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KREBS PIGMENTS DEPARTMENT
256 VANDERPOOL STREET
NEWARK, NEW JERSEY

NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

JACKSON LABORATORY

PIGMENTS GROUP RESEARCH REPORT

TITLE: PIGMENTS FROM DERIVATIVES OF 2-AMINO-BENZOIC ACID
(ANTHRANILIC ACID) AND RELATED INTERMEDIATES

Period Covered: February 3, 1947 - February 20, 1948.

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JACKSON LABORATORY

PIGMENTS GROUP RESEARCH REPORT

TITLE: PIGMENTS FROM DERIVATIVES OF 2-AMINO-BENZOIC ACID
(ANTHRANILIC ACID) AND RELATED INTERMEDIATES.

PERIOD COVERED: February 3, 1947 to February 20, 1948.

CHARGE: A-II-C-236

SUBMITTED BY: A. D. Reidinger

DATE SUBMITTED: 3/16/48

APPROVED BY: D. B. Killian

DATE ISSUED: 3/26/48

INTRODUCTION:

Investigation was made of the usefulness as diazo components of a number of intermediates related structurally to 2-amino benzoic acid (anthranilic acid). Some of these had been evaluated a number of years ago and in view of the results then obtained, further study appeared to be warranted. As a basis for comparison, couplings of anthranilic acid to various second components were used. Improvements in the Lake Red D type pigment (anthranilic Acid $\rightarrow$ Beta Naphthol) and in Pigment Scarlet Lake (anthranilic Acid $\rightarrow$ R-Salt) were looked for. It was also planned to check earlier work which indicated that pigment of "Watchung" Red shade (Permanent Red 2B Acid $\rightarrow$ BON) could be obtained from derivatives of anthranilic acid or their isomers.

SUMMARY AND CONCLUSIONS:

Of the intermediates tried, 4-chlor-2-amino benzoic acid appears to be of most interest. The manganese salt of the coupling to BON was a maroon pigment somewhat lighter than RT-521-D (TOB $\rightarrow$ BON, Mn) with much yellower undertone. It may have application in automotive enamels, particularly in metallic finishes in which a yellow tint is desirable. A sample, K-2512, has been placed on outdoor exposure in an alkyd enamel formulation (Series 7117 and PLM #143). The K-2512 formula is attached.

A sample (KS-144) representing the manganese salt of 6-chlor-2-amino benzoic acid $\rightarrow$ BON was also prepared for evaluation. This is a maroon about equal in depth to RT-533-D (PCAMSA $\rightarrow$ BON) and therefore lighter than the 4-chlor derivative. It is of interest because the intermediate can be made from a cheap by-product of the Chambers Works 6-chlor-2-nitro-toluene.

A close tinctorial match for "Watchung" Red, RT-428-D, was obtained from 2-chlor-5-amino benzoic acid coupled to BON (Ca salt), provided the color was flushed into varnish. The dried toner was weak. This intermediate is at present too expensive for consideration.

p-amino benzoic acid coupled to BON also approximated the "Watchung" Red shade. The higher cost of this intermediate compared to Red 2B acid would make its use uneconomic.

Aminoterephthalic acid coupled to Beta Naphthol (Ca salt) may be of interest as an intermediate for a Lake Red D type pigment. The product does not show the sensitivity to drier exhibited by Lake Red D but on the other hand has poorer lightfastness.

DISCUSSION OF RESULTS:

4-chlor-2-amino benzoic acid

- BON The Mn salt is described above. The Ca was similar in shade but duller and less lightfast.
- Beta Naphthol. The Ba salt showed no advantage over Lake Red D. The product was somewhat yellower and weaker and exhibited the characteristic sensitivity to metallic drier.
- R-Salt In the form of Pigment Scarlet Lakes of RL-211-D type, the products obtained were hard in texture and weak in tinting strength. Pulp of barium and strontium toners, tested by paper dyeings, showed no advantage over Pigment Scarlet in strength or in lightfastness. In the form of paper coatings (brushout) the strontium toner exhibited excellent light resistance.

5-chlor-2-amino benzoic acid.

- BON The manganese salt is a dull maroon of no interest.
- BN This product is similar to that from the 4-chlor isomer.
- PMP The Ba salt is a strong clear tinted yellow possessing very poor lightfastness.

6-chlor-2-amino benzoic acid.

- BON The Mn salt is discussed in the Summary. This product exhibited instability in the making formula and also in the enamel from it, which turned brown on aging. Development of the color at 80°C. instead of at a boil gave more consistent results. The Ca salt, prepared by a resinated formula, is a dark transparent red possessing excellent baking and bleed resistance.

2-chlor-5-amino benzoic acid

- BON The Ca salt is close to "Watchung" Red, RT-428-D, in shade and if flushed from the filter cake into varnish is equal in strength. Drying the color resulted in a hard, weak pigment. Lightfastness and bleed properties were inferior to the "Watchung" colors.

→ Beta Naphthol. Ba and Ca salts had more intense masstones and less bronzy finish than the corresponding anthranilic acid → BN pigments but were weaker due presumably to poor texture of the dry color.

→ PMP The Ba salt is a reddish shade yellow of fair lightfastness. The combination is probably too expensive to merit consideration.

2-chlor-5-amino-4-sulfo benzoic acid

→ BN Barium and calcium salts slightly weaker than obtained from the unsulfonated intermediate. Otherwise similar.

→ BON Calcium salt was weak as a dry color with somewhat poorer strength but more intense masstone than the unsulfonated intermediate.

→ R-Salt Barium lake of RL-211-D type was hard textured and weak in tinting strength.

P-Amino Benzoic Acid

→ BON The calcium salt is considerably yellower in shade than "Watchung" Red Toner, RT-428-D, is slightly worse in lightfastness and definitely inferior in bleed properties. Texture of the dried product was good. The higher cost of this intermediate compared to Red 2B Acid would make its use uneconomic.

Aminoterephthalic Acid

→ PMP Both Ba and Ca salts are very weak yellows, approximating Benzidine Yellow YT-459-D in shade. The Ca toner is lighter and stronger than the Ba salt and shows a definite advantage in lightfastness over YT-459-D. Its poor tinting strength would be a handicap to its promotion.

→ BN The Ba salt is a weak red of no interest. The Ca salt is superior tinctorially and although somewhat bluer in tint may be of interest as a Lake Red D type. It appears to be less sensitive to metallic driers than the latter pigment but is not as good in lightfastness.

→ BON The coupled dye was completely soluble as the soda salt and was not converted to the metal salts.

5-chlor Methyl Anthranilate

→ Beta Naphthol. The product of this combination is an orange somewhat yellower than Permatone Orange, YT-419-D, in shade with excellent lightfastness of full strength draw-down.

→ PMP A reddish yellow much weaker than the strong type Benzidine Yellow, YT-353-D, with about equal lightfastness.

Diazotisation of this intermediate was effected by use of nitrosyl sulphuric acid. Since coupling did not take place readily in acid solution, neutralization of the excess acid was necessary. As the 5-chlor derivative is soluble in hydrochloric acid solution, it may be possible to develop a better method for diazotization.

3:5 Dichlor Methyl Anthranilic acid

→ Beta Naphthol. An orange similar to Orange OF (DCB → PMP) in shade but considerably weaker. The difficulty of diazotizing and coupling may account for the lack of strength and also the poor lightfastness which was obtained.

→ Phenyl Methyl Pyrazolone. A reddish yellow similar to that from the 5-chlor derivative but considerably weaker.

5,5' Bisanthranilic Acid

→ R-Salt. A deep maroon pigment, considerably bluer than Azo Bordeaux Lake, EE-36-D, and superior in lightfastness. Because of hard texture of the dry color, evaluation was made by flushing from the water paste.

EXPERIMENTAL DETAILS:

The combinations tested and the corresponding notebook references are listed below:

Anthranilic Acid

→ 1-phenyl-3-methyl-5-pyrazolone	NB 1236	Expt. 4
→ Beta Naphthol	"	16, 21, 22
→ Beta oxy naphthoic acid	"	18, 25
→ R-Salt	"	36, 51

2-amino-4-chlor benzoic acid

→ PMP	NB 1236	Expt. 4, 9
→ BN	"	Expt. 22
→ BON	"	18, 25, 27
→ R-Salt	"	12

2-amino-5-chlor benzoic acid

→ PMP	NB 1236,	Expt. 4, 58
→ BN	"	22, 42
→ BON	"	19, 25, 27, 31
→ R-Salt	"	36, 51

2-amino-6-chlor benzoic acid

→ BON	NB 1260,	Expt. 15, 24, 35,
		40, 48, 53
	NB 1279,	Expt. 9, 14, 35, 46

2-chlor-5-amino benzoic acid

→ PMP	NB 1236,	Expt. 4, 58
→ BN	"	Expt. 22, 42
→ BON	"	19, 25, 27, 31
→ R-Salt	"	36, 51

2-chlor-5-amino-4-sulfo benzoic acid

→ BN	NB 1236,	Expt. 22, 42
→ BON	"	Expt. 19
→ R-Salt	"	Expt. 12, 36

P-amino benzoic acid

→ BON	NB 1236,	Expt. 27, 31
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Amino Terephthalic Acid

→ PMP	NB 1236,	Expt. 53
→ BN	"	"
→ BON	"	"

5-chlor Methyl Anthranilate

→ PMP
→ BN
→ BON

NB 1236, Expt. 33
" Expt. 30, 47
" Expt. 50

3:5 Dichlor Methyl Anthranilate

→ PMP
→ BN
→ BON

NB 1236, Expt. 33
" Expt. 30, 47
" Expt. 50

5,5' Bianthranilic Acid

→ R-Salt

NB 1279, Expt. 30

Attached is the formula for the preparation of K-2512 (4-chlor-2-amino benzoic acid → BON, Mn). The 6-chlor derivative was made in similar manner except that it was developed at 80°C instead of at boil.



FORMULA SHEET
(8-26-47)

COLOR CODE

Date Mar. 19, 1948

NAME Vernon Toner

N- 2512

REMARKS

Yellow Underdone Barren for evaluation.

REACTED ON

Lab. 1260-13

REACTANT

1.0

REACTANT No. 1260-13

Lab. 1260-13

Lab. No.	REACTANT	Wt. (g.)	Vol. (ml.)	Temp. (°C.)	REMARKS	Yield (g.)
44	Sodium Soda, 100% (ca. 50% NaOH sol'n.)	44	300	2500	To cold water, add	7
172	Sodium-sulfonate acid 100%	172	875	1625	ADD Heat to 104-106°F. Stir 10-20 minutes to dissolve (Test: slight on cy paper) Take to at 32-36°F. using ice	
240	Ice				Add	57
71	Sodium nitrate "as is" (Cr. 92% NaNO ₃)		30	250	dissolved in cold water. Stir 2-3 minutes Dump in as fast as possible	7
92	Sulfuric Acid 100% (ca. 31-45% H ₂ SO ₄ sol'n.)	92			Stir 40-60 minutes at 35-40°F. (Test: CR+, K+ thru out) Couple.	25
44	Sodium Soda, 100% (ca. 50% NaOH sol'n.)	44	180	1500	To cold water add	
200	"Althosol" Acid DON				Start agitator. Turn on steam Add in 3-5 minutes Heat to 130-140°F. Stir 10-20 minutes to dissolve. Take to at 59-61°F. with cold water and ice. Add all at once	82
160	Soda Ash		75	625	dissolved in water at 135-140°F.	3
10	Sodium Soda, 100% (ca. 50% NaOH sol'n.)	10			Couple into DON solution in 30-40 minutes. (Test: BY + thru out coupling). If necessary add (Final test: Diac -, DON +, pH 9.6 - 9.8)	
500	Salt		1220	10,000	Stir 30-40 minutes. Filter Filter and wash with about dissolved in cold water (Test Filtrate slight on BY)	71
			3000	25000	Reslurry filter cake in	

FORMER

LAB. FOR

COST GROUP

SIGNATURE

GOAL YIELD

FORMULA CHECK

- 2 -

COLOR CODE

DATE: Apr. 12, 1948 NAME

Haroon Tencer

IC 2512

REMARKS

REMARKS (continued)

QTY	DESCRIPTION	QTY	QTY	QTY	QTY
36	Pure Soap	20	275	Add	39
				dissolved in	
				cold water.	
				Then add	
15	Sodium Acetate	30	250	dissolved in	1
	Crystals			cold water.	
				Stir 5-10 minutes Add in 10-12 minutes	
315	Manganese sulphate	200	1650	dissolved in	326
	(ca. 86% MnSO ₄)			water at 122-125°F.	
				Stir 5-10 minutes	
				(Tests all normal 6.2 - 6.6)	
				Adjust to pH 7.6 - 8.2 with	
eg. 1	Caustic Soda, 50%			Heat to 210-212°F. in 20-35 minutes	
	(ca. 50% NaOH sol'n.)			Held at 210-212°F for 10 minutes	
		9500		Flowed to	
				Temperature 150-160°F.	
				Record pH (normal pH 7.2 - 7.6)	
				Filter, wash 20% H ₂ O	
				Dry at 140°F.	
				Pulverize	

PACKAGE 125

LOT NO. Drum

COST GROUP 36

SIGNATURE

A. D. REIDINGER

460 146. as is.

DUP050066914

NOTES FOR K-2512

This maroon is characterized by its yellow undertone and tint in relation to mazzon. The formula is based on procedures used for similar pigments and no information was obtained as to effect of variables.

Complete dissociation of 4-chlor anthranilic acid gave some difficulty due to the low solubility of its hydrochloride. The effect of a longer stirring period was not determined.

Coupling in the presence of sodium carbonate proceeds readily if the pH is maintained above 9.6. Addition of caustic soda may be made if necessary.

Isolation of the dye gave a darker bluer product than when carried straight thru. It may be possible to avoid washing with salt solution by adjustment of pH after coupling to about 8.0.

A. D. REIDINGER

3/19/48.

ADR:CC