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FINAL REPORT
ON
FRACTIONATION OF AROCLOR 1142 FOR IMPROVING PRODUCT STABILITY

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

Monsanto

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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.

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%).

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.

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.

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

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

'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.

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 ths 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 tctal 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.

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. ne 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 stabiliser, the lime concentration in the feed was doubled to 0.8% in all subsequent runs. All other factors such

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.

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%.

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,

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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8-8-66

MONS 057795

MONSANTO CHEMICAL COMPANY W. G. KRUMMRICH PLANT LABORATORY	DATE ISSUED 2/11/65	PAGE 1 OF 6	NUMBER 12,722
STANDARD ANALYTICAL METHOD	WRITTEN BY JJL		APPROVED BY DCA
	ATTACHMENTS WGK Method No. 12,741, Drawing Nos. 229 & 305		

PRODUCT
Aroclors

TEST
Thermal-Chemical Stability Test

THIS FORM ☐ SUPERSEDES METHOD _____ ISSUED ON 3/16/62
☒ REVISES INSTRUCTIONS

SCOPE

This method describes the procedure for determining the combined chemically and thermally unstable chlorides in chlorinated biphenyls. Sealed ampoules of the sample are exposed to heat under controlled conditions. The samples are then hydrolyzed by alcoholic NaOH. The resulting chlorides are finally titrated potentiometrically with standard silver nitrate solution.

EQUIPMENT

a. 32 mm. pyrex tubing - Kimball Glass Co., Toledo, Ohio, Cat. No. 46470, or equivalent.

This is used to make the ampoules. The tube is sealed on one end and drawn to a radius of 7-10 mm. at a point 150-200 mm. from the sealed end. Glass walls near the ampoule tip should be as thin as possible. (Refer to Drawing No. 229) These ampoules are washed with cleaning solution, then with a 10% nitric acid solution, followed by alternate rinses of distilled water and acetone. The final rinse should be an acetone rinse. The ampoules are dried in an oven at 240°C. for 4 hours immediately prior to using.

b. Oven - Blue M Electric Co., Blue Island, Illinois, Model No. OU580C - with a 1" hole drilled in the left side 10 inches back from the front and 12-1/2 inches up from the base. A stopper and thermometer are placed in this opening.

c. Thermometer, -5 to 360°C. range, - Fisher Scientific Co., St. Louis, Mo., Cat. No. 15-005, standardized at 240°C.

d. Micro buret, 1 ml. with 0.01 ml. divisions - Fisher Cat. No. 20-110, or equivalent.

e. pH meter - Leeds and Northrup Cat. No. 7664, or equivalent.

f. Silver billet electrode - Beckman Part No. 39261, or equivalent.

g. Glass electrode - Fisher Cat. No. 11-505-75, or equivalent.

h. Berzelius beaker, 200 ml. tall form, Fisher Cat. No. 2-546, or equivalent.

i. Funnel, pyrex long stem, modified. Refer to Drawing No. 305.

j. Usual laboratory apparatus.

REAGENTS

a. 0.1 N methanolic sodium hydroxide.

1. Sodium hydroxide - Fisher Scientific Cat. No. S-315.

2. Methanol - Union Carbide Co., St. Louis, Mo.

Dissolve 4.0 g. of sodium hydroxide in 500 ml. methanol in a 1 liter volumetric flask (The methanol should have a blank titration of not more than 0.05 ml. of 0.0025 N $AgNO_3$ per 100 ml. of methanol). Dilute to volume with methanol.

b. Sulfuric acid, AR grade, Mallinckrodt Cat. No. 2876, or equivalent.

Diluted 1:1 with distilled water.

NOTE: Pour the acid into the water.

c. Silver nitrate, AR, Mallinckrodt Chemical Co., St. Louis, Mo., Cat. No. 2169, or equivalent. 0.1 N solution, standardized.

Dissolve 17.00 g. $AgNO_3$ in distilled water and dilute to 1 liter. Standardize against Primary Standard NaCl using a silver wire/mercurous sulfate electrode system.

d. Silver nitrate solution 0.0025 N.

Dilute 25.0 ml. standardized 0.1 N $AgNO_3$ to one liter with distilled water. Store in a dark glass container.

N = 0.025 x N of $AgNO_3$ used.

e. Acetone, Mallinckrodt Cat. No. 2440, or equivalent.

A blank determination of 100 ml. acetone must not exceed 0.10 ml. 0.0025 N $AgNO_3$.

SAFETY

Aroclors are irritating to the skin. The vapors of the hot materials are irritating to the eyes and upper respiratory system. If accidental contact is made with the eyes, flush immediately with large quantities of water and get immediate medical attention. Methanol and acetone are highly flammable and normal precautions must be used when handling these reagents. Never use them around flames or spark-producing equipment.

This test is carried out at elevated temperatures. Be careful of thermal burns. A face shield should be worn when removing the ampoules from the oven for protection from possible breakage of the ampoule.

DETERMINATION

NOTE: All equipment used in this test must be chloride free. See Discussion.

1. Place a freshly cleaned, dry ampoule in a suitable holder on a beam balance.

2. Weigh to the nearest 0.1 g. and record the weight.

3. Place the modified funnel (see attached Drawing No. 305) in the ampoule. The tip of the funnel should extend into the main body area of the ampoule. The funnel should be supported in an iron ring on a ring stand.

4. Pour about 75 ml. of sample into a clean, dry 200 ml. beaker.

5. Carefully pour 50 $\pm$ 2 g. of sample through the funnel into the ampoule.

6. Allow the funnel to drain. Tapping the top of the funnel slightly may aid in removing the last drop from the funnel tip.

7. Carefully remove the funnel by gliding the bulbous end near the tip up the side of the neck of the ampoule. As the bulbous section nears the top of the ampoule, position the funnel tip in the center of the ampoule neck and complete the funnel removal in a smooth manner.

NOTE: If any sample drips from the funnel onto the neck of the ampoule, or if the funnel tip touches the neck of the ampoule while the funnel is being removed, discard the ampoule and start over.

8. Weigh the ampoule and sample to the nearest 0.1 g. on the beam balance and record the weight.

9. Seal the ampoule by using an oxygen-gas flame and pulling off a section 2" from the ampoule tip with a clean tweezers. Be careful not to expose the sample to overheating. Do not heat the glass to white heat. Radiation is detrimental to the sample. Do not allow combustion gases to enter the ampoule.

IMPORTANT: A very small torch flame must be used and the sealing accomplished very rapidly.

10. Place the ampoules in the support and put in the oven which has been previously heated and regulated at $240 \pm 2^{\circ}C$. Do not open oven after the samples are introduced until the required time has elapsed.

11. After the ampoules have been in the oven for 2 hours $\pm$ 2 min., remove them and allow them to cool to room temperature. Wear a face shield when removing the ampoules.

NOTE: Allow the Aroclor 1254 to cool to 50-60°C.

12. Cover the ampoule with a rag and break off the neck by striking it sharply with a spatula blade.

13. Pour the contents into a chloride free 200 ml. beaker.

14. Rinse the ampoule into the beaker with 10 ml. of acetone.

15. Add 25 ml. of acetone to the beaker.

NOTE: When analyzing 1254 Aroclor, rinse ampoule with second 25 ml. portion and combine it with the 10 ml. wash. Do not add additional 25 ml. acetone to the beaker. Total acetone volume should be 35 ml.

16. Pipet 25 ml. of methanolic NaOH into the beaker.

17. Introduce a clean stirring bar by using a chloride free tongs. Do Not touch it with the hands.

18. Cover the beaker with clean aluminum foil and immerse in a water bath at $40 \pm 1^{\circ}C$.

19. Place the water bath on the stirrer and stir the solution for 5 min., as fast as possible without splashing.

20. Remove the beaker from the bath and add 0.5 ml. 1:1 H_2SO_4.

21. Add 65 ml. acetone with a chloride free graduated cylinder.

MONS 057799

22. Titrate the sample potentiometrically with 0.0025 N $AgNO_3$ in 0.01 ml. additions from the micro buret. The endpoint is the point of maximum change in potential for the 0.01 ml. addition when using the line operated L and N pH meter and silver-glass electrodes.

23. Run a reagent blank using 100 ml. acetone, 25 ml. methanolic NaOH, and 0.5 ml. 1:1 H_2SO_4. Titrate as in Step 22.

CALCULATION

Gross chlorides, ppm =

$$\frac{(\text{ml. } AgNO_3 \text{ Step 22} - \text{ml. } AgNO_3 \text{ Step 23}) \times 0.0025 \times 35460}{\text{Sample Weight}}$$

Thermal-chemical chlorides = gross chlorides - free chlorides*

*Free chlorides are determined by Method No. 12,741.

Report all results to the nearest 0.01 ppm.

If duplicates do not check within 0.1 ppm, repeat the analysis.

DISCUSSION

1. All equipment used in this test should be successively washed with cleaning solution, distilled water, 10% nitric acid solution, then rinsed with distilled water and acetone in that order. A portion of the distilled water wash should be tested with $AgNO_3$ solution in a dark room to determine, by Tyndall beam, if it is chloride free. If a beam forms in the water wash within 1 minute after the $AgNO_3$ is added, the washing procedure must be repeated. It should be continued until the equipment is chloride free as indicated by this test.

2. Times and temperatures are critical in this test, and it is necessary to take all precautions to follow this procedure rigorously.

3. Ampoule dimensions, wall thickness and sealing technique must be carefully controlled in order to get reproducible results.

4. All ampoules must be thoroughly cleaned and thoroughly dried before being used in this analysis.

REFERENCE

1. W. W. Klemme's memo to P. G. Benignus, "Thermal-Chemical Stability Test", May 23, 1961.

2. Laboratory Notebook: 198, 3-5.

3. Anniston Method No. 039.

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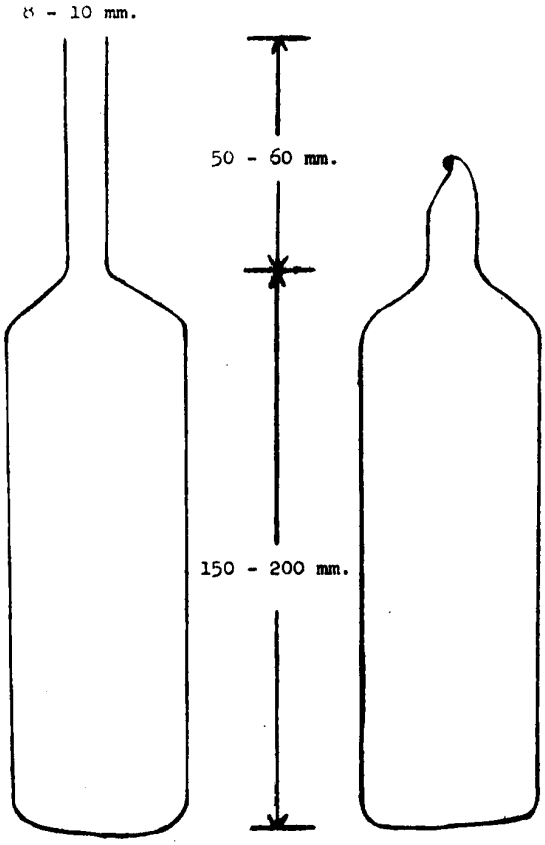


DETAILS OF AMPOULES

Drawing No. 229

MONS 057802

R Zie

CO[illegible]L

1700 S. SECOND ST	GENERAL OFFICES	ANNISTON
J. E. Smith -JFQ	R. E. Soden	W. B. Papageorge
W. R. Kellogg-Nitro	D. B. Hosmer	O. E. Dolin
H. C. Carder-WGK	N. L. Sample	L. C. Fuhmeister
O. DeGarmo	D. Danna (3)	R. G. Moody
H. L. Hubbard	J. A. Mullendore	P. H. Sturman
W. R. Richard	F. G. Benignus	J. W. Molloy
J. R. Savage-WGK		J. G. Bryant
L. L. Fellinger		W. B. Dunlap
D. Armstrong/J. J. Luecken-WGK		W. F. Taffee

PROGRESS REPORT
TECHNICAL SERVICES DEPARTMENT
ANNISTON, ALABAMA PLANT

JOB NO. 370-340 REPORT NO. 2 DATE July 15, 1965

TITLE: Aroclor 1242 Properties

OBJECTIVE: Report on factor analysis of isomer ratios versus various measured properties.

PERSONNEL: G. L. Arnett, E. A. Everage, V. R. Haupt. (L. C. Fuhrmeister)

REPORTED BY: V. R. Haupt

SUMMARY:

Each lot of Aroclor 1242 must meet certain specifications before it can be released for shipment. The measured properties are believed to be a function of the isomer ratios in the Aroclor. Sales lots of Aroclor 1242 have been analysed by gas liquid chromatography and together with the routine analytical data were sent to the Applied Math Group for factor analysis. Results of the analysis indicate a strong relationship of the measured properties with the isomer ratios. There appears to be certain isomer groupings that yield high dielectric constant while having a low stability. Further data is needed to confirm the dielectric constant relationships.

There are 58 compounds in Aroclor 1242. The eleven lowest boiling compounds plus a middle group (isomers 21-45) have an adverse effect on stability. Distillation can remove the low boilers and a different catalyst may decrease the middle group.

Future:

1. Resubmit data for factor analysis with stability as only dependent variable. EDC is August 15.
2. Submit additional data to verify factor analysis. EDC is October 1.
3. Regression analysis for stability and DK equations EDC is October 20.
4. Relate isomer ratios to chlorinator conditions. EDC November 1.
5. Optimize to show highest DK and best stability obtainable on paper with present chlorinator operation. EDC is December 31.
6. Field demonstration- Depends on step 5 results.

V. R. Haupt

MONS 057803

Details

Background

The Anniston control laboratory has been analyzing selected Aroclor 1242 sales lots by GLC in connection with the Aroclor Expansion Project. As the lots were both good and bad (bad lots from 1956) the isomer data plus routine lab analysis data were submitted to the Applied Math group for factor analysis. The 58 isomers were arranged in 24 groups of good GLC resolution. The factor analysis would arrange the 35 variables (eleven control analyses) in the minimum number of factors which would hopefully describe the relationship of the measured properties and the isomer ratios.

Factor Analysis Results

The factor analysis grouped the variables into 14 factors, one of which was eliminated as being insignificant. The measured or dependent variables submitted were:

Variable	No. of factors appeared in
1. Acid	One
2. Specific gravity	Four
3. Inorganic chlorides	One
4. Water	Three
5. Resistivity	Two
6. Dielectric constant (DK)	Three
7. Power factor	Eight
8. 10% distillation temperature	One
9. 90% distallation temperature	Two
10. Hydrolysis stability (HST)	One
11. Monsanto stability (MS)	One

Three of the 24 isomer groupings bordered on trace amounts and were dropped from the analysis.

Most of the variables fell into one factor and contained acid, specific gravity, chlorides, water, power factor, 10% distill temperature, HST and MS plus 14 isomer groups. This factor will be called the stability factor. The DK analysis method changed during the data period and as expected did not show up any firm relationships. The other factors do not seem highly important at this time so will be dropped from farther discussion.

Conclusions

The stability factor indicates the first eleven isomers are bad for stability. Isomers 12-20 are of good stability, isomers 21-45 are bad and 46-55 are of good stability. Unfortunately, the DK relationships do not coincide with the stability results which as expected presents a more complex relationship of isomer ratios and stability and DK. WGK is working on removing the low boiling bad stability isomers by distillation. This may also remove the 2,4' dichlorobiphenyl which has good stability. Research work indicates using different catalysts will change the isomer ratios. Therefore use of a different catalyst and perhaps plus distillation may give an improved stability plus DK. Optimizing the process for Aroclor 1242 will first require additional data to confirm the isomer relationship with stability and DK.

Future

The following plan will be used to optimize the present method of producing Aroclor 1242.

1. Resubmit data for factor analysis with stability as the only dependent variable. Determine how isomers vary with each other. EDC August 15.

2. Submit additional data (about 50) to verify the factor analysis. Only stability and DK will be used for the dependent variables. EDC October 1.

3. Get regression analysis for stability and DK equations. EDC October 20.

4. Determine isomer ratio relationships with chlorinator operating conditions and develop equations. EDC is November 1.

5. Optimize to get highest DK and best stability obtainable on paper with present chlorinator operations. EDC is December 31.

6. Field demonstration will depend on step 5 results.

V. R. Haupt

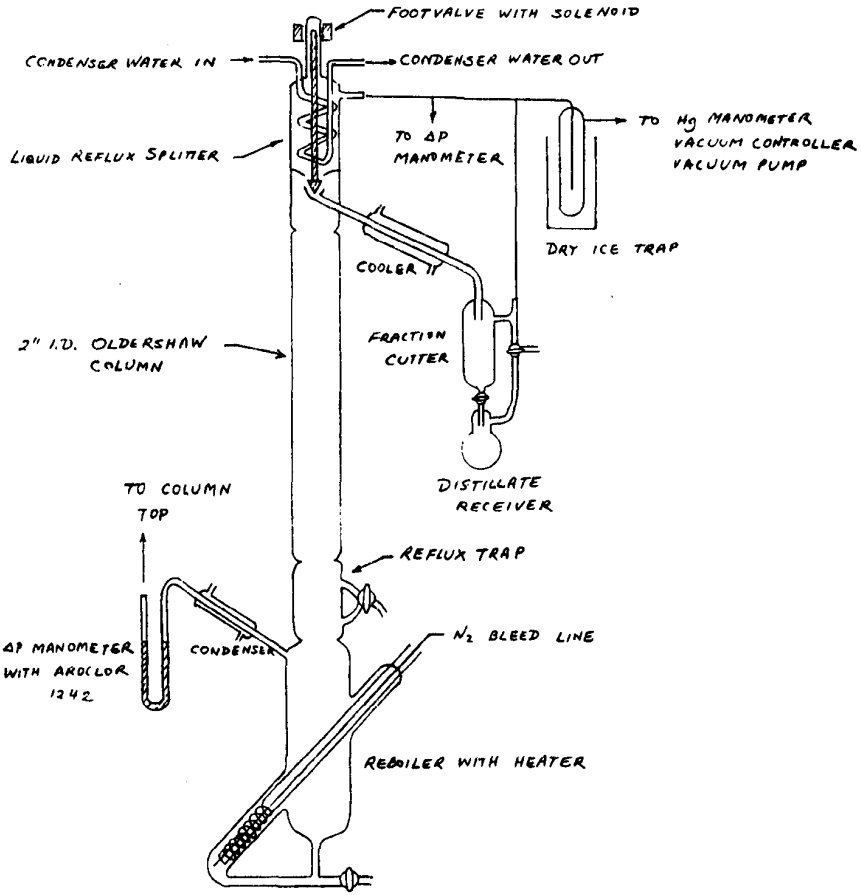


FIGURE 1 SCHEMATIC DIAGRAM OF THE BATCH COLUMN

R.Lee 1/18/66

MONS 057806

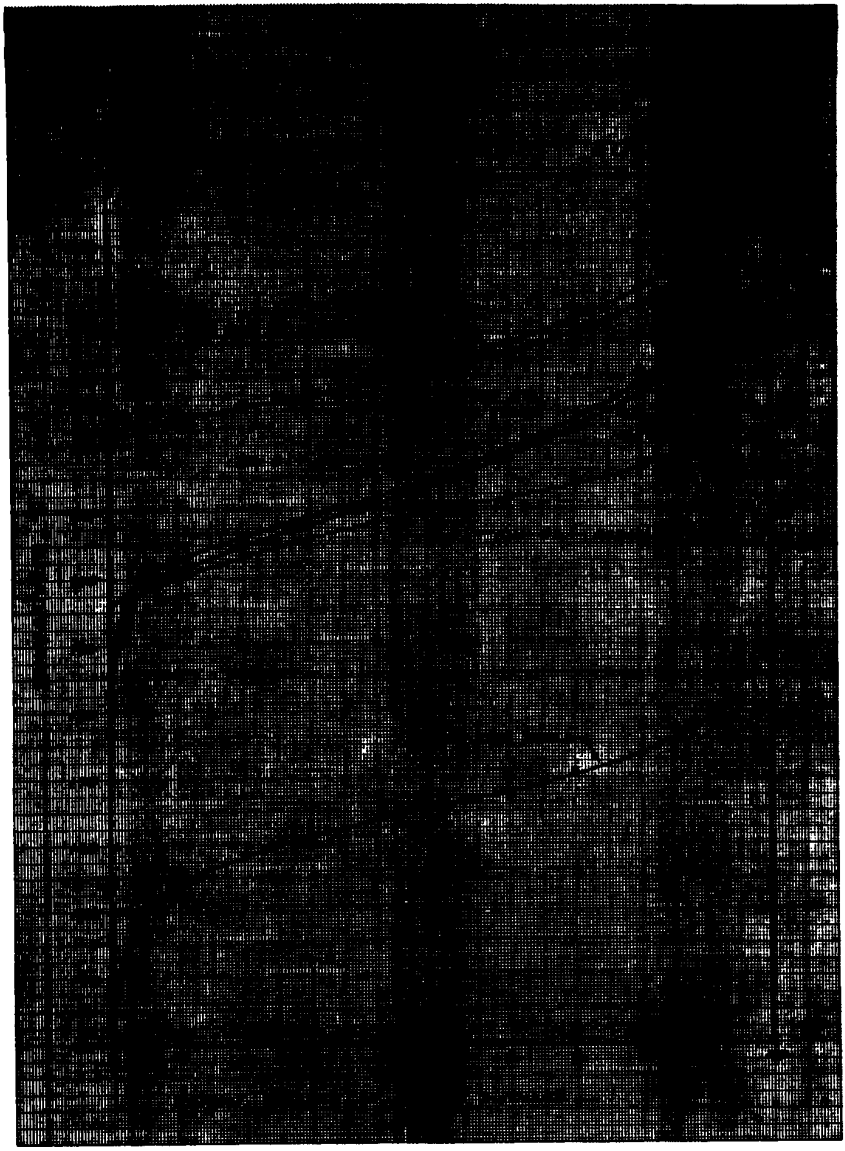
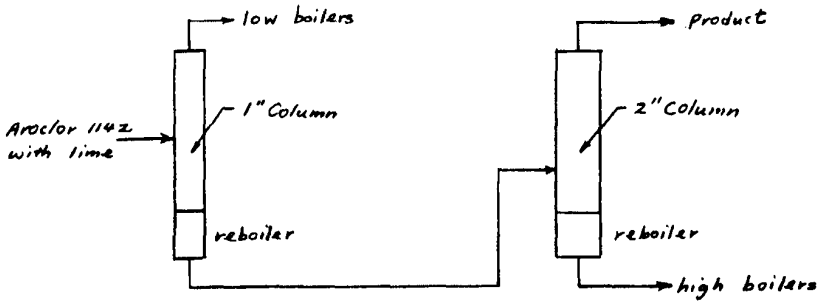


FIGURE 3 MODES OF OPERATING CONTINUOUS COLUMNS

R. Lee 9/23/65

Mode I



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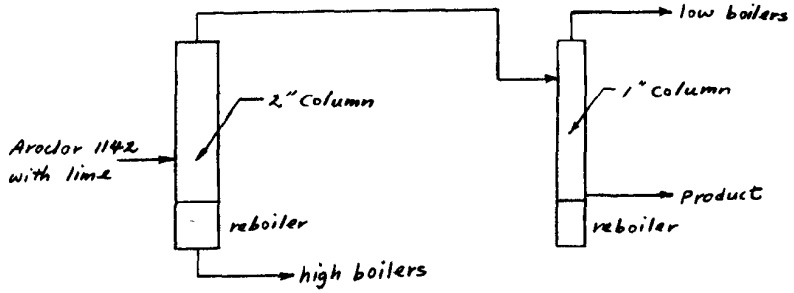
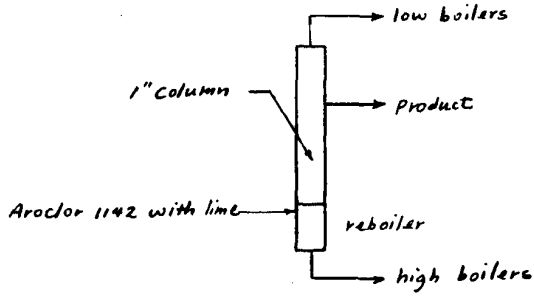


Mode III



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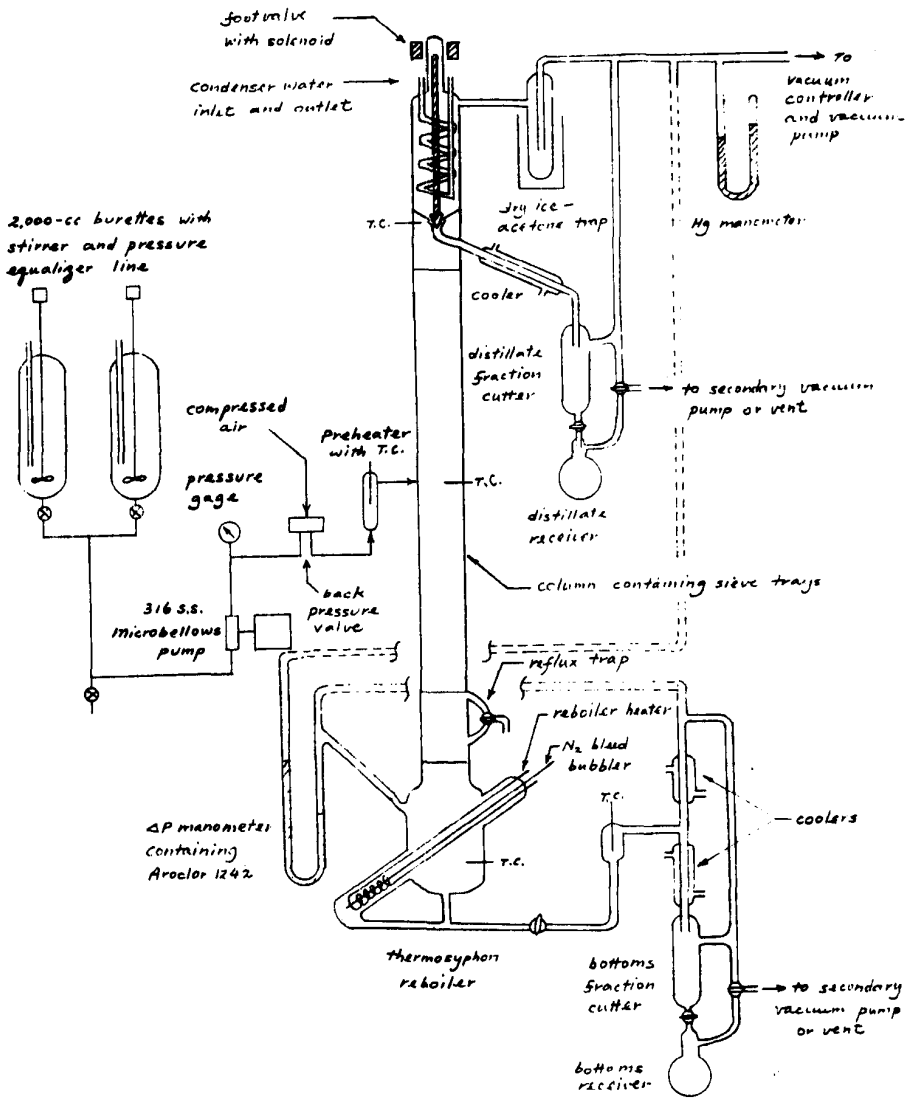

FIGURE 4 SCHEMATIC DIAGRAM OF A CONTINUOUS COLUMN

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R. Lee 2/14/66

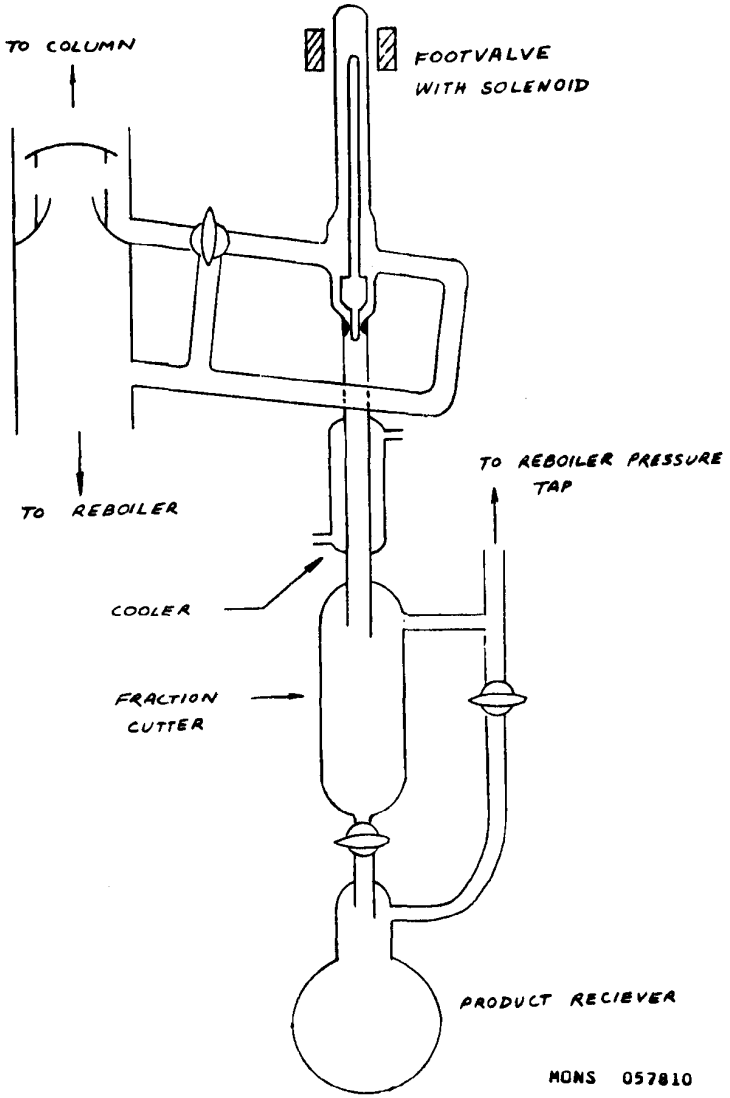
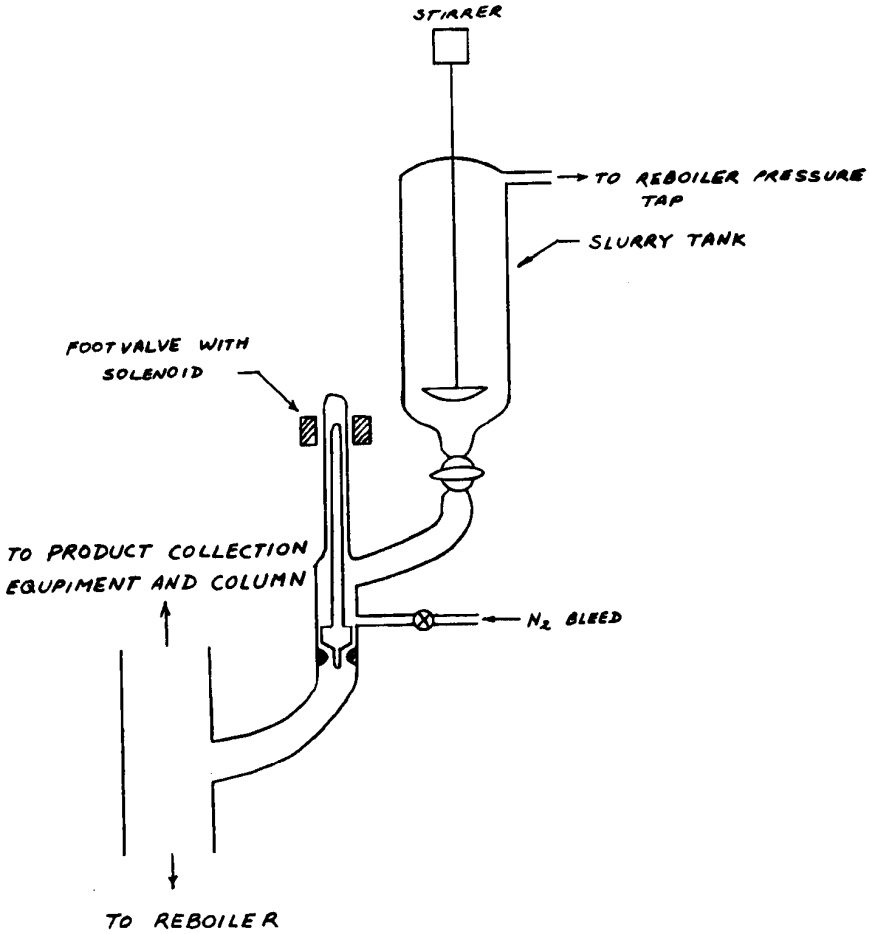


FIGURE 5. PRODUCT COLLECTION EQUIPMENT FOR MODE II OPERATION

R. Lee 1/21/66



MONS 057811

FIGURE 6. EQUIPMENT FOR CHARGING LIME TO REBOILER

R. Lee 1/20/66

TABLE I FRACTIONATION OF AROCLOR 1142 — SUMMARY OF DATA — BATCH DISTILLATION RUNS A.Lu 1/19/66

RUN No.	B1	B2	B3[B]	B4[C]	B5	B6	B7[C]
NBP	OR41604	OR41606	OR41608	OR41611	OR41613	OR41615	OR41618
COLUMN - OLDERSHAW							
diameter, in.	2	2	2	2	2	2	2
No. of actual trays	10	10	10	20	20	5	5
PRESSURE, mmHg							
Head	40	5	40	40	40	40	40
Reboiler	50 - 48.5	21.5 - 23	50.5	62	60	45.5	44
TEMPERATURES, °C							
Head	177 → 240	132 → 184	176 → 213	179 → 217	164 → 216[D]	183 → 241	183 → 220
Reboiler liquid	222 → 255	196 → 224	223 → 230	230 → 240	229 → 261	224 → 251	222 → 232
Reboiler heater	267 → 286	255 → 264	262 → 270	260 → 268	258 → 287	268 → 283	270 → 272
LIME ADDED TO FEED	0	0	0	0.4 %	0.4 %	0.4 %	0.4 %[E]
REFLUX RATIO, L/D	1:1	1:1	1:1	1:1	1:1	5:1	5:1
BOIL-UP, gm/hr.	1930	3290	4480	2700	2150	3550	2470
F-FACTOR (column top)	0.40	1.86	0.93	0.55	0.45	0.75	0.52
% DISTILLED	94.3	94.1	58.2	52.8	93.4	95.1	63.7
RUN DURATION, hr	5	3	~7	3	4	8	9
MATERIAL BALANCE, output/input %	99.9	100.2	100.4	–	99.4	99.3	–
PRODUCT QUALITY	T.C.Cl Fr.Cl Fract. Range	T.C.Cl Fr.Cl Fract. Range	T.C.Cl Fr.Cl Fract. Range	T.C.Cl Fr.Cl Fract. Range	T.C.Cl Fr.Cl Fract. Range	T.C.Cl Fr.Cl Fract. Range	T.C.Cl Fr.Cl Fract. Range
Thermal Chemical Stability as Chloride, ppm. [Free Chloride, ppm] (Fraction Range)	12.9 [0.17] (0.0 - 2.7 %) 1.45 [0.01] (2.7 - 5.5 %) 0.30 [0.02] (5.5 - 89.1 %) 0.94 [0.02] (89.1 - 91.8 %) 1.01 [0.02] (91.8 - 94.3 %) 0.19 [0.03] A (38.2 - 59.4 %) 0.18 [0.03] 0.30 [0.01] (10.9 - 78.1 %)	1.50 [0.03] (2.8 - 5.7 %) 0.38 [0.02] (5.7 - 87.4 %) 0.77 [0.01] (87.4 - 92.2 %) 0.38 [0.03] (92.6 - 61.2 %) 0.38 [0.03] (12.5 - 72.2 %)	0.60 [0.02] (22.5 - 25.3 %) 0.21 [0.02] (34.1 - 45.4 %)	0.11 [0.01] (30.8 - 52.8 %)	0.20 [0.01] (2.71 - 5.4 %) 0.18 [0.01] (5.4 - 92.0 %) 0.12 [0.02] (35.9 - 55.9 %) 0.51 [0.01] (56.5 - 92.0 %)	0.24 [0.02] (3.0 - 6.0 %) 0.11 [0.03] (6.0 - 88.3 %) 0.67 [0.04] (88.3 - 92.1 %) 0.14 [0.02] A (46.6 - 58.4 %) 0.15 [0.04]	0.20 [0.02] (11.2 - 24.5 %) 0.19 [0.03] (49.3 - 63.7 %)
NOTES	[A] Duplicate analysis		[B] Reboiler held at 250°C. for 5 hrs. after an initial cut from 0 to 22.5 %	[C] Incomplete run	[D] These low temperatures are questionable		[E] Feed was treated with lime for 1 hr. at 250°C. and then filtered prior to distillation

MONS 057812

A. Lee 9/20/65

TABLE II

FRACTIONATION OF AROCLOR 1142 — SUMMARY OF CONTINUOUS RUNS USING TWO-COLUMN SYSTEM

Run No.	1 [A]	2	3	4	5
NBP	OR 41626	OR 41633	OR 41637	OR 41606	OR 41635
Date	8/9/1965	8/16/65	8/20/65	8/27/65	9/2/65
COLUMN I					
% feed removed (including loss)	26 as distillate	18.6 as distillate	19.0 as distillate	16.9 as bottoms	18.9 as bottoms
EQUIPMENT					
Column type	Oldershaw	Oldershaw	Oldershaw	Oldershaw	Oldershaw
diameter, in.	1	1	1	2	2
No. of actual trays	15	15	17	15	25
Feed tray	5th	5th	10th	5th	5th
OPERATIONS					
% lime added to feed	0.0	0.0	0.0	0.0	0.0
Reflux ratio (col. top), V/D	4.30:1	1.99:1	3.00:1	1.34:1	1.61:1
Boil up (column top), g/hr.	618	373	692	3526	3410
F-factor (column top)	0.61	0.38	0.48	0.70	0.72
Run duration, hr.	8½	11	13	11½	11½
Column control	T_{head} [B]	T_{head}	T_{15th}	T_{10th}	T_{10th}
TEMPERATURES, °C					
Head	190	199	197	218	219
Control tray	190 (head)	199 (head)	201 (15th)	228 (1st)	226 (20th)
Feed preheater	216	217	214	232	238
Feed tray	216	215	218	240	208
Reboiler liquid	226	227	230	252	163
Reboiler heater	—	—	—	290	298
PRESSURES, mm Hg					
Head	40	40	40	40	40
Reboiler	58	56	61	60	76
COLUMN II					
% feed removed (including loss)	12.2 as bottoms	12.5 as bottoms	16.6 as bottoms	2.0 as distillate	1.9 as distillate
EQUIPMENT					
Column type	Oldershaw	Oldershaw	Oldershaw	Oldershaw	Oldershaw
diameter, in.	2	2	2	1	1
No. of actual trays	15	15	15	19	27
Feed tray	5th	5th	5th	10th	20th
OPERATIONS					
Reflux ratio (col. top), V/D	1.10:1	1.97:1	1.90:1	4.29:1	2.60:1
Boil up (column top), g/hr	3600	3650	3150	768	598
F-factor (column top)	0.78	0.77	0.69	0.51	0.99
Run duration, hr.	8	6	9	7½	9½
Column control	T_{10th} [C]	T_{10th}	T_{10th}	T_{15th}	T_{25th}
TEMPERATURES, °C					
Head	216	217	216	199	190
Control tray	227 (1st)	228 (15th)	226 (1st)	202 (15th)	196 (25th)
Feed preheater	239	228	229	215	211
Feed tray	238	235	236	219	205
Reboiler liquid	258	258	253	228	236
Reboiler heater	288	284	280	284	277
PRESSURES, mm Hg					
Head	40	40	40	40	40
Reboiler	61	61	59	61	69
MODE OF COLUMN OPERATION	I [D]	I	I	II [D]	II
OVERALL MAT'L BALANCE					
Output/input %	99.6	99.8	99.5	99.9	99.7
YIELD, wt. %	82.6	78.7	79.2	76.9	79.0
PRODUCT QUALITY					
Thermal chemical chloride, ppm	0.26 [0.03]	0.10 [D] [0.02]	0.27 [0.03]	0.25 [0.05]	0.10 [0.04]
[Free Chloride, ppm]	0.32 [0.01]	0.30 [0.02]	0.28 [0.02]	0.13 [0.04]	0.17 [0.02]
(Analysis of successive samples)	0.26 [0.02]	0.19 [0.01]	0.33 [0.04]	0.21 [0.03]	0.17 [0.02]
	0.32 [0.03]	0.19 [0.02]		0.23 [0.01]	0.17 [0.02]

NOTES

A Col. II was operated on 8/11/65

B "T_{head}" designates a method of column control in which the temperature in the column head was used to control the reflux ratio by operating the reflux splitter between total reflux and a finite reflux ratio.

C "T_{10th}" designates a similar method of column control in which the temperature at the 10th tray from the bottom of the column was used to control the reflux ratio

D Duplicate analysis

E See Figure 3.

MONS 057813

TABLE II (cont'd) FRACTIONATION OF AROCLOR 1142 — SUMMARY OF CONTINUOUS RUNS USING TWO-COLUMN SYSTEM

A. Lee 9/23/68

Run No.	6	7
NBP	OR41663	OR41668
Date	9/10/65	9/12/65
COLUMN I		
% feed removed as bottoms	15.9	13.8
EQUIPMENT		
Column type	Oldershaw	Oldershaw
Diameter, in.	2	2
No. of actual trays	25	25
Feed tray	5th	5th
OPERATIONS		
% lime added to feed	0	0.8
% lime added to reboiler	0.29	0.23
Reflux ratio (col. top), L/D	0.84:1	1.86:1
Boilup (col. top), gm/hr	2600	4020
F-factor (col. top)	1.0	0.85
Run duration, hr.	13½	7
Column control	T→R 20th	T→R 20th
TEMPERATURES, °C		
Head	174	218
Control tray	195 (20th)	226 (20th)
Feed preheater	178	219
Feed tray	225	249
Reboiler liquid	294	269
Reboiler heater	—	—
PRESSURES, mm Hg		
Head	10	40
Reboiler	48	83
COLUMN II		
% feed removed as distillate	10.9	12.0
EQUIPMENT		
Column type	Oldershaw	Oldershaw
Diameter, in.	1	1
No. of actual trays	27	27
Feed tray	20th	20th
OPERATIONS		
% lime added to reboiler	0.35	0.83
Reflux ratio (col. top), L/D	2.13:1	7.56:1
Boilup (col. top), gm/hr	487	1460
F-factor (col. top)	0.62	0.97
Run duration, hr.	13½	5
Column control	T→R 25th	T→R 25th
TEMPERATURES, °C		
Head	157	198
Control tray	167 (25th)	201 (25th)
Feed preheater	178	218
Feed tray	184	211
Reboiler liquid	221	202
Reboiler heater	256	270
PRESSURES, mm Hg		
Head	10	40
Reboiler	45	>80
MODE OF COLUMN OPERATION	II	II
OVERALL MAT'L BALANCE $\frac{\text{output}}{\text{input}}$ %	100.6	92.7
YIELD, wt. %	73.6	75.5
PRODUCT QUALITY		
Thermal chemical chloride, ppm	0.32 [0.02]	0.64 [0.02]
[Free chloride, ppm]	0.30 [0.02]	0.15 [0.04]
	0.39 [0.02]	0.15 [0.03]
	0.32 [0.02]	0.20 [0.03]
	0.42 [0.02]	

NOTE: See the first part of this table for explanatory notes on nomenclature.

MONS 057814

TABLE III FRACTIONATION OF AROCLOR 1142 —— SUMMARY OF CONTINUOUS RUNS USING ONE-COLUMN SYSTEM

R.Lee 1/18/66

RUN NO.	8	9
NBP	OR 41670	OR 41672
COLUMN — OLDERSHAW		
diameter, in.	1"	1"
total no. of trays	15	15
trays above product take-off	5	5
trays below product take-off	10	10
feed inlet point	Reboiler	Reboiler
OPERATIONS		
% feed removed as distillate	10.7	6.6
% feed removed as bottoms	18.7	9.0
% lime added to feed	0.8	0.8
Reflux ratio (col. top), L/D	10:1	~ 18:1
Boil up (column top), gm/hr	748	764
F-factor	0.50	0.51
Product reflux ratio, L/P	0.55:1	0.3:1
Run duration, hr.	7	8
Column control	manual	manual
Material balance, output/input %	98.3	99.8
MODE OF COLUMN OPERATION	III [A]	III
TEMPERATURES, °C.		
Head	200	202
Feed preheater	210	213
10th tray product take-off	217	220
Reboiler liquid	234	240
Reboiler heater	248	259
PRESSURES, mm Hg		
Head	40	40
Reboiler	-	59
YIELD, wt. %	71.4	87.2
PRODUCT QUALITY		
Thermal chemical chloride, ppm	T.C.Cl Free Cl	T.C.Cl Free Cl
[Free chloride, ppm]	0.18 [0.03]	0.29 [0.04]
	0.25 [0.03]	0.22 [0.05]
(Analysis of successive prod. samples)	0.20 [0.03]	0.20 [0.03]
NOTES	[A] See Figure 3	

MONS 057815

TABLE IX GLC ANALYSES OF FEED AND PRODUCTS FROM RUN B1

M. Lee 1/21/66

SAMPLE IDENTITY	CRUDE	DISTILLATE D-2	BOTTOMS B-2	DISTILLATE B-7	BOTTOMS B-7	DISTILLATE D-12	BOTTOMS B-12
COMPONENT No. 1	34	160	N.C.**	N.D.*	N.D.	N.D.	N.D.
2	28	176	4	N.D.	N.D.	-	-
3	9	48	5	N.C.	N.D.	-	-
4						-	-
5	912	4656	589	344	69	-	9
6	104	504	64	72	28	-	7
7	312	1104	293	312	94	-	
8	2112	6700	2044	2416	698	-	45
9A	344	976	312	432	148	-	10
10	5288	9568	5656	9152	3272	N.C.	
11						-	133
12	264	400	272	424	168	-	
13	2256	2916	2440	3616	1776	-	61
14	760	480	916	1128	908	32	29
15							
16	5432	2576	5728	7416	6304	197	215
17							
18	2544	1018	2648	3272	3144	118	121
19	1192	368	1208	1360	1608	116	94
20	328	136	328	424	432	N.C.	N.C.
21	1112	298	1092	1120	1516	199	105
22							
23	954	196	934	792	1224	431	114
24	690	188	644	488	1012	442	124
24A	1080	156	946	708	1558	1240	320
25	434	N.C.	382	290	646	3209	1280
26	772	N.C.	594	222	1142		
27	1130	168	960	558	1722	2232	292
28	298	N.C.	246	114	470	688	244
29	74	N.C.	60	N.C.	124	232	124
30	48	N.C.	38	N.C.	94		96
31	476	N.C.	326	72	650		564
32	966	N.C.	644	132	1318	6328	3296
33		N.D.	784	142	1594	5340	2996
33A	1174	-		N.C.			
34		-	N.C.	N.C.	N.C.	N.C.	196
35	956	-	536	58	1104	4904	4072
36		-	N.C.	N.C.			
37	128	-	92	N.C.	228	608	596
38	92	-	72	N.D.	154	328	408
39	N.C.	-	N.C.	-	N.C.	84	41
40	64	-	28	-	96	47	323
41	88	-	40	-	119	125	516
42	60	-	N.C.	-	88	172	341
43	110	-	48	-	134	144	705
43A	132	-	N.C.	-	148	136	713
44	N.C.	-	N.C.	-	94	68	53
45	N.D.	-	N.D.	-	N.D.	N.D.	
46	N.D.	-	-	-	N.D.	N.D.	102
47	N.D.	-	-	-	N.D.	N.D.	
48	70	-	-	-	130	56	729
49	N.D.	-	-	-	N.D.	N.D.	42
50	N.D.	-	-	-	-	N.D.	
51	N.D.	-	-	-	-	N.D.	N.D.
52	50	-	-	-	-	5	508
TOTAL COUNT	32,729	32,706	30,798	34,054	33,885	27,530	19,603
AREA % OF COMPONENTS 1 TO 11	27.9	72.9	29.1	39.5	12.6	0	1.0
12 TO 31	60.2	27.1	63.6	54.5	72.1	33.1	19.2
32 TO 52	11.9	0	7.3	1.0	15.3	66.9	79.8
FRACTION RANGE	-	2.7 - 2.8 %		36.2 - 36.3 %		91.8 - 91.9 %	

* N.D. = not detectable

** N.C. = not counted by the Infotronics Digital Readout System, but the small peak was visible on the chromatogram.

MONS 057816

TABLE I GLC ANALYSIS OF PRODUCTS FROM RUN B2

A. Lee 1/21/66

SAMPLE IDENTITY		DISTILLATE D-2	BOTTOMS B-2	DISTILLATE D-7	BOTTOMS B-7	DISTILLATE D-13	BOTTOMS B-13
COMPONENT NO.	1	59	N.C.	N.C.**	N.D.*	N.D.	N.D.
	2	12	3	273	"	"	"
	3	34	6	7	"	"	"
	4				"	"	"
	5	3088	910	576	51	"	"
	6	272	72	72	N.C.	"	"
	7	890	244	336	69	"	"
	8	5456	1554	3888	436	4	12
	9A	816	292	400	88	N.D.	N.C.
	10	8080	4464	5992	1109	59	50
	11					47	
	12	336	176	280	94	"	6
	13	2474	1880	2456	588	98	30
	14	448	624	744	298	206	14
	15						
	16	2560	4608	4800	2240	2368	180
	17						
	18	1048	2120	2136	1116	1506	109
	19	400	952	952	569	1074	75
	20	192	224	264	132	102	14
	21	318	888	792	1098	1254	90
	22						
	23	212	674	564	964	1150	84
	24	182	496	544	662	926	76
	24A	178	778	746	1196	2440	205
	25	70	346	292	474	824	92
	26	68	490	366	930	3336	424
	27	178	766	726	1290	3144	332
	28	66	176	292	368	928	113
	29	N.C.	32	N.C.	108	264	48
	30	62	22	N.C.	78	168	41
	31	86	278	232	664		504
	32	N.D.	356	550	1298	7704	1018
	33	"	596	452	1360	4288	1090
	33A	"	N.C.	N.D.	74	158	N.C.
	34	"	N.C.	N.D.	104	168	96
	35	"	442	364	1202		
	36	"	N.D.	N.D.		3864	1306
	37	"	34	"	288	712	230
	38	"	14	"	156	280	124
	39	"	N.D.	"	N.C.	75	41
	40	"	N.C.	"	148	206	131
	41	"	"	"	180	276	191
	42	"	"	"	144	178	134
	43	"	"	"	224	314	239
	43A	"	32	"	232	152	308
	44	"	N.C.	"	236	92	187
	46	"	N.D.	"	N.D.	N.D.	N.D.
	46	"	"	"	"	"	"
	47	"	"	"	"	"	"
	48	"	"	"	296	99	294
	49	"	"	"	N.D.	N.D.	N.D.
	50	"	"	"	"	"	"
	51	"	"	"	"	"	"
	52	"	"	"	274	31	245
TOTAL COUNT		27,606	24,719	28,702	20,671	37,509	8,142
AREA % OF COMPONENTS	1 TO 11	67.9	30.5	40.2	9.5	0.3	0.8
	12 TO 51	22.1	62.7	55.7	61.5	57.9	29.9
	52 TO EL	0	6.8	4.1	30.0	41.8	69.3
FRACTION RANGE		2.8-2.9 %		92.6-92.7 %		91.9-91.9 %	

* N.D. = not detectable.

** N.C. = not counted by the Informetrics Digital Readout System, but the small peak was visible on the chromatogram.

MONS 057817

TABLE II GLC ANALYSES OF PRODUCT SAMPLES

A. Lee 1/21/66

RUN NO.		86*	86	81	82	1	1	84*	2	2	3	4
SAMPLE NO.		D9→D11	D9→D10	D4→D10	D4→D11	D-5	D-10	D9→D11	D26	D28	D28+9	D28,13,15
COMPONENT NO.	1		N.C.***	N.C.	4	2	1	2	N.C.	N.C.	N.D.**	N.D.
	2	5	N.C.	2	5	4	4	9	4	5	N.D.	N.D.
	3	7	N.C.	4	5	4	3	11	4	4	N.C.	N.D.
	4											
	5	433	216	471	510	257	286	695	412	366	18	198
	6	91	91	91	105	72	80	130	96	97	40	9
	7	243	226	242	297	216	231	390	320	277	221	26
	8	1624	1556	1703	1877	1543	1605	2405	2272	1986	1804	203
	9A	316	314	288	383	293	282	507	432	386	342	33
	10	4750	4677	4851	5133	4760	4901	7619	7392	7044	7748	471
	12	219	218	197	239	231	226	351	352	329	32	3
	13	2079	2048	2074	2193	2140	2164	3334	3416	3279	3259	323
	14	788	766	598	622	774	770	1264	1208	1250	1437	125
	15											
	16	5278	5209	5358	5267	5346	5450	8466	9088	8973	9597	847
	18	2469	2435	2482	2413	2505	2541	3959	4272	4215	4472	394
	19	1169	1153	1165	1120	1168	1182	1875	1976	1979	2040	177
	20	317	306	280	316	308	297	508	456	507	472	41
	21	1052	1046	1046	984	1065	1047	1697	1716	1793	1952	170
	22											
	23	790	790	793	725	798	805	1267	1332	1357	1404	122
	24	560	572	549	510	582	558	898	948	982	980	84
	25	956	992	976	852	964	971	1533	1615	1670	1734	151
	26	389	401	397	345	399	392	622	694	695	721	67
	27	503	605	541	455	538	518	807	861	973	877	79
	28	884	969	912	783	921	906	1426	1574	1616	1638	142
	29	213	236	208	182	226	201	342	342	371	349	31
	29A	33	44	25	24	40	25	54	42	54	48	4
	30	23	29	17	17	19	17	27	27	37	30	2
	31	246	530	273	242	264	233	430	380	482	382	33
	32	502	619	529	458	501	465	805	745	919	722	64
	33	502	612	515	463	521	467	805	756	944	609	54
	34	19	24	14	14	27	9	30	17	28	14	1
	35	13	15	8	N.C.	26	4	21	13	16	7	N.C
	36	316	349	288	300	277	214	507	347	464	30	2
	37	66	73	40	50	83	33	106	85	105	65	5
	38	20	17	9	14	32	10	32	21	27	11	1
	39	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.
	40	N.C.	N.C.	N.C.	N.C.	13	N.C.	N.C.	N.C.	20	N.C.	N.C.
	41	15	7	8	15	14	10	24	15	21	N.C.	N.D.
	42	18	9	9	20	N.C.	N.C.	29	N.C.	N.C.	N.C.	
	43	N.C.	N.C.	N.C.	N.C.	13	N.C.	N.C.	N.C.	20	N.D.	
	44	20	N.C.	N.C.	24	N.D.	N.D.	32	N.D.	N.D.		
	45	N.C.	N.D.	N.D.	N.D.	-	-	N.C.	-	-	-	
	46	N.C.	-	-	-	-	-	N.C.	-	-	-	
	47	N.D.	-	-	-	-	-	N.D.	-	-	-	
	48	-	-	-	-	-	-	-	-	-	-	
	49	-	-	-	-	-	-	-	-	-	-	
	50	-	-	-	-	-	-	-	-	-	-	
TOTAL COUNT		26,946	26,942	26,955	26,958	26,950	26,932	43,210	43,244	43,282	43,634	10,527
AREA % OF COMPONENT 1 TO 11		29.7	28.8	28.4	30.8	28.5	29.5	29.7	25.3	23.5	23.3	11.9
12 TO 31		66.2	67.9	66.4	64.1	67.9	68.0	66.8	70.1	70.7	73.1	88.0
32 TO 42		5.5	6.9	5.2	5.1	5.6	4.5	5.5	4.6	5.8	3.6	1.6
FRACTION RANGE		6.0-16.3%	5.9-17.0%	6.8-18.3%	5.7-17.9%	8.0-18.4%	8.6-18.8%	6.0-18.3%	10.6-18.3%	10.6-18.3%	14.0-19.2%	8.0-19.0%
THERMAL CHEMICAL CHLORIDE ppm		0.11	0.18	0.30	0.38	0.32	0.25	0.11	0.19	0.14	0.27	0.13

* Same sample ** N.D.= not determinable

*** N.C. = not counted by the Infotronics Digital Readout System, but the small peak was visible on the chromatogram.

TABLE VII ELECTRICAL PROPERTIES OF PRODUCT SAMPLES

R. Lee 1/25/66

RUN NO.	SAMPLE NO.	DIELECTRIC CONSTANT @ 25°C. cycles/sec.				POWER FACTOR (%) at cycles/sec.				SPECIFIC RESISTIVITY ohm-cm.
		100	1,000	10 Kilo	100 Kilo	100	1,000	10 Kilo	100 Kilo	
-	PLANT	-	5.8	-	-	-	<0.1	-	-	-
B5	D4→D10	5.90	5.90	5.90	5.90	0.02	0.02	0.03	0.10	5.4×10^{14}
B6	D4→D11	5.89	5.89	5.89	5.89	0.02	0.02	0.02	0.02	2.7×10^{14}
1	D-16	5.85	5.85	5.85	5.85	0.01	0.03	0.03	0.15	3.6×10^{14}
2	D18	5.84	5.84	5.83	5.83	0.17	0.04	0.03	0.15	3.4×10^{12}

Reference: OR43549-52

MONS 052819