Serial No.

Copy No. 6

~~A. Siegel/A.A.Drizzolara~~
Library
Numerical
File

E. I. DU PONT DE NEMOURS & COMPANY
KREBS PIGMENTS DEPARTMENT
256 VANDERPOOL STREET
NEWARK. NEW JERSEY

TN-47-16 Copy #6

NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

JACKSON LABORATORY
PIGMENTS GROUP RESEARCH REPORT

MAROON TONER, RT-608-D
(4-CHLORANTHRANILIC ACID → BON, Mn)

Period Covered: SEPTEMBER 13, 1948 to FEBRUARY 10, 1949.

FILE: 2/23/49

DATE: 222.2

222.2

SERIAL NO. KN-49-16

Copy No. 6

Copy to:

1 - Numerical File
2 - Research File (222.2)
3 - Library File (222.2)
4 - Dr. J. E. Booge, Wilm.
5 - Dr. D. B. Killian, Newark
6 - Mr. A. Siegel/A.A.Brizzolara, Newark
7 - Dr. W. S. Struve, Jackson Lab.
8 - Mr. A. D. Reidinger, " "
9 - Mr. J. M. Tinker, " "
10 - Mr. J. M. Tinker, " "
11- Extra copy

MAR 1 1949
A.B.

JACKSON LABORATORY

PIGMENTS GROUP RESEARCH REPORT

MAROON TONER, RT-608-D
(4-CHLORANTHRANILIC ACID → BON, Mn)

SEPTEMBER 13, 1948 to FEBRUARY 10, 1949

CHARGE: A-II-C-236 ?
256.

SUBMITTED BY: A. D. Reidinger DATE SUBMITTED: 2/10/49

APPROVED BY: W. S. Struve DATE ISSUED: 2/23/49

INTRODUCTION:

K-2512, the manganese salt of 4-chlor-2-amino benzoic acid (4-chloranthranilic acid) coupled to beta-oxy-naphthoic acid, previously described in KN-48-4, was found upon exposure (6 months Florida)to exhibit lightfastness and durability on a par with arylide maroon, RT-551-D. Its attractive appearance in a metallic finish and its non-bleeding properties aroused considerable interest in the new combination as a possible addition to our line of maroons and it was decided to prepare sufficient sample for evaluation by F&F, Philadelphia and Parlin.

The product was coded ART-608-D and a new formula was written based on the straight thru process for RT-525-D (Mn Red 2B). Altho this procedure gave a lighter, yellower and also harder product than K-2512, it was considered suitable for costing purposes.

This report covers the work done in the study of the process, chiefly of the "isolated dye" procedure K-2512, which was found necessary in order to duplicate the sample originally evaluated.

SUMMARY:

At the outset it was found that the K-2512 process was sensitive to a number of variables which had not been studied previously. Optimum conditions of alkalinity and volume of development, amount of Para soap, and the effect of time and temperature of development were investigated.

With this information it was possible to prepare a two pound sample, KS-197, which altho not a close match for K-2512 was considered to be satisfactory for submission to Philadelphia. By rubout and in alkyd enamel, the new sample was dark, somewhat duller, and yellower than the original product.

Further study of the process did not reveal means of improving the tinctorial properties above the level of KS-197 and a sample of the same quality in filter cake form was prepared for evaluation by Parlin. However, since the product exhibited instability of color and of crystal form, it was not submitted.

Because of the additional amount of work which appeared to be required in developing a stable process, the problem was transferred from the Jackson Laboratory group to the Newark Laboratory.

Results of some promise were obtained on a straight thru process based on the K-2512 type of coupling. However, some variations occurred in the products obtained and further study would be required.

DISCUSSION OF RESULTS

The following results apply to the "isolated dye" formula, K-2512, or its modifications.

Raw materials - The 4-chloranthranilic acid used in the preparation of K-2512 and in part of the work reported here, was prepared by potassium permanganate oxidation of 4-chloro-2-amino toluene by the method referred to in Beilstein. Subsequently the procedure was modified in accordance with details given in an I.C.I. report, H-5246. Based on melting points and nitrite values, all intermediates used were of excellent quality.

Other materials were of the grade used in the Pigments Department.

Diazotization - Because of the low solubility of 4-chloranthranilic acid in hydrochloric acid, rate of diazotization is relatively slow. Precipitation of the amine and formation of a considerable amount of diazo-amino compound apparently occurs when the acid is added to the amine-sodium nitrite solution. The formation of diazo-amino compound is probably due to local deficiency of acid since on stirring for 30-45 minutes most of it breaks down and diazotizes. An undiazotized residue equivalent to about 3% of the weight of amine is filtered off before coupling.

Use of increased amounts of hydrochloric acid (50% and 100% more) improved the rate of diazotization and reduced the amount of undiazotized material. However, the products obtained were weak and duller in tint due possibly to improper balance of the alkalis used in coupling.

Coupling - A mixture of caustic soda and soda ash as alkalis for coupling appears to be most satisfactory. A larger amount of NaOH than in K-2512 is now used in order to obtain more rapid coupling.

Replacement of soda ash with ammonia in one experiment in which it was tried gave a lighter yellow product with harder dry texture.

Optimum coupling temperature appears to be from 10 to 15°C. At 25°C somewhat lighter, yellower and duller products were obtained. When coupled at 5-8°C, weakness has occurred but masstones appeared to run more consistently.

The presence of rosin in the coupling (20 grams per mol charge) did not have a pronounced effect. Slight dullness of masstone and tint was noted in a direct comparison.

Isolation of the Dye - No information was obtained as to the effect of development of the dye by heating before filtering or of using water in place of salt to wash the dye, or of omitting washing entirely.

Conditions for Strike and Development - Alkalinity of development appears to be the most important single variable. In all the recent work it was necessary to adjust the pH after adding manganese sulphate to 8.2 - 8.4 to obtain a normal product. Use of a definite amount of NaOH (18 grams per mol) is preferable to reliance on pH readings as a control. If insufficient alkali is used, a light, very dull color results. Use of higher amounts of alkali have relatively slight effects but do give darker products with yellower tints.

Reduction in development volume by 50% resulted in a lighter masstone and bluer dull tints while a two-fold increase had no effect.

Amount of Para soap may be varied from 50% less to 100% more than the formula amount without much effect but omission results in a duller and weaker product.

Amount of manganese sulphate was varied from 116 to 68% of the formula amount without change in tinctorial properties except that at the lowest amount, which is still 12% in excess of theory, a stronger product was obtained. Manganese content of the products varied relatively little and all were lower than anticipated from calculations based on the assumption of one atom Mn per mol of dye - 10.96 to 9.88% by analysis compared to 13% calculated.

Temperature and Time of Development - The following development conditions have been tried:

Temperature	pH	Time	
98 - 100°C	8.2-8.4	30 minutes	
98 - 100°C	8.2-8.4	10 "	(Standard)
98 - 100°C	8.2-8.4	2 "	
90 - 92°C	8.2-8.4	10 "	
92 - 93°C	8.1-8.2	10 "	
82 - 83°C	7.8-7.9	10 "	

The shorter development period, 2 minutes at 98-100°C instead of 10 minutes, gave similar tinctorial properties and may give better consistency since more rigorous conditions, e.g. 30 minutes at the boil, was found to be detrimental to the color. Similarly, development at 90-92°C had little effect on tinctorial properties compared to the standard procedure.

The combination of low temperature and low pH resulted in lighter masstones and more intense tints but did not appear to impart greater stability to the process since off-color was obtained in some instances.

Several procedures for adding manganese sulphate were tried. The method of RT-347-D in which the Na salt is acidified and the similar process for RT-521-D in which the manganese is added in the form of hydrate gave close matches for KS-197 referred to in Summary, although both were slightly duller in masstone than the control run for the series.

Straight Thru Process - The following methods of eliminating isolation of the coupled dye were tried.

An RT-525-D type process in which the Na salt is run into the $MnSO_4$ at a boil gave a lighter and yellower product than K-2512. Lightfastness and bleed properties were equally good but dry texture was poor. This process was also sensitive to the amount of alkali present during development.

A K-2512 type of coupling followed by addition of Para soap and manganese sulphate to the alkaline coupled dye, somewhat as in RT-565-D (yellow shade Mn Red 2B), gave promising results on several trials but subsequent study indicated it also was unstable. Somewhat better results were obtained by acidifying the coupling and striking at 50°C in RT-347-D process.

Replacement of soda ash with ammonia or additional NaOH gave inferior products on the latter formulation.

Instability in pulp form - The instability referred to in the summary was noted when samples of filter cake were composited by reslurrying in water, the color becoming very dull and changeable in masstone ink. It was not determined if this behavior is characteristic of the color. However, a sample of filter cake which had been stored for 7 weeks in that form did not show any significant change.

EXPERIMENTAL DETAILS:

Details will be found in Notebooks 1292 and 1320. An index is given of the variations studied.

Preparation of samples	(N.B. 1292, Expts. 46, 54 (N.B. 1320, " 4, 16
Raw Materials Tests	(N.B. 1292, Expt. 64 (N.B. 1320, Expts. 3, 5, 9
Diazotization	N.B. 1320, Expt. 7

Coupling Conditions	N.B. 1320, Expt.14
Alkalinity of Development	(N.B. 1292, Expt. 47 (N.B. 1320, Expts. 6, 13
Volume of Development	N.B. 1292, Expt. 53
Amount of Para Soap	N.B. 1292, Expt. 49
Amount of Manganese Sulphate	N.B. 1320, Expt. 15
Temperature and time of development	(N.B. 1292, Expt. 48 (N.B. 1320, Expt. 6, 27
Method of adding Manganese	N.B. 1320, Expt. 13
Straight Thru Process	(N.B. 1292, Expt. 43 (N.B. 1320, Expt. 20, 22, 23, 26

Composition of pigment codes referred to -

RT-347-D (Manganese toner of Tobias Acid
RT-521-D (coupled to Beta-oxy-naphthoic acid.
RT-525-D Manganese toner of Permanent Red 2B
RT-551-D 5-nitro-2-amino-anisole coupled to "Naphthanil" ASD.

A process embodying what is believed to be the optimum conditions is attached.

FORMULA SHEET

COLOR CODE DATE 2/8/49 NAME Maroon Toner K-

OBJECT Modification of K-2512

BASED ON N.B. 1320-16

BATCH SIZE-MOLS. 1.0 BATCH No. OF "K" SAMPLE

Wt. or Vol.	MATERIAL	100% WT.	GAL.	C. C.	MANIPULATION	Ng
44	Caustic Soda, 100%	44			Add to	
			300	2500	water. Then add	
175	4-chlor-anthranilic				Heat to 140-160°F and	
	acid 98-99%.				stir 20-30 minutes to dissolve	
					(Test: slight on cy paper)	
					Make to	
			720	6000	at 32°F with ice and water.	
2400	Ice				Add	
71	Sodium nitrite				Stir 2-3 minutes	
	"as is" (ca 99% $NaNO_2$				Dump in with good agitation	
100	Muriatic Acid 100%	100			Stir 25-35 minutes at 35-40°F	
	(ca 31.45% HCl soln.)				(Test: CR+, KI+ throughout)	
					Filter thru clarification press.	
					Collect filtrate. Add	
15	Sulfamic acid				dissolved in	
			6	50	cold water	
					(Test: KI - or v.s.)	
					Couple	
69	Caustic Soda 100%	69			Add to	
	(ca 50% NaOH soln.)		180	1500	water. Then add in 3-5 minutes	
200	"Lithosol" Acid BON				Heat to 130-140°F	
					Stir 10-30 minutes to dissolve.	
					Dilute to	
			420	3600	with cold water. Then add	
160	Soda Ash				Dissolved in	
			75	625	water at 135-140°F	
					Make to	
			720	6000	at 49-51°F with cold water and ice	
					Couple diazo into BON solution in	
					30-40 minutes at 50-60°F.	
					(Test: Diazo - BON+, pH 9.6-9.8)	
					Stir 30-40 minutes.	
					Filter and wash with	
700	Salt	1680	1680	14000	cold water	
					(Test: Filtrate slight on Ba)	

PACKAGE LBS. PER COST GROUP SIGNATURE

GOAL YIELD

DUP050067213

FORMULA SHEET

COLOR CODE DATE 2/8/49 NAME Maroon Toner K-

OBJECT Modification of K-2512

BASED ON N.B. 1320-16

BATCH SIZE-MOLS 1.0 BATCH No. OF "K" SAMPLE

No. of Charge	MATERIAL	100% WT.	GAL.	C. C.	MANIPULATION	ETC
					Reslurry press cake in	
			1200	10000	Stir 30-60 minutes	
					Make to	
			3000	25000	at 80-85°F	
					Add	
36	Para Soap				dispersed in	
			20	175	cold water	
75	Sodium Acetate				dissolved in	
	crystals		30	250	cold water	
					Stir 5-10 minutes.	
					Add in 10-12 minutes	
315	Manganese Sulphate				dissolved in	
	(Ca.80% $MnSO_4$)		200	1650	water at 122-125°F	
					Stir 5-10 minutes	
					(Test: pH normal 6.2-6.5)	
					Add in 2-3 minutes	
18	Caustic Soda 100%	18				
	(ca. 50% NaOH soln.)				Stir 5 minutes	
					(Test: pH normal 8.2-8.4)	
					Heat to 208-212°F in 40-45 minutes	
					Hold at 208-212°F for 2 minutes	
					Quench to 158-160°F volume	
			6000	50000		
					Record pH (normal pH 6.6-7.2)	
					Filter, wash SO_4 free	
					Dry at 140°F	
					Pulverize	

PACKAGE 125 LBS. PER Drum COST GROUP 36 SIGNATURE A.D.Reidinger

GOAL YIELD 460 lbs. "as is"