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256 VANDERPOOL STREET
NEWARK, NEW JERSEY

NEWARK PLANT
PigMENT COLOR RESEARCH REPORT

Final Report

(A)BT-376-D (DIOXAZINE VIOLET FR): SEMI-WORKS MANUFACTURE

Period Covered MARCH, 1953 to OCTOBER, 1953

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NEWARK PLANT

CHEMICAL DIVISION-COLORS

Final Report

TITLE: (A)BT-376-D (DIOKAZINE VIOLET FR): SEMI-WORKS MANUFACTURE

PERIOD COVERED: MARCH, 1953 to OCTOBER, 1953

CHARGE: A-I-C-52

SUBMITTED BY: O.J.C. KLEIN

APPROVED BY: J. H. COOPER

DATE SUBMITTED: AUGUST 13, 1954

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INTRODUCTION:

A flocculation resistant form of "Dioxazine Violet" had been made in the laboratory by precipitating, in the presence of "Dioxazine Violet", the aluminum salt of a sulfonated "Dioxazine Violet". It was considered advisable to prepare a large sample in the Semi-works, both to test the sulfonation and laking procedures, and to provide material for testing and sampling.

SUMMARY AND CONCLUSIONS:

1. Sulfonation and laking were successfully carried out in the Semi-works.
2. The products were quite close to the laboratory preparation tinctorially and in resistance to flocculation.
3. Resistance to flocculation varied with the system in which the pigment was dispersed.
4. The Semi-works process could probably be cheapened and simplified, since it was adapted without essential change from the laboratory process. No attempt was made to determine optimum conditions for any step.
5. The Semi-works process was coded ABT-376-D.

DISCUSSION:

The work on the preparation of ABT-376-D fell into several distinct divisions as follows:

- (a) Preparation of intermediates.
- (b) Synthesis of "Dioxazine Violet" crude.
- (c) Salt-milling and extraction of a portion of the crude to produce BT-309-P.
- (d) Sulfonation of a portion of the crude "Dioxazine Violet".
- (e) Preparation of the flocculation resistant pigment.
- (f) Testing and evaluation.

The intermediates and the crude toner were synthesized according to the formulas given in KM-50-12, in Semi-works lots 3274, 3344, and 3345.

The dried toner was salt-milled in the 200-gallon mill, and extracted, in Semi-works lots 3366 and 3367. The first lot was milled with oylpebs, and appeared to require an excessively long milling cycle. The ball charge was changed to a mixture of 1-inch and 1/2-inch balls for milling 3367, and strength about equal to lot 3366 was reached in about 24 hours. An equal mixture of lots 3366 and 3367, by rubout, was rated strong and intense against BT-311-D, lot 2380, a sampling lot, and was therefore considered satisfactory for further processing.

Sulfonation was carried out according to Part A of the process (A)BT-376-D, given in Exhibit III, in two Semi-works experiments, lots 3355 and 3357. The first was discarded because of contamination during processing. The sulfonation and subsequent droming proceeded without any process difficulties, except for slow filtration. The paste was analyzed by a Kjeldahl nitrogen determination, and the results expressed as the mono-sodium salt of "Dioxazine Violet". The yields from both batches, expressed as "Dioxazine Violet", were: lot 3355, 55.4%; lot 3357, 52.75%, based on lot 382 as a reference standard, taken at 100%. The extent of washing with Na_2SO_4 solution specified by the laboratory process seems excessive, and can probably be reduced, in view of the further washing given to the lake after the precipitation of the aluminum salt.

The laking process was carried out on the Semi-works products first on a laboratory scale, in Semi-works lot 3435. The quality, as shown in Exhibits I and II, was considered acceptable both by rubout and by flocculation test. During the process it was learned that a pH of about 11.5, obtained by addition of NaOH solution, was necessary to dissolve the sodium salt of the sulfonate. Yield was very slightly in excess of theory.

The large-scale laking was carried out without difficulty in a tile lined vat, according to the process in Exhibit III, Part B. No difficulties were encountered, but the pressing and washing times were long. Yield was approximately theoretical.

Quality of all samples was tested by rubout, and of the lakes by flocculation tests in alkyd as well. In general, the lakes were found to be quite similar, though yellower than the original KS-520-b sample by rubout, and equal to or better than KS-520-b or BP-279-D standard in flocculation in alkyd. Rubout results are tabulated in Exhibit I and flocculation tests in Exhibit II. It may be noted that in conformity with the expected behavior, the laboratory prepared flocculation resistant lake was better in GE-2527 than in GE-2454 alkyd. The Semi-works scale lake was not the equal of the laboratory preparation from the same raw materials, in resistance to flocculation, but was vvs better than the original KS-520-b sample. Flocculation test results were not completely consistent, as evidenced by the fact that KS-520-b flooded in one test (A, Exhibit II) and flocculated in another (D, Exhibit II).

REFERENCES:

1. Sulfonation of Dioxazine Violet: N.B. 1398-132.
2. KS-520-b, preparation of original sample: N.B. 1325-170-D
3. S.W. lots 3274, 3344, 3345, 3355, 3357, 3366, 3367, 3391, 3435, 3463.
4. Evaluation laboratory job numbers: 53-414, 53-445, 53-503.
5. Analysis of sulfonated KS-71: 1465-36.

EXHIBIT I

SUMMARY OF HIRSHOUT RESULTS

BT-309-P, BT-311-D, ABT-376-D, LABORATORY AND SEMI-WORKS

Code	Lot No.	Description	Standard	MT	DD	Str.	Tint
BT-309-P	3366	12-hr. mill sample, Lab. finished	BT-311-D, lot 382	lt.	wk., blue	weak	---
"	3366	24-hr. mill sample, " "	"	"	---	wk. (108-100)	blue, vs dull
"	3366	36-hr. mill sample, " "	"	lt.	vs wk., blue	weak	blue
"	3366	48-hr. mill sample, " "	"	lt.	vs wk., blue	s weak	blue
"	3366	Final sample, Semi-works	"	lt.	s wk., blue	weak	blue
"	3367	12-hr. mill sample, Lab. finished	"	lt.	s wk., blue	weak	blue
"	3367	24-hr. mill sample, " "	"	lt.	blue	wk. (108-100)	s blue
"	3367	Final sample, Semi-works	"	dk. int.	vs str.	weak	vs yellow
"	3367	" " " "	3367, 24 hrs.	lt., dull	vs yellow	weak	s yellow
"	3367	" " " "	BT-309-P, 3366	dk. int.	s str., yel.	vs str.	yellow, int.
ABT-376-D	3435	Laked in Lab, using S.W. BT-309-P	KS-520-b	---	---	---	yellow, s int.
"	3435	" " " "	*BT-311-D, 2380	dk. int.	s wk., s dull	weak	yellow, dull
ABT-376-D	3463	Final Semi-works product	KS-520-b	---	---	---	yellow, s int.
"	3463	" " " "	BT-311-D, 2380	dk. int.	wk., yel., s dull	weak	yellow, s int.
"	3463	" " " "	3366 + 3367	---	---	wk. (119-100)	dull
"	3463	" " " "	ABT-376-D, 3435	---	---	---	---
KS-520-b	3366 +	Original Lab Sample	BT-311-D, 2380	dark	weak	weak	dull
BT-309-P	3367	Mix of final Semi-works samples	BT-311-D, 2380	---	strong	strong	s int.
BT-311-D	382	S.W. File sample of an early lot	BT-311-D, 2380	dark	str., yel. int.	strong	yellow
BT-309-P	3366 + 3367	Mix of final Semi-works samples	KS-520-b	---	---	strong	vs blue, int.
BT-311-D	382	S.W. File sample of an early lot	KS-520-b	---	---	strong	int.

*BT-311-D, 2380 is a mix of salt-milled material set up as a sampling lot.

EXHIBIT II

SUMMARY OF FLOCCULATION TESTS

Sample	Standard	Sieved	Appearance	vs. Rubbed	Standard	Poured	Sample Rubbed	Flocculation (See note below)	Standard Poured	Sample vs. Rubbed	Standard Poured	Bleed vs. Standard
A. Ground in GE-2454, thinned with VMF naphtha + Mineral Spirits												
ABT-376-D	KS-520-b	vs str. & dull	s str.				7	---	vs worse	---		---
"	KS-71, lot 382	very str.	str.				7	---	better	---		---
"	BR-279-D, SD 2020	str., s int.	str., s int.				7	---	"	---		---
B. Ground in GE-2454, thinned with xylol												
ditto	KS-520-b	vs str. yel. s int.	wk., yel.				8	---	better	---		
"	KS-71, lot 382	str. yel. int.	yel. int.				8	---	better	---		
"	BR-279-D, SD 2020	str. yel. int.	str. yel. int.				8	---	better	---		
C. Ground in GE-2327												
ditto	KS-520-b	vs str. & yel. & int.	vs str. vs yel. & int.				7*	8	equal	7		vs better
"	KS-71, lot 382	yellow & intense	weak, yellow				7*	8	better	3		better
"	BR-279-D, SD 2020	vs str. & yel. & int.	wk. yel. vs dull				7*	8	equal	6		s better
"	BT-309-P, 3366 ± 3367	str. yel. int.	yellow				7*	8	better	3		better
D. Ground in GE-2454, thinned with VMF naphtha + Mineral Spirits												
ABT-376-D	ABT-376-D, lot 3435	vs str. vs int.	str. s int.				8	---	worse	---		vs better
"	KS-520-b	vs wk., vs dull	vs weak				8	---	vs better	---		s better
"	BR-279-D, SD 2020	str. yel. int.	str. yel. int.				8	---	vs better	---		vs better
"	BT-309-P, 3366 ± 3367	str. yel. int.	vs str. yel. vs int.				8	---	better	---		vs better

Note: In numerical rating of flocculation, 10 denotes no change in strength, and decreasing numbers show worse flocculation.

* The asterisk indicates that the sample became weaker on rubbing.

FORMULA SHEET



COLOR CODE (A) BT-376-DATE 8/23/54 NAME Dioxazine Violet Lake
 OBJECT Floculation resistant lake.

BASED ON SN lots 3357, 3463.

BATCH SIZE-MOLS BATCH No. OF "K" SAMPLE

LINE OR CMT.	MATERIAL	WGT. WT.	GAL.	C. C.	MANIPULATION	NO.
					PART A.	
					Prepare a quantity of sulfonated Dioxazine Violet as follows:	
					Set up a 30 gallon stainless steel drum in a deep pan. Equip drum with "Lightnin" agitator. Fill pan with ice and water.	
					Set up a pump to remove water from melted ice.	
					Add to drum	
156	Sulfuric Acid 98%				Keep drum covered to avoid water absorption.	
					Agitate acid, and cool to 59°F or lower.	
12.5	Crude for BT-309-P				Sprinkle in slowly so as not to exceed 59°F.	
					With steam pipe, heat water bath.	
					Raise temp. of slurry to 113°F (45°C)	
					Hold at 113°F for 1 hour.	
					To Vat 11, "14 Bldg., add	
			88		(20 inches). Have available	
400	Water				Add ice to vat, with agitation, till excess ice is present.	
	Ice				Move acid container to 11 Vat platform.	
					Drawn sulfonate in 11 Vat in 1-1/4 hours, keeping excess ice in Vat.	
					(Use glass jar and two 1/4" Tygon tubes as syphons.)	
					Heat slurry to 160°F with steam.	
					Hold at 155°-160°F. for 1/12 hrs.	
					Measure and record volume	
					Add by sifting	
+68	Sodium Sulfate anhyd.				2 lbs. per inch of volume	108
					Stir 1/2 hour after adding N-108	
					Filter in 16 frames, bronze press.	
					Wash with N-108 solution, 21 lbs. per 50 gallons of water, to	
					negative test on Congo Red paper.	
					Dump press.	
					Hold as presscake.	
					Weigh presscake.	

PACKAGE LBS. PER COST GROUP SIGNATURE

DUP050069951

FORMULA SHEET



COLOR CODE

DATE

NAME

K.

OBJECT

BASED ON

PAGE 2

BATCH SIZE-MOLS

BATCH No. OF "K" SAMPLE

LBS. OR GALS.	MATERIAL	100% WT.	GAL.	G. G.	MANIPULATION	NO.
					Analyze by Kjeldahl method and calculate to Dioxazine Violet.	
		LBS.			PART B.	
	Water		21		To 9 Vat (CPC Semi-works) add 7 inches	
	BT-309-P	54			Add	
			60		Stir to break down paste.	
					Make to (20 inches) and hold.	
					To a 30 gallon stainless steel drum	
					Add	
	Sulfonated Dioxazine Violet Crude	6			From Part A. Make to	
			20		with water.	
					Add immediately	
19	Caustic Soda, 50%	4.5			to a pH of 11.5. Should make a clear solution.	7
			24		Make to	
					with water.	
					Record pH of solution in drum	
					Add contents of drum to 9 Vat.	
					Stir to mix and take pH of slurry in 9 Vat. Record: pH	
					To	
	Water		12		Add	
	Alum	12			Stir to dissolve.	15
					Strike alum solution into 9 Vat in 30 minutes.	
					Stir 30 minutes.	
					Record: Final pH	
					Filter in two press loads, 16 frames each, in bronze press.	
					Wash practically sulfate-free.	
					Dump press.	
					Dry in Gordon-Davis dryer at 140°F.	
					Pulverize regular speed.	

PACKAGE

LBS. PER

COST GROUP

52

SIGNATURE

O. J. C. Klein

GOAL YIELD

DUP050069952

PROCESS NOTES

(A)BT-376-D

(A)BT-376-D is a flocculation-resistant lake of "Dioxazine Violet", composed of 90 mol percent of Dioxazine Violet (BT-309-P) on which is precipitated 10 mol percent of the aluminum salt of a sulfonated Dioxazine Violet. The "A" formula gives the Semi-works method of preparing both the sulfonated component and the lake.

Two sulfonations and one laking have been made in the Semi-works, as lots 3355, 3357 and 3463 respectively. In flocculation resistance, the product (lot 3463) was close to the original laboratory preparation, KS-520-b, in tinctorial properties and resistance to flocculation.

The composition and yields given below are calculated, based on components charged, and the Semi-works yield.

COMPOSITION:

	<u>#</u>	<u>%</u>
Dioxazine Violet Toner	54.0	86.4
Al salt of sulfonated toner	7.0	11.2
Moisture	1.5	2.4
Total	62.5	100.0

CALCULATED YIELD:

62.5 lbs. "as is".
61.0 lbs. anhydrous

Reference: KN-54-27


Signed: O. J. Klein 8/24/54

Approved: J. H. Cooper 8/24/54

jc

DUPONT NEWARK
PIGMENTS DEPARTMENT
SEP 9 1984