ORGANIC CHEMICALS DIVISION RESEARCH Report

REPORT NO.- 3281 JOB NO.- 2-02-760.01-4758

FINAL REPORT
ON
FRACTIONATION OF AROCLOR 1142 FOR
IMPROVING PRODUCT STABILITY

DATE - February 16, 1966 WRITTEN BY - R. Lee

Monsanto

ST. LOUIS, MO.

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St. Louis Research Report No. 3281

FINAL REPORT

ON

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JOB NO. 2-02-760.01-4758

Work Authorization No. 14-65

Date: February 16, 1966

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INTRODUCTION

In order to improve Monsanto's market position in Aroclor for electrical end use, this distillation work was undertaken to upgrade the thermal-chemical stability of Aroclor 1242. Currently the finished product has a stability that can be expressed as 0.4-0.6 ppm. 'thermal chemical' chloride. The goal of this project was to develop a continuous fractionation process to produce Aroclor with a 'thermal chemical' chloride of 0.15 ppm. or less.

'Thermal chemical' chloride is the unstable chloride in Aroclor generated from a two-hour exposure at 240°C. This measure of product stability has been generally adopted by the consumers of Aroclor. While Aroclor 1242 has to meet a number of stringent specifications such as color, specific gravity, dielectric constant, etc., the thermal chemical stability of the product needed improvement and was of primary concern in this research work.

One way of improving the quality of Aroclor is described in a British patent issued to Progile, a French corporation (Ref. 2). Crude was distilled using 40 theoretical plates and a vacuum of 5-10 mm. Hg by a batch process. Sizable fractions of low boilers and higher boilers were removed. They claimed excellent electrical properties for their product, although the product stability was not reported.

Distillation of crude Aroclor is also one of the purification steps in the current plant process. However, the distillation is straight-takeover involving no fractionation. The operation is semi-continuous at a vacuum of 30-50 mm. Hg. Only high boilers are removed. The feed to the still is crude Aroclor 1142 which is produced by reacting biphenyl with chlorine gas.

Briefly, the plant process is as follows: Crude Aroclor 1142 from the chlorinators is first aerated with dry air to remove free hydrogen chloride and then fed to the still. Hydrated lime, in an amount equivalent to about 0.3% of the Aroclor charge, is then added to the still at the beginning of a distillation cycle. The lime neutralizes any residual HCl in the still liquor and prevents sublimation of ferric chloride during the distillation period.

During the semi-continuous distillation, Aroclor 1142 is fed continuously to the still, and the distillate, Aroclor 1242, is also collected on a continuous basis. After charging about 75,000 pounds of Aroclor which is equivalent to filling 7 still receivers, the feed is cut off. The still is further boiled down to an upper temperature limit. Then the heel is dumped and another cycle is repeated.

The distillate, Aroclor 1242, is further treated with Attapulgus earth to remove water and ionic impurities. The treatment is followed by a filtration step to obtain the final finished product.

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The differences between Monsanto's distillation procedure and that described in Progile's patent are apparent. Based on Progile's patent, the W.G. Krummrich Plant Process Development Group did some exploratory distillation work to fractionate Aroclor 1142 (Reference 3). They found that Aroclor with 'thermal chemical' chloride as low as 0.12-0.17 ppm. could be prepared by removing fractions of low boilers and high boilers. Their successful batch distillation work led to the initiation of this project.

This project covered a period from July 6 to October 27, 1965, and was initiated under Manufacturing Work Authorization No. 14-65.

NOMENCLATURE

Aroclor - A Monsanto trade name for chlorinated biphenyl.

Aroclor 1142 - Plant crude chlorinated biphenyl containing approximately 42% chlorine.

Aroclor 1242 - Distilled chlorinated biphenyl containing approximately 42% chlorine.

Thermal Chemical Stability Test - A 2-hour test at 240°C. for determining the combined chemically and thermally unstable chlorides in Aroclor (see Analytical Procedures for details).

'Thermal Chemical' Chloride (T.C.Cl) - The amount of unstable chloride in Aroclor 1242 generated during the thermal chemical stability test. The level of 'thermal chemical' chloride is a measure of the stability of Aroclor; the lower the level, the more stable is the product.

Free Chloride - The unstable chloride in Aroclor 1242 prior to the Thermal Chemical Stability Test. Free chloride is always deducted from the total chloride to get the 'thermal chemical' chloride.

SUMMARY

Continuous and batch fractionations of Aroclor 1142 were carried out using bench-scale Oldershaw equipment for upgrading product stability from the current 0.4-0.6 ppm. level in 'thermal chemical' chloride to the target specification of 0.15 ppm.

In batch fractionation work, the variables studied included: number of trays (5 to 20), reflux ratio (1:1 and 5:1), column head pressure (5 and 40 mm. Hg) and lime addition (0 and 0.4%).

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For continuous fractionation work, a two-column system was used. The operating variables investigated were yield (74 to 83%), number of trays (15 to 27), reflux ratio (0.8:1 to 8:1), head pressure (10 and 40 mm. Hg) and mode of column operation. None of these variables appeared to control product quality. A one-column system was also tested for removing low boilers and high boilers.

Some limited experimental work was undertaken to stabilize feed material by treating Aroclor 1142 with $AlCl_3$. In addition, some gas chromatographic analyses were made of the distilled Aroclor in an attempt to correlate composition with stability.

CONCLUSIONS

1. Aroclor 1242 with a 'thermal chemical' chloride level of 0.17 ppm. can be produced by continuous fractionation. However, that is about the best that can be achieved by a continuous process. The yield was 74%.

2. Aroclor stability does not appear to depend significantly on the distillation conditions.

3. The addition of lime to feed material is the most important factor. But lime has a tendency to plug up fractionation equipment.

4. The best Aroclor product was obtained in a batch run using 5 trays and a reflux ratio of 5:1. The 'thermal chemical' chloride of the material was 0.11 ppm. The yield was 82%.

5. The product stability does not correlate well with either the low boiler or the high boiler content of the distilled material. However, removing some low boilers and high boilers from the crude is essential to product stability.

6. The electrical properties of the laboratory-prepared Aroclor 1242 were comparable to those currently produced in the plant.

RECOMMENDATIONS

1. Since the addition of lime to feed material is the single most important variable to product stability, it is recommended that other alkalis, e.g. K_2CO_3, KOH be tried. Note that the W.G. Krummrich Plant Process Development Group is doing additional research work in this area.

2. If a 'thermal chemical' chloride of 0.20-0.25 ppm. can be tolerated, the possibility of using a one-column system for fractionating Aroclor continuously deserves further testing.

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3. Treating Aroclor 1142 with lime and then distilling the filtered material can prevent lime from accumulating in the distillation column (such as in Run B7). This route was not fully explored in this work, and may deserve additional research work.

4. A better and faster method of characterizing Aroclor stability is very much needed. The current Chemical Thermal Stability Test is exceedingly elaborate and is susceptible to contamination. This analytical method was also judged as unsatisfactory in a separate research investigation (Ref. 6).

PATENT STATUS

No patentable information resulted from this work.

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Notebook Pages - OR 29566 - OR 29599
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EXPERIMENTAL WORK

A. Batch Fractionation

1. Equipment and Operating Procedures

A number of batch distillation runs were made prior to the continuous distillation work in order to develop the meticulous techniques for handling distilled Aroclor and to estimate the distillation requirements for a continuous process.

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The batch distillation column consisted essentially of 2-inch I.D. Oldershaw column sections and a thermal siphon reboiler. A schematic diagram of the column is shown in Figure 1. The column was vacuum jacketed, silvered and insulated with Aerocor in order to minimize heat loss. The number of trays in the column was varied from run to run ranging from 5 to 20. The usual accessories for distillate collection were used. The accessories included a condenser used as a cooler, a fraction cutter and a round bottom receiver. The column was vented through a dry ice trap which led to a vacuum controller and a vacuum pump. Vacuum control of the column was maintained using either a Hg monostat or a Moore flow regulator. Heat input to the reboiler was supplied by a coil heater constructed from 1/8" stainless steel tubing. Other accessory equipment around the column included either a U-tube Hg manometer or a McLeod gage for column head pressure measurements, a differential manometer containing Aroclor 1242 for pressure drop across the column, and a reflux trap which was placed between the reboiler and the trays. The reflux trap was used for boil-up measurements and for occasional sampling through a side take-off. Temperature measurements were made with thermocouples located at the top of the column, in the reboiler and inside the reboiler heater. The thermocouples were connected to a multi-point recorder.

To make a run, plant Aroclor 1142 (about 5000 gm.) and the desired proportion of lime were charged into the reboiler. With the vacuum pump on and the vacuum controller operating, the reboiler heater was turned on and the reflux splitter was set for total reflux operation. After the boilup reached the top of the column, the boilup rate was checked using the reflux trap. Minor adjustments in the heat input to the reboiler were sometimes necessary in order to operate the column at a high efficiency level. Generally, the total reflux operation lasted about an hour for equilibration prior to distillate take-off.

In general, about 92 to 94% of the charge was distilled over in a run. A large number of distillate cuts (generally 12 to 15) was collected. The initial and final cuts were usually small in order to obtain a close estimate of the fraction of acceptable product, or in other words, the yield of the batch process. The batch runs generally lasted 4 to 8 hours.

2. Results

A total of seven batch distillation runs were made. The operating conditions and the results of these runs are presented in Table I.

In the first two runs, Runs B1 and B2, a ten-tray section and a reflux ratio (L/D) of 1:1 were used. The purpose of these two runs was to evaluate the effect of pressure and hence the effect of temperature on product quality. The head pressure employed in Run B1 was 40 mm. Hg; that employed in Run B2 was 5 mm. Hg. Lime was not added to the feed materials in these first two

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runs. The results of both runs indicated that the low boilers (i.e. the initial cuts) and the high boilers (i.e. the final cuts) were highly unstable, giving high 'thermal chemical' chlorides ranging from 0.77 to 12.9 ppm. The center fraction, roughly from 6% to 88% of the charge distilled, was somewhat more stable. The 'thermal chemical' chloride of that composite fraction was 0.30 ppm. for Run B1 and 0.38 ppm. for Run B2. These chloride levels are comparable to those currently produced in the plant, but are not good enough. The temperature profiles of the column head and reboiler liquid versus percent of charge distilled are shown in Figure 2.

Run B3 duplicated Run B1 in every respect except for a higher boilup rate. The purpose of this run was to check if thermal degradation occurred under the distillation conditions. After a deep low boiler cut of 22.5%, the distillate take-off was stopped and the column pressure was brought up to atmospheric with nitrogen. The reboiler liquid was held at 250°C. for 5 hours. Then the column was restarted. The first cut after starting gave a high 'thermal chemical' chloride, e.g. 0.60 ppm. Another indication of thermal decomposition was evidenced by the lower initial column head temperatures after the column was restarted.

Because of the unsuccessful attempts to produce stable Aroclor, two modifications were made in Runs B4 and B5: the column size was increased to twenty Oldershaw trays and some lime (0.4% of the Aroclor charge) was added to the reboiler. Other operating conditions were about the same as Run B1. Runs B4 and B5 were duplicate runs as Run B4 was not completed because of equipment malfunction. The addition of lime and perhaps better fractionation increased the thermal chemical stability of Aroclor 1242 significantly. The main fraction in Run B5 (from 5.4 to 92.0% of the reboiler charge distilled) has a thermal chemical chloride of 0.18 ppm.

In order to determine the effect of fractionation on product quality, the column size was reduced to 5 trays in Run B6. The reflux ratio was increased from 1:1 to 5:1, however. Again, lime (0.4% of the Aroclor charge) was added to the reboiler charge. The main fraction (from 6.0 to 88.3% of the reboiler charge distilled) has a low thermal chemical chloride of 0.11 ppm.

The results of Runs B4, B5 and B6 indicated clearly that the addition of lime to reboiler charge was essential to the stability of the distilled product. In order to further resolve the role of lime and to avoid the difficulties associated with feeding a dilute slurry of Aroclor and lime in the subsequent continuous distillation work, another batch run was made. In Run B7, the Aroclor feed was treated with lime prior to fractionation. The feed treatment included contacting Aroclor 1142 with 0.4% lime at 250°C. for five hours. After the mixture had cooled down to room temperature, it was filtered using a Buchner filter. Except for the feed treatment, the operating conditions of Run B7 were identical to Run B6. Two center cuts from Run B7 gave

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'thermal chemical' chlorides of 0.20 and 0.17 ppm. These chloride levels were not as good as those obtained in Run B6. Based on the results of this run, lime was always added to Aroclor feed in the subsequent continuous distillation work.

B. Continuous Fractionation

1. Equipment and Operating Procedures

Following the batch fractionation work, a two-column continuous fractionation system was constructed. The layout and the components of both columns were nearly identical. A schematic diagram of one of the two columns is shown in Figure 4. Both columns had 15 Oldershaw trays in the first two runs. The number of trays in each column was increased as the experimental work progressed.

Each column consisted of a thermal siphon reboiler, Oldershaw column sections and a liquid reflux splitter. The distillate collection system was composed of a condenser for cooling, a fraction cutter and a receiver. Similar equipment was used for bottoms collection. Bottoms flow was governed by a constant level overflow from the reboiler. The materials of construction were glass, stainless steel and Teflon.

Column head pressure was measured with a Hg manometer. The column pressure drop was measured with a differential manometer containing Aroclor 1242. The differential manometer was connected to pressure taps at the reboiler and at the top of the column. Temperature measurements were made using thermocouples inserted in reboiler heater, reboiler liquid, feed tray, feed preheater, control tray and the top tray.

The feed system consisted of two 2000-cc. graduated burettes used alternately. Where there was lime in the feed material, an electrical stirrer was provided. The feed material was metered by a stainless steel microbellows pump. Other accessories in the feed system included a pressure gage, a back pressure regulator and a preheater. The preheater generally maintained the feed temperature near the boiling point.

The feed to the first column was Aroclor 1142 from the plant, mixed with 0.4% or 0.8% of lime. With agitation, the mixture formed a suspension and was pumped relatively easily.

The feed to the second column was either the bottoms or the distillate from the first column depending on the mode of operation.

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For a two-column system, two modes of operation were possible for the purpose of removing low boilers and high boilers. The two modes of operation, Mode I and Mode II, are shown in Figure 3. In Mode I, the low boilers, which constituted a small fraction of the feed, were removed in the first column. The bottoms was the feed to the second column. High boilers were removed as bottoms in the second column, and the product was the distillate. Because of the relative amounts of material involved, and in order to operate the two columns simultaneously, a 1"-I.D. Oldershaw column was used as the first column, and a 2"-I.D. Oldershaw column was used as the second column.

In Mode II, the high boilers were removed in the first column, and the low boilers were removed in the second. The distillate of the first column was the feed to the second column. The product was withdrawn as a liquid from the first tray above the reboiler. A schematic diagram of the equipment for withdrawing product is shown in Figure 5. For the reasons given above, a 2"-I.D. Oldershaw column was used as the first column, and a 1"-I.D. Oldershaw column was used as the second column in this case.

The distillate or the bottoms of the first column was transferred to the feed tanks of the second column by suction. For this purpose a round bottom receiver with a bottom outlet was connected to one of the two feed tanks by a long piece of Teflon tubing. Material was transferred periodically by applying vacuum to the feed tank.

To start a run, the first column was operated first. The usual start-up procedure of applying vacuum, turning on heaters and operating the column at total reflux was followed. After the boilup reached the top of the column, the column was allowed to equilibrate for 1/2 to one hour. Then the feed pump was turned on and the distillate and bottoms collection commenced at a constant reflux ratio. Minor adjustments in reboiler heat input and reflux ratio were made until the desired split of feed to distillate and bottoms was achieved. The column was then put under automatic control. Since the composition of the distillate was more critical than that of the bottom, the temperature near the top of the column was used for control. The temperature was sensed by a thermocouple connected to a Wert temperature controller. Below the set point, the Wert temperature controller activated the reflux splitter and the distillate was collected at a finite reflux ratio. Above the set point, the same mechanism turned off the reflux splitter allowing the column to operate at total reflux. At a given set temperature, the feed split was fixed.

As soon as the first column was operating under automatic control, the second column was started. The same start-up procedure was followed. In the same manner, the second column was controlled at the top of the column. Generally the reboiler of the second column was flushed out 3 to 5 times before a run was terminated. Successive samples of product were collected and analyzed in order to insure steady state operation. A run generally lasted 12 to 16 hrs.

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In Runs 6 and 7, it was thought that adding lime directly and continuously to reboiler might be beneficial to the product quality. For this purpose a special feeding device was constructed for metering 5 or 10% of lime in Aroclor 1242 and was added onto both columns. A schematic diagram of the equipment is shown in Figure 6. In essence, the feeding device consisted of a 500-cc. graduated burette and a foot valve. The foot valve was operated by a repeat-cycle timer for intermittent flow. Nitrogen bleed was provided near the bottom of the foot valve for suspending lime.

Later in the continuous distillation work, a one-column system was also tried. This was designated as Mode III operation (see Figure 3). The column was constructed using 1"-I.D. Oldershaw column sections and had 15 trays. The other accessories were similar to the two columns described above. By this mode of operation, Aroclor 1142 with 0.8% lime was charged into the reboiler where high boilers were also removed. A low boilers fraction was collected at the top of the column. The product was withdrawn from the 10th tray from bottom. The operation of this column was manual, i.e. no control device was used. A run generally lasted 7 to 8 hours.

2. Results

A total of nine continuous runs was made. The results and the operating conditions of these runs are summarized in Tables II and III. These runs may be divided into three groups according to the mode of column operation.

In the first three runs, the columns were operated according to Mode I (see Figure 3), that is, low boilers were removed as distillate from the first column, and the high boilers were removed as the bottoms from the second. In Run No. 1, 5.6% of the feed was removed as distillate in the first column and 12.2% of the feed was removed as bottoms in the second. The net yield of the product was 82.6% (see Discussion for the method of calculating the yield). The 'thermal chemical' chloride of the product was 0.29 ppm., and the free chloride was 0.02 ppm. These chloride values were averages of four analyses of successive samples. The succession of sample collection not only indicated steady state column operation, but also provided a more precise estimate of the product stability. The level of 'thermal chemical' chloride at 0.29 ppm. was somewhat better than the plant product (usually 0.4 to 0.6 ppm.) but did not meet the target specification of 0.15 ppm.

As an improvement over Run No. 1, a larger low boiler fraction was collected in Run No. 2. That is, 10.6% of the feed was removed as distillate in the first column. Because some lime precipitated out in the column which might decrease the beneficial effect of lime as a stabilizer, the lime concentration in the feed was doubled to 0.8% in all subsequent runs. All other factors such

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as column operation and equipment were maintained identical to Run No. 1. The yield of Run No. 2 was cut back to 77.7%. The product had an average 'thermal chemical' chloride of 0.21 ppm. which was an improvement over Run No. 1.

In Run No. 3, a minor equipment improvement was made by adding two trays to the top section of the first column. This permitted lowering the control point from the head to the 15th tray from bottom and should provide better separating power to the column. In addition, a larger high boilers fraction, that is, 16.6% in place of 12% for earlier runs, was removed as bottoms in the second column. The larger high boilers fraction caused a corresponding drop in yield to 74.2%. The resultant product had a 'thermal chemical' chloride of 0.30 ppm. This unexpected result contradicted the speculation that better fractionation and larger low boiler and high boiler cuts would give more stable product. It was reasoned at that time that perhaps some unstable low boilers were generated in the reboiler and escaped with the product in the second column. Hence a major equipment change was made by using Mode II operation in the subsequent runs.

In Run No. 4, by Mode II operation, the high boilers were removed as bottoms in the first column, and the low boilers were removed as distillate in the second. Product was collected from the first tray above the reboiler in the second column. For prolonged periods of operation, the reboiler should be flushed out to avoid color body and high boiler accumulation. However, for the relatively short laboratory runs the reboiler was not flushed. The average 'thermal chemical' chloride content of the product was 0.21 ppm.

For Run No. 5, an improvement in fractionation was made by adding ten trays to both columns. The first column then was a 2"-I.D. column with 25 trays; and the second column was 1" in diameter with 27 trays. Other operating conditions were not changed. The resultant product had a 'thermal chemical' chloride of 0.17 ppm. This product was the best obtained in the continuous work.

In Runs 6 and 7, lime was also added to both reboilers as a slurry in Aroclor 1242. In Run No. 6, a head pressure of 10 mm. Hg was used for both columns in order to lower the operating temperatures. In other respects, these two runs were similar to Run No. 5. Run No. 6 yielded a product with a 'thermal chemical' chloride of 0.34 ppm., and that for Run No. 7 was 0.28 ppm. The results of both runs were unsatisfactory.

Since the product stability did not appear to depend on fractionation, a one-column system containing 15 trays was used in Runs 8 and 9. The product, as mentioned earlier, was withdrawn in the middle of the column at the 10th tray from bottom. In Run No. 8, with a yield of 71.4%, the 'thermal chemical' chloride of the product was surprisingly low (0.21 ppm.) even though it did not meet the target specification of 0.15 ppm.

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In order to improve the yield of the process, another run, Run No. 9, was made. At a yield of 87.2%, the 'thermal chemical' chloride of the product was 0.24 ppm. Other specifics of these two runs are summarized in Table III.

C. Treating Crude Aroclor 1142

The possibility of improving crude Aroclor 1142 was investigated. A current theory on the instability of Aroclor is that the structures of some Aroclor molecules are less stable than others and tend to decompose during distillation. In particular, those Aroclor molecules which contain one or two chlorine atoms in a saturated carbon-carbon bond are regarded as unstable. These molecules could decompose giving a HCl molecule and a double bond. It was speculated that if HCl can be stripped off from these unstable Aroclor molecules prior to distillation, a more stable product can be produced.

The treatment involved reacting Aroclor 1142 with $AlCl_3$ at 180°C. for 5 hours using conventional laboratory glassware. Three separate experiments using three levels of $AlCl_3$ (0.05%, 0.25%, 0.50%) were carried out. These conditions were determined from a previous kinetic study to strip off HCl but provide minimum isomerization. (Extensive isomerization can be effected by using about 2% $AlCl_3$.) Samples of the treated crude were subjected to straight take-over distillations for obtaining heart cuts.

The sample treated with 0.05% $AlCl_3$ which represented a 79.1% heart cut had a 'thermal chemical' chloride of 0.27 ppm. and a free chloride of 0.10 ppm. The other sample treated with 0.5% $AlCl_3$ which represented a 74.9% heart cut had a 'thermal chemical' chloride of 0.28 ppm. and a free chloride of 0.06 ppm. Since these results were not promising, no further work was undertaken in this area.

D. Gas Liquid Chromatography

Concurrent with the distillation work to improve the stability of Aroclor 1242, gas liquid chromatographic (GLC) work was undertaken to identify the unstable components which generate 'thermal chemical' chloride and to correlate the product stability with composition.

The chromatographic method for analyzing Aroclor was developed earlier and is described in Reference #5.

Tables IV and V show the GLC analyses of the feed, distillates, and bottoms from Runs B1 and B2. Each set of distillate and bottoms samples was collected at the same instant. The sample sizes were small (about 1 to 2 cc.). The GLC analyses clearly showed that there were at least 50 components in the feed and that these components did not fractionate readily. The difficulty in fractionating the mixture of Aroclor is also reflected in the gradual temperature change in the reboiler and at the column head in the batch runs (see Figure 2).

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A number of samples, which were tested for stability, were also analyzed by gas liquid chromatography. These are presented in Table VI. An attempt was made to correlate stability (that is, 'thermal chemical' chloride) with the low boilers (which were arbitrarily chosen as the first 11 components) as well as the high boilers (which were arbitrarily designated as the 31st and later components). No correlation could be established. Apparently the stability of Aroclor does not depend only on the content of low boilers or high boilers.

DISCUSSION

A. Batch Fractionation

The results of batch fractionation work indicated that Aroclor 1242 with 'thermal chemical' chloride of less than 0.15 ppm. can be produced by using either (1) 20 actual sieve trays and a reflux ratio (L/D) of 1:1, or (2) 5 trays and a reflux ratio of 5:1 at 40 mm. head pressure. The yield was about 80%.

The addition of lime to the feed (0.4% by weight) was essential to the stability of the distillate. The optimum level of lime in feed, however, was not investigated, but could be easily determined in the plant if a batch fractionation process was adopted for the manufacturing process. Treating Aroclor 1242 with lime prior to the distillation (as in Run B7) was not as effective in producing stable product as charging lime directly to the reboiler. Lime is charged directly to the still by the present plant process and has not presented any serious operational difficulties.

Apparently low boilers were continuously generated during distillation (see Run B3) presumably due to thermal decomposition in the reboiler. Using a lower reboiler temperature, which was the result of using a 5 mm. head pressure in Run B2 versus 40 mm. pressure in all other runs, did not improve the stability of the product. It appeared that at these levels of vacuum the effect of pressure was not significant.

B. Continuous Fractionation

Continuous fractionation of plant crude Aroclor 1142 under various conditions failed to produce product with 'thermal chemical' chloride of less than 0.15 ppm. which was the target specification for stability. In general, the distilled products had 'thermal chemical' chlorides ranging from 0.17 to 0.34 ppm. In terms of free chloride, all the laboratory-prepared products met the current product specification (0.05 ppm) with values ranging from 0.02 to 0.04 ppm. The yield of the product ranged from 74 to 80%.

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The best product was obtained in Run 5, the 'thermal chemical' chloride being 0.17 ppm. and the free chloride being 0.02 ppm. The yield was 74.0%. For that run, the first column in which high boilers were removed contained 25 actual trays. The second column contained 27 actual trays and was used to remove low boilers. In the absence of any vapor liquid equilibrium data, column efficiency could not be determined.

For producing Aroclor with T.C. chloride of about 0.20 ppm., a number of other column conditions may be used including a one-column system (such as that used in Runs 8 and 9).

It is still uncertain which operating variables control the product stability or whether fractionation alone can consistently produce highly stable Aroclor (i.e. T.C. Cl less than 0.15 ppm.). The effects of low boiler and high boiler fraction sizes (which were reflected by yield values ranging from 74 to 83%), number of trays (15 to 27), reflux ratio (0.8:1 to 8:1) and head pressure (10 and 40 mm. Hg) on product stability did not show definite trends. The removal of low boilers and high boilers from crude Aroclor 1142 appeared to be a necessary, but insufficient factor, for product stability. The addition of lime to the feed improved product stability significantly, however, in continuous fractionation work, lime tended to deposit inside the column and plug up sieve trays.

There was almost no difference in product stability between the two modes of column operation which were Mode I (removing low boilers in the first column and high boilers in the second) and Mode II (removing high boilers in the first column and low boilers in the second). The operations involved were similar. Neither mode of operation presented any operational difficulties except for the occasional tendencies of column plugging caused by lime deposits.

Aside from the thermal chemical stability considerations, the laboratory distilled Aroclor 1242 had electrical properties similar to those currently produced in the plant (see Table VII).

It may be worthwhile to note that Mr. V.R. Haupt of the Technical Services Department at Anniston undertook a statistical study of the effect of isomer ratios versus measured properties. He concluded in an earlier report (see Appendix) that a middle fraction (components No. 21 through 45) also had an adverse effect on Aroclor stability. If his conclusion can be substantiated, it would seem that stable Aroclor cannot be produced by distillation without a tremendous yield loss.

In calculating the yield of the continuous runs, it was assumed that lime did not accumulate inside the columns and that all the lime charged with the feed exited as the bottoms along with high boilers. This assumption was admittedly not entirely valid, as some lime did precipitate out in preheaters, reboilers and on trays. However, in view of the quantity of lime involved,

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the assumption should not affect the yield value appreciably. As an example, the yield of Run No. 1 = feed + lime - distillate (or low boilers) - bottoms (or high boilers) = 100 + 0.4 - 5.6 - 12.2 = 82.6%. This method of calculation was used for all continuous runs.

MATERIAL SPECIFICATIONS AND ANALYTICAL PROCEDURES

No new raw material and finished product specifications are proposed as the result of this work. The current specifications may be found in the description of manufacturing process (Ref. 1). The target specification in terms of 'thermal chemical' chloride for this work is 0.15 ppm. or less. The current plant specification for the same is 0.4 ppm., max.

The method for the Aroclor Thermal Chemical Stability Test was developed by the W.G. Krummrich Plant Laboratory. A copy of the method is attached in the Appendix.

The gas chromatographic method for analyzing the composition of Aroclors was developed in Organic Research and is described in Reference 5.

TOXICITY AND HAZARDS

Aroclor has a medium toxicity range for liquid ingestion and high toxicity for vapor inhalation. This material can cause dermatitis, systemic poisoning from the fumes, and yellow atrophy of the liver. Especially at elevated temperatures, extreme caution should be exercised.

Lime is not toxic, but will burn skin upon contact. The dust could affect the mucous membranes.

The hazards and safety measures involved in handling these materials are described in detail in the description of manufacturing process (Reference 1). No new hazards are introduced as a result of this work.

ACKNOWLEDGMENT

The analytical support provided by Mr. R. L. Kuster of the W. G. Krummrich Plant Laboratory is gratefully acknowledged.

R. Lee

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