

Serial No. KN-47-47

Copy No. 1

Numerical File

JACKSON LABORATORY
PIGMENTS GROUP RESEARCH REPORT

KN-47-47
Title:- Metallized Pigments from Beta-oxy-naphthoic
acid K-2502, Aniline → BON, Nickel Complex
K-2511, Paranitroaniline → BON, Nickel
(and other amines)

Period Covered: 9-30-46 to 9-29-47

File: 222.2

Date: 2-9-48

2
N42145

Serial No. KN-47-47

Copy No. /

Copy to:

- #1 - Numerical File
- 2 - Research File (222.2)
- 3 - Library File (222.2)
- 4 - Dr. J. E. Booge, Wilmington
- 5 - Dr. W. F. Spengeman, Newark
- 6 - Mr. A. Siegel/ Mr. A.A. Brizzolara, Nwk.
- 7 - Dr. D. B. Killian, Jackson Lab., Wilm.
- 8 - Mr. A. D. Reidinger, " " "
- 9 - Mr. J. M. Tinker, " " "
- 10 - Mr. J. M. Tinker, " " "
- 11 - Imperial Chemical Industries Ltd.
- 12 - " " " "
- 13 - " " " "
- 14 - Extra Copy

JACKSON LABORATORY
PIGMENTS GROUP RESEARCH REPORT

Title: Metallized Pigments from Beta-oxy-naphthoic
acid K-2502, Aniline → BON, Nickel Complex
K-2511, Paranitroaniline → BON, Nickel
(and other amines)

Period Covered: September 30, 1946 - September 29, 1947

Charge: CR-236

SUBMITTED BY: A. D. Reidinger
A. D. Reidinger

DATE SUBMITTED: 12-11-47

APPROVED BY: D. B. Killian
D. B. Killian
1/12/48

DATE ISSUED: 2-9-48

INTRODUCTION:

Pigments of excellent lightfastness have been obtained at Jackson Laboratory by forming a complex metallic salt of diazotized arylamines coupled to beta-oxy-naphthoic acid. U.S. 2,396,328 (Du Pont) covers the preparation of metallic complexes, the first components of which are amines devoid of OH, COOH, and SO₃H groups. The products are red, maroon and brown, the former being usually somewhat dull compared to the simple metal salts. The nickel complexes are usually of better intensity than other metals, such as copper or cobalt.

It was planned to prepare samples of the most promising of the nickel compounds for evaluation and outdoor exposure.

SUMMARY AND CONCLUSIONS:

The following samples have been prepared and sent to Newark for testing. Final results on these products will be available in Exposure Reports and the other Paint Laboratory memoranda referred to below -

K-2502 - Aniline → BON, Ni Complex

This pigment is a light brown with a tint of reddish hue considerably duller than the average organic red. Lightfastness of the sample both in full shade and in zinc oxide extension was excellent by Fade-O-Meter test. The only modification of the original Jackson Laboratory formula was in heating the coupled dye to 60°C before isolating, which improved filtration rate and appeared to give increased depth and strength. For complete results refer to Paint Laboratory Memo #144 and Exposure Series #7118.

KS-103 - Aniline → BON, Ni Salt

A sample of the nickel salt containing 1/2 atom of Ni per mole of dye was also prepared. This is much more intense in mass tone than the metallic complex but is definitely inferior in lightfastness. Some interest in the metal salts of this combination has been observed, e.g. Harmon's Topaz Red (the Ca salt) and Calco's Red Lake R, and a number of similar derivatives have been evaluated at Newark.

Outdoor durability of KS-103 is being determined. See Exposure Series 7124.

KS-102 - Aniline → BON, Ni Complex in Pulp Form

A sample of K-2502 in pulp form was supplied to the Newark Laboratory for evaluation. Although excellent lightfastness is exhibited, dispersibility of the pulp is poor and use in this form would not be satisfactory. See General Service Laboratory Report #22.

K-2511 and KS-105 - Paranitroaniline → BON, Ni Complex

This product is a dull maroon with a bluish red tint of fair intensity. The present samples are noticeably duller than a preliminary Jackson Laboratory offering but was equal in lightfastness. Products

which were of equal intensity compared to the latter were poorer in fade resistance and improvement in lightfastness was obtained only by increasing the heating period from three to eighteen hours with resulting loss of masstone quality. Other details in Exposure Series 7118.

KS-104 - Paranitroaniline → BON, Ni Salt

Although somewhat deeper in masstone than the aniline salt, this pigment is much duller in tint and poorer in lightfastness. A sample is being tested for outdoor durability. See Exposure Series #7124.

Parachlor ortho nitro aniline → BON, Ni

The product obtained with this first component was deeper and more intense than the PNA counterpart, but was inferior in lightfastness. There is evidence that the Ni salt was obtained with only partial metallization. No sample was prepared for outdoor exposure.

Parachloraniline → BON, Ni

The metallized complex is a light brown similar to the aniline derivative. The nickel salt is much more intense but poorer in lightfastness. Neither appeared to have any advantage over the corresponding product made from aniline and samples were not prepared for outdoor evaluation.

Parachlor ortho toluidine → BON, Ni

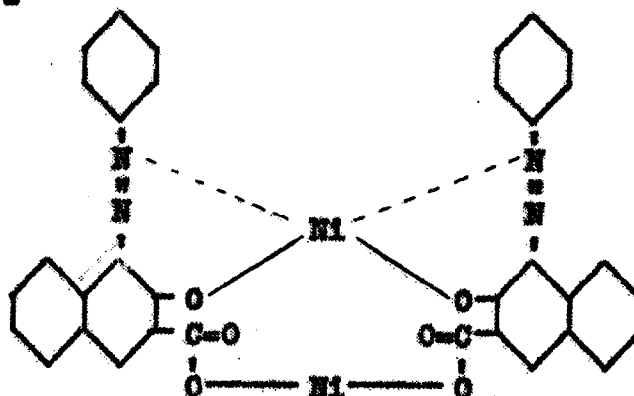
Difficulty was encountered in controlling the process for this combination. Although the pigment is more intense in masstone and bluer in tint than the corresponding aniline complex, it was decided not to do further work until the merits of the latter had been determined.

KS-106 - Beta Naphthylamine → BON, Ni

This product is characterized by its deep and relatively intense masstone. Metallization does not appear to be complete and lightfastness is consequently not as good as desired. However, outdoor tests are being made (Exposure Series #7124).

DISCUSSION OF RESULTS:

In all cases, difficulty was encountered in obtaining consistent results possibly due to the complex structure of the products in which the metal is presumably combined both as a simple salt with the carboxy group and in coordinate linkage with the azo groups in the following manner -



A limited process study was made particularly in the case of the paranitroaniline derivative. With this diazo component, coupling to BON was best carried out in buffered acid medium. Sodium carbonate or bicarbonate alkalinity gave lighter, yellower products with poorer lightfastness. Use of NaOH may be possible if excess alkali is neutralized after coupling.

The coupled dye was isolated and reslurried since a weaker product with poorer lightfastness was obtained in the one instance in which a straight thru procedure was tried.

Metallization was carried out with an excess of ammonia by heating at 90°C for 3 hours or longer. The PNA - BON, Ni complex was improved in lightfastness by an 18 hour development period but masstone color was duller. With sodium acetate as buffer or acid acceptor formation of the complex did not appear to be complete.

The other diazo components - aniline, etc. were coupled with soda ash as alkali. No other significant changes were made in the formula for coupling and metallizing the products from their amines.

For additional information on this type of pigment refer to

JLR-43-434 - Fast-to-Light Red Pigment
JLR-43-443 - Fast-to-Light Maroon Pigment

Copies of K-2502 and K-2511, which are representative procedures are attached.

EXPERIMENTAL DETAILS:

Refer to Notebooks 1235, 1236 and 1260.

Aniline - Beta oxy naphthoic acid

NB 1236, Expts. 7, 11, 15

NB 1260, Expts. 3, 18, 23

Para nitro aniline - Beta oxy naphthoic acid

NB 1235, Expts. 58, 60

NB 1236, Expts. 6, 10, 14, 20, 26, 48, 55, 56

NB 1260, Expts. 2, 5, 11, 16, 22

Para chlor ortho nitro aniline - Beta oxy naphthoic acid

NB 1235, Expts. 10, 12

NB 1236, Expts. 14, 46

Para chlor aniline

NB 1236, Expts. 14, 46

Para chlor ortho toluidine

NB 1260, Expts. 8

Beta Naphthylamine

NB 1260, Expts. 9, 29

FORMULA SHEET



COLOR CODE _____ DATE 8/13/47 NAME Brown Toner K-2502 (Exp)
 OBJECT To prepare Nickel derivative of (aniline + BON) for evaluation (Exp)
 DATED ON Lab. 1260-3A & B
 BATCH SIZE/NO. 2.0 BATCH NO. OF THE BATCH Lab. 1260-3A & B

QTY	NAME	WGT. GR.	WGT. OZ.	Q. C.	REMARKS	NO.
					To	
			60	500	cold water contained in vat add	
27	Aniline "as is"				Then add	
42	Muriatic acid 100%	182			Stir 10-20 minutes to dissolve	
	(+21.45% HCl sol'n.)				Cool to 32°F with ice	
1500	Ice				Then add in 2-3 minutes	
132	Sodium nitrite				dissolved in	
	"as is"		43	400	cold water	
					Stir 10-12 minutes. Temperature 32-35°F	
	Final volume approx. 3000		3000		Tests: GR+, KI slight	
96	Caustic Soda, 100%	96			Adjust volume to	
	(+50% sol'n.)		240	2000	with cold water. Turn on steam	
					Heat to 140-150°F. Add in 5-10 minutes	
280	Beta-naphthol				stir to solution	
	acid "as is"				Dilute with cold water to	
			900	7500	Add with agitation	
225	Soda Ash		150	1250	dissolved in	
					Adjust to 68-70°F with ice	
					Volume approximately	
			1200	10000		
					Couple diazo into BON solution	
					under surface in 25-30 minutes	
					Stir 25-30 minutes.	
					Tests: diazo-, BON+	
					Record pH ~ (normal pH 9.0 - 9.5)	
					Heat to 140°F in 15-20 minutes	
					Filter and wash negative to	
					Brilliant yellow paper with	
					5% salt solution prepared as follows.	
					To	
					cold water add	
250	Salt		600	5000	stir 15-20 minutes to dissolve	
					Pump thru press cake	
					Hold washed cake in pulp form	

PACKAGE _____ PREP. BY _____ COST GROUP _____ SIGNATURE _____

DUP050066711

FORMULA SHEET



COLOR CODE

DATE 8/13/77

PAGE 2
NAME

Brown Toner

K-2502
(Expo)

OBJECT

PACKING

UNIT OF MEASURE

QTY	DESCRIPTION	UNIT	QTY	QTY	REMARKS	REMARKS
			1200	10000	Resin press cake in cold water.	
					Heat to 190-195°F in 30-40 minutes	
40	Pura Bone		30	250	slurried in cold water	
					Prepare and add to C-12 run	
					To	
			240	2000	water at 135-140°F add	
570	Nickel chloride crystals, NiCl ₂ ·6H ₂ O				stir to solution	
					Then add	
200	Ammonia 28%				Stir 5-10 minutes. Use at once	
					Stir to dark color at 190-195°F for 3 hrs.	
					Press, wash free of Ni ⁺⁺ and Cl ⁻	
					Dry at 175°F.	

PACKAGE

170. PER

COST GROUP

SIGNATURE

A. D. REIDINGER

A. D. Reidinger

DUP050066712

CONFIDENTIAL

C-2502, a complex nickel derivative of indigo-VB, is a brown pigment possessing excellent lightfastness. The present formula was used in preparation of a sample for evaluation and has not been completely studied in respect for formula variations.

Exclusion of the complex dye before converting to the nickel complex and use of ammonia in the latter step appear to be preferable to a straight then procedure making use of sodium acetate and caustic soda in place of ammonia. However in view of the possible reduction in costs, these changes should require further study if the project becomes of interest.

The complex dye is heated at 140°F before filtering to improve filtration and drying rates. Washing with brine instead of water was necessary because of the solubility of the dye. Neutralization of the excess carbonic acid and removal of coloring may be better procedure.

Neutralization of the excess ammonia at the final stage had no effect on the color properties of the product and may be necessary if the formula is taken to the plant.

Use of 10% more in (60% of the formula amount) gave a better product.

A. D. HENNINGER
A. D. HENNINGER

7/23/57

172-776

DUP050066713

RECEIPT



COLOR CODE _____ DATE 8/13/47 NAME Maroon Toner
 OBJECT To prepare Fickel derivative of (Paranitraniline → BON)
 BATCH NO. Lab. 1260-11 A & B
 BATCH SIZE 2.0 BATCH NO. OF THIS BATCH Lab. 1260 - 11 A & B

QTY.	MATERIAL	WGT.	WGT.	TEMPERATURE	REMARKS
276	Paranitraniline			Slurry in	
	"as is"		180	1500	cold water
					Add
145	Sodium nitrite "as is"		45	375	dissolved in
					cold water. Stir 10 minutes
			480	4000	Make to
1600	Ice				at 32°F with ice and water
182	Muriatic acid 100%				Add in 4-6 minutes
	(+31.4% HCl soln.)				Stir 20-30 minutes until practically
					Diazo is slightly turbid yellow solution
					Tests: GR+, KI+ Temp. 35-40°F
15	Sulfamic Acid		20	160	Then add
					dissolved cold (KI- or vs)
128	Caustic Soda 100%	128			Adjust to
	(>50% soln.)		240	2000	with cold water. Turn on steam
380	Buthagol Acid BON				Heat to 140-145°F. Add in 5-10 min.
			1200	10000	stir to solution. Make to
60	Acetic acid 100%				at 68-70°F with ice and cold water
	(+60% CH ₃ COOH sol'n.)				Then add in 5-10 minutes
					Tests: EL vs. pH 6.5 - 6.9. Adjust if necessary
					Notes: BON should remain in solution
					Adjust temperature to 68-70°F.
					Couple the diazo into the BON solution
					in 25-30 minutes
					Tests: diazo-, BON (alk. spot) +, pH 4.2-4.5
					Stir 30-40 minutes
					Heat to 140°F in 20-30 minutes
					Filter and wash 01' free
					Hold in press cake form

PACKAGE _____ LBS. PER _____ COST GROUP _____ SIGNATURE _____

GOAL YIELD _____

DUP050066714

POTENTIAL SHEET



COLOR CODE

DATE

8/13/47

PAGE 2.

NAME

Hydrox Toner

K. 2511

COMENT

DATE ON

SECTION 4411.9

SECTION No. 47 1101 110111

PL. CT. 120	MATERIAL	REF. CT.	QAL.	G. S.	MANIPULATION	W.
			1200	10000	Reslurry mass cake in cold water. Add slurried in cold water	
80	Para Soap		48	430	Prepare and add in 8-10 minutes	
					To	
			240	2000	water at 135-140°F add stir to solution	
520	Nickel chloride crystals. $NiCl_2 \cdot 6H_2O$				Then add	
1080	Ammonia 28%				Stir 5-10 minutes. Use at once	
					Heat struck color to 190-195°F in 30-40 minutes	
					Stir at 190-195°F for 18 hrs.	
					Freeze, wash free of Ni^{++} and Cl^-	
					Dry at 175-180°F	

PACKAGE

LAB. FOR

COST GROUP

SIGNATURE

A. D. REIDINGER

A. D. Reidinger

REMARK

DUP050066715

NOTE FOR K-2511

K-2511 is a complex nickel derivative of paranitroaniline → ECH, related in chemical structure to K-2502. It is considerably deeper and more intense than the latter approaching a brown in shade.

COUPLING - The buffered acid coupling proceeds readily unless the pH drops below the recommended range, 4.2 - 4.5. In such case addition of a small amount of caustic soda can be made. The balance of components should be very close.

Coupling on the alkaline side (sodium carbonate as alkali) gave lighter and weaker products.

The coupled dye is heated to 140°F before filtering to improve rate of filtration and washing.

METALLIZATION - Isolation of the coupled dye before converting to the nickel complex resulted in a stronger more intense product than metallization of the coupled slurry.

Better lightfastness and darker bluer color was obtained by use of ammonia than with sodium acetate and caustic soda.

The 18 hour development period used in this formula was adopted for the preparation of a sample for evaluation since best lightfastness was obtained with the longer period. If the product proves to be of interest, further study of conditions could be undertaken.

Yield is the average of two experiments and while it is representative may not be equal to a real yield.

A. D. REIDINGER

7/29/47

ADR:CG