JLR-43-168, No. 8

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Pontachrome Flavine A

Problem Report

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Pontachrome Flavine A
(Project Number 1315)

B. G. Carson

JLR-43-168, No. 8 Serial Number 18713

Subject:

Pontachrome Flavine A (azo salicylic acid).

Object of Investigation:

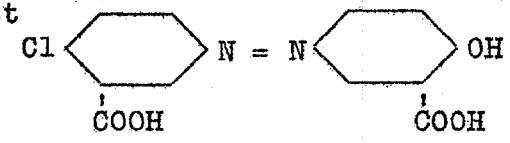
(a) To recheck the laboratory and theoretical yields for Pontachrome Flavine A 125%, (b) to determine the cause or causes for the low hydrolysis yield of this color, and (c) to make recommendations to the plant which would enable this yield to be improved.

Period Covered by Report:

May 22, 1942 to July 8, 1942; then intermittently to January 25, 1943.

Historical Background:

Pontachrome Flavine A (azo salicylic acid) has been known since 1914 when it was developed as Eriochrome Flavine A by Geigy and disclosed in German Patent 278,613; British Patent 22,070 (1914) and United States Patent 1,157,169. A process for its manufacture was developed in Jackson Laboratory in 1935. Subsequent manufacture of this dye in the Semi-Works and the Dye Works indicated that the over-all yield from phthalic anhydride to Pontachrome Flavine A was very low, but the total amount of the color needed for the trade each year was so small as not to warrant further process work. Early in 1942, however, the need for large quantities of this dye for use in Army olive drab mixtures made it necessary for the yields in the various areas involved to be studied. It was found that the greatest loss occurred in the Basic Colors Area where the final hydrolysis of the product



to the subject product

was carried out. The standard Dye Works yield for this hydrolysis is 77%. The actual yields for January and February of 1942 were very much below the standard yield.

Conclusions:

The primary objects of this investigation have been accomplished, (a) The laboratory yields previously reported in JLR-43-168, Number 1, Serial Number 15013 have been confirmed; hydrolysis of the order of 92-95% based on dyetest and on analyses can be obtained consistently in the laboratory. The theoretical yield is 740 pounds Pontachrome Flavine A, 125% per mole of Pontachrome Flavine A Base. (b) 1. The main cause for failure of the hydrolysis has been shown to be the presence of lead in the hydrolysis autoclave; (the Dye Works autoclave used for this hydrolysis has a poured lead gasket which must be replaced frequently on account of failure) large amounts of lead reduce the dye stoichiometrically, small amounts appear to hinder the hydrolysis all out of proportion to the amount of lead present. The exact course of the reaction in the presence of small amounts of lead has not been determined. 2. The condition of the walls of the autoclave has an appreciable effect on the yield from the hydrolysis. When the iron-walls are clean almost no hydrolysis occurs; when the walls have been conditioned by several (or many) runs good yields may be expected. 3. The hydrolysis reaction does not appear to depend on the presence of a copper catalyst, but better yields are obtained if copper in some form is used.

(c) It has been recommended to the plant that the lead gasket in the hydrolysis autoclave be replaced with one fabricated from copper, corrugated iron with asbestos filling or asbestos. On account of complete failure of the lead gasket, for the third time in seven months, a change has been made. In the meantime the plant yield had risen to 81% of theory. Some of this may be attributed to added experience in conducting the hydrolysis, much of it to a revised procedure of adding the copper sulfate catalyst as a solution instead of as a solid.

Summary:

The following facts dealing with the hydrolysis of Pontachrome Flavine A Base to Pontachrome Flavine A, 125% have been established:

(1) No changes in process between the Tentative Semi-Works Process and the present Dye Works Process have been such as to reduce the yield.

(2) No difference has been found among iron, copper, and nickel bombs which appear to influence the yield except that smooth-surfaced copper-lined bombs and smooth-surfaced nickel bombs appear to give good hydrolysis yields almost from the first charge whereas it takes several charges at times to bring the yield from an iron bomb up to its maximum.

(3) No essential difference has been found between the plant procedure of neutralizing with sulfuric acid and salting out the dye with sodium sulfate and the obvious method of neutralizing with hydrochloric acid and salting out with salt. The use of the latter procedure appears to give a stronger crude but no better yield.

(4) Additives such as ferric oxide, sodium sulfite, "Sitol" (a textile processing agent), pyridine and alcohol have no effect on the hydrolysis.

(5) Lead even in small amounts reduces the yield. In large amounts it acts apparently as a reducing agent in stoichiometric relations.

(6) Agitation during the hydrolysis is essential. No effort was made to correlate the rate of agitation with the yield.

(7) Poly TFE (a plastic) could be used as gasket material without changing in any way the quality or the yield of the dye.

(8) The $TiCl_3$ value of standard Pontachrome Flavine A, 125% does not agree with the nitrogen content by the Kjeldahl method. For the pure free-acid, salt-free product the $TiCl_3$ value is the same as the Kjeldahl value.

(9) The determination of yield data by means of the increase of inorganic chlorides content of the hydrolysis mixture is unreliable.

(10) Under any conditions of isolation found in which good dye is obtained there is a filtrate loss of 7.5-8.5%. The dye left in the filtrate is not Pontachrome Flavine A but is either unhydrolyzed base or monodecarboxylated material, both of which have tinctorial strength approximately half that of Pontachrome Flavine A, both of which are red and dull versus Pontachrome Flavine A.

(11) No catalyst other than copper or a copper salt has been found to be as effective as copper in catalyzing the hydrolysis.

(12) Pontachrome Flavine A is stable under the conditions of hydrolysis and undergoes no decarboxylation.

(13) Chloro-amino-benzoic acid prepared by the route: ortho-dichlorobenzene → ortho-chloro-benzonitrile → ortho-chloro-benzoic acid → 5-nitro-2-chloro-benzoic acid → 5-amino-2-chloro benzoic acid gives yields of Pontachrome Flavine A at least as good as standard Dye Works material.

Experimental Part

Most of the results of this investigation may be summarized by tables which are numbered below to correspond with the numbered statements of the summary. So many variables might have been checked on that it was decided to hold all volumes, charge sizes, temperatures, and times of hydrolysis constant after the first one or two series had been run until other factors had been checked. A typical hydrolysis is given below.

Typical Hydrolysis:

A bomb was loaded with .0327 moles Pontachrome Flavine A Base, 30.3 cc. 10 N NaOH, 0.238 g. $CuSO_4 \cdot 5H_2O$, and 40.0 cc. water. In charging the bomb the Pontachrome Flavine A Base was mixed with the caustic, the copper sulfate dissolved in the water, and the two mixtures mixed thoroughly either in the bomb or in a beaker. (When our 1-liter autoclave, Ex. 46, was charged the amounts were multiplied by 6 for convenience. When our 2-liter autoclave, Ex. 10, was charged the amounts were multiplied by 12.) The charge was heated with rotation for 8 hours at 154-156°C. after which time the contents of the bomb were removed with the help of as little hot water as possible, filtered to remove the copper sludge, and the volume of the combined filtrate and washings adjusted to 192 cc. to correspond to the volume of the Dye Works recipe. The temperature of the filtrate was then adjusted to 40° and acid (10 N HCl or 20 N H_2SO_4) added till the solution was faintly alkaline to Brilliant Yellow paper. After the first series was completed a pH meter was used during the neutralization and "faintly alkaline" was defined as having a pH of 6.8-7.2. After neutralization there was added 10% salt by volume, the precipitated dye was stirred at 40°C. for thirty minutes and filtered. Part of the filtrate was used to remove

the last portions of the dye from the beaker. When the presscake had become fairly dry it was removed from the filter and dried at 70°C. When dry the entire crude sample after being weighed was pulverized as completely as possible in a large glass mortar and dyetested for shade and strength or sent for analysis.

Any variations from this typical run, which was designed to duplicate the plant recipe in miniature, will be noted in connection with the tables in which those variations occur.

TABLE I

Comparison of Process Yields

Run	Tentative Semi-Works Process % (Theory)	Tentative Dye Works Process % (Theory)	Modified Dye Works Process (Recipe dated 3/18/42) % (Theory)
1	85.0	92.5	70.9
2	71.0	91.0	76.0
3	91.5		99.0
4			81.3
5			106.0
6			81.6
7			105.0
8			115.0
9			89.0
Av.	89.2	91.7	91.53

TABLE II

Yields From Different Types of Bombs

Run	Iron (D 13) %	Copper Line (B 51) %	Nickel (B 47) %
1	71.0	92.4	80.0
2	106.0	92.4	102.5
3	87.8	91.2	79.8
4	97.0	98.2	
5	85.0	89.1	
6	86.1	85.6	
7	92.5		
8	79.0		
9	100.0		
10	92.1		
Average	89.65	91.5	87.4

TABLE III

Comparison of Isolation Methods:
(a) Neutralization with Sulfuric Acid and Salting with Sodium Sulfate vs.
(b) Neutralization with Hydrochloric Acid and Salting with Sodium Chloride (10%)

No.	1	2	3	4	5	6	7	8	9	10
Method	A	A	A	A	A	B	B	B	B	B
Dry Weight g.	36.9	31.8	32.5	34.1	38.4	28.9	28.5	31.7	28.3	32.0
Strength	11:10	97.5 :100	95 :100	102.5 :100	121 :100	97.5 :100	88 :100	90 :100	88 :100	86 :100
Std.Wt. g.	33.5	32.6	34.3	33.3	31.7	29.2	32.4	35.2	32.1	37.2
Shade	T. N. Grn. T.Brt.	T. Grn. T.N. Brt.	N. Grn. T. Brt.	T. Brt.	T. Grn. T. Brt.	Close	T.N. Red T.N. Brt.	T. Red T.N. Brt.	T. Grn. T.N. Brt.	T. Grn. T.N. Brt.

Note: The above runs are aliquot parts of plant charge 221 which was obtained from the plant at the end of the hydrolysis. The material was filtered at 80°C. and divided into 10 equal portions. The average amount of standardized dye from each method is:

Method A : 33.08 g.
Method B : 33.20 g.

Abbreviations: Std. Wt. = standard weight; T. = trace; N. = noticeably; Grn. = green; Brt. = bright.

TABLE IV

Effect of Additives

Jackson Laboratory Notebook	Additive	Bomb No.	Type Bomb	Per cent yield
3831-90-1	1 g. Na_2SO_3	B50	Copper lined	91.2
-90-2	None	B51	"	89.1
-90-3	1 g. Na_2SO_3	D15	Iron	86.3
-90-4	None	B26	Iron	100.0
-90-5	0.5 g. Sitol	B52	Copper lined	100.0
-90-6	None	F3	Iron	93.7
-90-7	0.5 g. Sitol	D13	Iron	85.0
-90-8	None	A14	Iron	99.6
-97-1	None	B50	Copper lined	80.3
-97-2	1 g. Fe_2O_3	A14	Iron	85.1
-97-3	5 cc. Alcohol	D13	Iron	86.1
-97-4	1 g. Fe_2O_3	B51	Copper lined	85.6
-97-5	1 g. EtSH	F3	Iron	9.0
-97-6	None No $CuSO_4$ added	D13	Iron	82.5
-97-7	1 g. Ethyl Mercaptan	B52	Copper lined	34.0
175-C	5 cc. Pyridine	B52	"	85.0
175-E	5 cc. Pyridine 0.5 g. Pb (lead)	B30	Iron	68.0

TABLE V

Effect of Lead

JLNB	Run	Autoclave (Iron)	% Yield	Remarks
3831- 91	1	Ex. 46 (1-liter)	99.2	Asbestos gasket
94	2	"	99.0	"
98	3	"	87.2	"
103	4	"	81.7	Pb. gasket
106	5	"	85.0	"
108	6	"	81.3	"
112	7	"	84.0	"
113	8	"	less than 25.0	" plus 50 g. sheet lead
115	9	"	89.2	Asbestos gasket
118	10	"	98.5	"
122	11	"	100.0	"
125	12	"	29.8	30 g. Pb added
130	13	"	19.2	30 g. Pb added
3831- 92	1	Ex. 10 (2-liters)	34.2	Pb gasket
93	2	"	37.2	"
99	3	"	82.5	Asbestos gasket
102	4	"	87.9	" "
105	5	"	88.5	" "
107	6	"	82.2	" "
111	7	"	77.2	" "
114	8	"	75.5	* " "
116	9	"	89.2	" "
119	10	"	82.6	" "
123	11	"	88.0	" "
126	12	"	88.0	" "
129	13	"	84.8	" "
132	14	"	91.3	" "
136	15	"	93.6	" "
139	16	"	95.0	" "

*At this point it was discovered that a pipe leading from the autoclave contained a lead gasket about 12-15 inches from top of the autoclave. This was replaced with an asbestos one and the pipes washed out with hot 10% NaOH.

TABLE V-A

Effect of Lead Compounds

JLNB	Bomb	Type Bomb	Pb. Compound	% Yield
3831-101-1	B50	Cu. lined	None	92.0
101-2	B51	"	Pb. shot	less than 20%
101-3	B52	"	Pb. acetate	88.8
101-4	F3	Iron	PbO	70.0
101-5	D15	"	Granular lead	less than 20%
101-6	A14	"	None	84.0
101-7	D13	"	$PbCO_3$	92.0
101-8	A20	"	Pb. acetate	50.5

TABLE VI

Effect of Agitation

JLNB	Bomb No.	Type Bomb	Agitation	% Yield
3831-110-2	B52	Glass lined	None	51.0
110-3	B51	Glass lined	None	51.0
134-A	B26	Iron	Normal, No catalyst	63.5
134-B	B47	Nickel	Normal	102.5
134-C	A20	Iron	None	68.5
104-1	B50	Copper lined	Normal, No catalyst	86.6
104-5	A14	Iron	Normal, No catalyst	76.0
104-6	B30	Iron	Normal, No catalyst	55.1

TABLE VII

Effect of Poly TFE

JLNB	Bomb	Type Bomb	% Yield
3831-170	B52	Cu. lined *	75.0
3831-172	"	"	90.0

*The previous history of this bomb could not be determined. Both runs were normal runs with a 5.5 g. triangle of sheet Poly TFE inserted into the bomb before hydrolysis.

TABLE VIII

Analyses of Pontachrome Flavine A

JLNB	Material	% Purity by N (Kjeldahl	$TiCl_3$	Acid No.
3831-147	Free Acid	96.0	97.2	93.8
165-S	Standard, Lot 1	53.0	47.0	
165	Standard, Lot 1	53.3	47.2	
171	Free Acid	96.9		96.7
168	Free Acid	97.5		98.2

The free acid of Pontachrome Flavine A was prepared by dissolving 100 g. of Pontachrome Flavine A 125% in a liter of boiling water, adding HCl till the solution is strongly acid to Congo Red paper, filtering and washing with 5 200-ml. portions of hot water. 40.85 G. of the free acid 100% was obtained from a calculated amount of 41.02 g. based on a $TiCl_3$ determination of the standard product.

TABLE IX

Relation of Hydrolysis to Increase in Inorganic Chlorides by Analyses

JLNB	Type Run	% Chlorides at start	% Chlorides at end	Hydrolysis calculated %	Hydrolysis by dyetest %
3831-125	Pb present	3.09	3.28	18.1	29.8
126	Normal	3.16	4.02	91.6	88.0
136	Normal	3.18	4.20	109.0	93.6
144	Aliquot from chg. 280	6.46	6.54	145	85.4
144	Recheck "	6.31	6.62	171	85.4
162-A	Normal charge 6 hr. run	0.15	0.21	6.34	
162-B	Normal charge 4 hr. run	0.15	0.13	Negative	
162-C	Normal charge 3 hr. run	0.40	0.74	35.8	
162-D	Normal charge 1 hr. run	0.19	0.65	39.6	

TABLE X

JLNB	Type Run	Dye in Filtrates A Dye Isolated by $TiCl_3$ %	B Dye in Filtrate by $TiCl_3$ %	% Yield by Dyetest of a %
3831-102-AB	Neutralized with HCl. Add NaCl (salt).	70.7	8.65	85.0
102-CD	Neutralized with H_2SO_4. Add Na_2SO_4 (sodium sulfate).	82.4	8.51	85.3
103-AB	Neutralized with H_2SO_4. Added Na_2SO_4.	84.4	7.5	86.3
103-CD	Neutralized with HCl. Added NaCl.	82.4	7.2	87.8

Note: The constitution of the dye remaining in the filtrate was not determined. It is not Pontachrome Flavine A, but gives very weak, dull, red dyeings. Its tinctorial strength is approximately that of unhydrolyzed base or half that of Pontachrome Flavine A.

TABLE XI

Effect of Catalysts (?) Other Than Copper
JLNB-3831-142, 146, 163

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11
Bomb	B 26	A 14	D 15	B 47	A 14	B 30	A 20	B 30	A 20	A 20	B 30
Mols NaOH	0.303	0.303	0.303	0.303	0.303	0.303	0.303	0.303	0.303	0.303	0.303
Mols Base	0.0327	0.0327	0.327	0.0327	0.0327	0.0327	0.0327	0.327	0.327	0.327	0.327
Catalyst	$NiCl_2$	$NiCO_3$	Ni-pellets	None	$CuSO_4$	$Ni(OH)_3$	Ni-catalyst No. 3	Chromium	Nickel	Cobalt on Kieselguhr	Co-acetate
Wt. catalyst, grams	1.0	1.0	5.0	None	0.37	1.0	1.0	5.0	5.0	5.0	5.0
Crude Wt. dye, grams	14.5	16.0	14.7	19.3	16.4	10.6	12.8	9.0	17.4	13.8	19.05
Strength	75:105	9:10	85:105	1:1	85:100	95:75	16:7	7:8	90:103	13:8	1:1
Mol Yield, grams	633	545	555	590	590	257	137	305	610	253	620
% Yield	85.5	73.5	75.0	79.8	79.8	34.7	18.5	41.5	82.2	34.2	83.6
Shade	N.Green, N. Brt.	T.N. Green	Close								
Type Bomb	Iron	Iron	Iron	Nickel	Iron	Iron, pickled	Iron, pickled				

TABLE XII

Effect of Hydrolysis Conditions on
Pontachrome Flavine A

JLNB-3831-140,149

Run	1	2	3	4	5
Bomb	B-26	A-14	Ex-10	Ex-10	Ex-10*
Mols dye	.0327	.0327	.0327	.0327	.0654
Mols NaOH	0.303	0.303	0.303	0.303	0.606
Wt.$CuSO_4$ g.	0.37	0.37	0.37	0.37	0.74
Wt.H_2O g.	40.0	40.0	56.6	56.6	113.2
Isolation pH	6.8-7.2	6.8-7.2	appx.7.0	appx.7.0	appx.7.0
Crude Wt.	19.5	17.7	23.1	21.5	53.3
Strength	8:10	80:95	75:85	75:80	1:1
Mol Return, g.	730	643	753	703	815
% Return	98.6	87.0	101.0	95.0	110%
Shade	Close	Close	Close T.green	Close T.green	T.red T.bright

*Runs 3, 4, 5 are aliquot parts isolated from an autoclave run. Samples from this run were analyzed for azo nitrogen by $TiCl_3$ and for CO_2 before heating and for the same after heating 8 hours. The data for this determination follow:

Charge to Autoclave Ex. 10:

	g.
Pontachrome Flavine A, 125% (.0392 moles)	291.0
NaOH (30% solution)	510.0
Water	680.0
Copper Sulfate	4.44
Total	1485.44
Sample "A" for analysis	93.00
To Autoclave (0.3675 mole)	1392.44

After Hydrolysis:

Water to Wash Autoclave	527.00
Total Recovered Charge	1920.00
Sample "B"for Analysis	100.0
Left for isolation (.3482 mol)	1820.0

1.0 mol = 5215 g. solution
0.0327 mol = 171 g. solution

Analyses:

"A" 0.10% carbon dioxide
"B" 0.15% carbon dioxide
Difference 0.05% carbon dioxide
Increase 0.696 g. carbon dioxide = .0158 mol
= 4.3% mono-decarboxylation assuming carbon dioxide to have come from the Pontachrome Flavine A itself. Since the average amount of dye recovered from the hydrolysis was by dye-test 98.3% and since there appears to be a tendency for the recovered dye to be green and bright versus the starting material; the slight increase in the amount of carbon dioxide appears to have questionable significance.

TABLE XIII

Comparison of Samples of Amino-chloro-benzoic
(JLNB-4053-26,32)

	Plant Charge 4	3898-98-A	3898-103A
Coupling, % yield (By $TiCl_3$)	91.5 (4 runs)	96.1 (2 runs)	92.8 (2 runs)
Hydrolysis yield, %	93.8 (4 runs)	87.4 (2 runs)	88.2 (2 runs)
Overall yield, %	85.8 (4 runs)	84.0 (2 runs)	82.0 (2 runs)

Note: Both samples 3898-98-A, 103-A formed colorless diazo solutions. Each time the diazo solution from Plant Charge 4 was highly colored.

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Marjorie N. Reign