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FINAL REPORT

GREEN COLOR IN PYRANOL

Job No. 117-2319

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DSW 620950

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TABLE OF CONTENTS

		Page
I.	INTRODUCTION.	1
II.	SUMMARY	1
III.	CONCLUSIONS	1
IV.	RECOMMENDATIONS	2
V.	REFERENCES.	2
VI.	EXPERIMENTAL WORK	2
VII.	DISCUSSION.	9

DSW 620951

STLCOPCB4094979

I. INTRODUCTION

In late 1950, a project was initiated to investigate green color in Aroclor 1260. Off and on for about one year, General Electric picked-up and complained about a green color trend in Pyranol 1467. A review of reserve samples of Pyranol 1467 and its constituents, namely, Aroclor 1260 and TCB at WGK showed that the green color originated in the Aroclor 1260.

II. SUMMARY

Five samples of Aroclor 1260 were prepared. In these runs, effect of catalysts and catalyst concentration on color of Aroclor 1260 was studied. Plant iron catalyst, anhydrous $FeCl_3$, and a combination of plant iron catalyst and $FeCl_3$ were investigated.

Plant aroclor 1160 was distilled in the laboratory in the presence of lime and sodium carbonate to note color and recovery.

Three samples (1/2 gal. each) of Pyranol 1467 were prepared for complete analysis to compare quality of Pyranol 1467 when Aroclor 1260 was prepared in the plant(iron catalyst)and in the laboratory (plant iron plus $FeCl_3$ catalyst).

Aroclor 1260 was treated with varying amounts of Attapulgus earth to observe effect on color.

A short plant trial in which the plant iron catalyst was fortified with 0.3% $FeCl_3$ was made to determine if color of plant Aroclor 1260 would improve.

III. CONCLUSIONS

1. A trend toward color improvement of Aroclor 1260 was obtained in the laboratory when plant Fe catalyst was fortified with anhydrous $FeCl_3$.

2. The use of anhydrous $FeCl_3$ as catalyst for the preparation of Aroclor 1260 did not adversely effect the chemical, physical, or electrical properties of Pyranol 1467(a blend of Aroclor 1260, trichlorobenzene, and tin tetraphenyl).

3. Heavier Attapulgus earth treatment of Aroclor 1260(plant practice 0.05% by wt.) was very successful in appreciably improving the color. The initial color of Aroclor 1260 and the amount of Attapulgus earth used(up to 1%) were important factors on degree of color improvement of Aroclor 1260.

DSW 620952

STLCOPCB4094980

4. Because of the lower materials cost and less labor for use of anhydrous $FeCl_3$ as compared to heavier Attapulgus earth treatment, a short plant trial run of 4 batches was made where plant iron catalyst was fortified with 0.3% by weight of anhydrous $FeCl_3$ to note effect on color of Aroclor 1260.

5. The color of the Aroclor 1260 from the plant trial run was improved by approximately 50% having an average APHA color of 60 (50 to 70). Aroclor 1260 produced just prior to the test run ranged in color from APHA 90 to 125.

6. Low viscosity of Aroclor 1260 from the plant $FeCl_3$ run could not rightly be attributed to $FeCl_3$ but to some other factor. Aroclor 1260 prior to the $FeCl_3$ run had a low viscosity and tendency of plant Aroclor 1260 toward low viscosity was a problem in itself (reference to Aroclor Process Investigation Job No. 117-2602).

IV. RECOMMENDATIONS

In January 1951, Research recommended that consideration be given to 1) the addition of anhydrous $FeCl_3$, 0.3% by wt. of the biphenyl, to the chlorinator as fortifying catalyst for the production of Aroclor 1160 and 2) to heavier Attapulgus earth treatment of Aroclor 1260 as possible cures for the green color.

V. REFERENCES

1. Interim Report - Green Color in Pyranol, July 31, 1950, to Mr. D. M. Hosmer by P. Hodges and T. W. Dalton.

2. Report of Trip to Anniston Aroclor Plant Dept. 246 - Process, 4/6/51, to Mr. Dalton by P. Hodges.

3. Process for the Manufacture of Aroclors, Dept. 246, Sept.27, 1946, J. M. Lyles and J. Soffranko.

4. Process Description for the Manufacture of Aroclor in Dept. 246, Nov. 12, 1953, C. H. Schwarting.

5. Progress Reports, Job No. 117-2319, Green Color in Pyranol, Report Nos. 1-4, Nov. and Dec. 1950 and Jan. and May 1951.

VI. EXPERIMENTAL WORK

A. APPARATUS

Chlorinator was about a liter glass cylindrical shaped vessel which was equipped with a propellor type agitator, chlorine distributor (closed tube with perforations), thermometer, and condenser. A tube equipped with a hydrometer and thermometer for

DSW 620953

STLCOPCB4094981

drawing-up by vacuum a sample of chlorination mass to determine the specific gravity was a part of the chlorinator equipment.

Still was a round bottom flask. A 5-1/2 in. glass punched section wrapped with nichrome wire or a 6-1/2 in. packed section of 1/8 in. glass helices was used.

B. PROCEDURE - AROCLOR 1260

Typical chlorination procedure was to charge the chlorinator with molten diphenyl (550-600 gms) from Dept. 246 and the desired catalyst. The catalyst was 1) 5%(by wt. biphenyl) of plant iron turnings 2) 0.3% or 1% anhydrous $FeCl_3$. Chlorine was added to the batch over an 18 to 22 hr. period at about 80-90 gms./hr. The temperature was increased from 120°C to 145°C during the chlorinations. The batch was chlorinated to an end specific gravity of 1.557-1.562 at 90°C.

After completions of the chlorination, the batch was aerated at 140°C for ½ hrs. Either all or a part of the Aroclor 1160 was take-over distilled from lime. For most runs a punched glass spray section was used. A small packed column was substituted for the punched section in several runs to note effect on color.

The data for the various runs is summarized in the following Table I.

DSW 620954

TABLE I

SUMMARY OF DATA ON AROCLOR 1260

DESCRIPTION	NEUTRALIZER	COLUMN	% RECOVERED	COLOR - 425B BLUE % TRANSMISSION
Batch No. 1 5% Pl Fe	$Ca(OH)_2$ 0.4%	Spray Trap	96.5	56.0*
Batch No. 2 0.3% $FeCl_3$	$Ca(OH)_2$ 0.4%	Spray Trap	97.5	60.2*
Batch No. 3	$Ca(OH)_2$ 0.4%	Spray Trap Column	96.7 97.3	67.6* 67.0*
Batch No. 4 5% Pl Fe + 0.3% $FeCl_3$	$Ca(OH)_2$ 0.4%	Column	96.5	72.0*
Batch No. 6 5% Pl Fe + 0.1% $FeCl_3$	$Ca(OH)_2$ 0.4%	Column	97.5	61.0*
Lot U-18 (Pl 1260) Sept., 1947	--			71.2
Lot N-5 (Pl 1260) April, 1940	--			70.1
Lot C-13 (Pl 1260) July, 1950	--			70.0
Batch No. 145 (Pl 1260) October, 1950	--			69.5
Plant 1160 (10-3-50) Lab. Dist.	$Ca(OH)_2$ 0.4%	Spray Trap	94.2	65.4*
Plant 1160 (10-3-50) Lab. Dist.	$Ca(OH)_2$ 1.0%	Spray Trap	91.7	70.4*
Plant 1160 (10-3-50) Lab. Dist.	Na_2CO_3 0.57%	Column	95.0	66.4*

* Color data on laboratory prepared Aroclor 1260 is reported on untreated Aroclor 1260.

DSW 620955

STLCOPCB4094983

C. ATTAPULGUS EARTH TREATMENT

Some work on heavier Attapulgus earth treatment as a possibility of removing the green color was done. This phase of the study was very successful in gaining appreciable color improvement. The plant practice called for a 0.05% by weight as Attapulgus earth for treatment. Laboratory data showed that the quantity of earth necessary to improve notably or to eliminate the color was well above 0.05%. For example, the Aroclor 126[illegible] sample with the poorest color (Batch No. 1, 56% transmission) was treated at 110° for 4 hrs, heated to 150°C and filtered.

Attapulgus Earth % by wt.	Color 425B-Blue % Transmission
0	56.0
0.2	59.0
0.6	66.7
1.0	75.6

D. PYRANOL 1467

Samples of Aroclor 1260 which were prepared using $FeCl_3$ had to be thoroughly checked for their various properties to be certain that this aroclor 1260 is similar to plant production. Most laboratory runs were too small to obtain a complete analysis. However, in a special two runs sufficient Aroclor 1260 was prepared and blended with samples on hand from the smaller runs for a complete analysis as Pyranol 1467. It was analyzed as Pyranol 1467 to further extend the quantity of material.

One half gallon samples of Pyranol 1467 were prepared to check the chemical, physical, and electrical properties. This data which is included in Table II appeared on the whole to be in good agreement and it was concluded that anhydrous $FeCl_3$ catalyst did not effect the properties of Aroclor 1260 adversely. (See page 6 for Table II)

E. PLANT DEMONSTRATION

Although the laboratory data did not conclusively indicate that the addition of anhydrous $FeCl_3$ to the plant chlorinators and plant catalyst would eliminate the trend toward green color in Aroclor 1260, the laboratory data did show a color trend in a positive direction when anhydrous $FeCl_3$ was used to fortify the plant catalyst. $FeCl_3$ catalyst additions appeared to be a good lead to follow-up and a plant trial was warranted to evaluate the merits of anhydrous $FeCl_3$ catalyst as a possible cure for the green color.

Between 2/12/51 and 2/14/51, a short plant trial in which [illegible] chlorinator batches of Aroclor 1160 were prepared using 0.8% by wt. of anhydrous $FeCl_3$. The results of this run are summarized in Table III. (See page 7 for Table III) Lots 208, 210, and 211 to form composite D-5 was the Aroclor 1260 produced from this brief plant trial using $FeCl_3$. D-1, 2, 3, and 4 were prepared just prior to the $FeCl_3$ run.

DSW 620956

STLCOPCB4094984

TABLE II

PLANT B ANALYSES - PYRANOL 1467

SOURCE OF AROCLOR 1260		PLANT 1160 LAB. DIST. Fe CATALYST	PLANT 1160 PLANT DIST. Fe CATALYST	LAB. PREP. 5% PL Fe 0.3% $FeCl_3$	LAB. PREP. 5% PL Fe 0.3% $FeCl_3$
Property					
Color (APHA)		45	40	45	
Condition		Clear	Clear	Clear	
Specific Gravity at 15.5°C		1.564	1.564	1.570	1.668
Acid Number		0.002	0.002	0.002	
Inorganic Chloride		0.30 ppm	0.20 ppm	0.30 ppm	
Viscosity at 37.8°C.		54.8	53.5	54.4	55.1
Resistivity at 100°C		3445	3156	1175	2600
Dielectric Strength at 25°C		37	35	37	
Dielectric Constant at 100°C		3.87	3.86	3.83	4.15
Power Factor at 60 cycles		2.23%	2.26%	4.78%	3.28%
Power Factor at 1000 cycles		0.123%	0.145%	0.265%	0.21%
Refractive Index at 25°C		1.6148	1.6148	1.6149	1.6147
Distillation:					
First Drop		214°C	213°C	212°C	
Below 270°C		36%	36%	37%	
90%		402°C	400°C	401°C	
Pour Point		-36°C	-36°C	-34°C	
Moisture (H_2O)		30 ppm	25 ppm	30 ppm	
Tetraphenyl		0.146%	0.131%	0.174%	
Corrosion Test:					
Change in wt. of bright aluminum in contact with Pyranol, refluxed for 6 hours.		none	none	none	
Inorganic Chlorides	After test	0.80 ppm	0.50 ppm	0.30 ppm	
Acid number	After test	0.005	0.002	0.002	
Condition	After test	clear	clear	clear	
Color (APHA)	After test	50	40	45	

DSW 620957

STLCOPCB4094985

DSW 620958

TABLE III

AROCLOR 1260

PLANT $FeCl_3$ RUN

PROPERTY	$FeCl_3$ BATCHES				Fe BATCHES			
	LOT 208	210	211	D-5 COMPOSITE	D-1	D-2	D-3	D-4
App.	Gr.Yel.Liq.	Gr.Yel.Liq.	Yel.Visc.Liq.	Lt.Yel.Gr.Liq.	Gr.YelVisLiq.	Lt.Gr.Liq.	Lt.Gr.Liq.	Visc.Yel.Liq.
T	None	None	None	None	None	None	None	None
R	None	None	None	V.Slight	V.Slight	None	None	None
APHA	50	70	50	60	125	90	90	100
Acid No.	0.004	0.004	0.005	0.005	0.003	0.002	0.003	0.007
H_2O	0.0015%	0.0010%	0.0015	0.0030	0.0015%	0.0015	0.0015	0.0020
Inorg. Cl	< 0.000010%	0.000010%	0.000010	0.000010	0.000010%	0.000010	0.000010	0.000010
Sp.Gr. at 90°C	1.558	1.552	1.549	1.557	1.556	1.560	1.555	1.560
Visc. at 210°F	72.4 Sus.	72.4 Sus.	70.3	71.3	72.7	73.9	72.2	74.4
n_D^{25}	1.6460	1.6460	1.6455	1.6460	1.6461	1.6464	1.6463	1.6464
Dist.								
10%	387°C	386°C	386°C	386°C	385	390	390	388
50%	392	391°C	391	392	390	394	394	393
90%	400°C	400°C	400	400°C	402	403	401	401
Pour Point	32°C	32°C	32°C	34°C	26°C	30°C	30°C	32°C
Heat Loss	0.03%	0.07%	0.08	0.03	0.03	0.04	0.05	0.03
Corrosion	None	None	None	None	None	None	None	None
Condition	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear
APHA	80	80	50	60	125	90	100	100
Acid No.	0.003	0.005	0.006	0.005	0.003	0.002	0.004	0.007
Dielectric Strength	49KV	43	49	36				
Inorg. Cl	0.000010%	0.000010	0.000010	0.000010	0.000010	0.000010	0.000010	0.000010
Dielectric Constant	3.68	3.84	3.70	3.70				
Resistivity	28,000	1,500	16,000	23,800				
Power Factor	0.08%	0.17	0.08	0.086				

Batches prep[illegible] from Fe catalyst prior to $FeCl_3$ run.

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It was concluded that $FeCl_3$ was not affecting adversely the Aroclor 1260 and that the color was improved. However, the run was too short and longer plant demonstrations would need to be made.

The color was improved by approximately 50%(average of 60 APHA for three batches as compared to 90-125 APHA for four composites prior to the $FeCl_3$ run). However, low viscosities were encountered (71.3 sus average, 72-77 sus specifications). Because low viscosity of Aroclor 1260 was a productions problem in itself, several samples from plant $FeCl_3$ run were distilled in the laboratory to note if the low viscosity was not a result of incomplete recovery.

Description	% Recovery	Sp.Gr. at 90°C	Viscosity sus at210°F Uncorrected	Corrected
Chlorination Ba No. 3 Plant $FeCl_3$Run	95.0	1.557	70.8	69.9
Chlorination Ba No. 4 Plant $FeCl_3$Run	93.4	1.550	67.7	66.8
Plant Fe Batch Prior to $FeCl_3$ run. Same chlorinator no.4	94.1	1.553	69.1	68.2
Plant Fe Batch prior to $FeCl_3$ run. Same chlorinator No. 4 Distillation cut short to note effect of low recovery on viscosity	85.7	1.547	65.4	64.5
Plant $FeCl_3$Run Still Ba No. 2(134)	82.8	1.561	77.4	76.4
Plant 1160 dated 10/3/50 Lab. dist.	94.2	1.561	73.3	72.3
Plant 1160 dated 10-3-50 Lab. dist.	95.8	--	74.3	73.3
Plant 1160 dated 10-3-50 1% $Ca(OH)_2$	91.7	1.561	73.7	72.7
Plant Aroclor 1260 Ba 145	--	--	74.3	73.3
Plant Aroclor 1260 Ba 145 Treated	--	--	74.2	73.2
Lab. Ba No. 1 5% Fe	96.5	--	77.1	76.1
Lab. Ba No. 1 5% Fe	96.5	1.567	78.2	77.2
Lab. Ba No. 2 0.3% $FeCl_3$	97.5	1.567	79.2	78.2
Lab. Ba No. 3 1% $FeCl_3$	97.3	--	78.7	77.7

NOTE: Specific gravity at 90°C 1.550-1.560
Viscosity sus at 210°F 72-77 sus

DSW 620959

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The data show a 95.0% and 95.4% recovery with specification gravity but low viscosity for two chlorinator batches from the $FeCl_3$ run. Still Batch No. 2 from the same run gave a reasonable gravity and a viscosity of 76.4 sus. The low yield recovered on distillation is probably the result of still high boiler heel from previous all plant iron catalyst batches and does not represent a true recovery figure. Also, it is interesting to note that the last Fe batch prepared prior to the $FeCl_3$ run in the same chlorinator resulted in a maximum recovery of 94.1%, a specification gravity, but a very low viscosity (68.2 sus, corrected). Low viscosity of Aroclor 1260 from the plant $FeCl_3$ run cannot rightly be attributed to $FeCl_3$ but to some other factor in operations.

The specific gravity and viscosity data on a backlog of samples was obtained only when the plant low viscosity problem was encountered. It appears that the difficulty is centered in the chlorination step, since plant and laboratory Aroclor 1260 do not distill similarly. Plant material contains more high boiler which results in poorer recoveries (93-95% for the plant versus 96-97% for lab.). Batches were distilled at 7, 5, and 3 mm Hg pressure without noticeably improving the recoveries.

It is also questionable that the viscosity range and specific gravity range can be always met. Low gravities (1.550) tend to give out of specification grade low viscosities.

VII. DISCUSSION

A very intensive review of the tendency toward a green hue in Aroclor 1260 (consequently also in Pyranol) was made by production personnel. Various means to determine the cause or eliminate the color were unsuccessful. This information is discussed in references one and two and the correspondence on green color in Aroclor 1260.

Research directed its investigation primarily along this path: 1) to observe the effect of catalyst concentration on the color of Aroclor 1260 and 2) to note the results of heavier Attapulgus earth treatment of Aroclor 1260.

$FeCl_3$ Catalyst -- In the laboratory chlorinations, the catalyst (plant steel, anhydrous $FeCl_3$, and combinations of plant steel and anhydrous $FeCl_3$) and catalyst concentration were varied. Five batches of chlorinated biphenyl (Aroclor 1160) were prepared with agitation in glass equipment, aerated, and distilled. The laboratory and plant samples of Aroclor 1160 were distilled using either a 5-1/2 inch glass punched section or a column having a 6-1/2 inch packed section of 1/8 inch glass helices.

The results which are presented in Table I show a significant color trend when plant steel catalyst (5% by wt. of the biphenyl charge) was employed. Aroclor 1260 Batch No. 1, which had a color

DSW 620960

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of 56% Transmission (#25 B filter - Fisher Electrophotometer) was prepared. On the other hand, 5% by wt. plant steel catalyst fortified with 0.3% by wt. biphenyl charged as anhydrous $FeCl_3$ resulted in Aroclor 1260 having a color of 72% Transmission. All other samples had color values within this range. In September 1947 and April, 1940, times at which presumably a green color problem did not exist, colors of treated plant Aroclor 1260 were 71.2% and 70.1%, respectively.

What effect the addition of anhydrous $FeCl_3$ catalyst had on the chemical, physical, and electrical properties of Aroclor 1260 was not known. Therefore, to observe that no deleterious characterictics were encountered, sufficient Aroclor 1260 was prepared that samples could be submitted for complete analyses as formulations of Pyranol 1467. The analytical data, which are listed in Table II.

Attapulgas Earth Treatment -- Treating Aroclor 1260 with Attapulgus earth in quantities greater than 0.05% and up to 1% by wt. improved the color. The gain in color improvement through heavier Attapulgus earth treatment was more conclusive and positive than the use of $FeCl_3$ However, heavier Attapulgus earth treatment was less attractive to production because of the added cake load on the filter press, more labor, and loss of Aroclor 1260 in the press cake. Heavier Attapulgus earth treatment was to be considered in the plant, if $FeCl_3$ was not successful.

Cost Estimate

The addition of anhydrous $FeCl_3$ to the chlorinator or heavier earth treatment indicated a slight cost increase of the Aroclor 1260. The magnitude of this cost was:

Cost Increase
per 100 lbs. Aroclor 1260

Anhydrous $FeCl_3$ ($0.07713 per lb. - Jan. 1951)

$FeCl_3$ (0.3% by wt. biphenyl = 0.138 lbs.)	$ 0.0106

Attapulgus Earth ($0.012 per lb.)

1% A.E.	$ 0.012
Loss of 1260 in cake (1.lb.)	$ 0.060
Total	$ 0.072
0.5% A.E.	$ 0.006
Loss of 1260 in cake (0.5 lbs.)	$ 0.030
Total	$0.036

At a meeting at Plant B in January, 1951, attended by production and Research personnel, it was recommended that consideration be given to the addition of 0.3% by weight of the biphenyl charge as anhydrous $FeCl_3$ for the manufacture of Aroclor 1160 and for heavier treatment of the Aroclor 1260. Although a color trend in a positive direction was observed in the laboratory when anhydrous $FeCl_3$

DSW 620961

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of course, added the possibility of other variables, which were not studied, entering the problem and complicating the picture should not be discounted entirely. However, $FeCl_3$ catalyst addition appeared to be a good lead to follow-up and a plant trial was warranted to evaluate the merits of anhydrous $FeCl_3$ catalyst addition as a possible cure for the green color.

Because of the more appealing cost figures and the less labor involved, it was decided at the meeting that a plant demonstration, which would comprise the production of three to four batches of chlorinated Aroclor 1160 using an additional 0.3% by weight biphenyl charged as anhydrous $FeCl_3$ would be made.

From the short plant test run, some improvement in color was obtained by the use of $FeCl_3$. Due to the small quantity of material involved in the test run, it was necessary to distill the Aroclor from the heel of residue accumulated during normal production. It is possible that an extended run might have revealed further improvement in color.

At the time this plant run was made, low viscosity of Aroclor 1260 was also a problem. Laboratory distillations of laboratory and plant Aroclor 1160 were distilled to show that the use of $FeCl_3$ catalyst was not the cause of low viscosity.

However, because of this continued problem on low viscosity and the shortage of chlorine at that time, the use of $FeCl_3$ in a production of several weeks duration was not made.

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