shows the averages of the chlorination rates under the various conditions and gives the percentage increases in each case. An increase of nearly 60% was realized in the experimental Aroclor 1154 chlorinations over the regular plant operations. An increase of nearly 40% has already been shown in plant operations on No. 6 chlorinator over operations on the unmodified chlorinators. Table VII gives the analyses of the Aroclors from the experimental operations, all of which are within specifications.

Several experimental runs were carried out on Aroclor 1142 in chlorinator 5. Table I gives typical data for regular 1142 chlorinations as compared to the experimental chlorination data given in Table II. Comparison of data in these two tables shows that an increase of about 33% in plant production has been brought about in chlorinator 5, and that a further increase of 41% over this rate is possible, or a total overall increase of 88%. This comparison is tabulated in Table V. It should be pointed out, however, that this increase in production was accomplished on only one chlorinator, and that a similar increase on all the chlorinators would be largely dependent upon an adequate supply of chlorine to maintain these increased feed rates.

Table VI gives the analyses of the Aroclor 1242 samples from the experimental 1142 chlorinations. All of these samples were within specifications except that from Run 278 which had an unusually wide distillation range. Runs 303 and 341 were made at lower rates of chlorination and gave satisfactory Aroclors. It was then thought that finer dispersion of the chlorine by a glass cloth might make possible more rapid rates without producing off-grade Aroclor. Run 293 was made with such a cloth over the chlorine distirbutor and specification grade Aroclor resulted; however, the rate of chlorination was not as high as in Run 278. Subsequent examination of the glass cloth revealed that it had formed a matte-like material and had so constructed the flow of chlorine that the resulting pressure had ripped the cloth at the seam. For this reason, it was considered entirely unsatisfactory for this application. Furthermore, the data for Run 381 show that specification grade Aroclor 1242 can be produced at even a faster rate than employed in Run 278, and without further modification of the equipment. This rate of 786 pounds of chlorine per hour is the highest overall average rate yet attained in an experimental plant chlorination. It must then be concluded that the glass cloth is of no value in the chlorinator, and that the wide distillation range obtained in Run 278 was not due to the rapid chlorination rate, but was probably due to higher chlorinated trappings being charged to the chlorinator.

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From the foregoing facts it may be stated that an increase in production of about 30% has already been accomplished in the plant on No. 5 and No. 6 chlorinators, and that an additional increase of up to 40% over this 30% is within possibility depending largely upon the chlorine supply available.

Although no specific test was run on Aroclor 1260, regular production during periods of fast chlorination rates was satisfactory. Theoretically, there is also less chance of varying the isomer distribution of the Aroclor 1160 then of the 1142. Therefore, any change in properties is unlikely in view of the successful Aroclor 1242 and 1254 tests.

In consideration of the maintenance of equipment, the erosion of the distributor plate will be greater at the high chlorine feed rates. Observations have indicated that the plates may last only about a third as long as at the slow feed rates of 400-500 pounds per hour.

Increasing the number of holes in the distributor plate would help in lessening the erosion.

The replacement of catalyst may also be a more frequent practice. At the higher feed rates, the chances of localized high temperatures in the reaction zone are good and will allow more iron chloride to be formed, thus using up the iron turnings at a faster rate.

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