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FINAL REPORT
ON
AROCLOR 1242 - STUDY OF
UNSTABLE PRODUCT

Job No. 2-02-750.01-3269

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TABLE OF CONTENTS

INTRODUCTION

During July and August 1956 the Anniston plant experienced that the corrosion chloride stability of Aroclor 1242 was periodically out of specification. At the same time it was also reported that the plant had difficulty with free chlorine in the hydrogen chloride off-gas delivered to the muriatic acid towers. This lead to the conclusion of a catalyst deficiency in the chlorination process. In the plant the chlorination of biphenyl is carried out in the presence of iron turnings which, when subjected to chlorine, are converted to ferric chloride.

It was the purpose of this investigation to study the effect of varying amounts of ferric chloride catalyst on the stability of the chlorination product, and to determine the minimum catalyst requirements for the production of a stable Aroclor 1242.

SUMMARY

Several biphenyl charges were chlorinated with ferric chloride as a catalyst in concentrations from 0.01 to 0.05%. The chlorination products were treated with lime and attapulgus earth similar to the present plant practice. In several cases the amount of lime, or of attapulgus earth was increased in order to study the effect of such treatment. The yield and the corrosion chloride value (determined by Dr. Munch's group) indicated the effect of the varying catalyst concentrations on the stability of the chlorination product.

CONCLUSION

It was found that a minimum amount of 0.03% of ferric chloride is required for the production of a stable Aroclor 1242. Lower catalyst ratios resulted in increased addition chlorination, indicated by higher corrosion chloride values and lower yields. No improvement was found when the amount of lime or of attapulgus earth was increased, except in those cases where the amount of catalyst used was below the minimum charge required.

RECOMMENDATIONS

It is recommended that a ferric chloride concentration of 0.03 - 0.05% should be practiced for the chlorination of biphenyl at a temperature between 120-140°C in order to guarantee the production of a stable Aroclor 1242. The present plant practice, using 0.25% of lime for the distillation and 0.2% of attapulgus earth for resistivity improvement, should not be changed.

REFERENCES

1. Process Description for Aroclor, Department 246, by C. H. Schwarting and O. M. Schwartz, Nov. 12, 1953, revised: March 15, 1955.

2. Special Report, Job No. 117-1987, A Method for Determining the Stability of Trichlorobenzene, by O. W. Ashworth, April 25, 1948.

EXPERIMENTAL WORK

In a 2-l.ACE-reactor, equipped with gas-inlet, stirrer, thermometer, air-cooled condenser, and heating mantle, charges of 1000-1200 g. of biphenyl were chlorinated with 0.05, 0.03, 0.02, and 0.01% of ferric chloride as catalyst. The chlorinations were carried out between 120-140°C, and at such a rate that a specific gravity between 1.380-1.390/25°C. was reached within 10 or 12 hours. Then the addition of chlorine was discontinued, and the reaction product was blown with air for about four hours at 80-90°C, in order to remove absorbed hydrogen chloride gas and chlorine.

The crude chlorination product was weighed, 1.0 or 0.25% of lime were added and the material was distilled at 20 mm. Hg pressure. The amount of the distilled product determined the yield. This material was agitated with 1.0 or 0.2% of attapulgus earth at 80°C. for three hours and then filtered.

The corrosion chlorine analyses were carried out by Dr. Munch's group. The values listed in table I represent hydrogen chloride in ppm evolved at 210°C. after the first 8 and second 8 hour periods.

TABLE I

No.	% Catalyst	% Lime	% Earth	% Yield	Spec. Grav. 25°C.	Corrosion Chloride ppm 1st 8 hr	2nd 8 hr
332-A	0.05	1.0	1.0		1.391	0.049	0.055
332-B	0.01	1.0	1.0	81.0	1.257	205.	201.
332-C	0.01	0.25	1.0	63.0	1.254	224.	184.
333-B	0.02	1.0	0.2	93.0	1.388	28.7 31.1	17.7 22.6
333-B	0.02	0.25	0.2	90.0	1.388	49.4 46.4	17.1 37.8
333-A	0.03	0.25	0.2	98.6	1.389	0.10 0.12	0.02 0.06
334-A	0.05	0.25	0.2	99.0	1.393	0.16 0.22	0.10 0.25
334-A	0.05	1.0	0.2	98.5	1.392	0.23 0.11	0.09 0.13
449						0.15 0.13	0.06 0.05
512						3.15 3.38	3.50 3.66

DSW 167202

For the purpose of comparison the corrosion chloride values of a satisfactory plant lot, No. 449, and a rejected plant lot, No.512, were added in Table I.

TABLE II

Resistivity of Aroclor 1242

Sample No.	% Catalyst	% Lime Used	Resistivity ohm -cm x 10^{-9}	
332-A	0.05	1.0	14,400	
332-B	0.01	1.0	1,700	(390 after heating 16 hrs.)
332-C	0.01	0.25	870	
333-B	0.02	1.0	3,800	
333-B	0.02	0.25	1,700	
333-A	0.03	0.25	12,400	
334-A	0.05	0.25	10,200	
334-A	0.05	1.0	11,300	(14,700 after heating 16 hrs.)

Measurements were made on General Radio Resistivity Bridge Type 544 - BS4 at 500 VDC and 100°C. Readings were made after 30 seconds charge time and 30 seconds on operate setting.

In Table III are given the comparative results of numerous plant samples made before and during the reported plant difficulties.

TABLE III

Analyses of Plant Samples of Aroclor 1242

Sample Lot No.	Chlorides, ppm (210°C) 1st 8 hrs.	2nd 8 hrs.	Remarks
S-414	0.31	0.24	MONX 802 (Plant B)
	0.36	0.27	
	0.30	0.24	
512	3.15	3.50	GATX 2988 (Anniston)
	3.38	3.66	Rejected by G. E.
	3.09	3.33	0.25 ppm Cl
515	1.62	1.42	Anniston-Rejected by G.E.
	1.81	1.55	0.25 ppm Cl
510	1.66	1.36	" Rejected by G.E.
	2.09	2.00	0.3 ppm Cl
516	0.71	0.78	" OK by G.E.
	0.82	0.84	0.1 ppm Cl
502	1.87	1.73	Rejected by G. E.
	2.49	2.44	0.3 ppm Cl
449	0.15	0.06	" OK by G. E.
	0.13	0.05	0.1 ppm Cl
426	0.23	0.23	" OK by G. E.
	0.26	0.26	0.1 ppm Cl
423	0.26	0.33	OK by G. E.
	0.25	0.26	0.1 ppm Cl
S-415	0.21	0.23	Plant B
	0.26	0.23	
S-414 plus 0.41% Photo Aroclor	92.8	32.4	Photo catalyzed Aroclor
S-414 plus 2.03% Photo Aroclor	587	187	added to regular Aroclor
S-414	1.29	1.04	Tests made at 230°C
	1.59	1.32	to note effect of
512	8.54	8.05	temperature
	5.11	4.77	

All tests on chlorides were made by G. W. Ashworth. Samples of 250 gram size were used in the stability tests. Titration of the chlorides evolved was made using 0.005 N $AgNO_3$.

DSW 167204

DISCUSSION

The results of the experiments listed in Table I indicate a minimum catalyst requirement of 0.03% of ferric chloride for the production of stable Aroclor 1242.

When a catalyst concentration of 0.01% of ferric chloride was used, the chlorination stopped after about three hours. By supplying additional heat the chlorine consumption continued for another hour, then the reaction had to be discontinued, since considerable foaming occurred. The specific gravity was only 1.257 at 25°C.

Those experiments indicated in general that the stability of the chlorination end product depended on the degree of the addition chlorination. The less addition chlorination had taken place the more stable was the chlorination end product. It was noted that the degree of addition chlorination was not only a function of a minimum amount of catalyst but also a very definite function of a minimum reaction temperature. At reaction temperatures below 120°C. the addition chlorination increased considerably.

The addition of lime after the blowing of the chlorinated product with air before the distillation accomplished a dual purpose: converting the catalyst into a none volatile product, and eliminating small amounts of addition chlorination products. The present plant practice using 0.25% of lime seemed justified and should not be lowered.

DESCRIPTION OF THE RECOMMENDED PROCESS

Biphenyl should be charged with 0.05% of ferric chloride and chlorine should be introduced not before the reaction mixture has reached a temperature of 120°C. The rate of added chlorine should be regulated in such a way that this reaction temperature is maintained for the first period of the chlorination.

The first period of the chlorination represents the introduction of at least one chlorine into the biphenyl molecule. This chlorination product does not sublime and the rate of chlorination can be increased, which means that the reaction temperature can be raised to 160°C.

When a sample of the crude chlorination product indicate a specific gravity of 1.380-1.390/25°C. the addition of chlorine should be discontinued and the reaction mixture should be allowed to cool to about 80°C. and should then be blown with air for four hours at this temperature.

This crude air-blown chlorination product should be distilled over 0.25% of lime at reduced pressure.

The distilled material should be agitated with 0.2% of activated attapulgus earth at 80°C. for at least two hours and should then be filtered.

The resistivity measurements in Table II show a correlation between the more stable Aroclor and high resistivity values. The "Munch" test for chlorides indicates that a total of less than 0.5 ppm chlorides after heating for 16 hours at 210°C signifies a stable compound that will pass the G.E. corrosion test for 0.1 ppm chlorides.

The use of a large excess of lime in the distillation of unstable samples had some beneficial effect. The extent of this effect in the plant is not known, but it may explain why some lots were more unstable than others during the period when unstable Aroclor were made.

Resistivity of two samples was checked after heating for 16 hours at 100°C. A decrease in the resistivity of the sample made with 0.01% $FeCl_3$ is a further indication of instability, whereas the stable Aroclor from 0.05% $FeCl_3$ increased in resistivity.

Balsbaugh cells were used in the resistivity measurements because only small samples were available in some cases. The resistivities with these cells are invariably higher than the values obtained with the G.E. cells. Therefore these data are only comparative and do not show exactly what may be found in plant practice.

The data shown in Table III clearly points up the ability of the Munch test to pick up the corrosion chlorides in the Aroclor that was rejected by General Electric. Anniston had been unable to detect these unstable lots by their test method.

With modifications of their test method Anniston has now been able to duplicate the G.E. results. This is the first case of unstable chlorides in the Anniston production and shows that it is possible to produce the unstable material.

Tests were made using small amounts of unstable Aroclor added to stable material. The chlorides evolved show that only trace quantities in the order of 0.002% of unstable material will give corrosion chlorides in excess of 0.1 ppm by the G.E. test.

These results indicate the extreme importance of sufficient ferric chloride catalyst at all times in the chlorination step.

APPENDIX

The detailed experimental data and procedures are described in the notebook 1956, A-78332 - A-78335 and A 81878.

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