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PIGMENT COLOR RESEARCH REPORT
JACKSON LABORATORY
PIGMENTS GROUP RESEARCH REPORT

PIGMENTS FROM DERIVATIVES OF 2-AMINO-BENZOIC ACID AND RELATED INTERMEDIATES (Cont'd.)

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JACKSON LABORATORY

PIGMENTS GROUP RESEARCH REPORT

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

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INTRODUCTION:

This report is a continuation of KN-48-4 and KN-49-16 and covers additional work done on pigments from anthranilic acid derivatives. Because of the desirable tinctorial properties and the excellent outdoor exposure resistance in metallized enamel and lacquer films, exhibited by the manganese toner of 4-chloranthranilic acid and beta-oxy-naphthoic acid (coded RT-608-D), further investigation of substituted amino-benzoic acids as diazo components was carried out. This work had the objectives of obtaining data to support a patent application and to discover new products of related composition.

SUMMARY AND CONCLUSIONS:

The work covered by this report included the following topics -

1. Evaluation of other 4-substituted anthranilic acids as diazo components.

2. Study of effects of position of chlorine and other substituents in anthranilic acid.

3. Investigation of some poly-substituted anthranilic acids.

4. Evaluation of other metallic salts of 4-chlor-anthranilic acid and of 4-nitro-anthranilic acid coupled to beta-oxy-naphthoic acid.

5. Combination of anthranilic acid derivatives with other coupling components.

6. Esters of substituted anthranilic acids as diazo components.

7. Isomers of anthranilic acid as diazo components.

8. Evaluation of quality of 4-chloranthranilic and 4-nitro-anthranilic acid samples.

9. Study of diazotization technique.

10. Improvement in baking properties of RT-608-D.

Several 4-substituted anthranilic acids (4-bromo-, 4-methyl-, 4-nitro-, and 4-trifluoro methyl-anthranilic acid) were evaluated as diazo components in the beta-oxy-naphthoic type of pigment. Of these, the 4-nitro derivative appears to be of greatest value. The maroon produced by conversion to the manganese salt, (KS-275) was much yellower in shade than RT-608-D but exhibited excellent two-tone and was equal to or slightly better than the latter in outdoor durability. This amine is also estimated to be somewhat cheaper than 4-chlor-anthranilic.

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Evidence was obtained that substitution of chlorine in the 4-position, as in 4-chlor-anthranilic acid, resulted in tinctorial properties and outdoor durability superior to the 5- and 6-isomers. In the case of the nitro group the advantage of the 4-position over the 5- was apparent in respect to tinctorial properties but was not evident in exposure tests. These findings were used as the basis for a patent application.

Presence of other substituents in addition to those in the 4-position resulted in products which were duller in shade.

Several other metallic derivatives of the 4-chloranthranilic acid → BON dyestuff merit comment.

The strontium salt (KS-400) was a dark masstone, yellow undertone red with good lightfastness and bleed resistance. Altho suitable for use in vinyl plastic its cost was too high for this purpose.

Chromium derivatives were generally poor in color retention on outdoor exposure. However, a sample prepared in alcoholic medium (KS-409) was only slightly inferior to the manganese toner. Equal or slightly superior to the latter were mixed chromium/manganese derivatives made in ethylene glycol (KS-408) and in alcohol (KS-411), respectively. Only KS-408 was close to RT-608-D tinctorially.

The copper salt (KS-414) was equal and the nickel salt (KS-260) slightly inferior in color retention compared to the manganese derivative prepared as control. However, the latter was somewhat less lightfast on outdoor exposure than the standard sample of RT-608-D. Neither the copper or nickel derivative was as intense as RT-608-D.

A number of components, other than beta-oxy-naphthoic acid, were coupled to 4-chlor- and 4-nitro-anthranilic acids and converted to representative metallic derivatives. Of these the copper complex salt of the dyestuff - 4-nitro anthranilic acid coupled to Naphthanil RL (the p-anisidide of beta-oxy-naphthoic acid) - was of interest because of its tinctorial and working properties in enamel systems. This maroon, KS-389, (coded ART-647-D) is characterized by dark masstone and blue tint and in a metallized film exhibits excellent intensity and lightfastness.

Light reds of excellent lightfastness by Fade-O-Meter test were obtained by coupling the methyl esters of 4-chlor- and 4-nitro-anthranilic acids to Naphthanil ASE. Exposure of printing ink films is being made to determine their value as poster reds.

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None of the isomers of anthranilic acid or of several substituted derivatives which were tried gave products of noteworthy merit. The manganese salt of m-amino-benzoic acid and BON, and the strontium salt of p-amino-benzoic acid and BON, were yellow undertone reds which were evaluated in enamel and vinyl plastic films respectively but were found to be inferior to existing products.

Quality of 4-chlor-anthranilic acid was found to vary according to the method of preparation. Intermediate obtained in the laboratory by permanganate oxidation of para-chlor-ortho-toluidine was of much higher purity than material made at Orchem by amidation of 2,4 dichlorbenzoic acid. However, it appears that the amidation process can be controlled to give amine of satisfactory quality.

Similarly, 4-nitro-anthranilic acid was obtainable in pure form by permanganate oxidation of para-nitro-ortho-toluidine. However, a more economical method consisting of amidation of 2-chlor-4-nitrobenzoic acid is being studied by Jackson Laboratory chemists.

A procedure for diazotizing 4-chlor-anthranilic acid was worked out. An inverse method in which the solution of the sodium salt with the sodium nitrite is run into hydrochloric acid at 0-3°C has given the best results. 4-nitro-anthranilic acid is also readily diazotized by this method.

DISCUSSION:

1. Other 4-Substituted Anthranilic Acids

Use of 4-nitro-anthranilic acid as a component of a BON, manganese maroon necessitated variations in the process employed in the case of 4-chlor-anthranilic acid. These included development of the coupled soda salt at a boil in the presence of rosin and use of a greater amount of caustic soda during the development of the manganese toner. The properties of the product are described above.

Similarly, in the case of 4-methyl anthranilic acid, use of excess alkali was required to stabilize the toner (KS-273) during development. The product was only slightly bluer than RT-608-D but was noticeably inferior on outdoor exposure.

4-brom-anthranilic acid also produced a maroon (KS-427) slightly bluer in tint and metallier than RT-608-D which was inferior in light retention.

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Trifluor methyl anthranilic acid gave as a BON, Mn pigment, a light red (KS-399) which exhibited excellent lightfastness in the Fade-O-Meter. However, this did not show any advantage over RT-428-D (when tested in vinyl plastic) and, because of the prospective high cost of the intermediate, is not of practical interest.

2. Effect of Position of Substituents

BON-Mn pigments made from anthranilic acids containing chlorine as a substituent in the 4-, 5-, and 6-positions differ markedly in tinctorial properties and in outdoor durability. The product from 5-chlor anthranilic acid (KS-306) is a yellowish maroon, much duller than RT-608-D - the 4-chloro counterpart. On exposure it was inferior in color retention. From 6-chlor anthranilic acid a light bluish maroon (KS-144) was obtained, which also exhibited greater color change on exterior exposure.

A comparison of the products from 4- and 5-nitro anthranilic acid confirm the indication of superior color value obtainable from the 4-substituted amine. However, light resistance, in contrast to the relationship of the chlor-anthranilic acid pigments, was found to be equally good. Notwithstanding its merit in this respect, the dullness of the 5-nitro-anthranilic acid maroon would prevent its application as an automotive pigment. The detrimental effect of the 5-nitro derivative was also evident in a product prepared from mixed 4- and 5-nitro anthranilic acid.

3-nitro-anthranilic acid gave a BON, Mn pigment of deep maroon shade which was hard and weak as a dry color. When flushed into varnish, an intense blue undertone and tint were obtained which, however, exhibited poor lightfastness.

3. Poly-substituted Anthranilic Acids

2-amino-4-methyl-5-chloro-benzoic acid and 2-amino-4-chloro-5-methyl-benzoic acid, the carboxy analogs of Lake Red C Base and Red 2B acid, respectively, gave as BON-Mn pigments, dull reds of relatively light shade much inferior to the corresponding sulphonic acid derivatives. A deeper but also dull product was obtained from 2-amino-4-chlor-5-nitro anthranilic acid. From these results and those discussed above, it may be concluded that to obtain the desired type of BON-Mn pigment, only the 4-position in 2-amino-benzoic acid should be occupied by a substituent.

The calcium toner obtained with the carboxy analog of Lake Red C Base was a dark bluish red having very poor lightfastness. The amount of Red 2B acid counterpart was insufficient for preparation of calcium or other metallic derivatives.

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2-amino-3-naphthoic acid, which may be regarded as a substituted anthranilic acid (in 4 and 5 positions) produced a BON, Mn maroon, which was darker in masstone than RT-608-D but not sufficiently blue or intense to serve as a shading maroon. Blends with RT-608-D were dull and in addition exhibited poor lightfastness on outdoor exposure.

4. Other Metallic Salts.

A number of other metallic salts of 4-chlor anthranilic acid ⟶ BON were prepared and evaluated in addition to the manganese toner. On the basis of rubout and Fade-O-Meter tests none of these possessed lightfastness exhibited by RT-608-D. The calcium toner, KS-307, was a dull maroon which was poor in lightfastness, both in the Fade-O-Meter and on exterior exposure. The barium salt, KS-308, was a dull red of poor lightfastness, particularly when exposed to the weather. The strontium salt, KS-400, is described in the summary.

The chromium salt, K-259, was considerably duller in full shade enamel than RT-608-D and much inferior in the exposed metallized finish. Efforts were made to prepare the chromium complex in which the metal is coordinated with the azo nitrogen. Because of the low solubility of the dyestuff in water, other solvents - ethylene glycol and ethyl alcohol - were also employed. The structure of the resulting products was not established and it is possible that only normal metallic salts were obtained. The product made in alcohol slurry, KS-409, was rated only slightly inferior in outdoor durability to the manganese toner but was considerably lighter and yellower in shade.

The combined chromium-manganese derivative was also made, using both ethylene glycol and alcohol as the medium. These were equal and slightly superior, respectively, in exterior color retention compared to the manganese toner control.

Iron, cobalt, nickel and copper all produced maroons of dark masstone and dull undertone which, with the exception of the nickel derivative, were poor in lightfastness in the Fade-O-Meter. However, on exterior exposure tests the copper and nickel toners were equal to or only slightly inferior in color fastness to the manganese control for the series. Unfortunately, the slightly inferior performance of the latter compared to the standard sample of RT-608-D leaves this property in some doubt. Excessive reactivity in enamel was observed in the case of the nickel derivative.

Zinc and lead salts of 4-chlor anthranilic acid ⟶ BON possessed some merit in respect to tinctorial characteristics (intense full shade enamels) but were noticeably deficient in lightfastness when exposed outdoors.

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A number of metallic derivatives of the 4-nitro anthranilic → BON were also made and evaluated by rubout test. The chromium, nickel and copper salts were bluer and duller in varying degrees compared to the Mn toner KS-275 and were by Fade-O-Meter test poorer in lightfastness. The lead salt was bluer but not duller. However, lightfastness was inferior. As in the case of 4-chlor anthranilic acid, the Ba and Ca derivatives were not of interest (dull and poor in lightfastness). The strontium toner resembled the 4-chloro counterpart.

5. Other Coupling Components

4-chlor-, 4-methyl-, and 4-nitro anthranilic acids were coupled to the following components and the dyestuff converted to the metallic derivatives indicated.

- Naphthanils AS, ASD, RL, OL, SW, MX, TR, BG, BO, OP, KR, BR and EL. Copper and/or nickel complexes.

- Beta-Naphthol, Ba and Ca salts.

- R-Salt - Ba, Sr salts.

- Acetoacetanilide, Mn, Ca, Ba, Sr salt (4-chlor anthranilic acid only).

- Phenyl-Methyl-Pyrazolone, Mn, Ca, Ba, Sr salt. (")

- 2,4-Dihydroxyquinoline, Ni derivative.

Of greatest interest are the maroon pigments obtained from Naphthanil couplings by conversion to the copper complex as disclosed in USP-2,416,248 (DuPont). The anthranilic acid-Naphthanil AS copper combination has found application in paper dyeing because of its excellent lightfastness but it proved to be too dull and reactive in an automotive type enamel to be suitable for such use. The product obtained from 4-chlor anthranilic acid and Naphthanil ASD was somewhat more intense but also exhibited pronounced reactivity in alkyd enamel systems. Some improvement in both properties resulted from use of Naphthanil RL (p-anisidide of BON). However, the most satisfactory combination was found to be 4-nitro anthranilic acid and Naphthanil RL. The copper complex of this dyestuff, KS-389 (ART-647-D) ground to an enamel of good consistency. It is characterized by its deep masstone and strong blue tint and its excellent gloss both in full shade and metallized films. On exterior exposure it exhibited lightfastness equal to Naphthanil Maroon, RT-566-D, and its superiority in gloss retention, and in resistance to bronzing make it of interest as a blue type shading maroon.

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Of the other Naphthanils tried, MX merits further study in view of its lower price. Although the maroon obtained with 4-nitro anthranilic acid and this Naphthanil was yellower and somewhat weaker than the NRL product, it was similar in other respects.

4-methyl anthranilic acid in combination with NASD gave results by rubout tests which were comparable to the 4-chloro derivative.

Nickel and cobalt salts gave less desirable complexes than did copper, usually much duller. However, more light resistant ZnO tints could be obtained with nickel. No products of interest resulted from use of other metals - Mn, Cr, Ca, Sr, Ba.

Couplings of 4-chlor-, 4-methyl-, and 4-nitro-anthranilic acid to beta-naphthol gave no barium or calcium toners which would represent any improvement over Lake Red D (anthranilic acid → beta-naphthol, barium salt). Many of the combinations were inferior in tinctorial properties or in lightfastness.

Couplings of the same amines to R-Salt resulted in two products which possessed some merit. The strontium toners of all exhibited superior lightfastness compared to Pigment Scarlet Lake RL-211-D but none possessed equal strength if compared on the basis of equal dye content. The 4-chlor anthranilic acid derivative, KS-367, which was the stronger of the series, exhibited very good lightfastness and migration characteristics in vinyl but was not of interest because of its inherent weakness.

4-methyl-anthranilic acid when converted to a lake of RL-211-D type, produced a much bluer shade product than obtained from anthranilic acid. Other properties such as ink texture, baking and bleed resistance, and lightfastness of prints on outdoor exposure were fully equal to RL-211-D. Although the bluer shade of this product, KS-368, was desirable, the higher materials cost limit its possibilities.

4-chlor anthranilic acid coupled to acetoacetanilide and to 1-phenyl-3-methyl-5-pyrazolone gave no products of interest when converted to Ba, Sr, Ca and Mn salts. Those derived from acetoacetanilide were very weak, greenish shade yellows; those from phenyl-methyl-pyrazolone were of medium shade.

Nickel derivatives of anthranilic acid and 4-chlor- and 4-nitro anthranilic acids coupled to 2,4-dihydroxy quinoline were browns of excellent light resistance. The 4-chloro combination was fully equal to Green Gold, YT-562-D, in this respect as well as in representative bleed properties. On the basis of amounts of nickel chloride and NaOH used, these products appear to be complex salts in which the metal is at least partially coordinated.

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6. Esters of Substituted Anthranilic Acid

The methyl esters of 4- and 5-chlor anthranilic acids and of 4- and 5-nitro anthranilic acids were coupled to representative Naphthanils. Only the combinations of 4-chlor- and 4-nitro anthranilic acids with Naphthanil ASE and of 4-nitro anthranilic acid with Naphthanil SW were of particular interest. These were medium shade reds of excellent lightfastness (in full strength) very similar to the Poster Red, K-1335 (2:5 dichloraniline → NOL). The NASE products, KS-456 and 458 are being exposed in printing ink films. Whiting lakes were also made using these toners but when tested in composition linoleum failed to show any advantage over existing standards.

The 4-substituted anthranilic acid esters with NASD and NOL gave orange pigments similar in shade to Permatone Orange, YT-419-D. None possessed a distinct advantage in tinctorial properties or in lightfastness but the 4-nitro anthranilic ester → NOL product may merit consideration if 4-nitro anthranilic acid becomes available in volume.

7. Isomers of Anthranilic Acid

M-aminobenzoic acid coupled to BON gave only one metallic salt of interest - the manganese toner (KS-449). This product was a red considerably darker than RT-525-D (and slightly lighter and duller than RT-533-D) with equal lightfastness by Fade-O-Meter test. In enamel, however, it was inferior in exterior exposure characteristics. Other metallic salts (Ca, Ba, Sr, Ni, Cu, Zn, Pb) gave products of inferior lightfastness although the nickel derivative which was duller and bluer than RT-608-D, exhibited only a slight disadvantage in this respect. All were poor in dry texture and were flushed into the varnish to obtain satisfactory dispersion.

P-aminobenzoic acid formed a very dull manganese salt although brighter products of unstable form could apparently be obtained at low development temperatures. Of other metallic salts, the nickel and strontium toners (in pulp form) were of some interest. The former was somewhat lighter and bluer than RT-608-D with comparable lightfastness. The latter (KS-451) was similar in shade and lightfastness to the anthranilic and 4-chlor anthranilic acid counterparts but because of its poor texture was less satisfactory in vinyl plastics. Other metallic derivatives were dull or poor in lightfastness.

Some substituted m-aminobenzoic acids tested as components of BON, Mn pigments gave the following results. From 3-amino-4-chlor benzoic acid a maroon slightly lighter and bluer than RT-608-D was obtained which, however, was inferior in lightfastness by Fade-O-Meter test. 3-amino-4-methyl benzoic acid gave a yellowish red - even yellower in hue than obtained from the unsubstituted M-amino benzoic acid. The corresponding methoxy derivative from 3-amino-p-anisic acid resulted in a dull blue shade maroon of inferior lightfastness.

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One substituted p-aminobenzoic acid (4-amino-3-nitro benzoic acid) gave a brown BON-Mn derivative of no interest.

8. Quality of 4-Chlor-Anthranilic Acid

4-Chlor-anthranilic acid made by permanganage oxidation of para-chlor-ortho-toluidine was obtained in the laboratory with a purity of 97-100% (nitrite value). Melting points ranged from 231-234° to 236-237°C (uncorrected). A charge made in the Newark semi-works and deacetylated at the Chambers Works was of similar quality. However, yields by this route were economically low.

The intermediate initially made at Orchem by amidation of 2,4 dichlorbenzoic acid was of lower purity, nitrite value 90-96%. The impurities - 2,4 dichlorbenzoic acid and probably some 2,4 diaminobenzoic acid - interfered with diazotization and when present in sufficient amount resulted in inferior durability of the BON, Mn Maroon, RT-608-D. Subsequent modification of the process have yielded intermediate of greatly improved quality.

9. Study of Diazotization Technique

Direct diazotization of 4-chlor-anthranilic acid by addition of sodium nitrite was not successful due to the insolubility of the amine in acid medium. Use of an agent such as sodium xylene sulfonate increased the rate of absorption of nitrite but was not considered practical because of the cost.

Diazotization by rapid addition of the acid to the alkaline solution of amine and sodium nitrite was satisfactory on a small laboratory scale and when pure intermediate was used. However, increase in charge size with the less turbulent agitation prevented immediate diazotization of the amine and resulted in a considerable amount of undiazotizable material.

Best results were obtained by an inverse method in which the solution of the soda salt and of sodium nitrite (at 30-35°C) is run into hydrochloric acid (3.3 mols) at 0-3°C. Some undiazotized residue (about 2%) is usually obtained even with amine of good quality. This has been identified as partly 4-chlor-anthranilic acid and partly diazo-amino compound. When intermediate of poorer quality is used, the residue filtered from the diazo is greater, amounting to 10-15%.

4-Nitro-anthranilic is also readily diazotized by the above procedure. It was necessary, however, to increase the volume of the soda salt solution to avoid precipitation of the amine. Use of a higher temperature may have the same effect.

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10. Improvement in Baking Properties

The maroons from substituted-anthranilic acids exhibit the poor baking resistance of BON, Mn maroons. Some improvement, in the case was obtained by formation of the Mn salt in alcohol slurry instead (of of water. However, results were inconsistent and, since the pro- (RT-608-D, cedure was not economic, this lead was abandoned.

EXPERIMENTAL DETAILS:

Details may be found under the following references.

[4-Chlor-anthranilic Acid.]

→ Acetoacetanilide	N.B. 1353, Exp. 49	
→ Beta Naphthol	N.B. 1353, Exp. 1	
→ Beta-oxy-naphthoic acid.		
Various metals	N.B. 1320, Exp.	31, 32, 43, 54, 62, 63, 64, 65, 68, 69, 70, 71, 72.
	N.B. 1338, Exp.	56
	N.B. 1353, Exp.	20, 23, 28, 56, 62, 76.
	N.B. 1370, Exp.	25, 28, 31, 32, 34.
Process variations	N.B. 1353, Exp.	20, 41, 43, 45, 48, 50.
	N.B. 1370, Exp.	9, 10, 11, 12, 23, 24, 35, 42, 43, 53, 55.
Quality of amine	N.B. 1338, Exp.	14, 22, 42, 85.
	N.B. 1353, Exp.	13, 27, 75.
	N.B. 1370, Exp.	29, 40.
	N.B. 1385, Exp.	11, 12.
→ 2,4 Dihydroxy-Quinoline	N.B. 1396, Exp.	14.
→ Naphthenils	✓N.B. (1353) Exp.	30, 34, 35, 36, 37, 39, 40, 43, 73, 65, 71, 77.
→ Phenyl-methyl-pyrazolone	N.B. 1353, Exp.	52.
→ R-Salt	N.B. 1353, Exp.	7, 15.

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5-Chlor-anthranilic Acid	
→ Beta-oxy-naphthoic acid	N.B. 1338, Exp. 55, 68 N.B. 1353, Exp. 17, 18, 19, 20, 25, 29.
→ Naphthanils ✓	N.B. 1292, Exp. 31. N.B. 1353, Exp. 35.
6-Chlor-anthranilic Acid	
→ Beta-oxy-naphthoic acid	N.B. 1279, Exp. 9, 14, 35, 46. N.B. 1338, Exp. 74, 80.
→ Naphthanil / SD ✓	N.B. 1353, Exp. 35.
2-Chlor-5-amino-benzoic acid	
→ Naphthanils ✓	N.B. 1353, Exp. 9. N.B. 1370, Exp. 66.
4-Brom-anthranilic Acid	
→ Beta-oxy-naphthoic acid	N.B. 1370, Exp. 46. N.B. 1385, Exp. 5.
4-Methyl-anthranilic Acid	
→ Beta-Naphthol	N.B. 1353, Exp. 1.
→ Beta-oxy-naphthoic acid	N.B. 1320, Exp. 42. N.B. 1338, Exp. 23, 27, 38.
→ Naphthanil ASD ✓	N.B. 1353, Exp. 30, 34, 40.
→ R-Salt	N.B. 1353, Exp. 7, 15.
3-Nitro-anthranilic Acid	
→ Beta-oxy-naphthoic acid	N.B. 1385, Exp. 23.
4-Nitro-anthranilic Acid	
→ Beta-oxy-naphthoic acid	N.B. 1320, Exp. 42. N.B. 1338, Exp. 21, 25, 26, 29, 30, 37, 41, 62, 80. N.B. 1353, Exp. 45 N.B. 1370, Exp. 17, 63, 70. N.B. 1385, Exp. 1, 36.
→ Beta-Naphthol	N.B. 1353, Exp. 1.
→ R-Salt	N.B. 1353, Exp. 7, 15.
→ Naphthanils ✓	N.B. 1353, Exp. 30, 34, 43, 64, 66. N.B. 1370, Exp. 4, 18, 20, 22, 62, 70, 75. N.B. 1385, Exp. 3, 38.

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5-Nitro-anthranilic Acid

→ Beta-oxy-naphthoic acid N.B. 1338, Exp. 62, 80.
N.B. 1353, Exp. 24.
N.B. 1370, Exp. 30, 33.

→ Naphthanil ✓ N.B. 1370, Exp. 36.

4-Trifluormethyl-2-aminobenzoic Acid

→ Beta-oxy-naphthoic acid N.B. 1320, Exp. 9.

2-Amino-4-methyl-5-chlor-benzoic Acid

→ Beta-oxy-naphthoic acid N.B. 1353, Exp. 2.
N.B. 1370, Exp. 72.
N.B. 1385, Exp. 47, 49.

2-Amino-4-chlor-5-methyl-benzoic Acid

→ Beta-oxy-naphthoic acid N.B. 1370, Exp. 5, 6, 72.

2-Amino-4-chlor-5-nitro-benzoic Acid

→ Beta-oxy-naphthoic acid N.B. 1338, Exp. 73.

M-Aminobenzoic Acid

→ Beta-oxy-naphthoic acid N.B. 1385, Exp. 13, 17, 18, 28, 29.

P-Aminobenzoic Acid

→ Beta-oxy-naphthoic acid N.B. 1385, Exp. 13, 14, 15, 20, 28, 29.

3-Amino-4-chloro-benzoic Acid

→ Beta-oxy-naphthoic acid N.B. 1385, Exp. 19, 30, 45.

3-Amino-4-methoxy-benzoic Acid

→ Beta-oxy-naphthoic acid N.B. 1385, Exp. 23, 30.

3-Amino-4-methyl-benzoic acid

→ Beta-oxy-naphthoic acid N.B. 1385, Exp. 19, 30.

4-Amino-3-nitro-benzoic Acid

→ Beta-oxy-naphthoic acid N.B. 1385, Exp. 45.

2-Amino-3-Naphthoic Acid

→ Beta-oxy-naphthoic acid N.B. 1353, Exp. 38, 41, 67.

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