PROGRESS REPORT
TECHNICAL SERVICES DEPT. - W.G. KRUMMRICH PLANT

JOB NO.	REPORT NO.	DATE
91370:3198	3	9/8/65

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TITLE: Aroclor - Improve Electrical Grade Quality

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PROBLEM: Report status of work to improve Aroclor quality.

SUMMARY: An improvement in Aroclor quality (stability) is needed to protect our market against foreign competition.

A designed experiment indicated that a quality improvement was possible by upgrading the chlorinators, but a plant test to confirm the designed experiment failed to show an improvement. A plant test using revaporized chlorine was also run. Again, there was no significant improvement. These tests did show, however, that some improvement could be made by improving the effectiveness of earth treatment.

Currently there are three areas of work to improve stability. These are distillation, chemical treatment, and chlorination improvements.

Distillation was proven by PR & D as a means to improve stability, in batch equipment. Research is currently developing design data for continuous distillation. When this is complete an equipment and operating cost estimate will be made (EDC 11/1/65).

PR & D is currently investigating chemical treatment to improve quality. Preliminary results are promising. When this work is complete the results will be confirmed with a plant test and an equipment and operating cost estimate will be made (EDC 11/1/65).

DSW 311682

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A study of the chlorination step indicates quality can be improved by designing a new chlorinator. Further work may be done in this area, dependent upon the results of the distillation and chemical treatment work.

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DETAILS

Background

As reported previously an improvement in Aroclor quality (stability) is needed to protect our market position against foreign competition.

PR & D laboratory work showed very stable Aroclor could be made from present production material by distillation, and the removal of unstable high and low boiling fractions. This work, and a plant test, indicated that plant equipment to improve stability by distillation would be quite costly, and would substantially increase manufacturing cost.

At this time work was initiated to improve the chlorination step. It was felt that by proper control of the chlorination the amount of unstables could be minimized, and the cost of distillation equipment and magnitude of the yield loss to reach the quality goal would be reduced.

A designed experiment was run on the chlorinators to determine the significant variables affecting stability. There was no method for directly measuring the stability of chlorinator batches so that an apparent correlation between certain low boilers, which could be measured, and stability (low low boilers, good stability) was used. There was a large experimental error in the results of the designed experiment, but it indicated that using the existing operating conditions with a particular two of the five chlorinators would give the lowest amount of low boilers, and by the correlation the best stability.

A complete description of the distillation work and the designed experiment can be found in Progress Reports Nos. 1 and 2 of this job.

Confirmation of Designed Experiment

A plant test was run to confirm the results of the designed experiment. This was done by separating crude made in the two chlorinators which, according to the designed experiment, should produce low low boiler material, from other crude. The low low boiler material was air blown, distilled, and earth treated separately also. The results of this test are listed in the Appendix, Table 1.

A composite of the first two test batches, sampled after air blowing, had a high low boiler content, and the test was started over. The next five batches were sampled at the completion of chlorination, and had low low boiler content. During the processing of these batches it was necessary to stop the distillation with two batches in the still, to prevent driving over unstable high boilers. This meant that the low boilers would be concentrated in the distillate, but the content should still have been substantially below normal.

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Although a composite sample of the five test chlorinator batches was low in low boilers (40 ppm biphenyl)) the stability, following distillation and earth treatment, was about normal, 0.46 and 0.58 ppm TCCl. Also, the biphenyl content of the finished test material was higher, 360 ppm, than could be explained by the concentration effect described above. This suggests a breakdown of heavier chlorinated products to low boilers. As expected, there was a very unstable fraction at the start of the distillation.

A sample taken just before plant earth treating was earth treated in the lab and analyzed 0.35 ppm TCCl, 0.11-0.23 better than plant treated material.

Two samples from the non-experimental system were taken during the test and analyzed 0.35, 0.36 ppm TCCl and about 2800 ppm biphenyl. Although the biphenyl content was much higher than the test material the stability was essentially the same. Obviously, more will have to be done to improve stability than simply changing chlorinator conditions to reduce certain low boilers.

Study of Chlorination Step

It was known from the distillation work that there are both low and high boiling unstable fractions. After a qualitative study of the chlorination kinetics, and considering the results of the designed experiment and some data on snift gas impurities it was theorized that the low boiling unstables were raw material impurities and the high boiling unstables were overchlorination products.

The product of chlorination is a mixture of biphenyl chlorinated to various levels, called homologs. The average chlorine concentration of the mixture corresponds to a specific homolog, and depends upon the kind of Aroclor. There are, of course, a number of isomers for each homolog.

It seems reasonable that the higher weight homologs are unstable, and that their presence in the mixture accounts for the unstable high boilers. It is probable that these high boiler products are the result of local over reaction in the chlorinators. An evaluation was made of the present chlorinators, and it was concluded that more stable Aroclor (less high boilers) could probably be made in a chlorinator of improved design.

This discussion is a simplification. Within each homolog the isomers probably differ in stability. Anniston is, at the present time, trying to correlate isomers to stability.

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Revaporized Chlorine Test

As stated above it was felt that the low boiling unstables are the result of raw material impurities. At the present Monsanto makes the purest biphenyl available in the United States so that no gains can be easily

made here. To check the effect of impurities in the chlorine snift gas, which is normally used, a plant test was run using revaporized chlorine. Revaporized gas has less contaminates, including low boiling organics, than snift gas.

A total of five chlorinator batches were made. Except for the use of revaporized chlorine standard operating procedures were followed. Care was taken to prevent contamination with normal production material. The results of the test are listed in the Appendix, Table 2.

The Aroclor made with revaporized chlorine was not significantly different than normal, 0.37 and 0.42 ppm TCCl. The second batch made after the test, using snift gas, analyzed 0.43. No sample was taken right at the start of distillation but a crude sample was distilled in the lab using an Oldershaw column. There was still an unstable low boiling fraction, and the sample did not appear significantly different than normal production samples distilled and analyzed in the same manner. It appears that the use of revaporized chlorine does not significantly improve stability, although the forward flow samples during the test had good stabilities. This test will be repeated at a future date.

Again, material earth treated in the lab was somewhat better, 0.32 ppm TCCl, than the same material earth treated in the plant. Based on this limited data, it would seem a slight improvement can be made in stability by improving earth treatment.

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Present Status and Future Work

At the present time there are three areas being investigated for improving Aroclor stability. Their present status and the future work planned is as follows:

1. Distillation

   Research is currently developing design data for two continuous distillation columns to remove unstable fractions from crude Aroclor. The use of distillation to improve stability was proven by the PR & D laboratory, in batch equipment. The questions left to resolve are the equipment and operating conditions necessary for a continuous process. When the Research work is complete an estimate for the equipment and operating cost will be developed.

2. Chemical Treatment

   Work is now in progress by PR & D to improve stability by a chemical treatment. Preliminary results are very promising. When this work is complete the work will be confirmed with a plant test. Again, providing this approach is successful, an equipment and operating cost will be made. It may turn out that it will be necessary to include some distillation equipment along with the chemical treatment. Work to improve earth treatment will be included here.

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3. New Chlorinator

This approach is an outgrowth of the designed experiment work. The principle here is to design a chlorinator which reduces the amount of high boilers made in the chlorinators. This eliminates, or at least reduces the cost of, distillation equipment to improve stability. The present goal is to reduce thermal chemical chlorides to 0.15 ppm. At the present time, no actual design work on a new chlorinator has been done, due to a lack of kinetic data. The attractiveness of this approach depends upon the results of the distillation and chemical treatment work. If the equipment and manufacturing costs of these approaches are high, work to design a new chlorinator is justified, and will be done. The estimate for distillation and chemical treatment should be complete by 11/1/65.

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Appendix

Table 1 - Plant Test, 6/15 - 16/65, 1242

Crude made in chlorinators nos. 2 and 3 was isolated and processed. The following samples were taken.

Sample	Analyses		
1. Composite of five test chlorinator batches (feed to stills).	40 ppm biphenyl 200 ppm 2 - chlorobiphenyl 50 ppm 3 & 4 - chlorobiphenyl		
2. *Forward flow of test material from still			
	Time of Distillation	Stability, TCCl	ppm Biphenyl
	0 hrs.	2.33 ppm	> 5000
	1	0.31	3000
	$3\frac{1}{2}$	0.37	--
	$6\frac{1}{2}$	0.47	410
	$9\frac{1}{2}$	0.42	250
3. *Blend tank (2 samples) test material		0.35	360
4. Blend tank, plant earth treatment, test material		0.46 0.58	
5. *Controls - samples from non-experimental system taken during test, still forward flows		0.35 0.36	~ 2800

* These samples were earth treated in the lab.

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Table 2 - Plant Test, 7/22 - 23/65, 1242

Five batches were made in chlorinator nos. 1, 3 and 4 with revaporized chlorine and processed. The following samples were taken.

	Sample	Analyses, ppm TCC
1.	*Forward flow of test material from still.	
	Time	
	< 5 min.	0.10
	2 hr.	0.21
	4½ hr.	0.27
2.	*Blend tank of test material.	0.32
3.	Blend tank, plant earth treatment (2 samples).	0.37, 0.42
4.	Second 1242 batch after test, made with snift gas.	0.43
5.	Composite of test chlorinator batches, lab distilled using Oldershaw column.	
	1st fraction, 10%	1.37
	2nd fraction, 10% to 235°C	0.19
	3rd fraction, 235 to 245°C	0.69

* These samples were earth treated in the lab.

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