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FINAL REPORT
ON
MONOCHLOROBIPHENYL

DATE - June 5, 1975 WRITTEN BY - D. R. Cova

Monsanto

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MONSANTO INDUSTRIAL CHEMICALS COMPANY

St. Louis Research & Development

Research & Development Report No. 3933

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Written by: D. R. Cova

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ABBREVIATIONS

CBP	Chlorobiphenyl
DCBP	Dichlorobiphenyl
MCBP	Monochlorobiphenyl
PCB	Polychlorobiphenyl
o	ortho
m	meta
p	para

INTRODUCTION

An impure form of Monochlorobiphenyl (MCS 1109) was first made in the Aroclor Department at the W. G. Krummrich Plant in 1971-72. Production was stopped after a few runs. Dow Chemical Co. was interested in the product at that time. In 1973 their interest crystallized into some definite proposals. At that poing (May, 1973) we began research work to provide Dow with representative samples and to develop a process for Monochlorobiphenyl. The Process for Engineering Design (Ref. 1) was issued on 7/29/74. A successful plant run (in the W. G. Krummrich Plant Aroclor Department) was carried out over the time period October 1974 to January 1975. A 7,000 gallon lot of product was generated and shipped to Dow Chemical Co. Research work ended in March, 1975.

Dow Chemical Company's interest in Monochlorobiphenyl was as an intermediate to make o-phenylphenol and, possibly, also a small amount of p-phenylphenol. At present they obtain Monochlorobiphenyl as a by-product of their phenol plant.

SUMMARY

Aroclor 1111 was fractionated in a 30-tray Oldershaw column to simulate the Aroclor 1016 fractionation system in the Aroclor Department at the W. G. Krummrich Plant. Experiments were carried out to optimize the reflux ratio program and other parameters of column operation.

Residue from this fractionation was chlorinated to various levels from 30% to 54% chlorine. The residue was converted to Aroclor 1016, 1242, and 1254. Aroclor 1142 made from residue was isomerized over $AlCl_3$ catalyst to reduce the level of 4,4'-DCBP in the Aroclor. Isomerization conditions were adjusted to maximize 4,4'-DCBP reduction and to minimize corrosion of steel during isomerization.

CONCLUSIONS

1. Monochlorobiphenyl can be manufactured in the Aroclor Department at the W. G. Krummrich Plant in present equipment (with some minor modifications). Capacity has been estimated to be 1.4M lbs./month.

2. Residue from Monochlorobiphenyl fractionation can be converted to Aroclor 1242' which is a suitable replacement for Aroclor 1242 as a transformer fluid. Transformer fluid sales have been such that the amount of Aroclor 1242' produced concurrently with 8M lbs./yr. of MCBP would approximately satisfy this market.

3. Residue from MCBP fractionation can be readily converted to suitable Aroclor 1254. There is, however, no economic incentive for doing so, because this would over-supply this market.

RECOMMENDATIONS

1. We recommend that further research work be carried out on alternate catalysts to $FeCl_3$ for the low level chlorination of Biphenyl to make crude Monochlorobiphenyl.

2. We recommend that low level oxychlorination of Biphenyl to Aroclor 1111 be investigated.

3. Further work should be carried out on residue disposition, especially on conversion of residue to suitable Aroclor 1016.

PATENT STATUS

Nothing of a patentable nature was developed. No disclosures were submitted.

REFERENCES

Note: The references tabulated below do not include any which have been attached to this report in the various appendices.

1. Cova, D. R., "Process for Engineering Design for Monochlorobiphenyl", Report No. P-1766, Job No. 43-000-760.22-1016005, July 29, 1974.

2. Sharma, Ram Karan and Howard B. Palmer, "Vapor Pressure of Biphenyl Near Fusion Temperature", J. Chem. Eng. Data, 19, No. 1, 6-8 (1974).

3. Scheidt, Francis Matthew, "Selective Monochlorination of Biphenyl Using Clay Catalysts", Patent Specification No. 1272699, filed Nov. 19, 1970, Great Britain, assigned to Dow Chemical Co.

4. Thompson, Q. E., "Tentative Process for the Preparation of Arbclor 1105", Report No. P-1620, Job No. 2-21-760.01-1754059, June 18, 1971.

5. Cova, D. R., "Tentative Process for Refining of MCS 1109", Report No. P-1621, Job No. 2-21-760.01-1754005, June 15, 1971.

6. Cova, D. R. and Q. E. Thompson, "Tentative Process for the Manufacture of MCS 1109 at Newport, England", Report No. P-1625, Job No. 2-21-760.01-1754005, Aug. 2, 1971.

EXPERIMENTAL WORK AND DISCUSSION

A. Selection of Chlorination Level

11% chlorine was selected as the optimum level of chlorination for MCBP fractionator feed. This selection was based on work carried out in 1970-71 on development of a process for MCS 1109. MCS 1109 was an impure form of MCBP containing 18 to 22% biphenyl and up to 1% of dichlorobiphenyls. The reader is referred to the Tentative Processes of references 4, 5 and 6 for further details.

B. Fractionation to Make MCBP

1. General Procedure

This fractionation is carried out in semi-continuous fashion in a 30-tray column under vacuum. The 30-tray column was chosen to simulate the Aroclor 1016 column at the W. G. Krummrich Plant. Column head pressure was set to give stillpot pressure equivalent to that expected in the plant. Likewise the ratio of column holdup to stillpot charge (about 0.05) was maintained close to that experienced in the plant.

After a period of total reflux, distillate flow is started at a relatively low reflux ratio. At the same time Aroclor 1111 is fed into the stillpot at the same rate as distillate is taken off. At some point the Aroclor feed is cut off, and the intermediate cut from the previous run is fed in. At some point during this time, reflux ratio is increased to keep the o-chlorobiphenyl (o-CBP) concentration low in the distillate. When all of the intermediate fraction has been fed in, the reflux ratio is increased to 15/1. From here on, fractionation is in the batch mode. An increase in head temperature signals the end of the forefraction and the beginning of the intermediate fraction. The intermediate fraction is collected separately and is held for recycle to the next fractionation batch. The forecut can be recycled back to the chlorination reactor. Leveling off of the head temperature indicates depletion of biphenyl from the head of the column. This signals that the end of the intermediate fraction is near at hand. When the biphenyl concentration has fallen sufficiently, the distillate flow is diverted to the main fraction receiver and the reflux ratio is lowered (generally to 8/1). Main fraction is taken off until the level of m-chlorobiphenyl (m-CBP) in the main fraction approaches 4.0%. At this point, distillation is stopped. In our laboratory experiments additional small fractions are taken around

each cut point. After all these fractions have been analyzed they are mixed in the proper order and amount to make up the four fractions called for: forecut, intermediate cut, main fraction, and residue.

2. Samples for Dow

Two samples of MCBP for Dow were generated in the laboratory by fractionating Aroclor 1110 in a 30-tray column. The two distillations were carried out semi-continuously, feeding the stillpot while the forecut was taken off. The forecut was quite large since Aroclor 1110 contains about 45% unreacted biphenyl. Biphenyl was difficult to separate requiring a high reflux ratio (15/1) through the intermediate fraction. The intermediate fraction was large. In the first distillation the cut point was chosen too early and the main fraction contained too much biphenyl. It was recharged to the second distillation and refractionated.

After fractionation various cuts were blended back together to make two samples, each meeting a different specification. The second sample was short of material and had to be diluted out with additional distillate from an early Dayton Pilot Plant fractionation. Analyses of the two samples and specifications are given in Table XXIV, Appendix H. The two samples were shipped to Dow, who, after testing, concluded that sample MCS 1547 with the less rigid specifications would be adequate for their needs. They then requested a large sample (20 drums of 55 gallons each) of the MCS 1547 material.

3. Fractionation in the Dayton Pilot Plant

It was decided to make the twenty drums of MCS 1547 at the Dayton Pilot Plant. A large distillation system with a packed column is available there. 125 drums of Aroclor 1110 were shipped to Dayton. The material was fractionated in five batches of 20 or 21 drums total charge plus feed. The batches were run semi-continuously through the forecut. After the first two batches it was found that the intermediate cut was very large to the detriment of the main fraction. In the remaining batches the intermediate fraction from the previous runs was fed to the stillpot. With this procedure a reasonably sized main fraction could be obtained.

After fractionation was completed, various cuts were blended together in the stillpot to make MCS 1547. Since only 10 drums at a time could be blended, two lots of MCS 1547 were produced and shipped to Dow. Analysis of

the two lots and the specifications are given in Table XXV, Appendix H.

The Dayton Pilot Plant report is attached in Appendix F.

4. Process Simulation

Up to this point we had not given serious consideration to simulating the plant process. MCS 1547 would be made in the 30-tray fractionating column in the Aroclor Department at the W. G. Krummrich Plant. What was needed was optimization of the reflux ratio program and a material balance suitable for a more accurate economic evaluation and for the Process for Engineering Design report. These needs were met in a series of distillation runs in the 30-tray column in the laboratory.

This series of runs was a recycle series in that the intermediate fraction from one run was fed to the stillpot during the next run. The distillations were carried out semi-continuously with feed to the stillpot during the forecut. Aroclor 1111 was fed first and then at the appropriate point the feed was switched to the intermediate fraction from the previous run. Stillpot pressure was set to correspond to that used in the plant when making MCS 1109 (a less pure monochlorobiphenyl). Column holdup to stillpot charge ratio was set to correspond to that in the plant.

Appendix A contains component material balances for this series of runs. From these experiments a feed/charge ratio and a reflux ratio program was selected, as described below.

5. Feed/Charge Ratio and Reflux Ratio Program

The purpose of the semi-continuous mode of operation is to reduce time spent in charging the stillpot, batch heatup, establishing the concentration gradients at total reflux, and dumping residue. For this reason, it is desirable to maximize the feed/charge ratio. As the fractionation proceeds in the semi-continuous mode, biphenyl is selectively removed from the system. Column feed must be stopped before the biphenyl is depleted. Otherwise, o-CBP will reach the head of the column and be taken over in the forecut. The optimum feed/charge weight ratio was found to be 0.63 (the feed here consists of both Aroclor 1111 and the intermediate cut from the previous batch).

The reflux ratio program was optimized, and the final program decided upon was as follows. After a total reflux period to establish the column gradients, distillate

flow is started to the forecut receiver at a reflux ratio of 3/1. At the same time Aroclor 1111 is fed to the stillpot at the same rate as distillate is taken off. After 91.4 lbs. of distillate has been collected, the reflux ratio is increased to 5/1. After 102.1 lbs. of Aroclor 1111 has been fed, its flow is stopped and the intermediate cut from the previous run is fed (on the virgin batch where there is no intermediate fraction to be fed, an additional 40.3 lbs. of Aroclor 1111 is fed to the stillpot). When 40.3 lbs. of intermediate fraction has been fed, the feed is stopped and the reflux ratio is increased to 15/1. After a total of 155.3 lbs. of forecut has been collected, the distillate flow is diverted to the intermediate cut receiver. After 40.3 lbs. of intermediate fraction has been collected, the distillate flow is diverted to the product receiver and the reflux ratio is lowered to 8/1. 100 lbs. of MCBP is distilled off at this reflux ratio. At the end of this period the fractionation is stopped, and 71.4 lbs. of residue is pumped from the stillpot to the residue receiver.

The forecut contains 4.9% o-CBP. Increasing the reflux ratios during this cut to 5/1 and 8/1 (instead of 3/1 and 5/1) would reduce this concentration to about 2-1/2%. Since the forecut is returned to the chlorination step where it is converted to Aroclor 1111, most of the o-CBP is recovered (except for that converted to dichlorobiphenyl). It is estimated that operation at the lower reflux ratios will mean a loss in yield of only 0.4%.

The reflux ratio of 15/1 at the end of the forecut and through the intermediate is essential to reduce the size of the intermediate fraction and to maximize the size of the product fraction.

A reflux ratio of 8/1 is recommended for the main fraction. It was found that a lower reflux ratio (5/1), while it gave an adequate product (though higher in p-CBP), gave an increased residue. The increase was about 8 lbs. per 100 lbs. of MCBP.

6. Instantaneous Distillate Concentrations

In two of our fractionations, sets of small (1-2 cc) samples were taken. These represented instantaneous distillate samples which proved to be very useful in comparison with fractionations in the plant column. In plant scale fractionations, instantaneous samples are easily had whereas composite samples are more difficult to obtain and are necessarily of a historical nature.

Figure 5 in Appendix G depicts the fall of biphenyl concentration in the distillate through the intermediate fraction and into the main fraction. The concentrations are plotted against percent of the charge plus total feed distilled. On the semi-logarithmic plot the curve is a straight line with a break at low concentrations. This break may represent analytical error, a small degree of decomposition in the stillpot to form biphenyl, or biphenyl holdup in an area infrequently washed by distillate.

Figure 7 (Appendix G) depicts the changes in concentration through the main fraction and beyond it if the fractionation is continued further. Concentration curves for m-CBP, p-CBP, and 2,2'-dichlorobiphenyl (2,2'-DCP) are depicted.

C. Product Compositions and Tentative Specifications

The original MCS 1547 product specifications gave a product containing 11% or less p-chlorobiphenyl (p-CBP). In November 1973, Dow requested MCBP containing at least 14% p-CBP. In order to meet this specification it was necessary to distill further into the residue. This necessitated loosening specifications to the following:

	Specifications	Typical Product
Biphenyl	0.6% max.	0.47%
o-Chlorobiphenyl	75.0% min.	78.3%
m-Chlorobiphenyl	5.5% max.	4.64%
p-Chlorobiphenyl	14.0% min.	15.6%
Total Polychlorobiphenyl	1.3% max.	0.85%

In the second column of the above table is a typical analysis of laboratory product.

Shortly thereafter, Dow had another change of heart and decided that they preferred the low-para MCBP. Low-para MCBP, which is identical with MCS-1547, has the following specifications:

	Specifications	Typical Product
Biphenyl	0.6% max.	0.50%
o-Chlorobiphenyl	80.0% min.	85.75%
m-Chlorobiphenyl	4.0% max.	3.08%
p-Chlorobiphenyl	Remainder	10.25%
Total Polychlorobiphenyl	1.0% max.	0.41%

The second column of the above table gives an analysis of typical laboratory product. Comparing material balances for the low- and high-para products showed that the low-para product would generate more residue per 100 lbs. of product (15.5 lbs. more residue per 100 lbs. of MCBP. Therefore, the low-para process increased the problem of residue disposal.

D. Environmental Impact

A prime concern with any Aroclor product is its effect in the environment. This was closely scrutinized through toxicity tests and analyses for trace components.

EC-201 and EC-202 forms were submitted to the Medical Department on both MCS 1546 and MCS 1547. Both products were approved for sale to Dow Chemical Co. for conversion to phenylphenols.

Acute toxicity screening, chick edema factor and a 90-day feeding test in rats were run on typical MCBP. Rat inhalation and acute toxicity to fish were also requested. The rat inhalation test ran into problems and had to be restarted. It is still underway. In the acute fish toxicity test, both trout and bluegill showed a 96 hour TLV of 3.2 ppm.

Memos and reports concerning the above have all been compiled in Appendix E of this report.

Analyses for trace components in MCBP were carried out by both Monsanto and Dow Chemical Co. In general, there was good agreement between the two laboratories. Dow also analyzed phenylphenol samples (which they produced from our MCBP samples) for trace levels of chlorinated compounds.

All the above analytical results have been compiled in Appendix B of this report. Tables XIII and XIV give analysis (by J. P. Mieure) of 5 different samples of MCBP. The preponderance of polychlorobiphenyls in these samples consisted of one isomer, 2,2'-DCBP. All the remaining trace components added up to no more than 500 ppm.

Tables XVI and XVII and the memo from E. S. Tucker to W. R. Richard relate to analysis of phenylphenols made from MCBP. The levels of chlorinated compounds are quite low.

E. Residue Disposition

It is obvious from the material balances of Appendix A that there is considerable residue generated (generally about 72

lbs. of residue per 100 lbs. of MCBP). There were two possibilities available for handling this residue. One was hydrodechlorination to a lower chlorine level and recycle to the process. The feasibility of this was shown by Q. E. Thompson. He was able to remove chlorine in a low pressure reaction under hydrogen using a palladium catalyst and lye to neutralize the HCl formed. This process appeared to be relatively expensive (see cost estimate in Appendix J), so we concentrated our efforts on the other possibility, which was chlorination to a higher Aroclor as 1242, 1016 or 1254.

1. Early Experiments on Residue Chlorination

Aroclor 1016 was made from the residue of low-para MCBP. The MCBP residue was straight takeover distilled to remove lime. This distillate was chlorinated to Aroclor 1142 and then fractionated semi-continuously in a 30-tray column to give Aroclor 1016. Analysis of this product at the W. G. Krummrich Analytical Laboratory gave 0.30% High-Boiling Homologs (HBH). The specification on HBH is 0.40%. Infrared analysis showed that the same compounds were present as in standard Aroclor 1016, but the various concentrations were different. On cooling the sample down, a white solid formed between -5 and -10°C. This solid (which is 4,4'-dichlorobiphenyl) did not redissolve on warming up to room temperature.

Aroclor 1016 was also made from the residue of high-para MCBP. The procedure was the same as above. This product was placed in a freezer whose temperature cycled between -14 and -20°C. After two weeks the white solid had formed. In standard Aroclor 1016 from the W. G. Krummrich Plant no solid formed. The conclusions from infrared analysis of the product were the same as with the previous sample.

HBH analysis gave 0.38%. Electrical properties were good (0.00066 dissipation factor, 4.80 DK, and 344 x 10^4 resistivity). This material contained twice the concentration of 4,4'-dichlorobiphenyl as does standard Aroclor 1016. In general, those compounds containing para-chlorine were increased in concentration, while those having no para chlorine were reduced in concentration. This is as expected since MCBP residue contains over 50% p-CBP (Appendix A).

In an attempt to resolve the problem of solids formation at low temperatures, Aroclor 1016 from MCBP was diluted down to 30% and 40% concentrations with standard Aroclor 1016. After two weeks in the freezer both mixtures gave solids formation. After two more weeks the 40%

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mixture still had solids, but none were detected in the 30% mixture.

Aroclor 1242 was made from high-para MCBP residue by straight takeover distilling the residue from the Aroclor 1016 fractionation above and mixing it with the 1016 in aliquot portions. Part of this Aroclor 1242 mixture was placed in the freezer where, after 3 weeks, crystals were detected in it. The remainder of the mixture was converted to Aroclor 1154 by further chlorination, then to Aroclor 1254 by straight takeover distillation. This Aroclor 1254 sample was placed in the freezer. After nine days crystals were found in the material. This material was then diluted 50/50 with standard Aroclor 1254 from the W. G. Krummrich Plant and placed in the freezer along with the standard Aroclor 1254. After two weeks neither sample had formed crystals.

The above Aroclor 1254 sample (undiluted with standard 1254) and standard Aroclor 1254 were each diluted to 70% and 60% concentration with trichlorobenzene (TCB). These four samples were placed in a freezer held at -40°C. The purpose of this test was to duplicate transformer conditions in a cold climate. After six days both samples that contained 40% TCB showed crystals. The other samples containing only 30% TCB contained no crystals although the mixture made with standard Aroclor 1254 was cloudy. Apparently, TCB is the material solidifying.

The undiluted Aroclor 1254 sample tested out satisfactorily for electrical properties (0.00054 dissipation factor and 4.36 decay). Infrared analysis of the sample showed it to be similar to standard Aroclor 1254 with small concentration differences. At this point Aroclor 1254 from MCBP residue appears to be equivalent to standard Aroclor 1254 for transformer use. As expected, chromatographic analysis shows changes in isomer concentration from standard Aroclor 1254.

Unfortunately, conversion of residue to Aroclor 1254 is not economically feasible, because the amount of residue generated would far exceed projected Aroclor 1254 sales. Aroclor 1254 sales are at present approximately in balance with the quantity of Aroclor 1254 made by chlorination of the still residue from Aroclor 1016.

2. Solubility of 4,4'-DCBP in Aroclor

The solubility of 4,4'-DCBP in Aroclor 1016 was determined to make sure that we had a problem as regards 4,4'-DCBP

level. The data are plotted in Fig. 3 (Appendix C) and they show that indeed a problem does exist. Normal Aroclor 1242 with 2.5 area % 4,4'-DCBP is supersaturated at temperatures below -10°C. To ensure that no problems with 4,4'-DCBP precipitation occur during the use of Aroclor 1242 made from residue, the level of 4,4'-DCBP in the product should be no higher than that in normal Aroclor 1242, 2.5 area %.

The data of Fig. 3 (Appendix C) were determined by holding saturated or supersaturated Aroclor 1016 (made from residue) in the presence of solid 4,4'-DCBP at a given temperature until equilibrium was attained. A sufficiently long time was taken to ensure equilibrium (24 hours at 50°C, a few months at +20°C, and a week at -20°C). After this time the supernatant liquid was sampled by decanting or filtering (at the equilibrium temperature) and analyzing this liquid by GLC for 4,4'-DCBP. The curve of Fig. 3 looks reasonable in having approximately the shape predicted by regular solution theory.

Some of our Aroclor samples were held in freezers at -20°C and other temperatures. Nothing startling came from this except the confounding of some results when crystals of water formed in a few of the samples.

3. Level of 4,4'-DCBP in Chlorinated Residue

The major component of MCBP residue is p-CBP. This is a precursor of 4,4'-DCBP. When the residue is chlorinated the level of 4,4'-DCBP first increases to a maximum then falls as chlorination proceeds through the dichlorobiphenyl stage into trichlorobiphenyl. Figure 4 (Appendix C) is a plot of concentration of 4,4'-DCBP versus specific gravity at 65°C around the region of Aroclor 1142 (a specific gravity of 1.355 indicates Aroclor 1142). As can be seen, the 4,4'-DCBP level is about 3.1-3.2 area % compared to 2.5 area % in normal Aroclor 1142. This is the best we have been able to do, and it should be comparable to what can be done at WGK in the batch chlorinators.

Chlorination conditions of 150°C and 0.5% $FeCl_3$ and of 250°C and 0.025% $FeCl_3$ were tried. Both gave Aroclor 1142 with higher levels of 4,4'-DCBP than did the normal chlorination conditions of 150°C and 0.05% $FeCl_3$. A fritted glass sparger was then used instead of the usual chlorine sparger (a glass tube with 4 or 5 holes of about 1 mm diameter at one end). It is known that small chlorine bubbles lead to a wider homolog spread (see

Progress Report No. 5 on MCS 1043), so, as expected, the 4,4'-DCBP level was higher than normal.

We found one more variable which adversely affects 4,4'-DCBP level in Aroclor 1142 made from residue. The Aroclor 1111 originally used in our process development work was made in the batch chlorinators in the Aroclor Department at the W. G. Krummrich Plant. We found that Aroclor 1142 made from residue where this was the starting material consistently gave higher levels of 4,4'-DCBP than was the case where the Aroclor 1111 had been made in the laboratory. This was tracked down to contamination of the W.G.K. Aroclor 1111 with Aroclor 1154 (made previously in the batch chlorinators). This level of contamination was about 0.5%. This was concentrated up to about 3% in the MCBP residue. Its effect on chlorination was to reduce the amount of chlorination required to produce Aroclor 1142. Since less chlorination was carried out, a higher level of 4,4'-DCBP was left in the Aroclor 1142. This is a problem which is apt to occur in the plant on a changeover to MCBP production. We can handle this by chlorinating to a slightly higher specific gravity. This reduces the 4,4'-DCBP level and still maintains the product within specifications (the experiment on 227274 and 227276). A specific gravity of 1.362 at 65°C is the maximum however. Beyond this point the product would be out of specification.

4. Resolution of 4,4'-DCBP Problem

This area presented the last large obstacle to a successful MCBP process. The problem of residue disposal was resolved by a combination of chlorination and isomerization. Four possible routes were looked at and these are discussed below.

a. Isomerization Followed by Chlorination

In this procedure distilled MCBP residue was isomerized over $AlCl_3$ and then was chlorinated to Aroclor 1142. The concentration of $AlCl_3$ was varied from 2% down to 0.5%. Reaction temperature was varied from from 170 to 280°C. Optimum conditions for isomerization were 200°C and 0.5% $AlCl_3$. Chlorination then was carried out over the $AlCl_3$ catalyst at a temperature of 150°C.

Aroclor 1242 made from this process appears to be satisfactory insofar as it was tested (see Table XXVIII, Appendix K). Thermal chlorides was out of

spec, but this appeared to be more a problem of laboratory technique than the process, since Aroclor 1242 made in the laboratory by the standard process from biphenyl also gave poor thermal chlorides. The level of 4,4'-DCBP was down to satisfactory levels in the Aroclor 1242. This route worked through the removal of the precursor of 4,4'-DCBP by converting it (p-CBP) to the meta isomer in the isomerization step.

Work on this route was discontinued because of problems that were encountered. One of these was sublimation of $AlCl_3$ out of the reactor during chlorination. This was sufficient to deposit solids in the condenser and vent lines. Distillation of the Aroclor 1142 left larger than normal residues. This is an indication of the formation of highly chlorinated biphenyl compounds (or polymerization of biphenyl) and would have been very undesirable. Finally, there was a corrosion problem on steel during isomerization. This occurred in some experiments but not others (Appendix D).

b. Isomerization, Distillation, Chlorination

This route was essentially the same as the previous one, differing from it in that the isomerized residue was straight takeover distilled before chlorination to Aorclor 1142. This route also appeared to give suitable product, although some strange colors were observed during titration in some of the stability tests. This procedure eliminated the problem of $AlCl_3$ sublimation, but the problems of high residue (because of two distillations) and corrosion were still with us. Also, another processing step had been added. Work was also discontinued on this.

c. Chlorination Over $AlCl_3$

In this route the residue was chlorinated over $AlCl_3$ to Aroclor 1142. Aluminum metal was also used as catalyst, FeCl, being added to act as catalyst until $AlCl_3$ had been formed from the Al. It was found that under the proper conditions (at least 0.4% $AlCl_3$) the Aroclor 1142 formed contained less than 2.5 area % 4,4'-DCBP. Unfortunately, the amounts of catalyst required caused corrosion problems (Appendix D). Catalyst sublimation and large residues on distillation were further reasons for the elimination of this route from consideration.

d. Chlorination Followed by Isomerization

In this route distilled residue was chlorinated over 0.05% $FeCl_3$ at 150°C to Aroclor 1142. 0.25% $AlCl_3$ was then added and the material was isomerized over a 5-hour period at 250°C. The final product Aroclor 1242 contained less than 2.5 area % 4,4'-DCBP. This route eliminated the problems of sublimation and large residue formation. Corrosion of steel during isomerization was reduced to tenable levels (see Appendix D). A suitable product was obtained which met all specifications except two (see Table XXVII, Appendix K). The refractive index of the product was higher than normal, and the dielectric constant was lower than normal. The latter change is an asset for transformer use, which is the only use of Aroclor 1242 at the present time. The infrared spectrum and chromatogram of the product were also different from those of normal Aroclor 1242. These differences were caused by changes in the concentration of various isomers. It might be noted at this point that all Aroclor 1242 made from residue by any of the above routes or by stright chlorination of residue over $FeCl_3$ had infrared spectra and chromatograms that differed from those of normal Aroclor 1242 (compare Figs. 12 and 13, Appendix M).

Table XX, Appendix C, shows the levels of 4,4'-DCBP obtained under the various conditions of our experiments.

5. Corrosion

One of the difficulties encountered in using Al or $AlCl_3$ catalyst was equipment corrosion. A large number of short-term tests were run under varied conditions. Steel, Monel and Hastelloy C were tested. When optimum conditions were found, a long test was run (30 hours of test comprised of 5 isomerization batches). Corrosion rates on this test were 4.0 mils/yr on steel, 1.3 mils/yr on Monel, and 1.2 mils/yr on Hastelloy C. Corrosion was uniform (see attached memo from O. W. Siebert). These optimum conditions (optimum from the standpoint of both low corrosion rates and sufficient isomerization) were 0.25% $AlCl_3$ concentration and a temperature of 250°C. Lower temperatures (down to 180°C) had no effect on corrosion rate. $AlCl_3$ concentration had a large effect, corrosion increasing rapidly with increase in $AlCl_3$ concentration (see Table XXI, Appendix D). There was some variation in corrosion rates in the short-term tests, probably due in part to the short exposure times. Because of this it was highly desirable to test further.

Corrosion of steel in the isomerization of Aroclor 1142 was tested again at $AlCl_3$ concentrations of 0.25 and 0.40%.

The higher concentration was tested because of the possibility of at times needing a greater degree of isomerization. This is provided by the higher $AlCl_3$ concentration. Each test consisted of nine isomerization batches (5 hours at 250°C on each batch for a total exposure at temperature of 45 hours). Two fresh steel coupons were used in each test. At the 0.25% concentration, penetration rates were 2.6 and 3.3 mils/yr and 4.1 and 5.0 mils/yr at 0.4% $AlCl_3$. The coupons were examined by Mr. O. W. Siebert of CED who concluded that steel would be satisfactory for this process step.

6. Lime Treatment of Isomerized Aroclor 1142

Aroclor 1142 must be lime treated before it is distilled. The purpose of lime treatment is to react out dissolved HCl, "kill" (i.e., deactivate) the catalyst, and give an Aroclor 1142 distillate of suitable quality. $AlCl_3$ must be a difficult catalyst to deactivate. It was found in early experiments that if the distillation was carried out immediately after the lime was added, the distillate became colored as distillation proceeded. This problem was resolved by holding the material at 150°C for 2 hours. This bit of technology was found in an old Therminol 77 report.

7. Aroclor 1242 Quality

In order to produce Aroclor 1242 or 1016 of suitable quality for testing (especially as regards the stability tests), we incorporated an elaborate cleanout and handling procedure. The procedure is given in Table XXXII, Appendix N. This procedure was used in all experiments except the early ones.

The results of tests of Aroclor 1242 and 1016 are given in Table XXVIII, Appendix K. As can be seen from the table, the thermal chlorides stability test was quite difficult to pass. This was due to the problems of maintaining proper cleanliness in the laboratory. Two samples of Aroclor 1242 were made from biphenyl by the standard process. Both failed the thermal chlorides test. On the other hand, we were able to make Aroclor 1016 and 1242 from residue which passed this test.

Table XXVIII shows that Aroclor 1242 made from residue will pass every specification except refractive index and dielectric constant. The refractive index is higher than normal and the dielectric constant is lower. The infrared spectra and chromatograms will also be different from those shown by normal Aroclor 1242. Figs. 12 and 13, Appendix N, are chromatograms for Aroclor 1242 from residue and from biphenyl, respectively.

F. Test Run at W. G. Krummrich Plant

1. Biphenyl Chlorination

Biphenyl was chlorinated to Aroclor 1111 in the continuous 4-stage chlorination unit. WGK Analytical Research & Development Report No. 2565 is attached to this report (Appendix G). This gives the composition of the reaction mass exiting each stage (chlorinator 6 is the first stage, and 9 is the last stage). Table XXIII, Appendix G, gives a comparison of laboratory Aroclor 1111 composition with that from the plant. The laboratory material is slightly more chlorinated. Other than that, the two materials are quite comparable.

A difficulty encountered in the plant was the carryover of excessive amounts of liquid with the HCl offgas from the last stage at the higher biphenyl feed rate. Plant reaction mass was tested in the laboratory to determine if foaming was occurring at the higher rate of HCl evolution. The result was negative: no foaming occurred. At this time the carryover problem is believed to have been caused by a level buildup in the 4th stage brought about by too small of an opening in the reactor effluent valve.

2. Fractionation

The Aroclor 1111 was fractionated in the 30-tray Aroclor 1016 column. Quality and yield of the product were as predicted. Figure 5, Appendix G, compares the variation in biphenyl concentration in the distillate versus percent of the charge distilled in the plant run with that obtained in the laboratory. This shows that the laboratory simulated the plant closely. It had been intended to use the refractive index of the distillate to determine the start of the MCBP fraction. However, the sensitivity was too low. From the plant and laboratory data, we have concluded that column head temperature rise can be used to determine this cut point. This point is discussed further below.

The end of the MCBP fraction was determined by GLC analysis of material collected in product storage and in the distillate receiver along with reference to Figure 7, Appendix G, which depicts the change in distillate composition with percent distilled around the end of this fraction.

A presently unresolved problem is excessive vibration in or near the stillpot at furnace heat inputs of over 80% of the maximum. This was a new experience since

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this system had been previously run at 100% of furnace capacity in making MCS-1109.

WGK Analytical Research & Development Report #2567 is attached (Appendix G). This gives distillate and storage tank analyses from the plant fractionation. The analysis of the sample shipped to Dow Chemical Co. is given in Table XXVI, Appendix H.

3. Column Control

Column control is discussed in the Process for Engineering Design (Ref. 1) with the exception of the following. Since refractive index was not suitable to determine the start of the MCBP fraction, we cast about for another method. We have decided to use the rise in column head temperature (as biphenyl is depleted from the system) in the following fashion. After the head temperature has risen 10°C above the biphenyl plateau, a certain number of gallons of distillate are taken forward into the slop cut receiver. As soon as this amount of distillate has been collected, distillate flow is switched to the MCBP fraction receiver. Figure 6, Appendix G, plots biphenyl concentration in the MCBP fraction versus percent of the charge distilled from the 10°C rise point on. An error of ± 2°C in determining this rise will cause a ± 2-1/2% change in the size of the MCBP fraction and less than ± 0.1% change in MCBP fraction biphenyl concentration.

4. Residue Chlorination and Isomerization

Column residue was distilled in the laboratory and then converted to Aroclor 1242' (chlorination, then isomerization over $AlCl_3$) using $AlCl_3$ catalyst purchased for the test run. Satisfactory material was made. The 4,4'-DCBP level was lower than expected, indicating a "hotter" lot of catalyst. This proved to be the case when isomerization level was adequately low in a much shorter time than expected.

Analyses and pertinent reports are contained in Appendix G of this report.

G. Chlorination of Biphenyl Over Various Catalysts

A number of different possible catalysts were tested for chlorinating biphenyl to the monochlorobiphenyl level. Each test was carried out with a catalyst concentration of 1% and a temperature of 150°C (except for the Pentonite clay where a temperature of 80°C was used). $FeCl_3$ is the normal catalyst, so an experiment with 1% $FeCl_3$ was run to give us a baseline.

In each experiment the theoretical amount of chlorine to give 100% conversion to monochlorobiphenyl was added to the reaction mass (except BF, where more chlorine was added). Table XXVII, Appendix I, gives the percent chlorine in the product, the chlorine efficiency, and the ratio of o-chlorobiphenyl (o-CBP) to p-CBP. The ratio of these two isomers may vary with the degree of chlorination, so in order to provide a fair test these ratios were plotted against the percent chlorine in the product and compared to that obtained under normal chlorination conditions (0.05% $FeCl_3$). This is given in Fig. 9, Appendix I. It is obvious from this figure that $FeCl_3$ is still the catalyst of choice since it tends to make more o-CBP and less p-CBP.

Reference 3, a patent assigned to Dow, claims the selective chlorination of biphenyl to o-CBP using moistened Bentonite Clay as catalyst. We had not as yet duplicated their results. Our one run with Bentonite Clay did not contain as much moisture as called for in the patent.

H. Physical Properties

Some physical properties of MCBP and of process streams were determined. These are collected in Appendix K.

I. Miscellaneous Experiments

1. Dow inquired as to the possibility of increasing the concentration of p-chlorobiphenyl in MCS 1547 or of our supplying them with more p-chlorobiphenyl. It was thought that isomerization might increase the para isomer content, but past work by L. Bannister showed that o-chlorobiphenyl isomerized to the meta isomer (which has no use) rather than to the para isomer. He used $AlCl_3$ catalyst over the concentration range of 1/4 to 2% and reaction temperatures of 160 to 200°C.

2. The p-CBP concentration of MCBP was varied in an attempt to reduce the crystallizing point sufficiently low to make a suitable solvent for tolylxylylsulfone. The lowest crystallizing point found was 9°C, and this concept was dropped.

3. In one experiment the MCBP fractionation was carried further to remove the p-CBP from the residue as a tail cut. This tail cut was chlorinated to 30% chlorine, then mixed with the MCBP residue in aliquot portions and fractionated to make MCS-1043. The product was not suitable because is contained too much 4,4'-dichlorobiphenyl.

4. Early experiments in which residue was chlorinated to Aroclor 1142 then fractioned to form Aroclor 1016 ran into the problem of high 4,4'-DCBP level. In later experiments the Aroclor 1142 was isomerized over $AlCl_3$ before fractionating into Aroclor 1016. This resolved the problem of 4,4'-DCBP level but gave a product with a low dielectric constant (4.61 in the experiment on page 227266 versus a specification of 4.70-4.90). This lower dielectric constant was due to the changed isomer concentrations caused by isomerization. Aroclor 1016 made by fractionating chlorinated residue (no isomerization) on 207183 had a dielectric constant of 4.80.

5. We attempted in one experiment to fractionate out a concentrated fraction of 4,4'-DCBP from Aroclor 1142 made from residue. We failed to achieve any significant concentrating of the 4,4'-DCBP. Apparently the mixture is too close-boiling to separate readily.

6. In another experiment in this area we chlorinated residue to a specific gravity of 1.362 at 65°C (about Aroclor 1142 1/2). This gave a sufficiently low level of 4,4'-DCBP. This Aroclor was then fractionated in the same manner as in producing Aroclor 1016. The data are given in Table XXXI, Appendix N. It appears that a suitable product may be obtained if we can accept a higher residue formation (25% of the charge as residue compared to 20% in the present process). GLC analysis (by the long method) for pentachlorobiphenyl and higher were 0.4% compared to 0.57% average for the plant. The High-Boiling Homologs (HBH) analysis was high, 0.4% compared to 0.2% average in the plant. This latter analysis (a short GLC procedure) however is not as quantitative an indicator of pentachlorobiphenyl concentration as is the longer GLC analysis.

7. $FeCl_3$ was tried as an isomerization catalyst. There was no reaction at 273°C and a catalyst concentration of 2%.

8. A 50/50 mixture of biphenyl and Aroclor 1016 was held at 260°C over 2% $AlCl_3$. There was only a slight reduction in biphenyl content indicating little transfer of chlorine from the Aroclor 1016 to the biphenyl.

9. $SnCl_4$ was used as a chlorination catalyst. It gave interesting results in chlorinating biphenyl to Aroclor 1111. The levels of 2,2'-DCBP and of m-CBP were reduced considerably to 0.36% and 0.70%, respectively, compared to 1.6% and 3.1% in Aroclor 1111 produced over $FeCl_3$ catalyst. The crude was treated with lime and then fractionated. The distillate was clear of tin indicating that the

lime had reacted with the catalyst. Analysis for tin in the residue, however, indicated that most of the catalyst had vaporized during chlorination. We attempted to chlorinate to Aroclor 1142 using $SnCl_4$ catalyst, but the reactivity was too low (large amounts of chlorine being bypassed) and catalyst was being vaporized out of the reaction mass too rapidly, so the experiment was discontinued.

10. At one time we considered taking a tail cut in the MCBP fractionation and leaving mostly dichlorobiphenyls in the residue. The tail cut which would be essentially p-CBP was to be chlorinated to Aroclor 1254 and the residue to Aroclor 1242 or 1016. This was dropped because the amount of tail cut would have produced too much Aroclor 1254 to be sold.

11. In one experiment (265317, 265320) distilled residue was chlorinated to a specific gravity of 1.362 at 65°C. This corresponded to 42.7% chlorine and was high enough to give a low 4,4'-DCBP content (2.6 area %). The material was distilled and Porocel treated. Its pour point was right at the specification level, -14°C, but the viscosity at 100°F was out of specification (95.9 SUS as compared to a required range of 82-92 for Aroclor 1242).

12. An experiment was run in which MCBP residue was chlorinated to 42.5% Cl and then fractionated as in the manner of the Aroclor 1016 process. Analytical results versus Aroclor 1016 specifications are shown in Table III of the attached memo (D. Cova to R. Koch, 11/21/74, in Appendix K). As Aroclor 1016 this product was out of specification on specific gravity, refractive index, viscosity, High Boiling Homologs (HBH) and A.C. inorganic chlorides. This last result is most likely a laboratory artifact. Of the others, higher than normal viscosity and HBH are real problems, although it may be possible to sidestep the HBH issue by changing to a longer GLC procedure which determines pentachlorobiphenyl and more highly chlorinated biphenyls more accurately. By this procedure, this product compared favorably with normal Aroclor 1016 (see Table III of the above memo).

13. We carried out some experiments in which we tried to reduce the 4,4'-DCBP level of Aroclor 1142 made by chlorinating MCBP residue. It was thought that if the chlorination cycle could be extended slightly, this would allow enough chlorination to occur to give a lower 4,4'-DCBP level. The cycle was extended by adding biphenyl to the distilled residue. Up to 13.3% biphenyl was added to distilled MCBP residue without any effect whatsoever on the 4,4'-DCBP level of the Aroclor 1142. Probably the

faster rate of chlorination of biphenyl compared to chlorinated biphenyls and the fact that some 4,4'-DCBP is formed in biphenyl chlorination prevented a lowering of the 4,4'-DCBP level in the Aroclor 1142 formed.

14. The solubility of HCl in Aroclor 1142 at temperatures ranging from 120 to 250°C and under atmospheric pressure of HCl was determined. The data are plotted in Fig. 10, Appendix N.

15. The levels of pentachlorobiphenyls and more highly chlorinated biphenyls (or penta $^+$) were determined for Aroclor 1242' from MCBP residue and compared to that for normal Aroclor 1242 made from biphenyl. The product from MCBP residue contained ~4% penta$^+$ as compared to ~5% penta$^+$ in normal Aroclor 1242. The product from residue also compared favorably on HBH, ~5% HBH versus ~6-8% in normal Aroclor 1242 (see Table II in the memo, D. Cova to R. Koch, 11/21/74, in Appendix K).

16. HCl offgas from the chlorinators at WGK is passed through a scrubber to remove PCB's from the gas. The scrubbing liquid is distilled residue from the Aroclor 1016 process. When the plant is making Aroclor 1111 (for MCBP manufacture) the offgas will contain biphenyl which is relatively volatile. It has been found in the plant that chlorination of biphenyl occurs in the plant scrubber. We added biphenyl to a sample of scrubber liquor and simulated this low temperature chlorination in the scrubber. The sample and a control were then chlorinated to Aroclor 1154 and worked up to Aroclor 1254. The sample with chlorination in the scrubber showed a poorer Monsanto stability and higher unstable chlorides. This may not have been a fair test since the amount of chlorination in the scrubber was much higher than would be expected in the plant.

17. Since contamination of MCBP residue with more highly chlorinated Aroclor was shown to have an adverse effect on 4,4'-DCBP concentration of the Aroclor 1142 produced, it was decided to determine the liquid holdup of a WGK batch chlorinator after dropping a batch. This was done by chlorinating bipehnyl to Aroclor 1121 in such a unit after Aroclor 1154 had been made in the unit. The reaction mass was then analyzed for residual Aroclor 1154. In this way, the holdup was shown to be only about 3 gallons.

18. A proposed temperature cycle for chlorination of MCBP residue in the plant was tested in the laboratory. In this cycle the temperature is allowed to rise to 190°C and is held there. This reduces heatup time for the following isomerization step. There was no adverse effect on 4,4'-DCBP concentration (see Table XX, Appendix C).

DESCRIPTION OF RECOMMENDED PROCESS

The reader is referred to the Process for Engineering Design for Monochlorobiphenyl (Reference 1).

MATERIAL SPECIFICATIONS AND ANALYTICAL PROCEDURES

The reader is referred to the Process for Engineering Design for Monochlorobiphenyl (Reference 1) for material and product specifications and for all analytical procedures except the GLC procedures and that for HCl in Aroclor which are given in Appendix L.

COST ESTIMATES

Cost estimates are given in Appendix J.

TOXICITY AND HAZARDS

The reader is referred to the Process for Engineering Design for Monochlorobiphenyl (Reference 1).

ATMOSPHERIC AND STREAM POLLUTION

The reader is referred to the Process for Engineering Design for Monochlorobiphenyl (Reference 1).

ACKNOWLEDGEMENT

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D. R. Cova

js

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APPENDIX A

MATERIAL BALANCES FOR MONOCHLOROBIPHENYL FRACTIONATION

Notebook Page No. 207156-7

Calculated 1/28/74

TABLE I

	CHARGE	CRUDE FEED	INTERMED. FEED	FORE FRACTION	INTERMED. FRACTION	MAIN FRACTION	RESIDUE
Biphenyl	45.08			94.45	32.25	.48	06
Ortho	27.02			5.48	67.62	85.56	2 26
2,2'-Dichlor	1.52			.00	.00	.45	5.59
Meta	3.77			.01	.04	3.87	11.65
Para	17.66			.03	.08	9.52	61 35
Dichlors	4.22			.00	.00	.00	16.45
Trichlors	.28						1.11
Tetras	.37						1.46
TOTAL	287.22	215.22	.00	221.52	52.09	100.0	129.02

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Notebook Page No. 207158-59-60 Calculated 1/28/74

TABLE II

	CHARGE	CRUDE FEED	INTERMED FEED	FORE FRACTION	INTERMED. FRACTION	MAIN FRACTION	RESIDUE
Biphenyl	46.34		32.25	98.96	34.65	.47	.01
Ortho	26.83		67.72	1.04	64.70	85.91	.56
2,2'-Dichlor	1.90		.00		.00	.43	7 78
Meta	3.18		.04		.03	3.43	9.34
Para	15.90		.08		.07	9.47	57 16
Dichlors	5.49		-		-	.00	24 19
Trichlors	.22		-		-	-	97
Tetras	.00		-		-	-	-
TOTAL	209.02	114.74	38.34	150.15	38.48	100.00	73.47

MONS 021545

Notebook Page No. 207161

Calculated 1/28/74

TABLE III

	CHARGE	CRUDE FEED	INTERMED. FEED	FORE FRACTION	INTERMED FRACTION	MAIN FRACTION	RESIDUE
Biphenyl	46.41		34.65	97.64	26.70	.54	.00
Ortho	26.74		64.70	2.32	72.70	82.93	.88
2,2'-Dichlor	1.44		.00	-	-	.64	5.63
Meta	3.21		.03	.02	.04	3.89	9.26
Para	16.13		.07	-	.09	11.74	57.13
Dichlors	5.52					.03	24.87
Trichlors	.17						.78
Tetras	.32						1.45
TOTAL	226.80	111.67	41.15	163.73	40.91	100.00	74.98

MONS 021546

Notebook Page No. 207167-8

Calculated 1/28/74

TABLE IV

	CHARGE	CRUDE FEED	INTERMED. FEED	FORE FRACTION	INTERMED FRACTION	MAIN FRACTION	RESIDUE
Biphenyl			25.09	97.36	35.11	48	.20
Ortho			74.29	2.64	64.41	82.40	.79
2,2'-Dichlor			.00		.00	.69	5.50
Meta			.04		.03	3.85	8.12
Para			.10		.08	12.18	52.06
Dichlors						.03	28.76
Trichlors						-	1.60
Tetras						-	3.00
TOTAL	204.01	95.56	39.39	136.56	38.61	100 00	63 79

MONS 021547

Notebook Page No. 207169-70

Calculated 1/28/74

TABLE V

	CHARGE	CRUDE FEED	INTERMED. FEED	FORE FRACTION	INTERMED FRACTION	MAIN FRACTION	RESIDUE
Biphenyl	46.20		31.64	97.74	33.89	.20	.05
Ortho	27.21		67.84	2.26	65.56	84.19	1.35
2,2'-Dichlor	1.40		.00		.00	58	5 49
Meta	3.01		.04		.03	3.62	8.78
Para	15.23		.08		.08	11.00	53.85
Dichlors	7.02					.02	31.35
Trichlors	.32						1.44
Tetras	.12						.52
TOTAL	236.86	108.56	50.54	158.53	60.18	100.00	77.25

MONS 021548

Notebook Page No. 207173

Calculated 1/28/74

TABLE VI

	CHARGE	CRUDE FEED	INTERMED FEED	FORE FRACTION	INTERMED FRACTION	MAIN FRACTION	RESIDUE
Biphenyl			33.89	97.57	31.77	.60	
Ortho			65.56	2.40	67.70	85.17	
2,2'-Dichlor			.00		.00	56	
Meta			.03		.03	3 31	
Para			.08		.07	10.01	
Dichlors						.01	
Trichlors							
Tetras							
TOTAL	201.37	84.67	50.84	144.25	29.87	100.00	62 76

Notebook Page No. 207190, 93

Calculated 1/28/74

TABLE VII

	CHARGE	CRUDE FEED	INTERMED. FEED	FORE FRACTION	INTERMED. FRACTION	MAIN FRACTION	RESIDUE
Biphenyl	46.87		30.31	95.30	28.35	.37	.01
Ortho	26.98		69.15	4.67	71.54	82.08	92
2,2'-Dichlor	1.40					.69	5.64
Meta .	2.80		.03		.03	3.79	7.91
Para	15.40		.07		.07	13.02	54.50
Dichlors	5.83					.03	27.44
Trichlors	.12						.56
Tetras	.64						3.02
TOTAL	223.33	115.62	34.95	167.01	35.03	100.00	71.86

MONS 021550

Notebook Page No 207197-B

Calculated 1/28/74

TABLE VIII

	CHARGE	CRUDE FEED	INTERMED FEED	FORE FRACTION	INTERMED. FRACTION	MAIN FRACTION	RESIDUE
Biphenyl	46.43		28.35	95.13	30.26	.22	10
Ortho	27.38		71.54	4.87	69.66	82 38	5 13
2,2'-Dichlor	1.93					59	7.85
Meta	2.74		.03			3.53	7.78
Para	15.38		.07			13 28	51 86
Dichlors	5.35					.00	23 83
Trichlors Tetras	.77						3 44
TOTAL	240.45	115.35	37.18	171.09	41.94	100 00	79 95

MONS 021551

Notebook Page No. 257419

Calculated 1/28/74

TABLE IX

	CHARGE	CRUDE FEED	INTERMED. FEED	FORE FRACTION	INTERMED. FRACTION	MAIN FRACTION	RESIDUE
Biphenyl				96.24	33.45	.30	.00
Ortho				3.74	66.46	85.96	2.04
2,2'-Dichlor						52	6 02
Meta					.03	3 05	8.71
Para					.05	10.15	57 67
Dichlors							25.43
Trichlors							
Tetras							
TOTAL	223.0	115.4	30.8	161.8	30.8	100.0	76.6

MONS 021552

Notebook Page No. 25745J

Calculated 1/28/74

TABLE X

	CHARGE	CRUDE FEED	INTERMED FEED	FORE FRACTION	INTERMED. FRACTION	MAIN FRACTION	RESIDUE
Biphenyl				95.81	40.62	56	02
Ortho				4.15	59.30	82.22	1.37
2,2'-Dichlor						76	5.90
Meta						3 48	7 32
Para						13 00	57 60
Dichlors						.01	27 19
Trichlors							.58
Tetras							
TOTAL				126.37	47.99	100.00	63 18

MONS 021553

Notebook Page No. 257442

Calculated 1/28/74

TABLE XI

	CHARGE	CRUDE FEED	INTERMED. FEED	FORE FRACTION	INTERMED. FRACTION	MAIN FRACTION	RESIDUE
Biphenyl			33.45	95.82	27.40	.48	.25
Ortho			66.46	4.17	72.53	83.56	3.02
2,2'-Dichlor						.35	5.75
Meta						3.63	8.90
Para						11.99	56 17
Dichlors							25.41
Trichlors							.49
Tetras							-
TOTAL	271.08	135.44	37.16	198.66	51.72	100 00	93.30

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TABLE XII

ANALYSES OF INSTANTANEOUS DISTILLATES
MONOCHLOROBIPHENYL
OR 207190-93

Charge = 4807

KWH
1-28-74

CUT #	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V
Di	98.89	98.27	93.64	97.61	78.99	85.69	84.00	42.92	5.42	3.22	1.36	0.54	0.07	0.02	0.01	0.13	0.01	0.01	0.01	0.0	0.01	0.02
OPTHO	1.13	1.71	6.35	2.36	19.06	14.31	58.85	86.89	98.31	96.66	98.39	98.96	97.50	87.18	35.81	8.76	2.66	0.66	0.14	0.07	0.07	0.06
UNK					-	-	-	-	-	-	-	-	-	-	0.06	0.07	0.07	0.07	0.06	0.33	—	0.01
2,2'					-	-	-	-	-	-	-	-	0.01	0.20	2.62	4.84	5.78	5.46	6.21	7.60	10.76	8.17
META					0.01	-	0.02	0.07	0.09	0.08	0.07	0.19	0.72	3.43	16.81	16.85	15.49	13.92	11.50	8.53	4.07	1.94
P-PA					0.02	0.004	0.05	0.18	0.14	0.15	0.18	0.29	1.70	9.19	42.19	69.85	75.98	79.60	81.89	81.83	65.46	49.50
6-11 Di															0.11	0.40	0.19	0.28	0.61	1.94	19.63	50.31
WEIGHT	301	665	1191	1992	1939	3143	3270	2906	2524	2598	2317	2831	3390	3583	3709	3886	4004	4123	4244	4364	4485	4536
% DISTILLED CUMULATIVE	6.43	13.79	24.78	30.00	40.23	54.68	67.22	73.06	78.51	84.05	89.52	95.02	68.65	73.27	77.16	80.84	83.30	85.77	88.27	90.78	93.30	94.36

APPENDIX B

ANALYSES AND METHODS FOR TRACE COMPONENTS IN MONOCHLOROBIPHENYL AND PHENYLPHENOLS PRODUCED THEREFROM

TABLE XIII

TRACE COMPONENT ANALYSIS IN MCBP SAMPLES

Peak No.	Peak Identity	First Lab Sample of MCS 1546 MIC 207152 Blend 1	First Lab Sample of MCS 1547 MIC 207152 Blend 2	Blend From Recycle Series MIC 207162
1-10	?	20-30 ppm total	20-30 ppm total	~ 10 ppm total
11	Biphenyl	-	-	-
12	?	50 ppm	20 ppm	40 ppm
13	?	50 ppm	50 ppm	100 ppm
14	o-Chlorobiphenyl	-	-	-
15	?	30 ppm	30 ppm	30 ppm
16	?	30 ppm	50 ppm	70 ppm
17-19	m & p-chlorobiphenyl and 2,2'-di-chlorobiphenyl	-	-	-
20	a dichlor	28 ppm	65 ppm	90 ppm
21	?	6 ppm	<5 ppm	<5 ppm
22	a dichlor	8 ppm	22 ppm	30 ppm
23	a dichlor	10 ppm	35 ppm	30 ppm
24	?	17 ppm	6 ppm	3 ppm
25	?	8 ppm	3 ppm	<3 ppm
26	?	8 ppm	4 ppm	<3 ppm
27	4,4'-dichlor	<5 ppm	80 ppm	<10 ppm
28	?	10 ppm	4 ppm	Probably less than 50 ppm
29-34	?	~150 ppm total	~50 ppm total	

Note: Peaks 1 through 28 were determined with a 4 meter x 1/8" dia. Santicizer 409 column at 200°C and a helium flow of 40 ml/min. Peaks 29 through 34 were detected using an OV-17 column 4 meters x 1/8" dia at 260°C. Flowrate was 20 ml/min. The detector was a flame ionization unit in both cases.

TABLE XIV

TRACE COMPONENT ANALYSIS IN MCBP SAMPLES

Peak No.	Peak Identity	First Lab Sample of MCS 1547 MIC 207152 Blend 2	MIC 207162 Low-Para MCBP	MIC 207175 High-Para MCBP
1-10	?	20-30 ppm total	~10 ppm total	<10 ppm total
11	Biphenyl	-	-	-
12	?	20 ppm	40 ppm	50 ppm
13	?	50 ppm	100 ppm	40 ppm
14	o-Chlorobiphenyl	-	-	-
15	?	30 ppm	30 ppm	30 ppm
16	?	50 ppm	70 ppm	80 ppm
17-19	m & p-chlorobiphenyl and 2,2'-di-chlorobiphenyl	-	-	-
20	a dichlor	65 ppm	90 ppm	190 ppm
21	?	<5 ppm	<5 ppm	<3 ppm
22	a dichlor	22 ppm	30 ppm	40 ppm
23	a dichlor	35 ppm	30 ppm	40 ppm
24	?	6 ppm	3 ppm	<3 ppm
25	?	3 ppm	<3 ppm	<3 ppm
26	?	4 ppm	<3 ppm	<5 ppm
27	4,4'-dichlor	80 ppm	<10 ppm	<5 ppm
28	?	4 ppm		
29-34	?	~50 ppm total	probably less than 50 ppm	Very low

Note: Peaks 1 through 28 were determined with a 4 meter x 1/8" dia Santicizer 409 column at 200°C and a helium flow of 40 ml/min Peaks 29 through 34 were detected using an OV-17 column 4 meters x 1/8" dia. at 260°C. Flowrate was 20 ml/min. The dtector was a flame ionization unit in both cases.

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