Progress Report

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Title	TSD Job & Report No.
MONOCHLOROBIPHENYL: PLANT DEMONSTRATION OF THE CONVERSION OF MONO RESIDUE INTO AROCLOR 1242'	91370:9002 (9)
	Business Group: SPECIALTY PRODUCTS

Product Code	Product	Dept. No.
811.11	AROCLOR	246

Personnel	Report Date
K. E. Boucher (W. C Engman)	2/25/75

SUMMARY:

Monochlorobiphenyl was made in the Aroclor department last September, 1974, to provide Dow one tank car for their evaluation. While producing 5,660 gallons of Monochlorobiphenyl, some 4,000 gallons of distilled Monochlorobiphenyl residue was collected. To complete the field demonstration of the new Monochlorobiphenyl process, this Mono residue was converted into Aroclor 1242'. Aroclor 1242' differs from the normal Aroclor in that it has a lower dielectric constant and a higher refractive index.

During the week of February 10, 1975, 1500 gallons of distilled residue was chlorinated to 1142, isomerization over $AlCl_3$, lime treated, then distilled again, Porocel treated, and stored as Aroclor 1242'. About 1,064 gallons of Aroclor 1242' was made. Monochlorobiphenyl process is given in Report No. P-1766, Process for Engineering Design for Monochlorobiphenyl, 7/29/74, by D.R. Cova.

Results of the Aroclor 1242' demonstration and possible areas for improvements are now given:

1. Quality was good; normal electrical properties were obtained. All the electrical specifications were met except for a slightly lower dielectric constant, higher refractive index, lower specific gravity, and lower viscosity. The low gravity/viscosity are due to not distilling over enough Aroclor during the still pot boildown. About 580 gallons of residue were drained from the still following the boildown.

2. The isomerization reaction was extremely fast. Process calls for a five hour hold period at 250°C to reduce the 4,4' dichlorobiphenyl level to 2.5%. The $AlCl_3$ catalyst used in this demonstration was tested by Research and is considered 'hot'.

MONS 021673

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SUMMARY (Continued)

The 2.5% 4,4'DCBP level was reached at 200°C, within 1-1/2 hours after heating past 155°C. Recommended catalyst concentration of 0.25% was used, and the option of aging for an additional five hours past the recommended hold period using a higher 0.40% catalyst concentration was not needed.

3. The 4,4' Dichlorobiphenyl decreased from 3.5% to about 1.8% in the third hour after reaching 250°C. The 4,4' DCBP level then remained essentially constant. This is well below the 2.5% 4,4' DCBP level required. If such low levels can consistently be achieved, we recommend the isomerization step be continuous rather than batch to significantly reduce operator workload.

4. The isomerization reaction started at temperatures considerably below 250°C. If we can have some of the isomerization occur at 200°C better equipment utilization and less process risk would be possible. Now an extremely long isomerization cycle (>6 hours) would create a bottleneck. We recommend a two-step isomerization: (1) the initial reaction would occur at 200°C using the existing blend tanks for up to 9 hours, (2) any finishing necessary can be achieved by heating to 250°C in #1 still.

5. The lime concentration recommended by Research is 0.5%, more than twice now used to treat crude Aroclor 1142. The lime is used to prevent the $FeCl_3$ and $AlCl_3$ catalyst from coming over during final distilling as well as neutralizing dissolved HCl. Research and the plant have considered possible ways to remove HCl gas prior to lime treatment. We recommend the HCl be removed by placing the isomerized crude under vacuum and approach the boiling point. This step would be included in the isomerization finishing step at 250°C using #1 still vacuum controls.

ACKNOWLEDGEMENTS:

My thanks to the many people who helped in making this a successful demonstration: Area 5 Shop, Production, WGK Laboratory, and Research. My special thanks for the suggestions and comments of Gary Johnson who wants a continuous process, Linus Horcher for his prompt analytical results and Dario Cove who developed the process.

Kenneth E. Boucher

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Technical Services Department

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BACKGROUND

The September demonstration run provided a good quality finished product. Monochlorobiphenyl tentative specifications versus actual analysis were:

Component	Monochlorobiphenyl Specification	Actual Result
Biphenyl	0.6% max.	0.32%
o-chlorobiphenyl	80.0% min.	83.97%
m-chlorobiphenyl	4.0% max.	4.04%
p-chlorobiphenyl	remainder	10.87%
Polychlorobiphenyl	1.0% max.	0.75%
Sp. Gr. 25/15°C	1.152-1.162	1.159
Refractive Index 25°C	1.6092-1.6112	1.6108

Only significant problem was that the Aroclor column could only run at 80% of design due to excessive vibration of the still pot. Improved mechanical support of the still pot furnace return piping will be recommended.

PROCESS FLOW FOR AROCLOR 1242' DEMONSTRATION

Department equipment was used as given below. Major difference between the demonstration and the plant design scope is that #1 still will be used for isomerization rather than #2 still.

Unit	Use
#1/#2 Blend	To store mono residue
#2 chlorinator	For batch chlorination
#2 Blow Tank	Feed tanks for #2 & #4 stills
#2 Still	First for isomerization, then the lime treatment
#4 Still & Receiver	To distill Aroclor 1142'
#5 Absorber	For Porocel treatment
#16 Storage	Aroclor 1242' product storage

RESULTS

1. **Materials**

Quantities involved in this demonstration are shown:

Mono Residue - 1500 gallons	
Crude Aroclor 1142'	~1724 gallons
Aroclor 1242'	1064 gallons
#4 Still residue	~ 580 gallons

Three chlorinator batches were made, each using 500 gallons of Mono residue.

RESULTS (Cont'd)

2. Quality

Table I shows analysis versus specifications for Aroclor 1242.

TABLE I

QUALITY OF AROCLOR 1242' MADE FROM MONOCHLOROBIPHENYL BY CHLORINATION/ISOMERIZATION

	SPECIFICATION	PRODUCT MADE* IN THE LABORATORY FROM RESIDUE	PRODUCT MADE IN AROCLOR DEPT.
Distn Range	>235°C at 10%, <360°C at 90%	335/346	333/347
Refractive Index @ 25°C	1.6240-1.6260	1.6285	1.6265
Pour Point	<-14°C	-16°C	-20°C
Power Factor @ 100°C, 60 cycle, max., @ 100°C, 1000 cycles	0.5 Internal 1.0 Customer	0.38	0.084
Dielectric Constant @ 60 cycles, 100°C @1000 cycles, 100°C	4.74-4.95	4.69	4.69 4.69
Resistivity @ 100°C		6.8×10^{13}	24.27×10^{13}
Dielectric Strength @ 25°C	>35 KV	>50 KV	45 KV
Inorganic (Free) Chlorides	0.05 ppm, max.		0.01 ppm
Thermal Chemical Chlorides	<0.65 ppm	0.36-0.85	0.24 ppm
Monsanto Stability	<.4 ppm	0.14-0.73	0.06 ppm
Westinghouse Hydrolyzable Chlorine	<1.0 ppm	0.40 ppm	0.53 ppm
Hydrolytic Stability	<0.5 ppm	0.06 ppm	0.10 ppm
Corrosion	0.0	0.0	0.0
A.C. Color	<60 APHA	15 APHA	15 APHA

RESULTS (Cont'd)

TABLE I (Cont'd)

QUALITY OF AROCLOR 1242' MADE FROM MONOCHLOROBIPHENYL BY CHLORINATION/ISOMERIZATION

	SPECIFICATION	PRODUCE MADE* IN THE LABORATORY FROM RESIDUE	PRODUCT MADE IN AROCLOR DEPT.
A.C. Condition	Clear	Clear	Clear
A.C. Acidity	<0.010	0.001	0.001
A.C. Inorganic Chlorides	<0.05 ppm	0.05 ppm	0.02 ppm
Viscosity @ 100°C	82-92 SUS	87.5 SUS	80.6 SUS
Specific Gravity @ 25°C	1.381-1.392		1.379
Moisture (H_2O)	35 ppm,max		10 ppm
Acidity (Mg KOH/g)	0.010 max.		0.001
Turbidity			None
Appearance			Water white liquid
Residue			Very slight
Color (APHA)			15 APHA

3. CYCLES

Chlorination: Chlorination cycles were varied by using different programmed chlorine feed rates for each of the three batches. No entrainment in the off-gas HCl was detected.

TABLE II

Batch	Cl_2 Feed Program 1st Hour #/hr Cl_2	After 1st Hour #/Hr. Cl_2	Chlorination Time	Estimated Total Cycle Time
1	800	800	172 minutes	192 min (3 hr, 12 min)
2	800	1000	145 minutes	165 min. (2 hr, 45 min
3	800	1200	130 minutes	150 min. (2 hr., 30 min

Each chlorination was done at 150°C using 4 lbs of $FeCl_3$ and 500 gallon of Mono residue.

ISOMERIZATION

Isomerization was begun on 2/12/75 at 9 A.M. with the addition of 45 pounds of $AlCl_3$ to some 1729 gallons (0.25% $AlCl_3$) of crude 1142'. Then the still was heated using a direct fired Aroclor furnace. Table III gives the results. The still was heated to 250°C and held at 250°C for one hour. Sample analysis then indicated the isomerization was completed. At 2:30 P.M., the #2 still furnace burners were turned off and the batch was allowed to cool until 6 A.M. when the lime was added

TABLE III

1142' ISOMERIZATION DEMONSTRATION

2/12/75

TIME (HRS)	#2 STILL TEMP.	REACTION TIME (after reaching 250°C)	AREA % 4,4' DICHLORO-BIPHENYL (DCBP)
0	115°C		3.48%
1	155°C		3.36%
2	180°C		2.69%
3	215°C		2.22%
4	235°C		1.98%
4-1/2	250°C	0	1.87%
5-1/2	250°C	1	1.89%
6-1/2	245°C	2	1.92%
7-1/2	238°C	3	1.82%
8-1/2	230°C	4	1.84%
9-1/2	225°C	5	1.85%
21	178°C	16-1/2	1.84%

Process calls for 2.5% 4,4'DCBP. This was reached near 200°C about 1-1/2 hours after passing 255°C. As far as 4,4' DCBP is concerned, the isomerization was essentially completed when 250°C still temperatures was reached.

LIME TREATMENT

At least two hours lime treatment time is required. At 6 A.M., 100# of lime was added to the 1725 gallons of crude and agitated for two hours in #2 still. The slurry was then transferred to the #2 blow tank.

DISTILLATION

#4 still was charged, heated @ 40 mm Hg vacuum before starting feeding a continuous flow of crude from #2 blow tank. Cycle times are given Some 1064 gallons of distilled Aroclor 1242' was collected and about 580 gallons of residue was drummed from #4 still.

DISTILLATION (Cont'e)

#4 STILL CYCLE

OPERATION	CYCLE TIME-HOURS	TEMPERATURE
Charged #4 still	1-1/2	
Heat-up still @ 40 mm Hg	1-1/3	
Continuous feed	2-1/6	226-229°C
Boildown 40% level to 15%	1-5/6	234-235°C
TOTAL	6-5/6	

Gallons per hour while distilling forward: 1064 gallon = 266 gph versus 192 gph required for 8M #/yr capacity. 4 hrs

DISCUSSION OF RESULTS

The results of the demonstration were reviewed with the need in mind to provide facilities for manufacturing 8M pounds of Monochlorobiphenyl per year. Through use of the data received during the demonstration the process risk could be reduced and by following through with the various operating workload could be somewhat analyzed. Here are some comments that were made by Production during the demonstration:

1. The still operator will have many additional responsibilities due to the isomerization step. Can some steps be automated?

2. The amount of lime addition for making Aroclor 1242' is over twice that needed for Aroclor 1016. Can lime addition be reduced?

3. A significant amount of time may be needed for the isomerization step. The #1 still could be a bottleneck if the cycle extends over five (5) hours. Can some of the isomerization occur in the #1 still feed tanks?

4. Heat-up in #2 still took almost 4-1/2 hours. Can the heat-up cycle be reduced?

To accomplish the above desireble improvements, the following changes are recommended in the Monochlorobiphenyl process.

1. Make the isomerization step continuous. The quickness at which the 4,4' DCBP was reduced to a 2.5% level and the fact that a much lower level was reached (1.85% 4,4 DCBP) suggests that continuous isomerization is possible.

DISCUSSION OF RESULTS (Cont'd)

2. Add an additional HCl removal step to possibly reduce lime usage Much of the dissolved HCl gas in crude 1142' would be removed if a vacuum was pulled on the crude after isomerization. Less lime might then be needed to keep the catalyst in the batch when distilling.

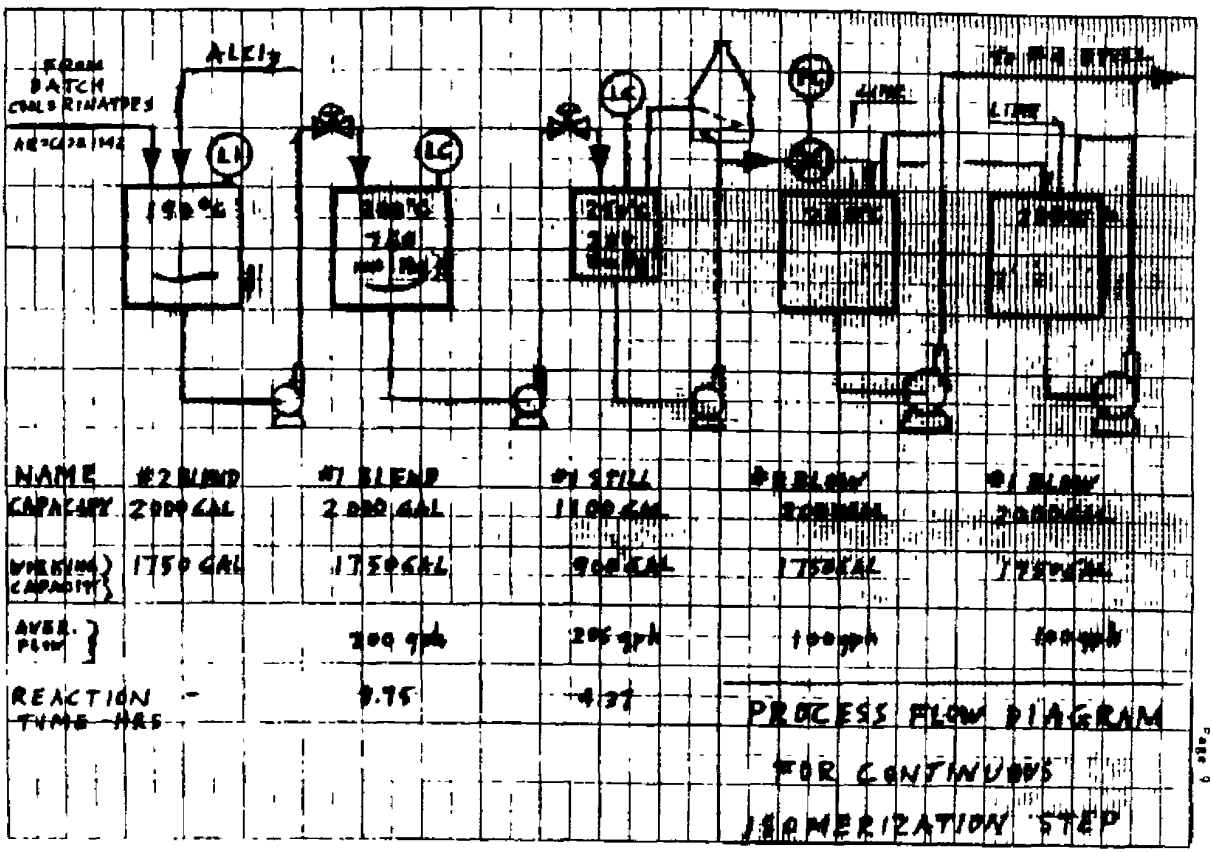
3 More time could be allowed for the isomerization if the reaction could be allowed to begin in the feed tanks, controlled at 200°C, with 200# steam. The demonstration shows a significant amount of reaction occurs at 200°C. The reaction then would be finished off at 250°C in a still using a gas furnace. This would amount to a two step isomerization reaction.

4. The 200°C reaction temperature could be more economically and quickly reached if the final chlorinator temperature of 190°C was allowed. The initial chlorination would still be at 150°C for the first hour; with the remaining 1-1/2 hour being at 190°C. We now chlorinate at 190°C in the last of four continuous chlorinators when producing Aroclor 1142 crude.

To better visualize the revised isomerization process, see the process flow diagram sheet.

The isomerization step during the demonstration was allowed to proceed after the required 2.5% 4,4' DCBP was reached. Even after no significant change in 4,4' DCBP occurred we found isomerization continued. In Table IV, major changes in isomer distribution are given throughout the isomerization process step. There is an indicated increase in tetra's and penta's. This may indicate some increase in high boilers. Data is extracted from the attached WGK Analytical R&D report, No 2644 from L. Horcher and K.L. Schutzenhofer.

K-E



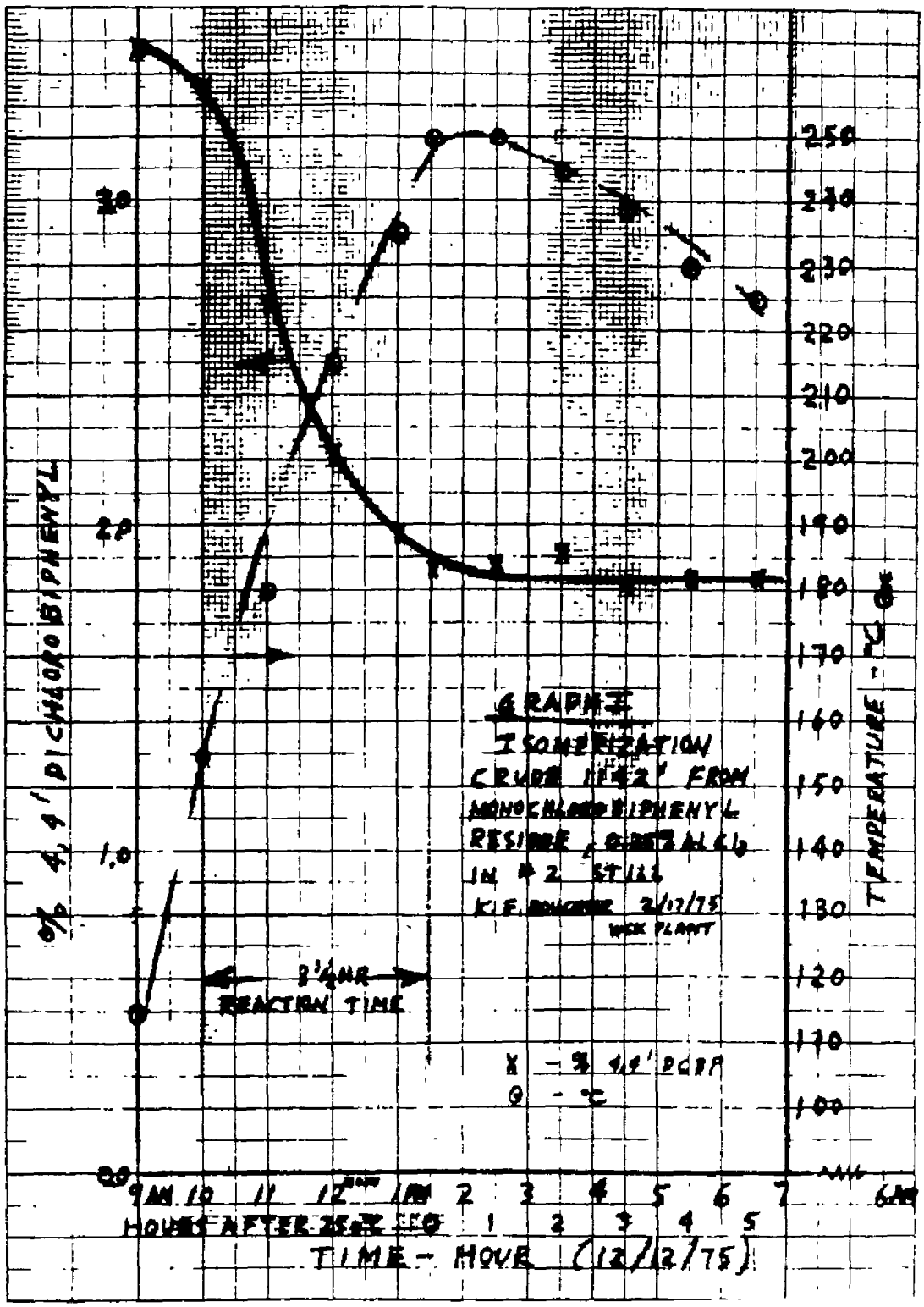
MONS 021681

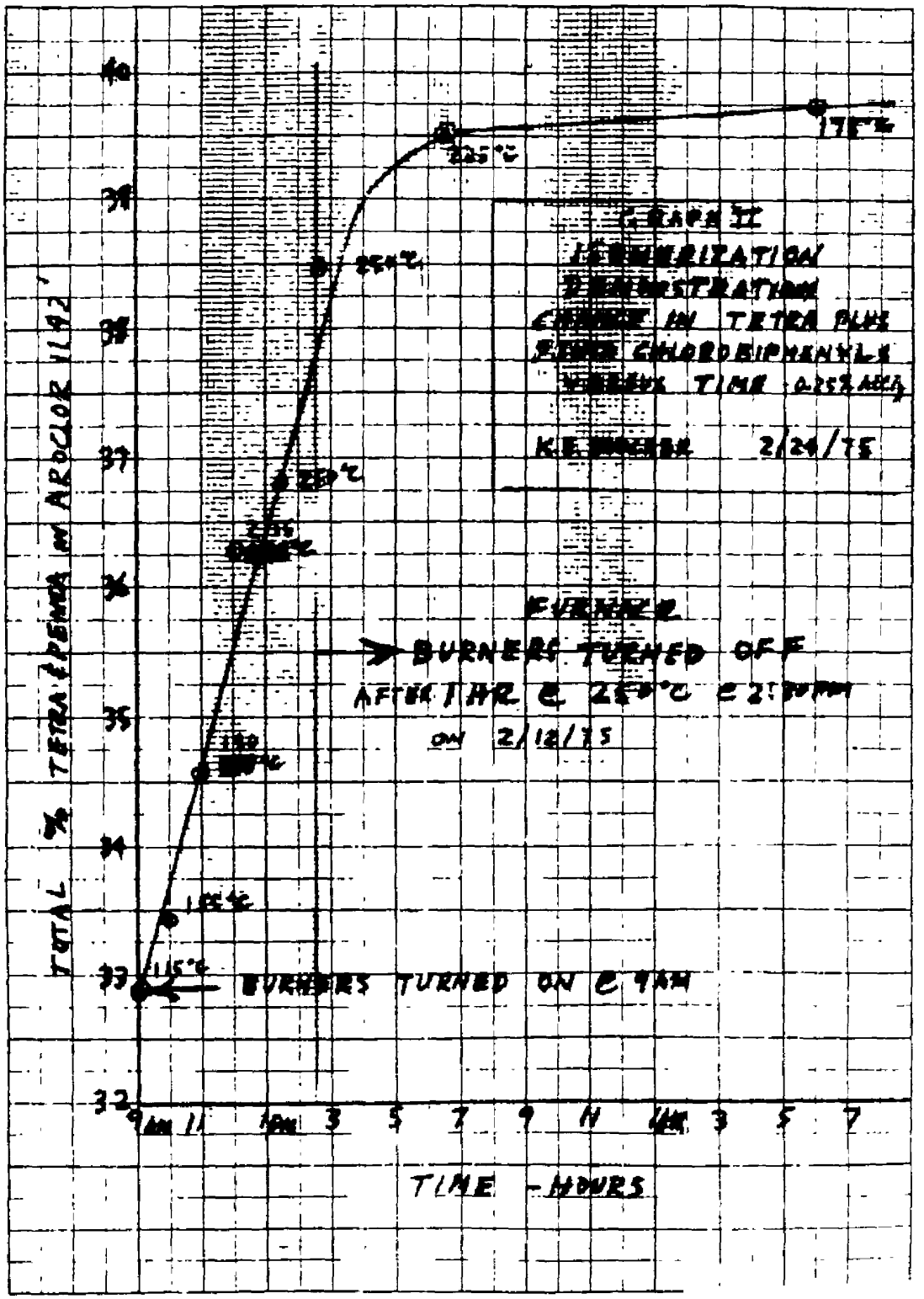
DISCUSSION OF RESULTS (Cont'd)

TABLE IV

1242' ISOMERIZATION RUN - AREA PERCENT
0.25% $ALCl_3$

Time	9 AM	10 AM	11 AM	12 NOON	1:30 PM	2:30 PM	6:30 PM	6:00 AM
Time in Still	0 hr.	1 hr.	2 hr.	3 hr.	3-1/2 hr.	4-1/2 hr	8-1/2 hr	16-1/2 hr
Temp.	115°C	155°C	180°C	218°C	250°C	250°C	225°C	178°C
Component Reducing:								
1. 2,2'	0.91	0.71	0.53	0.43	0.46	0.29	0.26	0.21
10. 2,4'	9.24	6.61	3.33	1.85	1.15	1.03	0.88	0.91
12. 2,5,2'	9.09	8.97	8.67	8.03	7.62	7.19	6.77	6.72
17. 4,4'	3.48	3.36	2.69	2.22	1.87	1.89	1.85	1.84
19. 2,5,4'	23.31	23.31	22.29	20.47	18.03	16.48	14.81	14.74
21. 3,4,2'	7.35	7.39	7.23	6.81	6.10	5.63	4.89	4.87
27. 2,3,4'	4.44	4.12	3.60	2.87	2.13	2.06	2.00	2.04
Total Reductions:	57.82	54.47	48.34	42.68	37.36	34.57	31.46	31.33
Increasing:								
9. 2,3'	0.76	1.96	3.14	2.85	2.09	1.72	1.45	1.40
13. 3,3'	0.26	0.27	0.63	2.03	3.79	4.61	5.50	5.59
15. 3,4'	0.27	1.68	4.02	5.61	6.17	6.00	5.89	5.89
18. 2,3,2'	4.30	4.56	5.23	6.35	10.15	11.55	12.91	13.19
22. & 23. Tetra'e	0.51	0.52	0.63	0.87	1.13	1.25	1.31	1.35
Other Tetra'e + Penta'e peat 26.	26.10	26.61	27.63	28.98	29.29	30.82	31.78	31.81
TOTAL INCREASE	32.20	35.60	41.28	46.69	52.62	55.95	58.84	59.21
COMPONENT TOTAL	90.02	90.07	89.62	89.37	89.98	90.52	90.30	90.54


% 4,4' DICHLOROBIPHENYL
TEMPERATURE - °C
GRAPH I
ISOMERIZATION
CRUDE 1142' FROM
MONOCHLOROBIPHENYL
RESIDUE
IN #2 STILL
K.F. BOUCHER 2/17/75
WCK PLANT
REACTION TIME
X - % 4,4' DCBP
⊙ - °C
HOURS AFTER 25°C
TIME - HOUR (12/12/75)


GRAPH II
ISOMERIZATION
DEMONSTRATION
CHANGE IN TETRA PLUS
PENTA CHLOROBIPHENYLS
VERSUS TIME 0.25% ACID
K.E. [illegible] 2/24/75
FURNACE
BURNERS TURNED OFF
AFTER 1 HR @ 250°C @ 2:30 PM
ON 2/12/75
BURNERS TURNED ON @ 9AM
115°C
225°C
250°C
TOTAL % TETRA & PENTA IN AROCLOR 1142
TIME - HOURS
40
39
38
37
36
35
34
33
32
9AM 11 1PM 3 5 7 9 11 1AM 3 5 7

CONCLUSIONS AND RECOMMENDATIONS

1. The isomerization step of the new Monochlorobiphenyl process was successfully demonstrated with the Aroclor 1242' meeting the critical specification for electrical grade.

2. Recommended changes to the new Monochlorobiphenyl are as follows:

   a) Convert the isomerization step from batch to continuous.

   b) Insert a vacuum treatment step for removal of dissolved HCl in an attempt to reduce lime addition.

   c) Have isomerization done in two steps to allow better utilization of equipment and to provide more than adequate time for completing the reaction.

   d) Finish the chlorination of Mono residue at 190°C to minimize the heat-up time to reach isomerization reaction temperature.

Future Work consists of:

1. Completing the plant engineering scope for the manufacture of Monochlorobiphenyl.

2. Providing additional research work to check:

   a. Chlorination of Mono residue at 190°C. — O.K.

   b. Distillation of plant isomerization mono residue to see if the viscosity and specific gravity specifications will be met.

   c. Simulate proposed continuous isomerization process.

   d. Determine if high boilers are actually significantly increased during isomerization. — N/A

3. The remaining 2500 gallon of Mono residue will be converted into Aroclor 1254. Also the Aroclor 1242' produced by this demonstration will be converted into Aroclor 1254.

Kenneth E Boucher

Kenneth E. Boucher
Technical Services Department

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