The Hydrolysis of certain Arylamides used as Dye Intermediates and the Preparation of certain related Thiol-acids and Arylamides.

A Thesis submitted in fulfilment of the requirements for the Degree of Doctor of Philosophy in the Faculty of Science of the University of Glasgow.

by

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Note:- The references listed above are also cited in their appropriate places in the text.

PART I.

The Hydrolysis of certain Arylamides used as Dye Intermediates.

The Naphtol - AS - dyestuffs[*] of the I.G.Farbenindustrie A-G. belong exclusively to the Azo series of dyestuffs and form an extremely important and modern branch of colour chemistry. They are insoluble azo dyestuffs produced on the fibre by the combination of a NAPHTOL (usually an arylamide of 2-hydroxy-3-naphthoic acid) and a diazotised amine.

In the eighties of last century the Para-red process for dyeing cotton was discovered. The process consists of padding the cotton cloth in an alkaline solution of β-naphthol containing a little Turkey red Oil (sodium sulpho ricinoleate), drying the impregnated cloth and then treating in a second bath with a diazotised solution of p-nitroaniline to which sodium acetate has been added. In this way the dyestuff is developed on the fibre.

The observation, that the arylamides of 2-hydroxy-3-naphthoic acid in alkaline solution are substantive and stable and that, without intermediate drying, they can be absorbed by cotton in the presence of formaldehyde and

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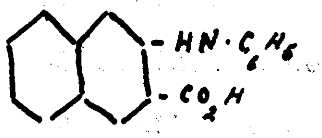
[*] The correct spelling of the registered British Trade mark is NAPHTOL-AS and is used throughout in this paper.

and protective colloids (sodium ricinoleate etc.) has revolutionised the production of fast dyeings and prints on cotton fabrics. These arylamides can be coupled with diazotised bases to form dyestuffs which, compared with Para red, not only show a better fastness to washing, light and acids but also give very bright dyeings. In consequence of the great expansion of this discovery there is a large assortment of these Naphtol-AS products on the market. By the use of various substituted 2-hydroxy-3-naphthoic acid arylamides and of high molecular aceto-acetic arylamides etc., and coupling these with the large variety of amines, (after diazotisation), now on the market it is possible for the modern dyer to produce shades of excellent fastness from the purest yellow through all colours of the spectrum to black not only on vegetable fibres such as cotton, linen, jute, and hemp but on wool (cf. Everest and Wallwork, J. Soc. Dyers & Colourists, 1934, 50, 38), silk (cf. H. Görlich, Textilber., 1935, 16, 441), rayon, acetate rayon (cf. R. Metzger and H. Röhling, Textilber., 1937, 18, 644), and wool-spun rayon unions (cf. W. Kirst, Textilber., 1937, 18, 739).

The shades obtained possess exceedingly good strength and many can be classed, as regards fastness properties, with the Indanthrone Vat dyestuffs. One of the more recent combinations - Naphtol AS-ITR + Fast Red ITR Base not only resembles Turkey red (i.e. Alizarin dyed on aluminium mordant) in brightness of shade but surpasses it in fastness and in simplicity of production.

The first arylamide of 2-hydroxy-3-naphthoic acid to be described was the anilide, which was obtained by Schöpff (Ber., 1892, <u>25</u>, 2740) by heating equimolecular quantities of 2-hydroxy-3-naphthoic acid and aniline in presence of phosphorus trichloride. According to Schöpff (loc.cit.) when excess of aniline is used the main product is 2-anilino-3-naphthoic acid (1) while the anilide of 2-anilino-3-naphthoic acid (2) and the anilide of 2-hydroxy-3-naphthoic acid (3) are formed as by-products.



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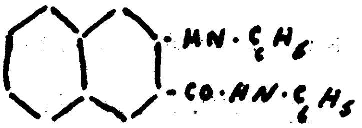

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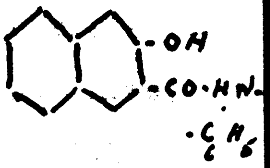
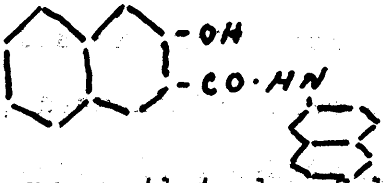


(3)

Nine years later, that is in 1901, Strohbach (Ber., 1901, <u>34</u>, 4152) described the preparation of the β-naphthylamide



It would appear that when Schöpff and Strohbach published their papers neither had any idea of the important properties possessed by the anilide and β-naphthylamide of 2-hydroxy-3-naphthoic acid and it was not until about the year 1912 that the Griesheim Elektron Co. (member of the present I.G.Farbenindustrie A-G.) issued their first patent (English Pat., 6,379, 1912; cf. also Badische An. and Sod. Fab. D.R.P., 221, 481, of 1909) and their commercial application as components of azoic colours commenced.

At the present time there are about two dozen Naphtols and about three dozen Amines ("Fast Bases") available for commercial purposes.

In this investigation the constitution of some of these Naphtols is considered. As stated above these are mainly arylamides of 2-hydroxy-3-naphthoic acid although a few are arylamides of other acids. F.M.Rowe and his collaborators have studied the action of dilute sulphuric acid, boiling at 140-145°C. (cf. Rowe and Levin, J. Soc. Dyers & Colourists 1924, 40, 227; Rowe & Levin, Ibid., 1925, 41, 354; F.M.Rowe, Ibid., 1930, 46, 227;) and more recently (F.M. Rowe & C.H. Giles, Ibid., 1935, 51, 287) of concentrated sulphuric acid on members of the Naphtol AS series and have found that, in general, when the arylamine component does not contain an alkoxyl group, hydrolysis takes place readily and the arylamide is decomposed into 2-hydroxy-3-naphthoic acid and the arylamine. When concentrated sulphuric acid is used, however, the 2-hydroxy-3-naphthoic acid is sulphonated under the conditions employed; also the arylamine is formed in improved yield.

When an alkoxyl group is present in the arylamine residue of the Naphtol, however, it is decomposed into unstable amino-phenols during the hydrolysis with dilute and concentrated sulphuric acid. For example, F.M.Rowe (Ibid. 1930, 46, 227) found that, Naphtol AS-OL, which is the O-anisidide of 2-hydroxy-3-naphthoic acid, on hydrolysis with boiling dilute sulphuric acid gave 2-hydroxy-3-naphthoic acid and O-amino-phenol. In 1934, S. Ueno and T. Suzuki (Jour. Soc. Chem. Ind. Japan, 1934, 37, 233B-234B) were able to show that Naphtol AS-ITR and Naphtol AS-LT were the 5-chloro-2-4-dimethoxyanilide and the 5-methoxy-2-toluidide, respectively of 2-hydroxy-3-naphthoic acid. These authors treated the above mentioned Naphtols with an aqueous caustic soda solution of about 50 per cent strength at about 200°C. for several hours in an autoclave, fitted with a stirrer and were successful in decomposing them into the original acid and amino components; the alkoxyl group remaining unaffected. In this way, therefore, Ueno and Suzuki were successful in overcoming the defects of the sulphuric acid methods of hydrolysis.

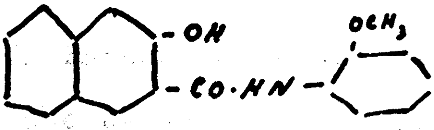
In the present investigation use has been made of potassium hydroxide in alcoholic solution as the hydrolysing agent. The Naphtol is dissolved in alcoholic caustic potash solution (16 grams. caustic potash, pure sticks, dissolved in 100 c.c. of alcohol) and boiled for about six hours under a reflux condenser. At the end of this period the alcohol is distilled-off and the residue poured into three times its bulk of cold water. The solution so obtained is extracted with ether, which removes the arylamine. The ethereal layer is washed with water until free from alkali and then transferred to a suitable flask and the ether distilled-off. The crystalline residue , usually obtained on cooling, is purified by crystallisation from a suitable solvent; water being extremely suitable for most of the alkoxy-amines examined. In cases where the arylamine was a liquid it was usual to identify by conversion into the acetyl derivative. The aqueous portion after the ether extraction contains the acid in the form of its potassium salt which is decomposed into the free acid on acidification with hydrochloric acid. When the acid is 2-hydroxy-3-naphthoic acid this is precipitated on acidification and is isolated by filtering off and washing free from mineral acid and potassium chloride with cold water. The acid can then be identified after crystallisation from a suitable solvent. In the case of 2-hydroxy-3-naphthoic acid dilute alcohol is most suitable for this purpose.

In all the Naphtols examined it was found that the alcoholic caustic potash decomposed them into the original acid and the original arylamine - the alkoxyl group present in the arylamine residue being unaffected by the hydrolysis.

In this way it has been possible to show that:-

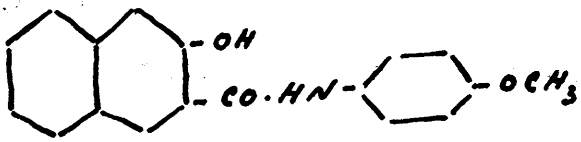
1) Naphtol AS-OL (I.G. Farbenind. A-G.) is the o-anisidide of 2-hydroxy-3-naphthoic acid.-

I.



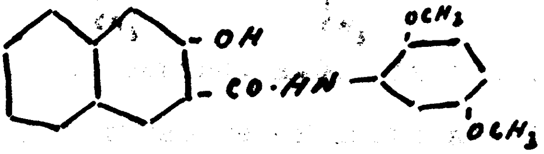
2) Naphtol AS-RL (I.G. Farbenind. A-G.) is the p-anisidide of 2-hydroxy-3-naphthoic acid.-

II.



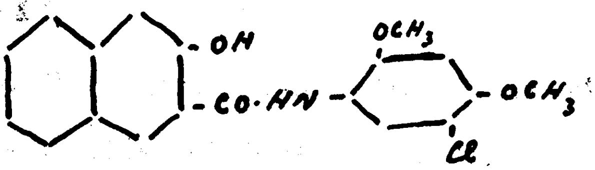
3) Naphtol AS-BG (I.G. Farbenind. A-G.) is the 2:5-Dimethoxy-anilide of 2-hydroxy-3-naphthoic acid.-

III.



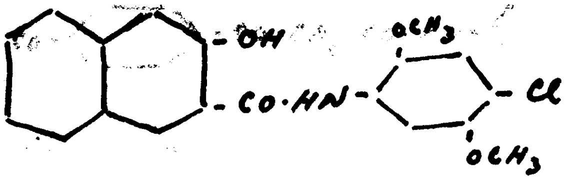
4) Naphtol AS-ITR (I.G. Farbenind. A-G.) is the 5-chloro-2:4-dimethoxyanilide of 2-hydroxy-3-naphthoic acid.-

IV.



5) Naphtol AS-LC (I.G. Farbenind. A-G.) is the 4-chloro-2:5-dimethoxyanilide of 2-hydroxy-3-naphthoic acid.-

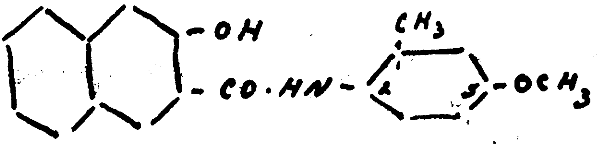
V.



6) Naphtol AS-LT (I.G. Farbenind. A-G.) is the 5-methoxy-

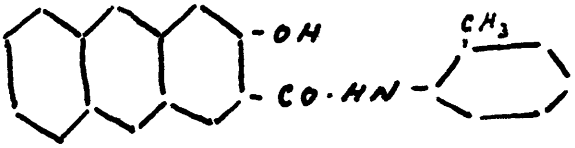
-2-toluidide of 2-hydroxy-3-naphthoic acid.-

VI.



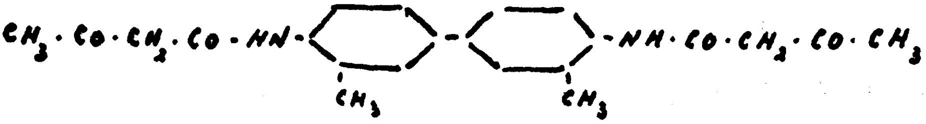
7) Naphtol AS-GR (I.G. Farbenind. A-G.) is the o-toluidide of 2-hydroxy-anthracene-3-carboxylic acid.-

VII.



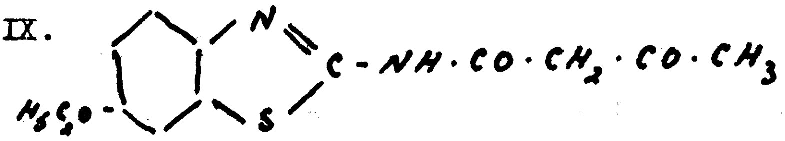
8) Naphtol AS-G (I.G. Farbenind. A-G.) is diaceto-acetic-o-tolidide.-

VIII.



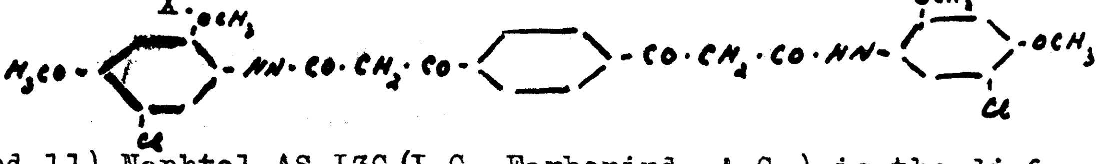
9) Naphtol AS-L4G. (I.G. Farbenind. A-G.) is the 2-amino-6-ethoxybenzothiazole derivative of aceto-acetic acid.-

IX.



10) Naphtol AS-LG (I.G. Farbenind. A-G.) is the di-2,4-dimethoxy-5-chloro-anilide of Terephthaloyldiacetic acid.-

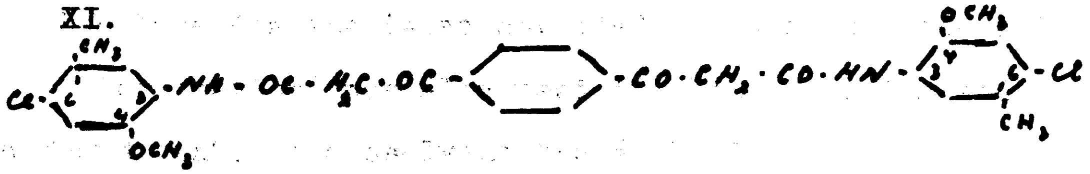
X.



and 11) Naphtol AS-L3G (I.G. Farbenind. A-G.) is the di-6-chloro-4-methoxy-3-toluidide of Terephthaloyldiacetic

acid.-

XI.



In each instance confirmation of these constitutions was obtained by direct synthesis.

To try out this method of hydrolysis further arylamides of several acids were prepared and characterised. In each case hydrolysis with alcoholic caustic potash caused the arylamide to be decomposed into the original acid and the arylamine. In addition to alcoholic potash as the hydrolysing agent, mono-, di- and tri-ethanolamines have been tried. Unsuccessful results were obtained when using solutions of the ethanolamines in alcohol but when the arylamides were dissolved in the ethanolamines themselves (i.e. without dilution with any solvent) and boiled for 6-7 hours, under a reflux air-condenser, on a sand-bath, complete decomposition of the arylamide into the amino and acid components ensued. The separation of the amino and acid components after the hydrolysis was carried out in a manner similar to that used in separating these components after hydrolysis with alcoholic potash and which has already been described. The mono-, di-, and tri-ethanolamines used were supplied by the Union Carbide and Carbon Corporation of New York (London Agents - General Metallurgical and Chemic

Ltd., Moorgate, London E.C.2).

Ethylene diamine (also supplied by Union Carbide and Carbon Corporation) was also used in this connexion and it was found that, on dissolving the arylamide in the ethylene diamine and boiling the mixture under a reflux air-condenser on a sand bath for 6-7 hours complete decomposition of the arylamide took place; the original acid and amino component being obtained in the usual manner.

Piperidine was also tried but no hydrolysis of the arylamides occurred.

The general principle which can be stated as a result of this investigation is that, 16 per cent alcoholic potassium hydroxide solution, mono-, di-, and tri-ethanolamine and ethyl-ene diamine, at the boil, hydrolyse, completely and smoothly, arylamides of hydroxy carboxylic acids into the original acid and arylamine component. When the arylamine component contains an alkoxyl group this latter remains unaffected and so the defects of the sulphuric acid methods of hydrolyses used by F. M. Rowe and his collaborators (loc. cit.) are thus eliminated. As was to be expected, however, hydrolysis of arylamides of aceto-acetic acid, benzoyl acetic acid, and terephthaloyl - diacetic acid, with these hydrolytic agents, caused the acid component to be completely decomposed with the result that it could not be isolated and so identified;

the arylamine component in these cases was, of course, easily obtained and identified.

The arylamides of the various acids prepared will now be theoretically discussed under the following sectional headings:-

Section I:- Arylamides of 2-hydroxy-3-naphthoic acid.

Section II:- Arylamides of 5:6:7:8-Tetra-hydro-2-hydroxy-3-naphthoic acid.

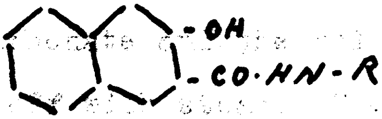
Section III:- Arylamides of 2-hydroxy-anthracene-3-carboxylic acid.

Section IV:- Arylamides of Aceto-acetic acid.

Section V:- Arylamides of Benzoyl-acetic acid.

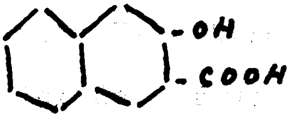
Section VI:- Arylamides of Terephthaloyldiacetic acid.

Section I. Arylamides of 2-hydroxy-3-naphthoic acid.



As already mentioned in the general theoretical section the majority of the Naphtols most used in commerce are arylamides of 2-hydroxy-3-naphthoic acid. 2-Hydroxy-3-naphthoic acid (I) crystallises

I.



in small yellow rhombic plates, from ~~which~~ dilute alcohol (50 parts water: 50 parts ethyl alcohol), which melt at 216°C., and gives in aqueous solution a characteristic blue coloration with ferric chloride solution.

The usual method, described in the literature, for the preparation of the arylamides of 2-hydroxy-3-naphthoic acid is to heat equimolecular proportions of the arylamine and the acid with phosphorus trichloride or thionyl chloride in an indifferent solvent such as toluene or xylene. For example, according to Ullmann "Enzyklopaedie der technischen Chemie", 2nd. Edition, Vol.7, page 819, the anilide of 2-hydroxy-3-naphthoic acid is prepared by suspending 188 kgm. of 2-hydroxy-3-naphthoic acid (100%) in 500 kgm. of toluene and mixing with 94 kgm. aniline, and treating the mixture with 65 kgm. of phosphorus trichloride at 80°C. over a period of 3 hours. The reaction mixture is then boiled for a further 3 hours, made slightly alkaline with sodium carbonate and the toluene and excess aniline distilled off with steam. The yield of anilide is stated to be 95-98% of Theory (cf. Chem. Fabrik. Griesheim Elektron, D.R.P. 293, 897; Chem. Zentr., 1916, II, 617; Frdl., 12, 912; also Schöpff Ber., 1892, 25, 2744). Another method mentioned in the literature consists in heating the methyl ester of 2-hydroxy-3-naphthoic acid and the arylamine with phosphorus oxychloride. Thus Strohbach (Ber., 1901, 34, 4152) prepared the β-naphthylamide of 2-hydroxy-3-naphthoic acid by melting together 28 gm. 2-hydroxy-3-naphthoic acid methyl ester and 20 gm. β-naphthylamine, and adding to the cooled melt 15 gm. phosphorus oxychloride and heating to 180-200°C. until the evolution of hydrochloric acid is completed. The powdered melt is boiled with water and the β-naphthylamide filtered off and finally recrystallised from a pyridine-water mixture.

During the course of this work it has been found that very good yields (over 90%) of arylamides of 2-hydroxy-3-naphthoic acid are obtained by dissolving equimolar proportions of 2-hydroxy-3-naphthoic acid and arylamine in a minimum amount of pyridine at 70°C., adding phosphorus trichloride over a period of a quarter of an hour and heating at 110-115°C. for 4 hours. The condensation product at this stage is usually a thick viscous syrup. On cooling, alcohol is added and the whole boiled - the arylamide separating out or crystallising out on standing overnight. The arylamide is filtered-off at the pump, washed with alcohol and finally dried. The filtrate contains some arylamide and this is isolated by first adding a little glacial acetic acid and finally water. The volume of water added should be 2 times the volume of the filtrate. The water must be added carefully and the whole well stirred during the water addition otherwise a sticky viscous semi-solid product is formed which only solidifies with difficulty. The precipitated arylamide is filtered off, dried and recrystallised as before. Thus, for example, confirmation of the constitution of Naphtol AS-LT which had been shown on hydrolysis with 16% alcoholic caustic potash solution to be the 5-methoxy-2-toluidide of 2-hydroxy-3-naphthoic acid was obtained by heating equimolar proportions of the acid and 5-methoxy-2-toluidine with a small amount of pyridine and the requisite amount of phosphorus trichloride at 115°C. for 4 hours (Full details are given in the experimental section). The yield of arylamide was 93% of theory. No depression of the melting-point of recrystallised Naphtol AS-LT was observed on mixing with the 5-methoxy-2-toluidide of 2-hydroxy-3-naphthoic acid (recrystallised) so obtained.

The following arylamides of 2-hydroxy-3-naphthoic acid have been prepared in connexion with this study.

1) The o-anisidide of 2-hydroxy-3-naphthoic acid to confirm the constitution of Naphtol AS-OL.

2) The p-anisidide of 2-hydroxy-3-naphthoic acid to confirm the constitution of Naphtol AS-RL.

3) The 2:5-dimethoxy-anilide of 2-hydroxy-3-naphthoic acid to confirm the constitution of Naphtol AS-BG.

4) The 5-chloro-2:4-dimethoxyanilide of 2-hydroxy-3-naphthoic acid to confirm the constitution of Naphtol AS-ITR.

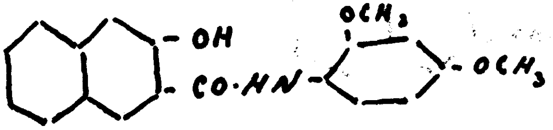
5) The 4-chloro-2:5-dimethoxyanilide of 2-hydroxy-3-naphthoic acid to confirm the constitution of Naphtol AS-LC.

6) The 5-methoxy-2-toluidide of 2-hydroxy-3-naphthoic acid to confirm the constitution of Naphtol AS-LT.

The following arylamides of 2-hydroxy-3-naphthoic acid were also prepared with a view to confirming the hydrolytic action of 16% alcoholic caustic potash, of the ethanolamines and of ethylenediamine on such arylamides.-

7) The 2:4-dimethoxyanilide of 2-hydroxy-3-naphthoic acid

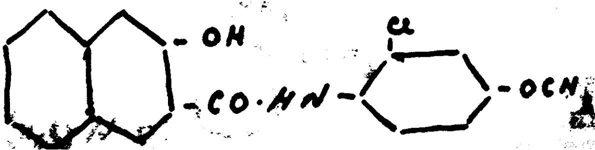
VII.



from 2-hydroxy-3-naphthoic acid and 2:4-dimethoxyaniline.

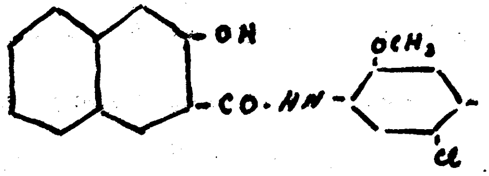
8) The 2-chloro-4-anisidide of 2-hydroxy-3-naphthoic acid from 2-hydroxy-3-naphthoic acid and 2-chloro-4-anisidine

VIII.



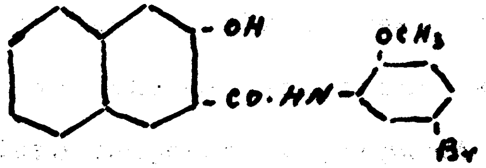
9). The 5-chloro-2-anisidide of 2-hydroxy-3-naphthoic acid from 2-hydroxy-3-naphthoic acid and 5-chloro-2-anisidine.-

IX.



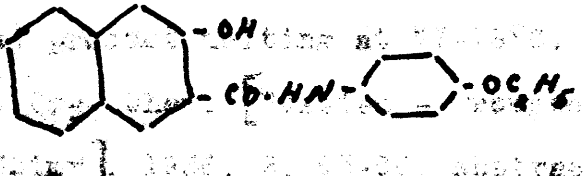
10). The 5-bromo-2-anisidide of 2-hydroxy-3-naphthoic acid from 2-hydroxy-3-naphthoic acid and 5-bromo-2-anisidine.-

X.



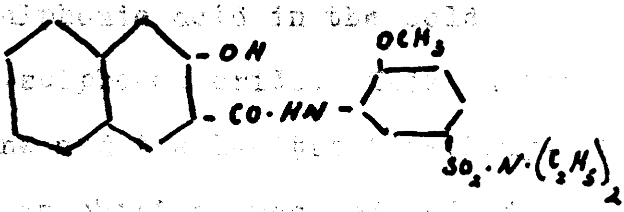
11). The p-phenetidide of 2-hydroxy-3-naphthoic acid from 2-hydroxy-3-naphthoic acid and p-phenetidine.-

XI.



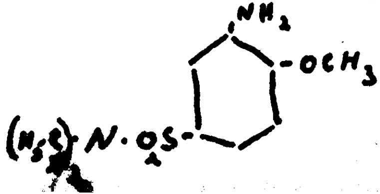
12). The 1-amino-2-methoxybenzene-5-sulphondiethylamide of 2-hydroxy-3-naphthoic acid from 2-hydroxy-3-naphthoic acid and 1-amino-2-methoxy-benzene-5-sulphondiethylamide.

XII.



According to Fierz-David-"Künstliche organische Farbstoffe", Ergänzungsband, Berlin, 1935, page 36, Fast Red ITR Base of the I.G.Farbenindustrie A-G. is 1-amino-2-methoxybenzene-5-sulphondiethylamide.-

XIII.



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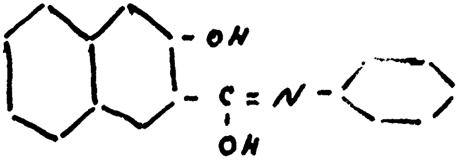
(Found N=10.61%, S=12.5% - calculated for $C_{11}H_{18}O_3N_2S$ - N=10.8% & S=12.4%). On recrystallisation from dilute alcohol (50 pts. alcohol and 50 parts water) Fast Red ITR Base crystallised in monoclinic colourless crystals which had a melting point of 105°C. In D.R.P.575, 216, of 26th. April 1933 (cf. also D.R.P.480, 814 of 13th. Sept., 1929) the preparation of 1-amino-2-methoxy-benzene-5-sulphondiethylamide by reduction of the corresponding nitro-compound is described and the melting-point is given as 104-105°C. The nitro compound is prepared by the condensation of 1-nitro-2-methoxy-benzene-5-sulphonic acid chloride and diethylamine and is described as a pale yellow crystalline (prisms) product melting at 77-78°C. In 1936 A. Jerschow, (Ind. Org. Chem. [Russian - Promyschlennost organitscheskoi Chimii], 1936, 2, 95-96, abstracted Chem. Zentrl., 1937, 108, I, 1020) published a proof of the constitution of Fast Red ITR Base. This author treated o-nitro-anisole with chloro-sulphonic acid in the cold and obtained o-nitro-anisole-5-sulpho-chloride. This latter was condensed with diethylamine and the 1-nitro-2-methoxy-benzene-5-sulphondiethylamide so obtained was reduced with zinc dust in a neutral medium and 1-amino-2-methoxy-benzene-5-sulphondiethylamide obtained; and this was found to be identical with Fast Red ITR Base.

Dyeing Properties of 2-hydroxy-3-naphthoic acid Arylamides.

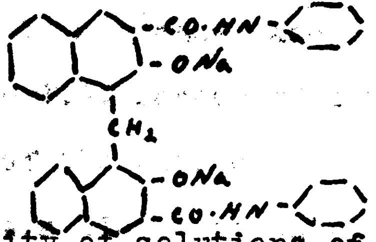
The increased substantivity of 2-hydroxy-3-naphthoic acid arylamides for cotton fibres as compared with that of β-naphthol, is attributed to the presence of the acylamino group, the relative stability of the combination with the cellulosic fibre being due to its strong association and residual valency. The affinity of vat dyes of the acylamino-anthraquinone type for cotton is explained on the same principle. In 1935, H.Krzikalla and B. Eistert, both of the I.G. Farbenindustrie A-G. Dyestuff laboratories (J. pr.Chemie, 1935, 143,50-58) carried out an investigation to ascertain whether the homologue of the anilide of 2-hydroxy-3-naphthoic acid (Naphtol AS), the anilide of 2-hydroxy-naphthyl-3-acetic acid, in which the acylamino group is separated from the naphthalene nucleus by a methylene group, is also more substantive than β-naphthol. The anilide of 2-hydroxy-naphthyl-3-acetic acid was prepared by the action of diazomethane on o-acetyl-β-hydroxy-naphthoic chloride and boiling the product with aniline. These Authors found that it yielded yellower dyeings than those from the anilide of 2-hydroxy-3-naphthoic acid and was not much more substantive than β-naphthol. The influence of the methylene group in lowering the substantivity of 2-hydroxy-3-naphthoic acid arylamides is attributed to its effect in interrupting the chain of conjugated double bonds and preventing enol formation. On the basis of these in-

:vestigations and in view of the low substantivity of 2-hydroxy-3-naphthoic-N-methyl-anilide and β-naphthol-3-sulphonanilide, it is concluded that the anilide of 2-hydroxy-3-naphthoic acid has the enolic structure --



The arylamides of 2-hydroxy-3-naphthoic acid are themselves water-insoluble bodies. Accordingly they can only be practically applied by being transferred into their sodium salts and in that form dissolved in water. To make these sodium salts in solution sufficiently stable for the purposes of the dyeing process, the addition of a protective colloid (e.g. sodium sulphoricinoleate) is essential. For the production of solutions of arylamides of 2-hydroxy-3-naphthoic acid the following method was adapted:-

The arylamide was pasted up with sodium sulphoricinoleate and caustic soda. During this process the sodium salt of the arylamide is formed and shows visibly by the greenish yellow colouring of the paste. Care must be taken that no small particles of arylamide remain unpasted as the arylamide which has not been transferred into its sodium salt cannot (or only with much difficulty) be dissolved. In view of this it was found advisable to warm the pastes to ensure complete formation of the sodium salt. The pastes prepared in this manner were made up to the necessary volume with hot water and complete solution obtained by subsequent boiling. Formaldehyde solution is added to the clear solution of the arylamide on cooling down to around 30°C. The addition of formaldehyde is necessary in order to prevent decomposition of the sodium salt of the arylamide on the fibre into free arylamide and caustic soda with consequent weakening of the dyeings. This is probably due not only to the action of the carbonic acid present in the air (cf. E.B.Higgins, J. Soc. D. and C., 1927, 43, 213) but even more to the hydrolysis which frequently occurs when salts of weak acids, e.g.arylamides, are present in solution with strong bases. The hydrolysis is greatly accelerated, however, by carbonic acid, both factors acting together when the impregnated material is exposed to the air. According to K. Brass and P.Sommer (Ber., 1928, 61, 993-1002) arylamides of 2-hydroxy-3-naphthoic acid react with formaldehyde in alkaline solution, in the same way as β-naphthol, to form methylene derivatives. Thus, when formaldehyde is added to an alkaline solution of the anilide of 2-hydroxy-3-naphthoic acid, the yellow di-sodium salt of the anilide of methylene-di-β-hydroxy-naphthoic acid is precipitated quantitatively by addition of common salt after some hours. Thus the stability of solutions of arylamides of β-hydroxy-



naphthoic acid after addition of formaldehyde appears to be due, therefore, to the presence of the methylene group in the ortho position to the hydroxyl group but the degree of dispersity and the colloidal nature of the higher molecular methylene derivatives are also partly responsible. In coupling with diazonium compounds 1 mol. of the methylene derivative reacts with 2 mols. of the diazonium compound with simultaneous elimination of the methylene group, forming the same azo compound as would be produced with the arylamide itself. The methylene bridge, therefore, does not appear to interfere with the coupling in any way.

With the addition of formaldehyde to the arylamide solution the latter is now ready for use. The bleached cotton yarn is padded in this liquor at around 30°C. for half an hour, as the arylamides are not instantly absorbed by the cotton fibre and it is only after acting upon it for some time that a balance results between the arylamide absorbed and that remaining in the bath. It may also be mentioned that the affinity of the arylamides of β-hydroxy-naphthoic acid is greater in the cold and is reduced at higher temperatures. The temperature of impregnation is, in general, about 30°C. In any case, according to trade circulars issued by the I.G. Farbenindustrie A-G. regarding the application of the Naphtols, temperatures above 45°C. should be avoided as a liquor containing formaldehyde is liable [illegible] to precipitate the arylamide of β-hydroxy-naphthoic acid at this temperature and this results in weak dyeings.

After impregnation with the arylamide solution, the yarn is squeezed thoroughly and then entered into a solution of the diazotised base in water. The yarn is worked in this developing bath for about 20 minutes, removed, and rinsed thoroughly with cold water to remove completely the diazo solution still adhering to the yarn. After rinsing, the yarn is soaped at around 85-90°C. for half an hour in a bath containing 1-2 gm. soda ash and 2-3 gm. soap (a good quality tallow soap [=61.5% 63% Fatty acids], was used in all cases) per litre. Finally, the dyed yarn is rinsed in luke-warm water and dried. The procedure for diazotising each of the various bases used is described in detail in the experimental section.

Each of the 2-hydroxy-3-naphthoic arylamides prepared by the author has been padded on cotton yarn and coupled with the following diazotised bases.-

1) 2:5-dichloroaniline (Fast Scarlet GG Base of the I.G. Farbenind. A.G.).

2) 5-chloro-2-toluidine (Fast Red TR Base of the I.G. Farbenind. A-G.).

3) 5-nitro-2-anisidine (Fast Red B Base of the I.G. Farbenind. A-G.)

4) o-amino-azo-toluene (Fast Garnet GC Base of the I.G. Farbenind. A-G.)

5) o-dianisidine (Fast Blue B Base of the I.G. Farbenind.A-G.).

and 6)/

and 6) 4'-methoxy-4-amino-diphenylamine (Variamine Blue
B. Base of the I.G. Farbenind. A-G.)

The shades produced varied from reddish-orange through the various shades of red to blue. It was observed that the shades produced by the various arylamides and the same base were very similar. The degree of fastness of the dyeings obtained from the various arylamides with the same diazotised base varied but this was not studied in any detail. As a matter of fact the question of fastness of the azoic dyeings has been the subject of many communications. For example, the following references may be mentioned in this connexion - P. Bean and F. M. Rowe (J. Soc. D. and C., 1929, 45, 67); "I.G. Ratgeber für das Färben von Baumwolle", Frankfurt, 1933, pages 558-569, while there has just been published by R.B. Foster, P.R. Mehta & K. Venkataraman (J. Soc. D. & C. 1938, 54, 209-215) a comprehensive paper on the fastness to Kier-boiling of these dyestuffs. A second paper by R. B. Foster, I.R. Ramachandran & K. Venkataraman loc. cit. 216-225) deals with the fastness to rubbing of the Naphtol AS-series of Azoic dyestuffs.

The shades produced on cotton yarn by the following arylamides of 2-hydroxy-3-naphthoic acid.-

1) The 5-methoxy-2-toluidide of 2-hydroxy-3-naphthoic acid (Naphtol AS-LT).

2) The 2:4-dimethoxy-5-chloro-anilide of 2-hydroxy-3-naphthoic acid (Naphtol AS-ITR).

3)/

3) The 2:5-dimethoxy-4-chloro-anilide of 2-hydroxy-3-naphthoic acid (Naphtol AS-LC).

4) The 2:4-dimethoxy-anilide of 2-hydroxy-3-naphthoic acid.

5) The 1-amino-2-methoxy-benzene-5-sulphondiethylamide of 2-hydroxy-3-naphthoic acid.

in combination with the diazotised bases already mentioned, are shown in the special "Dyeings" section at the end of the experimental part of this Thesis.

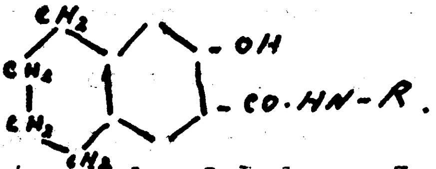
These five arylamides were taken as representative of the 2-hydroxy-3-naphthoic acid derivatives examined.

Hydrolysis of arylamides of 2-hydroxy-3-naphthoic acid.

Hydrolysis of all the arylamides of 2-hydroxy-3-naphthoic acid by 16% alcoholic caustic potash, mono, di-, and tri-ethanolamines, and ethylene diamine under the conditions outlined in the general theoretical section yielded in each instance -2-hydroxy-3-naphthoic acid and the arylamine.

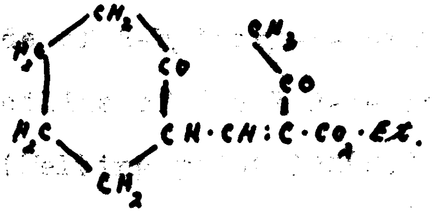
Full details of the hydrolytic conditions are given in the experimental section.

Section II. Arylamides of 5:6:7:8-Tetra-hydro-2-hydroxy -3-naphthoic acid.



5:6:7:8-Tetra-hydro-2-hydroxy-3-naphthoic acid was first described by G. Schroeter (Annalen, 1922, 426, 83-160. See especially pages 107-109 and 147). Schroeter prepared the acid from 6-hydroxytetralin by heating this compound under pressure with carbon dioxide in the presence of alkalis (Kolbe reaction). In 1935, R. Robinson and J. Walker (J. Chem. Soc., 1935, 1530-1533) synthesised the acid by condensing crude methoxymethylene-cyclohexanone (prepared by methylating hydroxymethylene-cyclo-hexanone in aqueous potassium hydroxide solution with methyl sulphate) with ethyl sodioacetoacetate. An intermediate product (pro:bably I) was formed in poor yield.

I.



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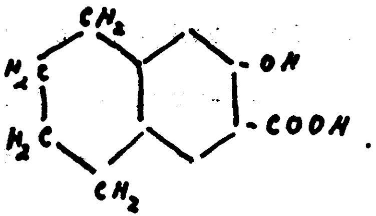


On further treatment with boiling alcoholic sodium ethoxide condensation and hydrolysis occurred and 6-hydroxytetralin-7-carboxylic acid (5:6:7:8-Tetra-hydro-2-hydroxy-3-naphthoic acid - II) was formed.

In French patent 814, 169, granted 17th. June. 1937. to the I.G. Farbenindustrie A-G. (abstracted Chem. Zentrl., 1938, 109, I, 434-435), the hydrogenation of aromatic or heterocyclic polynuclear hydroxy compounds in alkaline solution with hydrogen under pressure in the presence of hydrogenation-catalysts is discussed. Of special interest in this connexion is the description of the preparation of 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid from 2-hydroxy-3-naphthoic acid. For example 940 parts of 2-hydroxy-3-naphthoic acid are dissolved in a solution of 300 parts of potassium hydroxide in 5500 parts of water and hydrogenated at 120°C. under a pressure of 180 atmospheres in presence of a Nickel-Cobalt catalyst until no more hydrogen is absorbed. Thereupon the solution is separated from the catalyst by filtration and acidified with dilute sulphuric acid which precipitates the 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid. The yield of tetra-hydro acid is stated to be 85% of theory. Under similar conditions, it is claimed that the anilide of 2-hydroxy-3-naphthoic acid (Naphtol AS) provides the anilide of 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid (Melting point 183°C.) in 90% yield.

A supply of 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid was very kindly offered to the author by the I.G.Farbenindustrie A-G. The acid crystallised from dilute alcohol (50 parts alcohol: 50 parts water) in long narrow rectangular plates which had a melting-point of 178-179°C.

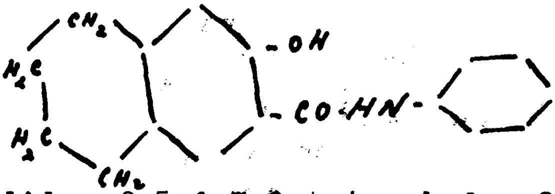
(Schroeter [loc. cit] gives M.Pt.177-178°C; Robinson & Walker [loc. cit.] gives M.Pt.178°C.). The acid was sparingly soluble in boiling water and gave a violet coloration on addition of ferric chloride solution to its aqueous solution (cold); the colour being similar to that given by the addition of ferric chloride solution to an aqueous solution of salicylic acid. It is worth noting that an aqueous solution of 2-hydroxy-3-naphthoic acid gives a blue coloration on addition of ferric chloride solution. On boiling the acid with acetic anhydride an acetyl derivative ($O.Ac - C_{10}H_{10} \cdot CO_2H$) was obtained and had a melting-point of 146-147°C. (Schroeter, loc. cit. found 142-143°).

The preparation of several arylamides of 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid is described in U.S. Patent 2,040, 397 (granted to H. Morschel of Germany, assignor to General Aniline Works, Inc., New York). The method of preparation described in this patent is to treat the acid with a slight excess of arylamine in an inert organic solvent such as toluene, nitrobenzene, etc. The mixture is heated to 80°C. and at this temperature phosphorus trichloride is added over a period of 1 hour. After boiling for 12 hours sodium carbonate solution is added and the solvent blown-off with steam. The reaction product which separates is filtered-off with suction. The arylamide so obtained is then recrystallised from a suitable solvent.

For the purpose of the present investigation the following arylamides of 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid were prepared:-

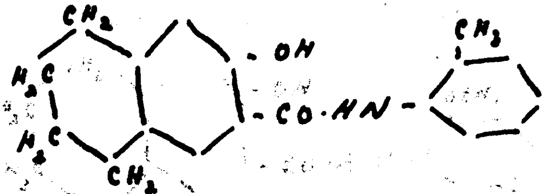
1) The anilide of 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid.-

(III).



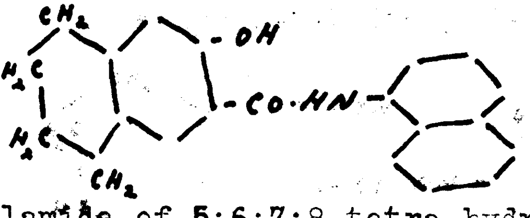
2) The o-toluidide of 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid.-

(IV).



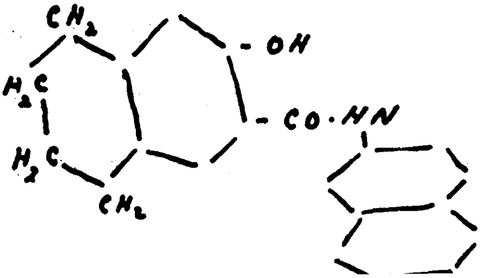
3) The α-naphthylamide of 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid.-

(V).



4) The β-naphthylamide of 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid.-

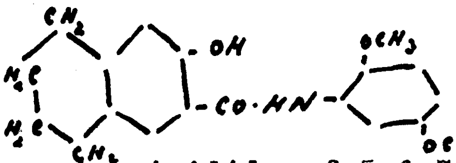
(VI).



5/

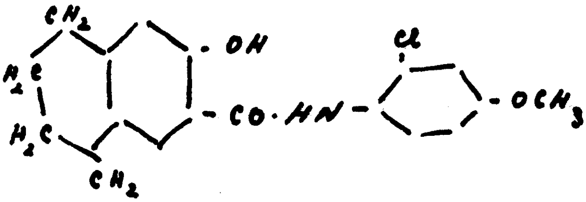
5) The 2:5-dimethoxy-anilide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.-

(VII).



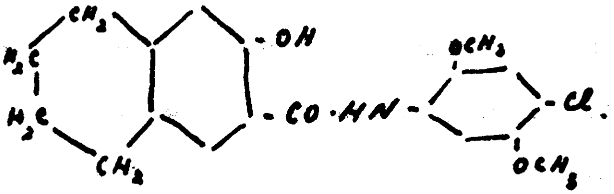
6) The 2-chloro-4-anisidide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.-

(VIII).



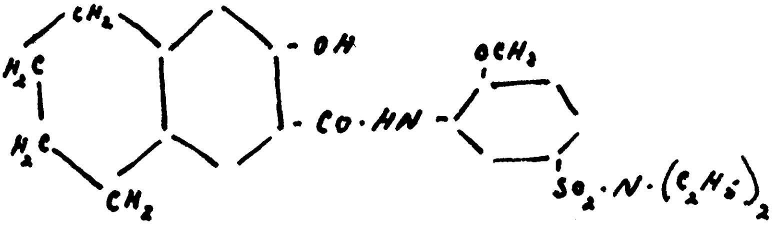
7) The 2:5-dimethoxy-4-chloro-anilide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.-

(IX).



and 8) The 1-amino-2-methoxy-benzene-5-sulphondiethylamide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.-

(X).



Some of the above mentioned arylamides were prepared in a manner similar to that described in U.S.Patent 2,040,397. referred to earlier; others were prepared by the "Pyridine" method, already used with success by the author for the preparation of arylamides of β-hydroxy-naphthoic acid (q.v.). The preparation of the majority of the arylamides mentioned had been completed before the above mentioned American Patent became generally available in the literature (U.S. Pat.2,040,397. was abstracted in Chem. Zentrl., 1936, <u>107</u>, II, 871). In any case it may be mentioned that the method of preparation referred to in U.S. Patent 2,040,397. is the one generally referred to in the literature for the preparation of arylamides of hydroxy-acids.

All of the arylamides of 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid prepared were colourless or pale yellow coloured crystalline bodies with sharp melting-points. They were all insoluble in boiling water but dissolved in warm aqueous solutions of sodium hydroxide with a bluish fluorescence (arylamides of 2-hydroxy-3-naphthoic acid dissolve inaqueous sodium hydroxide solutions with a greenish-yellow fluorescence).

Dyeing Properties of the arylamides of 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid.

The arylamides of 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid were applied to cotton yarn in a manner similar to that already described for the application of the arylamides of β-hydroxy-naphthoic acid. They are on the whole more easily soluble in aqueous sodium hydroxide solutions than the corresponding arylamides of β-hydroxy-naphthoic acid and partly in consequence of this do not give such strong dyeings when coupled with the diazotised bases. On padding the cotton yarn in the sodium salt solution of the arylamide for half an hour at 30°C. and squeezing thoroughly and evenly the yarn was quite white (cotton yarn when padded in the sodium salt solutions of the arylamides of β-hydroxy-naphthoic acid and squeezed was yellow in colour). On entering the impregnated yarn into the diazotised base coupling took place. In general poor shades (dull salmon pinks, browns and plums) were obtained with the various diazotised bases used. These arylamides, therefore, do not appear to have any ~~much~~ commercial value as dye intermediates.

Each of the arylamides of 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid prepared has been padded on cotton yarn and coupled with the same diazotised bases as were used in the experiments with the arylamides of β-hydroxy-naphthoic acid, viz:-

1) 2 : 5 - dichloro-aniline.
2) 5 - chloro - 2 - toluidine.
3) 5 - nitro - 2 - anisidine.
4) o - amino - azo - toluene.

5) o-dianisidine.
6) 4'-methoxy-4-amino-diphenylamine.

The shades produced by the various arylamides with the same diazotised base were similar.

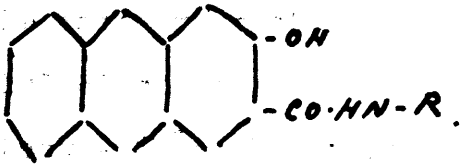
The various shades produced on cotton yarn by 1). the 2:5-dimethoxy-4-chloro-anilide of 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid and 2). the 1-amino-2-methoxy-benzene-5-sulphondiethylamide of 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid, which were considered representative of this group, in combination with the above mentioned diazotised bases are shown in the special "Dyeings" section.

Hydrolysis of the arylamides of 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid.

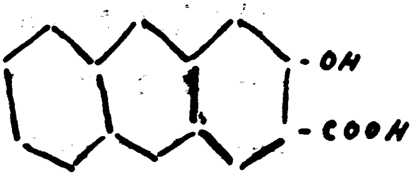
Hydrolysis of all the arylamides of 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid by 16% alcoholic potassium hydroxide, mono-, di-, and tri-ethanolamines, and ethylene diamine under the conditions already outlined yielded 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid and the arylamine.

Details of the hydrolytic conditions employed are given in the experimental section.

Section III. Arylamides of 2-hydroxy-Anthracene-3-carboxylic acid.

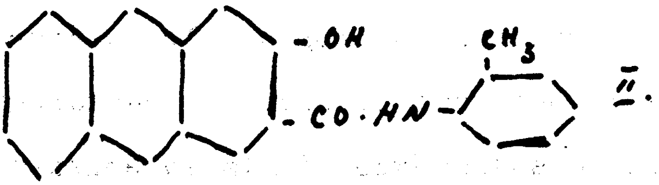


On hydrolysis of Naphtol AS-GR with 16% alcoholic potassium hydroxide solution, under the conditions already specified, it was observed that the acid produced was not 2-hydroxy-3-naphthoic acid (no characteristic blue coloration with ferric chloride). The acid, on recrystallisation from nitrobenzene, had a melting-point of about 298°C. (with decomposition), and analysis showed the acid to be probably a hydroxyanthracene carboxylic acid. The arylamine obtained on hydrolysis of the Naphtol was found to be o-toluidine. An examination of the literature showed that the I.G. Farbenindustrie A-G. had been granted a German Patent (D.R.P.554,786 granted 14/7/32) for the manufacture of arylamides of 2-hydroxy-anthracene-3-carboxylic acid (I), which were claimed to be valuable as dyestuff-intermediates. In October 1935, the I.G. Farbenindustrie A-G. were kind enough to supply the author with a good supply of this acid. The acid obtained was cry-



I.

:stallised from nitrobenzene (with the addition of norit) and no depression in melting-point was observed when the acid was mixed with the acid (recrystallised from nitrobenzene) obtained on hydrolysis of Naphtol AS-GR. H. E. Fierz - David in his book - "Künstliche organische Farbstoffe" Ergänzungsband, Berlin, 1935 page 38 and published in the late autumn of that year, mentions that Naphtol AS-GR is the o-toluidide of 2-hydroxy-anthracene-3-carboxylic acid (II).



Confirmation of this statement and of the hydrolytic experiments referred to above was obtained by direct syn:thesis of the Naphtol from the acid and o-toluidine.

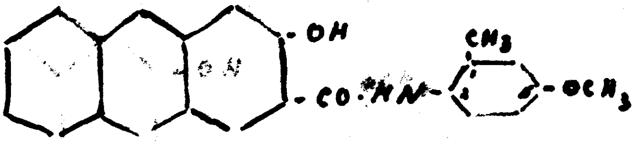
The preparation of 2-hydroxy-anthracene-3-carboxylic acid is described in D.R.P. 547,352 (I.G.) granted 22/3/32, in D.R.P. 553,538 (I.G.) granted 27/6/32, and in D.R.P. 564,129 (I.G.) granted 14/11/32.

In D.R.P.547,352, 2-hydroxy-anthracene-3-carboxylic acid is prepared from 2-chloro-anthracene-3-carboxylic acid (prepared by the reduction of the corresponding anthraquinone derivative with zinc dust and ammonia) by heating with a 15% aqueous solution of potassium hydroxide for 5-6 hours at 200-210°C. in a copper lined autoclave fitted with a stirrer. The reddish yellow solution so obtained is acidified with dilute mineral acid at the boil. The 2-hydroxy-anthracene-3-carboxylic acid thus precipitated is filtered off with suction, washed and dried. Similarly, the acid may be obtained by heating 2-chloro-anthracene-3-carboxylic acid with, water, potassium carbonate and some copper sulphate (dissolved in water) for 7 hours at 160-170°C. in a nickel-autoclave. D.R.P.553, 538 describes the preparation of the acid either from an alkali salt of 2-hydroxy-anthracene or from the free hydroxy compound in presence of alkali carbonates, by heating at high temperatures and pressures in an atmosphere of carbon dioxide. For example - I. the potassium salt of 2-hydroxy-anthracene is heated in an atmosphere of carbon dioxide in a pressure vessel for 9 hours at a pressure of 60 atmospheres and at a temperature of 260°C. or II. 2-hydroxy-anthracene and 3 parts potassium carbonate are heated for 11 hours in an atmosphere of carbon dioxide under a pressure of 80 atmospheres and at a temperature of 220-230°C. In D.R.P. 564,129 the acid is prepared by stirring 2-sulpho-anthracene-3-carboxylic acid into molten caustic potash at 200°C. and gradually raising the temperature to 260°C.- the melt assuming a yellow colour. Stirring is continued for 1 hour at 150°C.

after which time the melt is allowed to cool, diluted with water and the 2-hydroxy-anthracene-3-carboxylic acid finally precipitated by the addition of hydrochloric acid. The only arylamide of 2-hydroxy-anthracene-3-carboxylic acid in use commercially at the present time is the o-toluidide which is, as already mentioned, Naphtol AS-GR. The author, has, in addition to preparing the o-toluidide, prepared the following arylamides of 2-hydroxy-anthracene-3-carboxylic acid:-

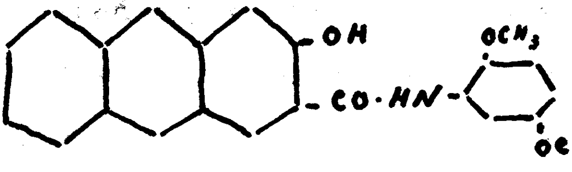
1). The 5-methoxy-o-toluidide of 2-hydroxy-anthracene-3-carboxylic acid.-

III.



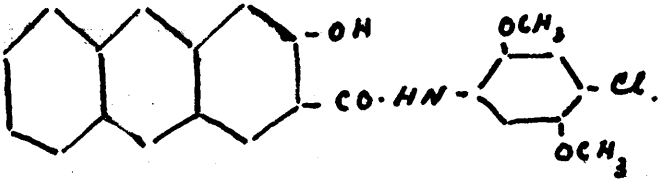
2). The 2:5-dimethoxy-anilide of 2-hydroxy-anthracene-3-carboxylic acid,-

IV.



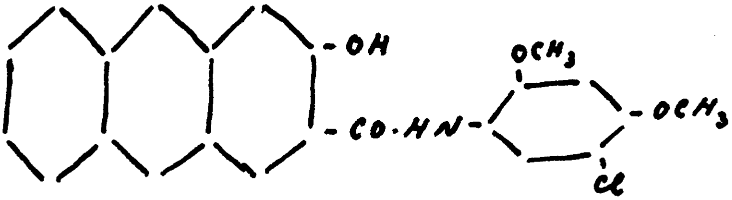
3). The 2:5-dimethoxy-4-chloro-anilide of 2-hydroxy-anthracene-3-carboxylic acid.-

V.



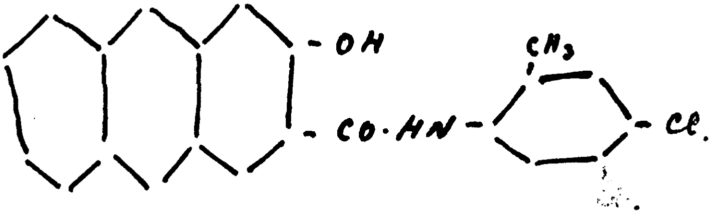
4). The 2:4-dimethoxy-5-chloro-anilide of 2-hydroxy-anthracene-3-carboxylic acid.-

VI.



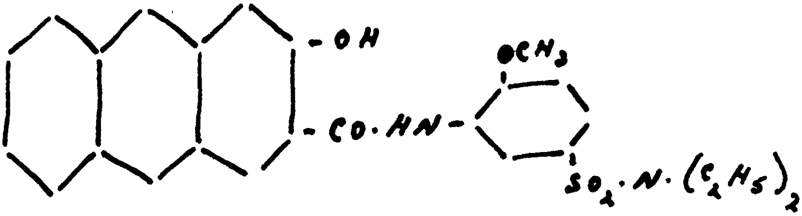
5). The 5-chloro-o-toluidide of 2-hydroxy-anthracene-3-carboxylic acid.-

VII.



and 6). The 1-amino-2-methoxy-benzene-5-sulphondiethylamide of 2-hydroxy-anthracene-3-carboxylic acid.-

VIII.



Some of the above mentioned arylamides were prepared by heating equimolar quantities of the acid and the arylamine in toluene solution to 70°C. adding phosphorus trichloride drop by drop and finally heating the mixture at around 110°C. until the evolution of hydrochloric acid has ceased. The arylamide which separates out on cooling is filtered-off, boiled with sodium carbonate solution (to remove acid) and then recrystallised from a suitable solvent. The cheapest and most convenient crystallising medium for these arylamides was found to be nitrobenzene.

This method of preparing the arylamides of 2-hydroxy-anthracene-3-carboxylic acid is the one recommended in D.R.P.554,786. It was also found that these arylamides could be prepared by the "Pyridine" process already used by the present author in preparing arylamides of 2-hydroxy-3-naphthoic acid and 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid. The procedure was similar to that used in the preparation of the arylamides of these two acids and consisted in dissolving 2-hydroxy-anthracene-3-carboxylic acid and the arylamine in a small amount of pyridine, adding phosphorus trichloride in small amounts at a time, when the temperature had reached 70°C., finally raising the temperature to 115°C. and heating at this temperature for four hours. During the course of the reaction the reactants were efficiently stirred. On adding alcohol when the temperature of the mixture had fallen, the arylamide separated out on standing. The arylamide was filtered-off with suction, washed with alcohol, dried and finally re-crystallised from nitrobenzene. Yields of over 90% of the theoretical were obtained.

All the arylamides of 2-hydroxy-anthracene-3-carboxylic acid prepared were either mustard yellow or orange coloured crystalline products. They were all insoluble in boiling water but dissolved in aqueous alkali hydroxide solutions with a reddish-orange colour. All the arylamides examined melted sharply at high temperatures.

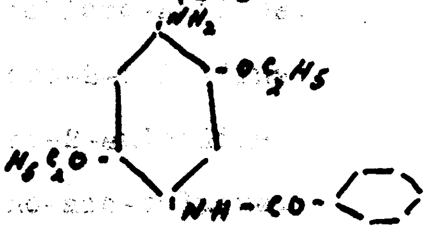
Dyeing Properties of 2-hydroxy-anthracene-3-carboxylic acid arylamides.

The outstanding property of the 2-toluidide of 2-hydroxy-anthracene-3-carboxylic acid (Naphtol AS-GR) is that it gives green shades on cotton yarn when this latter is impregnated with the sodium salt solution of the arylamide, squeezed and then coupled with either of the following diazotised bases:-

1). o-dianisidine (Fast Blue B Base I.G.).

2. 1-amino-4-benzoylamino-2:5-dimethoxy-benzene.
(Fast Blue BB. Base - I.G. -

for constitution cf. Lecture delivered by Dr. K. Holzach before the I.V.C.C., Stuttgart 28th. May 1936; cf. also Fierz - David - "Künstliche organische Farbstoffe" Ergänzungsband 1935, page 37).



and 3). 4'-methoxy-4-amino-diphenylamine (Variamine Blue B. Base - I.G.).

The green shade produced from the 2-toluidide of 2-hydroxy-anthracene-3-carboxylic acid and diazotised 1-amino-4-benzoylamino-2:5-dimethoxy-benzene has good fastness to light and chlorine and is fast to caustic kier boiling under pressure. All of the arylamides of

2-hydroxy-anthracene-3-carboxylic acid prepared gave similar green shades with these three bases, and so far as is known the arylamides of this acid are the only arylamides which can produce green shades with certain diazotised bases; hence the importance of Naphtol AS-GR in the Naphtol AS range of dye intermediates. The shades produced by the arylamides of 2-hydroxy-anthracene-3-carboxylic acid with the other diazotised bases, which are being used in these experiments, do not appear to be of great commercial value - the shades varying from a dull red to a dull plum.

Each of the arylamides of 2-hydroxy-anthracene-3-carboxylic acid prepared has been padded on cotton yarn and coupled with the usual group of diazotised bases which are again repeated for the sake of convenience.-

1). 2:5-dichloro-aniline.

2). 5-chloro-2-toluidine.

3). 5-nitro-2-anisidine.

4). o-amino-azo-toluene.

5). o-dianisidine.

6). 4'-methoxy-4-amino-diphenylamine.

The shades produced by the various arylamides with the same diazotised base were alike.

The range of shades produced on cotton yarn by 1). the 2-toluidide of 2-hydroxy-anthracene-3-carboxylic acid (Naphtol AS-GR); 2). The 2:5-dimethoxy-anilide of 2-hydroxy-anthracene-3-carboxylic acid, and 3). The 2:5-dimethoxy-4-chloro-anilide of 2-hydroxy-anthracene-3-carboxylic acid, which were taken as representative of this group of arylamides, in combination with these diazotised bases are shown in the "Dyeings" section.

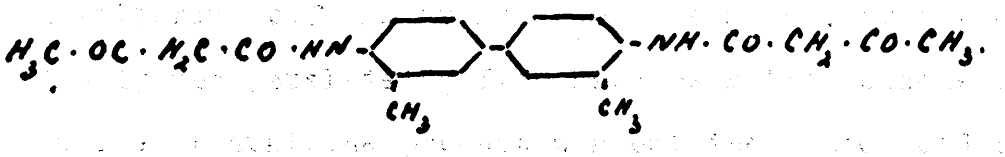
Hydrolysis of 2-hydroxy-anthracene-3-carboxylic acid Arylamides.

Hydrolysis of the 2-hydroxy-anthracene-3-carboxylic acid arylamides by 16% alcoholic potassium hydroxide, mono, di-, and tri-ethanolamines, and ethylene-diamine, under the conditions, which have been used by the author in this work, yielded 2-hydroxy-anthracene-3-carboxylic acid and the arylamines.

Section IV. Arylamides of Aceto-acetic acid.

$$R-NH\cdot CO\cdot CH_2\cdot CO\cdot CH_3.$$

Saunders (J. Soc. D. & C., 1924, 40, 49) and Rowe and Levin (Ibid., 1924, 40, 228) state that Naphtol AS-G is diaceto-acetic-o-tolidide (I).-



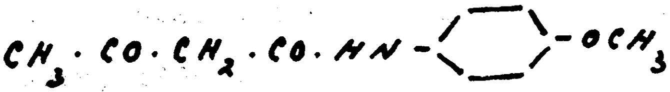
I.

On subjecting Naphtol AS-G to hydrolysis with 16% alcoholic potassium hydroxide solution (boiling for 2 hours) and working up the products of hydrolysis in the manner already described, o-tolidine was obtained. Thus, the arylamine component of Naphtol AS-G is o-tolidine. Attempts to isolate the acid were unsuccessful as the aceto-acetic acid was decomposed under the conditions of hydrolysis. Later it was found that complete hydrolysis of Naphtol AS-G took place on boiling the Naphtol for 5 hours under a refluxing condenser with $^{N}/1$ alcoholic potassium hydroxide. On working up the products of hydrolysis in the usual manner, o-tolidine was easily isolated but as was to be expected no acid could be obtained.

Analysis of recrystallised Naphtol AS-G (crystallised from benzene-nitrobenzene- 50/50 - M.Pt.- 208°C.) agreed with the suggestion that this Naphtol is diaceto-acetic o-tolidide. Naphtol AS-G was then synthesised by heating equimolecular proportions of ethyl aceto-acetate and o-tolidine using mono-chloro-benzene as solvent and with a small quantity of N. NaOH as catalyst, for 5 hours. The diaceto-acetic-o-tolidide crystallised out on cooling. On filtering off the crystals with suction, drying and finally recrystallising from benzene-nitro-benzene (50/50) a white crystalline product was obtained which did not depress the melting point of recrystallised Naphtol AS-G on mixing. The method used for the preparation of diaceto-acetic-o-tolidide was an adaptation of a general method for the preparation of aceto-acetic arylamides which has been proposed by J. K. Thomson (Thesis, Glasgow, 1935). This author in his dissertation has described a large number of these arylamides which have been prepared by this method; the method being notable for the high yields of aceto-acetic arylamides obtained.

In view of the large number of aceto-acetic arylamides prepared by Thomson no useful purpose would have been served by repetition. As a matter of interest, however, aceto-acet-p-anisidide (II) was prepared from ethyl aceto-acetate and p-anisidine by Thomson's method, (cf. Thomson's Thesis - page 120).

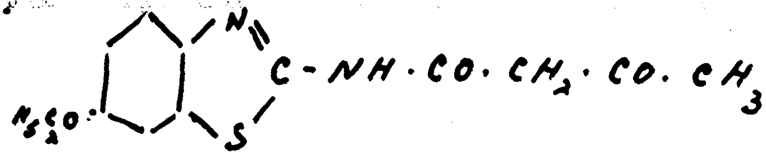
II.



In October, 1933, the I.G. Farbenindustrie A-G. introduced a new naphtol which they called Naphtol AS-L4G. This Naphtol dissolves readily in aqueous sodium hydroxide solutions and possesses low substantivity. Further, in combination with the various "Fast Bases" available Naphtol AS-L4G produces yellow shades, (so, of course, does Naphtol AS-G), which are distinguished by very good fastness to light. The yellow shades from Naphtol AS-L4G are dischargeable which makes this Naphtol extremely important in calico-printing. It should be mentioned that the yellow shades produced from Naphtol AS-G are not dischargeable.

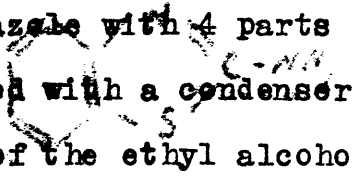
Hydrolysis of Naphtol AS-L4G with N/1 alcoholic potassium hydroxide solution yielded as the arylamine component of the Naphtol, 2-amino-6-ethoxybenzthiazole, (this was confirmed by analysis and comparison with an authentic sample), but no acid could be distinguished. Analysis showed that this Naphtol is probably 2-acetoacetylamino-6-ethoxybenzthiazole. (III).

III.



The preparation of 2-acylacetylamino-arylthiazoles is described in D.R.P.603, 623 (granted to the I.G. Farbenind. A-G. 8th. October, 1934). The method of preparation according to this patent, consists in heating a 2-amino-arylthiazole and an acyl-acetic ester until the alcohol, which is a product of the reaction, has been completely removed. In an example quoted 1 part of 2-amino-benz-thiazole is mixed with 4 parts of ethyl aceto-acetate in a flask fitted with a reflux condenser until no more ethyl alcohol distills over. This is usually accomplished in about 15 minutes. After cooling, the reaction product separates out and is filtered-off with suction, washed with alcohol and dried. The product obtained in this way is 2-aceto-acetylamino-benzthiazole. The preparation of 2-acetoacetylamino-6-ethoxybenzthiazole is not described in this patent but the preparation of the corresponding 2-benzoylacetyl-amino-6-ethoxybenzthiazole is briefly referred to. This latter compound has been prepared by the author and will be described in Section V.

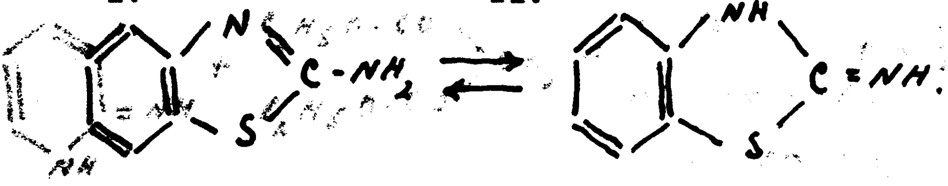
2-Acetoacetylamino-6-ethoxybenzthiazole was prepared by the author by heating 1 part of 2-amino-6-ethoxybenz:thiazole with 4 parts of ethyl aceto-acetate, in a flask fitted with a condenser, at 160°C. for 15 minutes, when all of the ethyl alcohol formed had distilled over. On



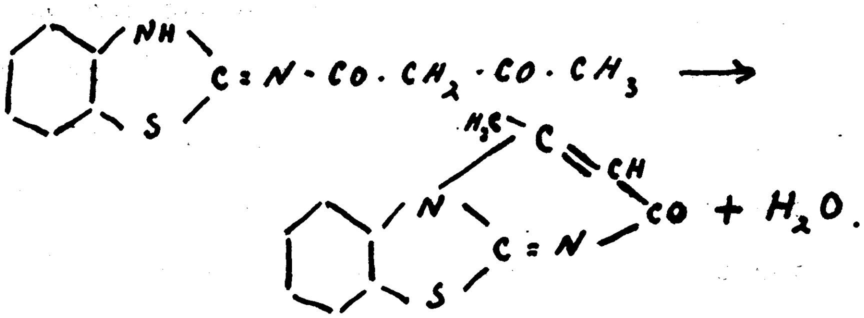
On cooling the reaction mixture a white crystalline product separated out. This was filtered at the pump, washed with alcohol and dried. The white lustrous crystalline product obtained on recrystallising from alcohol had a melting point of 200°C. and showed no depression in the melting point when mixed with Naphtol AS-L4G (recrystallised from alcohol). Naphtol AS-L4G is therefore 2-acetoacetylamino-6-ethoxybenzthiazole.

While it is well known that by heating aromatic amines with acylacetic-esters, alcohol is split off and the acylacetyl compounds of these amines are formed, it was rather surprising that 2-amino-benzthiazoles should have reacted in such an analogous manner and was not to be expected as in many of their reactions (e.g. the diazo reaction) they do not behave like aromatic amines. According to Richter - Anschütz - Reindel - "Chemie der Kohlenstoffverbindungen" 12th. Edition, Leipzig, 1931, Vol. 3, page 145, the reactions of 2-aminobenzthiazole (I). are better explained by representing it in the tautomeric imino form (II).

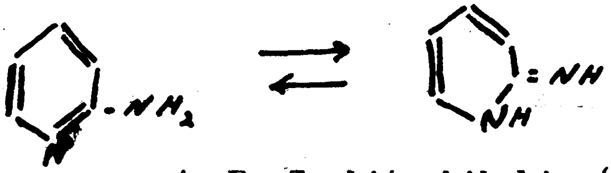
I. II.



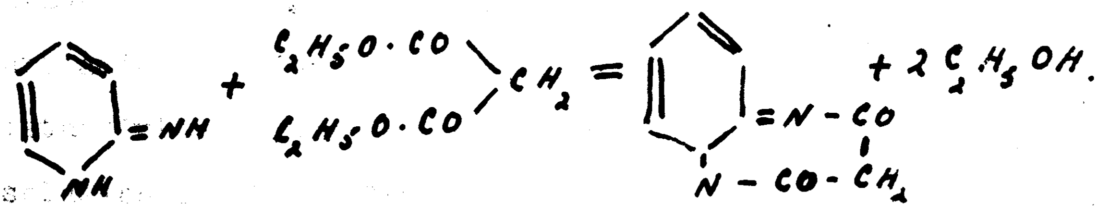
The great reactivity of the 2-amino-arylthiazoles is shown by thefact that they form ring compounds. Thus, for example, on heating a mixture of 2-amino-benzthiazole with ethyl aceto-acetate for several hours at a high temperature, after the alcohol has been split off, ring closure takes place and a compound of the following type is formed. (cf. D.R.P. 603, 623).



In this connexion it is worth noting that 2-amino-benzthiazole apparently behaves in a similar manner to 2-amino-pyridine which exhibits the same type of tautomerism.-



and moreover, as A. E. Tschitschibabin (Berichte, 1924, 57, 1168) has shown condenses with malonic ester to form a ring compound according to the following equation.-



To prevent ring closure when preparing 2-acylacetyl-

:amino-benzthiazoles from 2-amino-benzthiazole and acylacetic esters it is therefore necessary to take care that heating is not prolonged after the alcohol has been distilled-off.

Dyeing Properties of Aceto-acet-arylamides.

The aceto-acet-arylamides are all very soluble in aqueous sodium hydroxide solutions and possess low substantivity. In combination with the numerous "Fast Bases" on the market they produce yellow shades which are on the whole of good fastness. Various aceto-acet-arylamides, e.g. the anilide, are constituents of the well known Hansa Yellows which have a wide industrial application. Taking Naphtol AS-G and Naphtol AS-L4G as the representatives of this group having the greatest use in the dyeing and printing industry we find that both dissolve readily in aqueous solutions of sodium hydroxide and have poor affinity for the cotton fibre. They are therefore primarily suitable for dyeing piece goods in which case it has been shown that dyeings produced with an intermediate drying show a fuller and more brilliant shade. On impregnating cotton yarn with aceto-acet-arylamides it is necessary, in order to improve the substantivity of the arylamide, to add to the sodium salt solution of the arylamide 30 grams. per litre. of Glauber's salt. The affinity for the cotton fibre then corresponds approximately to that of some of the arylamides of 2-hydroxy-3-naphthoic acid.

As already mentioned Naphtol AS-G dyeings are not dischargeable. This fact has, of course, certain disadvantages in calico-printing, as, for example, white discharge styles cannot be produced. On the other hand the fact has certain advantages as, for example, in the production of special coloured discharge styles, (e.g. a green shade may be produced by incorporating in the discharge paste an Indanthrone Blue Vat dyestuff). Dyeings derived from Naphtol AS-L4G ~~is~~ are dischargeable and the yellow shades produced in combination with the "Fast Bases" are very fast to light; furthermore they are fast to washing, chlorine and peroxide. Naphtol AS-L4G combinations are therefore extremely suitable for curtains and furnishing fabrics. (cf. W. Christ, Textfiber., 1934, 15, 18 - 20). It was found by the author that Naphtol AS-G and Naphtol AS-L4G dyeings could be differentiated by taking a few threads of the yellow dyed material and treating them with nitric acid (conc.) On this treatment Naphtol AS-G. dyeings turn a characteristic green colour, while Naphtol AS-L4G dyeings remain unaffected.

The shades produced on cotton yarn with diacetoacetic-o-tolidide (Naphtol AS-G) and 2-acetoacetylamino-

6-ethoxybenzthiazole (Naphtol AS-L4G) in combination with the following diazotised bases are shown in the "Dyeings" section.

1). 2:5-dichloro-aniline.

2). 5-chloro-2-toluidine.

3). 5-nitro-2-anisidine.

4). o-amino-azo-toluene.

5). o-dianisidine.

and 6). 4'-methoxy-4-amino-diphenylamine.

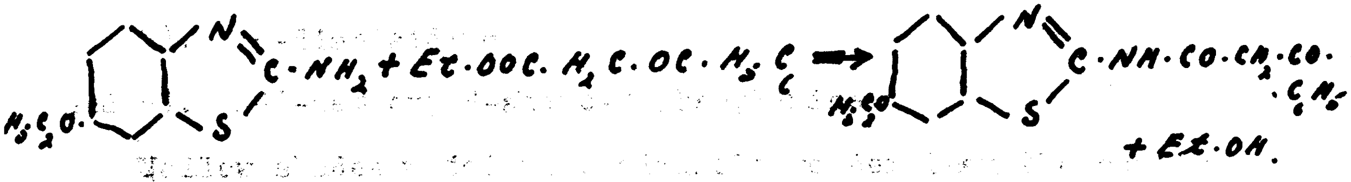
Hydrolysis of Aceto-acet-arylamides.

Hydrolysis of the aceto-acet-arylamides by $^{N}/_{1}$ alcoholic potassium hydroxide, mono-, di-, and tri-ethanolamines and ethylene diamine under the usual conditions employed by the author yielded the amino-component but no acid could be isolated which, of course, was to be expected owing to the unstable nature of aceto-acetic acid under such conditions.

Section V. Arylamides of Benzoyl-acetic acid.

$$C_6H_5\cdot CO\cdot CH_2\cdot CO\cdot HN-R.$$

The only arylamide of benzoyl-acetic acid prepared and examined by the author was 2-benzoylacetylamino-6-ethoxy-benzthiazole and was prepared in order to compare it with the 2-acetoacetylamino-6-ethoxybenzthiazole already described. 2-Benzoylacetylamino-6-ethoxybenzthiazole was readily prepared by heating the ethyl ester of benzoyl acetic acid with 2-amino6-ethoxybenzthiazole in a flask fitted with a condenser at around 116°C. until all the ethyl alcohol had distilled off (about 15 mins.). On cooling, the crystalline arylamide separated out, and was filtered off at the pump, washed with alcohol and dried.



2-Benzoylacetylamino-6-ethoxybenzthiazole differed from 2-acetoacetylamino-6-ethoxy-benzthiazole in that it was only sparingly soluble in hot alcohol (the acetoacetylamino compound was very soluble in hot alcohol). The 2-benzoylacetylamino-6-ethoxybenzthiazole crystallised from Benzene-nitrobenzene (90/10) in small find pale sulphur yellow coloured needles which melted at 208°C.

As regards the dyeing properties of 2-benzoylacetylamino-6-ethoxybenzthiazole it may be said that it behaved in a similar manner to the aceto-acet-arylamides. It was readily soluble in aqueous sodium hydroxide solutions and possessed low substantivity, although it appeared to be very slightly better in this latter connexion than the corresponding aceto-acetylamino compound. On padding cotton yarn in the sodium salt solution of the arylamide to which Glauber's salt at the rate of 30 grams. per litre had been added, squeezing the impregnated yarn evenly and coupling with the following diazotised bases.-

1). 2:5-dichloro-aniline.
2). 5-chloro-2-toluidine.
3). 5-nitro-2-anisidine.
4). o-amino-azo-toluene.
5). o-dianisidine.
and 6). 4'-methoxy-4-amino-diphenylamine.

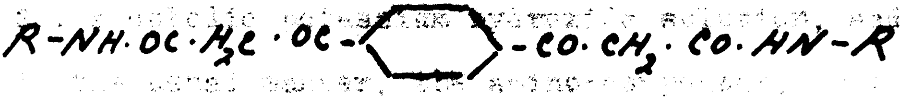
Yellow shades which were slightly redder than the corresponding acetoacetylamino-compound were obtained.

Hydrolysis.

On hydrolysing 2-benzoylacetylamino-6-ethoxybenzthiazole with 2N. alcoholic potassium hydroxide solution for 5 hours and working up the products of hydrolysis in the usual manner 2-amino-6-ethoxybenzthiazole was obtain-

:ed but no acid could be isolated. The faintly acid aqueous layer after ether extraction, however, gave a reddish-violet coloration with ferric chloride solution.

Section VI. Arylamides of Terephthaloyldiacetic acid.

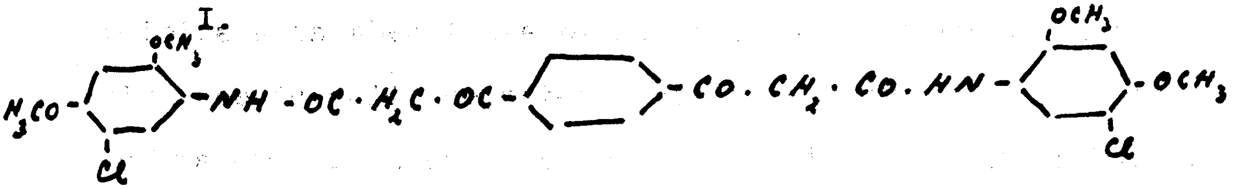


In the spring of 1933 the I.G. Farbenind. A-G. introduced two new Naphtols viz:- Naphtol AS-L3G and Naphtol AS-LG, both of which in combination with the "Fast Bases" on the market produced yellow shades. These two Naphtols possess high substantivity and are therefore extremely suitable for machine and tub dyeing. The yellow shades produced from these two Naphtols and the Fast Bases are of excellent fastness to light and are better even in this respect than the greenish yellow vat dyestuffs. Furthermore, they are very fast to washing, chlorine, soda boiling, etc., and are not dischargeable. In this latter connexion it is worth noting that the dyeings show outstanding fastness to kier-boiling (cf. W. Christ, Textilberichte, 1934, 15, 18-20). Because of their high substantivity it is not necessary to add any Glauber's salt to the sodium salt solutions in order to increase affinity for the cotton fibre. In fact, according to Christ (loc. cit.) 90% of these two Naphtols are absorbed from the padding bath by the cotton fibre without the addition of salt. Naphtol AS-L3G produces greenish yellow tones while reddish yellow shades are produced from

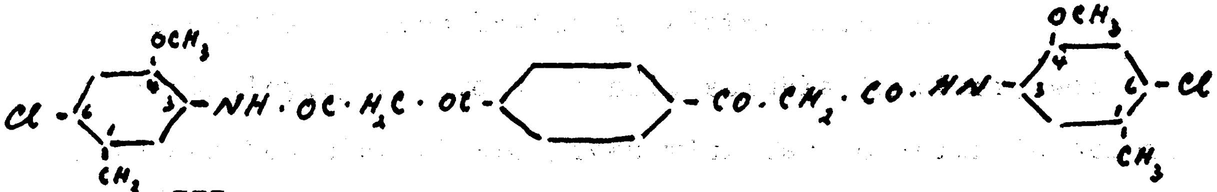
Naphtol AS-LG.

On hydrolysing Naphtol AS-LG and Naphtol AS-L3G with 2N. alcoholic potassium hydroxide solution, and working up in the usual manner, the amino-component, in the case of Naphtol AS-LG, was found to be 2:4-dimethoxy-5-chloro-aniline while in the case of Naphtol AS-L3G the amino-component was found to be 6-chloro-4-methoxy-3-amino-toluene. In each instance, however, no acid (except a little terephthalic acid) could be isolated owing to decomposition. Analyses of both Naphtols after recrystallisation from nitrobenzene and a study of the Patent literature suggested that these two Naphtols might be derivatives of terephthaloyldiacetic acid. The preparation of arylamides of terephthaloyldiacetic acid is described in D.R.P. 556,479, (awarded to the I.G. Farbenind. A.G. 15/8/32). No details of the methods employed for preparing these arylamides are given in this patent; more stress being laid on their application as dye intermediates. However, the author has found that arylamides of this type are easily prepared by gently boiling the arylamine with a slight excess of ~~the~~ diethyl terephthaloyl diacetate for about 10-15 minutes on the sand-bath. On cooling, a yellow coloured solid mass is obtained, which on extraction with boiling alcohol crumbles up and becomes a yellow amorphous powder. On recooling, this is filtered at the pump, washed with alcohol and dried at 100°C. By this method yields of the arylamides of over 90% of theory are obtained. In this way the author has been able to synthesise Naphtol AS-LG(I) from diethyl terephthaloyldiacetate and 2:4-dimethoxy-5-chloro-aniline and Naphtol AS-L3G(II) from diethyl terephthaloyldiacetate and 6-chloro-4-methoxy-3-amino-toluene. As a matter of interest the di-2:5-dimethoxy-4-chloro-anilide(III) was also prepared.

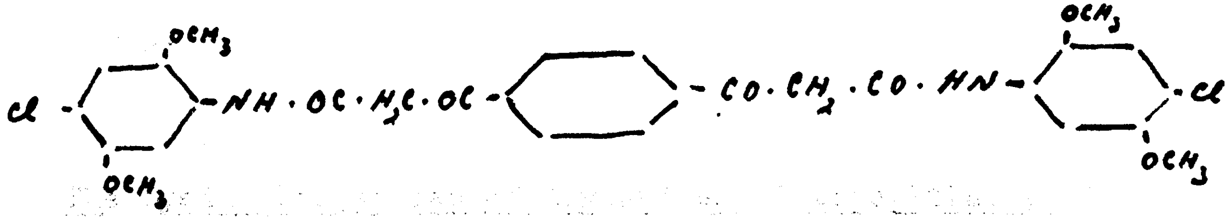
I.



II.



III.



The preparation of the di-ethyl terephthaloyldiacetate has been described by L. Berend and P. Herms (Jour.f.prakt. Chemie, 1906, [2], 74, 125) and is obtained by dissolving terephthaloyl-diacetoacetic-diethyl ester (prepared by the same authors [loc. cit., 125] by application of the Claisen reaction, from terephthaloyl chloride, ethyl aceto-acetate and sodium ethoxide; this mixture being allowed to stand overnight at 0-10°C.) in 10% alcoholic ammonia solution with stirring and afterwards slowly heating the resultant solution on the water-bath up to 60°C. Thereupon the solution suddenly becomes brown and on allowing to stand in the ice-chest overnight a thick brown precipitate separates out. The precipitate is then filtered off and washed in ethereal solution with acetic acid and water. After removing the last traces of water and on evaporation of the ether a white solid mass remains which on recrystallising from alcohol (norit) gives large angular leaves having a melting point of 70°C. Diethyl terephthaloyldiacetate is easily soluble in ether, acetic acid and hot alcohol and gives with ferric chloride solution the characteristic red-violet reaction of the $(-CO\cdot CH_2-CO-)$ group.

The Dyeing Properties of Arylamides of terephthaloyldiacetatic Acid.

As already mentioned the shades produced by this group of arylamides and the "Fast Bases" are yellow. The shades produced on cotton yarn with the di-2:4-dimethoxy-5-chloroanilide of terephthaloyldiacetic acid, (Naphtol AS-LG), which was taken as representative of this group, in combination with the following diazotised bases are shown in the "Dyeings" section.

1). 2:5-dichloro-aniline.

2). 5-chloro-2-toluidine.

3). 5-nitro-2-anisidine.

4). o-amino-azo-toluene.

5). o-dianisidine.

6). 4'-methoxy-4-amino-diphenylamine.

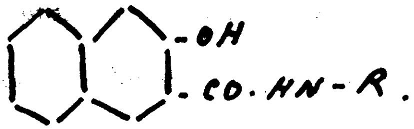
Hydrolysis of Arylamides of Terephthaloyldiacetic acid.

As mentioned above, hydrolysis of these arylamides with 2N. alcoholic potassium hydroxide solution gave the arylamine but no acid could be isolated except a little terephthalic acid which was obtained on acidifying the concentrated aqueous alkaline solution with hydrochloric acid, -- the alkaline hydrolysis of the terephthaloyl diacetic acid apparently producing terephthalic acid.

Similar results were obtained when mono-ethanolamine and ethylene diamine were used as the hydrolysing agents.

EXPERIMENTAL SECTION.

Section I. Arylamides of 2-hydroxy-3-naphthoic acid.



Naphtol AS-OL. This Naphtol crystallised from alcohol in colourless crystals which melted at 167°C.

Hydrolysis with 16% Alcoholic potassium hydroxide. On boiling crystallised Naphtol AS-OL with 16% alcoholic potassium hydroxide for 7 hours under a reflux condenser on a sand-bath and at end of this period distilling off the excess alcohol and then pouring the residue in the flask into 3 times its bulk of cold water a clear solution was obtained. The clear solution was transferred to a separator and extracted with ether. The aqueous layer was run off into a beaker and the ether which had dissolved was evaporated off by placing the beaker and contents in a boiling water bath. After the small amount of ether had been evaporated off the aqueous solution was cooled and hydrochloric acid added until the solution reacted acid to congo red paper, at which stage a white flocculent precipitate came down. This was filtered off, washed free from mineral acid and potassium chloride and dried at 100°C. in the steam-bath.

The dry solid obtained was recrystallised from dilute alcohol (50 pts. alcohol and 50 parts water) and the product identified as 2-hydroxy-3-naphthoic acid (M.Pt. 216°C.; no depression of melting point on mixing with an authentic sample of 2-hydroxy-3-naphthoic acid and further gave the characteristic blue coloration with ferric chloride).

The ethereal layer in the separator was washed several times with cold water until free from alkali (litmus). The ethereal layer was then transferred to a suitable flask and the ether evaporated off. The residue in the flask was a brown coloured oil which on boiling with acetic anhydride gave an acetyl derivative which had a melting-point of 84°C. A small portion of the oil was dissolved in hydrochloric acid (conc.) and diluted with water and diazatised. On coupling with sodium-β-naphtholate a scarlet coloured azo dyestuff was precipitated which was filtered and washed well with water. On recrystallising the dry dyestuff from toluene a bronze-red crystalline product M.Pt.180°C. was obtained. This agreed with the melting point given for o-anisidine-azo-β-naphthol by F.M. Rowe and C. Levin (J.Soc. Dyers & Colourists, 1924, 40, 218). The arylamine component of Naphtol AS-OL is therefore o-anisidine.

Synthesis of Naphtol AS-OL. As the above hydrolysis of Naphtol AS-OL showed that this Naphtol was the o-anisidide of/

of 2-hydroxy-3-naphthoic acid, equimolecular proportions of 2-hydroxy-3-naphthoic acid and o-anisidine were dissolved in toluene and treated with phosphoreus trichloride at 70°C. The mixture was then boiled for 5 hours. The mixture was then made alkaline with sodium carbonate and the toluene steam-distilled off. The anisidide was obtained in 88% yield, and on recrystallising from alcohol had a melting-point of 167°C. No depression in the melting-point was observed on mixing with crystalline Naphtol AS-OL.

The conclusion that Naphtol AS-OL is the o-anisidide of 2-hydroxy-3-naphthoic acid confirms the findings of Rowe (Ibid., 1930, 46, 228).

Naphtol AS-RL. This Naphtol crystallises from glacial acetic acid in almost colourless leaflets M.Pt. 230°C.

Hydrolysis with 16% Alcoholic potassium hydroxide. On hydrolysing crystalline Naphtol AS-RL with 16% alcoholic potassiun hydroxide under a reflux condenser at the boil for 7 hours and pouring the residue, after distilling off the excess alcohol, into water a clear greenish fluorescent liquid was obtained which on extraction with ether in the usual manner gave as the ether soluble product a white crystalline product which had M.Pt. 57°C. On admixture with an authentic sample of p-anisidine no depression of the melting point was observed. On working up the aqueous portion in the manner already described 2-hydroxy-3-naphthoic acid was isolated.

Synthesis of Naphtol AS-RL. In order to prove the correctness of the hydrolysis experiments equimolecular proportions of 2-hydroxy-3-naphthoic acid and p-anisidine were dissolved in toluene and phosphorus trichloride added at 70°C. The whole was then boiled for 6 hours. On working up in the usual manner a yield of p-anisidide of 2-hydroxy-3-naphthoic acid equal to 85% of Theory was obtained. On admixture of the product re-crystallised from glacial acetic acid with recrystallised Naphtol AS-RL no depression of the melting-point was observed. This proof that

Naphtol AS-RL is the p-anisidide of 2-hydroxy-3-naphthoic acid agrees with the conclusions of Rowe & Levin (J. Soc. Dyers & Colourists, 1924, 40, 227).

Naphtol AS-BG. This Naphtol crystallised in colourless needles from alcohol and had a melting-point of 184°C.

Hydrolysis with 16% Alcoholic potassium hydroxide. On hydrolysing crystalline Naphtol AS-BG with 16% alcoholic potassium hydroxide by boiling in the usual manner for 6 hours and working up the products of hydrolysis in the manner already described, 2:5-dimethoxyaniline (pearly plates from water M.Pt. 81°C. - no depression on admixture with an authentic sample of 2-5-dimethoxyaniline) and 2-hydroxy-3-naphthoic acid were obtained.

Hydrolysis with Monoethanolamine.

The monoethanolamine used in this experiment was supplied by The General Metallurgical and Chemical Company Limited and was a product of Carbide and Carbon Chemicals Corporation of New York. The product was water-white and had a specific gravity of 1.019 at 20/20°C. 93% distilled over between 165° and 173°C. On boiling crystalline Naphtol AS-BG with monoethanolamine for 6 hours under a reflux condenser on a sand bath, and pouring the reaction mixture into 10 times its bulk of cold water a clear solution was obtained. On extracting the cold greenish fluorescent liquid with ether in a separator, washing the ethereal layer free from alkali (litmus) and distilling off the ether a brownish crystalline product was obtained on cooling. This product on recrystallising from water was found to be 2:5-dimethoxyaniline (pearly white crystalline plates M.Pt. 81°C.). The aqueous layer on removal of the small quantity of ether present (in solution) was acidified with hydrochloric acid and the precipitated 2-hydroxy-3-naphthoic acid filtered off and washed with cold water until free from mineral acid and potassium chloride. The acid gave the characteristic blue coloration with ferric chloride solution and no depression of the melting point was observed on admixture with an authentic sample of 2-hydroxy-3-naphthoic acid.

Similar results were obtained when Naphtol AS-BG was hydrolysed with di-ethanolamine, tri-ethanolamine and ethylenediamine in like manner to monoethanolamine.

The specifications of these three products which were supplied by General Metallurgical and Chemical Company were as follows:-

Diethanolamine.-

Specific gravity ... 1.089.
Water .... not more than 1.5%.
Mono-ethanolamine... not more than 2.0%.
Di-ethanolamine .... not less than 95%.
Tri-ethanolamine ... not more than 2%.

Triethanolamine.-/

Triethanolamine.-

Specific Gravity	1.200.
Water	not more than 1.0%
Mono-ethanolamine ..	not more than 2.5%.
Di-ethanolamine	not more than 15%.
Tri-ethanolamine ...	not less than 80%.

Ethylene-diamine.-

Specific gravity ...	0.985 at 20/20° C.
Purity	69% by weight.
Boiling range	115-120°C.- 98%. above 122° C. - Nil.

On hydrolysing Naphtol AS-BG with triethanolamine it was observed that both the 2:5-dimethoxyaniline and the 2-hydroxy-3-naphthoic acid were rather difficult to purify.

Synthesis of Naphtol AS-BG. In order to prove that Naphtol AS-BG is the 2:5-dimethoxyanilide of 2-hydroxy-3-naphthoic acid, equimolecular proportions of 2-hydroxy-3-naphthoic acid and 2:5-dimethoxyaniline were dissolved in toluene, treated with phosphorus trichloride at 70°C. and boiled for 6 hours. On working up the reaction product in the usual manner a yield of arylamide equal to 93% of Theory was obtained. Admixture of the arylamide (recrystallised from alcohol) with Naphtol AS-BG (also recrystallised from alcohol) did not depress the melting-point which was 184° C. This confirms the conclusions of F. M. Rowe (J. Soc. D. & C., 1930, 46, 228).

Napthol **AS-ITR.** This Naphtol crystallised from Benzene-nitrobenzene (50/50) and had M.Pt. 197-198°C. In combination with Fast Red ITR Base (1-amino-2-methoxy-benzene-5-sulphondiethylamide) this Naphtol produces shades similar to Alizarin on aluminium mordant and having the fastness properties of the Indanthrone Vat dyestuffs. In 1934, Ueno and Suzuki (J. Soc. Chem. Ind. Japan, 1934, 37, 233B-234B.) were able to show, by hydrolysis with 50% aqueous caustic soda solution in an autoclave at 200°C. for several hours, that this Naphtol was the 2:4-dimethoxy-5-chloroanilide of 2-hydroxy-3-naphthoic acid.

Hydrolysis of Naphtol AS-ITR with 16% alcoholic potassium hydroxide. On hydrolysing this Naphtol with 16% alcoholic potassium hydroxide solution the author has been able to confirm Ueno and Suzuki's results, for on extracting the products of hydrolysis, dissolved in water, with ether, 2:4-dimethoxy-5-chloroaniline (M.Pt. 91°C. [from water] and no depression of melting-point on admixture with an authentic sample of 2:4-dimethoxy-5-chloro-aniline) was obtained. $C_6H_2(OCH_3)_2 \cdot Cl \cdot NH_2 = C_8H_{10}NCl$ requires N = 7.5%; Cl = 18.9%; (OCH_3) = 33.1%. Found - N = 7.8% (MICRO); Cl = 19.1% (MICRO) and (OCH_3) = 32.9% (MICRO).

The aqueous layer from the ether extraction on treating in the usual manner was found to contain 2-hydroxy-

-3-naphthoic acid.

Hydrolysis of this Naphtol with monoethanolamine and ethylene-diamine under the same conditions as described under Naphtol AS-BG (page 64.) also gave 2:4-dimethoxy-5-chloroaniline and 2-hydroxy-3-naphthoic acid.

Synthesis of Naphtol AS-ITR. To confirm the results of the hydrolyses experiments an attempt at synthesising this Naphtol was made by dissolving equimolar quantities of 2:4-dimethoxy-5-chloroaniline (18.75 gm.) and 2-hydroxy-3-naphthoic acid (18.8 gm.) in 10 c.c. of pyridine and heating the mixture to 70°C. and until complete solution. 6 c.c. of phosphorus trichloride were then added over a period of ½ an hour while the whole was well stirred. The mixture was then heated in the oil-bath at 115°C. for 4 hours; the mixture being frequently stirred during this period. Towards the end of this time the mass became quite viscous and had a deep golden yellow colour. On cooling, alcohol was added and the whole boiled for about ½ an hour on the water-bath. On re-cooling and allowing to stand overnight a yellowish brown solid had separated out. This was filtered off with suction and well washed with alcohol. The residue in the filter was dried in the steam bath at 100°C. Yield 29.2 gms. The filtrate was taken and cold water slowly added while the whole was well stirred. Soon a light brown precipitate was obtained and this was allowed to settle and finally filtered at the pump and dried at 100°C. Yield 2.8 grams.

Total Yield - 32.0 gm. = 92.3% of Theory. The arylamide was recrystallised from Benzene-Nitrobenzene (50/50) and light-brown crystals were obtained which had a melting-point of 198°C. and which was not depressed when admixed with Naphtol AS-ITR (recrystallised from the same solvent).

Naphtol AS-LC. This Naphtol was introduced by the I.G. Farbenind. A-G. in May, 1936, and in combination with the "Fast Bases" gives yellowish brown, red, maroon and blue shades possessing excellent fastness to light, washing and chlorine. The dyeings are dischargeable. Naphtol AS-LC is very substantive and is particularly suitable for dyeing in vats and in machines. Naphtol AS-LC recrystallises from benzene in cream coloured plates M.Pt. 188°C.

Hydrolysis of Naphtol AS-LC.

Hydrolysis of Naphtol AS-LC with 16% alcoholic potassium hydroxide, by boiling for 6 hours under a reflux condenser and separating the amino-component and the acid component obtained in the usual manner, gave 2:5-dimethoxy-4-chloro-aniline and 2-hydroxy-3-naphthoic acid. 2:5-Dimethoxy-4-chloro-aniline was recrystallised from water and gave small white needles - M. Pt. 118°C. On admixture with an authentic sample of 2:5-dimethoxy-4-chloro-aniline no depression of the melting-point was observed. $C_8H_{10}O_2NCl$ requires N = 7.5%; found -N = $7.4\%^{I.}$ and $7.5\%^{II.}$

The presence of 2-hydroxy-3-naphthoic acid was confirmed by comparison with an authentic sample of this acid and by its characteristic blue coloration with ferric chloride solution.

Hydrolysis of Naphtol AS-LC with mono-ethanolamine and ethylene-diamine under the conditions previously employed when using these substances (see under Naphtol AS-BG. p.64) gave 2:5-dimethoxy-4-chloro-aniline and 2-hydroxy-3-naphthoic acid.

Synthesis of Naphtol AS-LC.

In order to confirm the results of the hydrolyses experiments, 2:5-dimethoxy-4-chloro-aniline (9.4 gms. = $^1/20$ mol.) and 2-hydroxy-3-naphthoic acid (9.4 gm. = $^1/20$ mol.) were dissolved in 5 c.c. pyridine by heating the mixture to 70°C. 3.0 c.c. Phosphorus trichloride were added over a period of $\frac{1}{2}$/an hour and then the whole heated for a further four hours at 115°C. On working up in the manner described under Naphtol AS-ITR, a yield of 2:5-dimethoxy-4-chloro-anilide of 2-hydroxy-3-naphthoic acid equal to 94% of Theory was obtained. The arylamide was recrystallised from benzene and had M. Pt. 188°C. The melting-point of 2:5-dimethoxy-4-chloro-anilide of 2-hydroxy-3-naphthoic acid was not depressed when mixed with Naphtol AS-LC (recrys. from benzene).

Analyses.

Found for Naphtol AS-LC - N = $\overset{\text{I.}}{4.00}$% and $\overset{\text{II.}}{3.90}$%.

Found for 2:5-dimethoxy-4-chloro-anilide of 2-hydroxy-3-naphthoic acid - N = $\overset{\text{I.}}{3.99}$% and $\overset{\text{II.}}{4.05}$%.

$C_{10}H_6$ /

$C_{10} H_6 (OH) \cdot CO \cdot HN \cdot C_6 H_2 \cdot Cl. (OCH_3)_2 = C_{19} H_{16} O_4 NCl$ requires N = 3.91%.

Naphtol AS-LC is therefore the 2:5-dimethoxy-4-chloroanilide of 2-hydroxy-3-naphthoic acid.

Naphtol AS-LT. This Naphtol crystallises from alcohol in large lustrous plates with a slight pink tinge melting at 194°C. Ueno and Suzuki (loc. cit.) hydrolysed this Naphtol with 50% aqueous caustic soda solution in an autoclave, fitted with a stirrer, and heating at 200°C. for several hours. By this means these authors obtained 5-methoxy-2-toluidine and 2-hydroxy-3-naphthoic acid. The present author was able to confirm this by hydrolysing the Naphtol with 16% alcoholic potassium hydroxide solution for 6 hours at the boil. The oily amino-component gave an acetyl compound M. Pt. 133°C. (cf. Ueno and Suzuki - loc. cit.) and further, on boiling up this amino-component with light petroleum (B.P. 40/60°C.), filtering and boiling up the filtrate with Norit and re-filtering a water-white solution was obtained which on standing overnight in the ice-chest deposited large crystals (almost colourless) which melted to a light brown coloured oil when placed on the palm of the hand. The crystals had M.Pt.14°C. This behaviour agreed with that of an authentic sample of 5-methoxy-2-toluidine. The presence of 2-hydroxy-3-naphthoic acid was confirmed by means of a mixed melting point determination when no depression was observed.

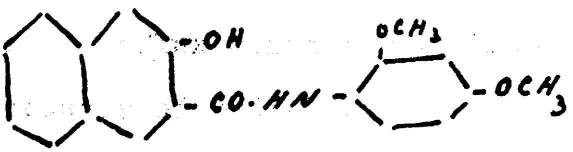
Synthesis of Naphtol AS-LT.

4.6 gm. ($^1/30$ mol.) of 5-methoxy-2-toluidine and

6.27 gm. ($^1/30$ mol.) of 2-hydroxy-3-naphthoic acid were dissolved in 4 c.c. pyridine by heating to 70°C. in an oil-bath; 2 c.c. of phosphorus trichloride was then added over ½ an hour, and the whole then heated at 115°C. for 4 hours. On working up the reaction mixture in the usual way a yield of arylamide equal to 95% of Theory was obtained. The aryl:amide was easily soluble in hot alcohol and crystallised out in white lustrous plates which had no pink colour, and which melted at 194°C. On mixing with Naphtol AS-LT (recry:stallised from alcohol) no depression of the melting point was obtained.

Naphtol AS-LT is therefore the 5-methoxy-2-toluidide of 2-hydroxy-3-naphthoic acid; thus confirming the conclusions of Ueno & Suzuki (loc. cit.).

2:4-Dimethoxy-anilide of 2-hydroxy-3-naphthoic acid.



No reference to this compound could be found in the literature.

The standard "Pyridine" method was used for preparing this arylamide; the following quantities being used.-

9.4 gm.($^1/20$ mol.)	2-hydroxy-3-naphthoic acid.
7.7 gm.($^1/20$ mol.)	2:4-dimethoxy-aniline.
5.0 c.c.	Pyridine.
3.0 c.c.	Phosphorus trichloride.

On adding alcohol to the cooled condensation product and boiling until complete solution had occurred and then cooling again the bulk of the arylamide crystallised out. The total yield of arylamide obtained was 14.2 grms. = 87.6% of Theory. The arylamide was easily soluble in hot alcohol from which it crystallised in almost colourless leaves which melted at 155°C.
(Found N = (I) 4.1%, (II) N = 4.3%; $C_{19} H_{17} O_4 N$ requires N = 4.3%).

The arylamide dissolves readily in hot caustic soda solutions with the characteristic green fluorescence.

Hydrolysis with 16% alcoholic potassium hydroxide. On boiling the 2:4-dimethoxy-anilide of 2-hydroxy-3-naphthoic acid with 16% alcoholic potassium hydroxide solution for six hours under a reflux condenser on a sand-bath and working up the products of hydrolysis in the usual manner, 2:4-dimethoxy-aniline (crystals from light petroleum (B.P.40/60°) - M.Pt. 34°C; no depression of the melting-point on admixture with an authentic sample of 2:4-dimethoxy aniline) and 2-hydroxy-3-naphthoic acid were obtained.

Hydrolysis with Ethylenediamine.

2:4-Dimethoxy-aniline and 2-hydroxy-3-naphthoic acid were obtained on hydrolysing this arylamide with ethylene diamine for 6 hours at the boiling-point under a reflux condenser.

2-Chloro-4-anisidide of 2-hydroxy-3-naphthoic acid.

(HN: Cl: OCH_3 = 1: 2: 4).

This arylamide is briefly referred to by F. M. Rowe (J. S. D. & C., 1931, 47, 32 cf. also English Patent 193,866) but no analysis or details of its chemical properties are given.

The arylamide was easily prepared by dissolving equimolecular quantities of 2-chloro-4-anisidine and 2-hydroxy-3-naphthoic acid in toluene, adding phosphorus trichloride drop by drop at 70°C. over a period of half an hour and finally boiling for five hours. On cooling, the mixture was made alkaline with sodium carbonate solution and the toluene and unchanged reactant materials distilled off in steam. The arylamide was obtained in 86% yield.

The following quantities of materials were used.-

9.4 gm.($^1/20$ mol.)	2-hydroxy-3-naphthoic acid.
7.9 gm.($^1/20$ mol.)	2-chloro-4-anisidine.
25 c.c.	Toluene.
3 c.c.	Phosphorus trichloride.

The 2-chloro-4-anisidide of 2-hydroxy-3-naphthoic acid was recrystallised from nitrobenzene and had a melting-point of 228°C. The arylamide was readily soluble in warm aqueous caustic soda solutions and dissolved giving the characteristic yellowish-green fluorescence.

(<u>Found</u> /

(**Found** N = (I) - 4.1%; (II) - 4.1%. - $C_{18}H_{14}O_3NCl$ requires N = 4.3%).

Hydrolysis with 16% alcoholic potassium hydroxide solution.

On boiling the 2-chloro-4-anisidide of 2-hydroxy-3-naphthoic acid with 16% alcoholic potassium hydroxide solution in a flask fitted with a reflux condenser, for 6 hours and working up by the standard method, 2-chloro-4-anisidine (Crystals from water M.Pt. 62°C. - no depression of melting-point on admixture with an authentic sample of 2-chloro-4-anisidine) and 2-hydroxy-3-naphthoic acid were obtained.

5-Chloro-2-anisidide of 2-hydroxy-3-naphthoic acid.

(HN: OCH_3: Cl = 1: 2: 5).

The application of the 5-chloro-2-anisidide of 2-hydroxy-3-naphthoic acid for the production of shades fast to kier-boiling is described in English Patent 193,834 (I.G. Farbenind. A-G.) but no details of its preparation or chemical properties are given.

The arylamide was readily prepared by dissolving equimolecular proportions of 5-chloro-2-anisidine and 2-hydroxy-3-naphthoic acid in toluene, adding phosphorus trichloride drop by drop at 70° C. and finally boiling the mixture for five hours. On working up the reaction mixture in the usual manner for this method a yield of arylamide equal to 91% of theory was procured.

The following quantities of materials were used:-

9.4 gm.($^1/20$ mol.)	2-hydroxy-3-naphthoic acid.
7.9 gm.($^1/20$ mol.)	5-chloro-2-anisidine.
25 c.c.	Toluene.
3 c.c.	Phosphorus trichloride.

The 5-chloro-2-anisidide of 2-hydroxy-3-naphthoic acid was recrystallised from acetone and had a melting-point of 211°C. The arylamide dissolved with the characteristic yellowish green fluorescent colour of 2-hydroxy-3-naphthoic acid arylamides, in warm aqueous sodium hydroxide solutions.

(Found /

(Found N = (I) - 4.3%; (II) - 4.2% - $C_{18}H_{14}O_3NCl$ requires N = 4.3%).

Hydrolysis with 16% alcoholic potassium hydroxide solution.

Hydrolysis of 5-chloro-2-anisidide of 2-hydroxy-3-naphthoic acid with 16% alcoholic potassium hydroxide solution under the usual conditions and working up the products of hydrolysis by the standard method gave 5-chloro-2-anisidine (Crystals from water M.Pt. 84°C. - no depression of the melting-point detected on mixing with an authentic sample of 5-chloro-2-anisidine) and 2-hydroxy-3-naphthoic acid.

5-Bromo-2-anisidide of 2-hydroxy-3-naphthoic acid.

($HN: OCH_3: Br = 1: 2: 5$).

The application of the 5-bromo-2-anisidide of 2-hydroxy-3-naphthoic acid for the production of shades fast to kier-boiling is referred to in English Patent 193,834 (I.G. Farbenind. A-G.) but no analysis or details of its chemical characteristics are given.

The arylamide was readily prepared by mixing the following quantities of reactants:-

9.4 gm. ($^1/20$ mol.)	2-hydroxy-3-naphthoic acid.
10.1 gm. ($^1/20$ mol.) ...	5-bromo-2-anisidine.
25 c.c.	Toluene.
3 c.c.	phosphorus trichloride.

These materials were allowed to react in the usual manner and then worked up in the manner which is more or less standard for this method of preparation of arylamides of the β-hydroxy-naphthoic series. The yield of arylamide in this instance amounted to 87% of theory.

The 5-bromo-2-anisidide of 2-hydroxy-3-naphthoic acid was recrystallised from benzene-nitrobenzene (75/25) and had a melting-point of 216-217°C. The arylamide dissolved readily in aqueous sodium hydroxide solutions - the solutions having the characteristic yellowish-green fluorescence.

(Found N = (I) - 3.71%; (II) - 3.76%. $C_{18}H_{14}O_3NBr$ requires N = 3.8%).

Hydrolysis with 16% alcoholic potassium hydroxide solution.

Hydrolysis of the 5-bromo-2-anisidide of 2-hydroxy-3-naphthoic acid with 16% alcoholic potassium hydroxide solution under the usual conditions and working up the products of hydrolysis by the standard method yielded, 5-bromo-2-anisidine (Crystals from water M.Pt.98°C. - no depression of the melting-point being observed on admixture with an authentic sample of 5-bromo-2-anisidine) and 2-hydroxy-3-naphthoic acid.

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p-phenetidide of 2-hydroxy-3-naphthoic acid.

No reference to analysis or chemical properties of this arylamide could be found in the literature.

The p-phenetidide of 2-hydroxy-3-naphthoic acid was readily prepared by mixing the following quantities of materials:-

9.4 gm. ($^1/20$ mol.) .... 2-hydroxy-3-naphthoic acid.
6.9 gm. ($^1/20$ mol.) .... p-phenetidine.
25 c.c. .... toluene.
3 c.c. .... phosphorus trichloride.

The method of procedure was the usual one adopted when toluene was used as the diluent. The p-phenetidide was obtained in 93% yield and was readily soluble in warm aqueous sodium hydroxide solutions; the solutions exhibiting the usual yellowish green fluorescence. The p-phenetidide of 2-hydroxy-3-naphthoic acid recrystallised from acetone and formed pale pink crystals which melted at 216°C. (Found N = (I) - 4.4%; (II) - 4.6%. $C_{19}H_{17}O_3N$ requires N = 4.6%).

Hydrolysis with 16% alcoholic potassium hydroxide solution.

Hydrolysis of this arylamide with 16% alcoholic potassium hydroxide solution under the usual conditions and working up the products of hydrolysis by the standard method yielded p-phenetidine (light brown oil - acetyl derivative, [phenacetine], M.Pt.- 135°C., which gave no depression of melting-point when mixed with an authentic sample of phenacetine), and 2-hydroxy-3-naphthoic acid.

1-Amino-2-methoxy-benzene-5-sulphondiethylamide of 2-hydroxy-3-naphthoic acid.

No reference to this compound could be found in the literature.

This arylamide was prepared by (I) the"toluene" method and (II) the "pyridine" method.

I) The "toluene" method.

The following quantities of materials were used:-

9.4 gm. ($^1/20$ mol.)	2-hydroxy-3-naphthoic acid.
12.9 gm.($^1/20$ mol.)	1-amino-2-methoxy-benzene-5-sulphondiethylamide.
25 c.c.	toluene.
3 c.c.	phosphorus trichloride.

These materials were allowed to react in the usual manner and then worked up in the usual way when toluene is used as the diluent. The yield of arylamide amounted to 90% of Theory. On recrystallising from alcohol-benzene (20/1) the arylamide melted at 207-208°C.

II) The "pyridine"method. The following quantities of materials were used.-

9.4 gm. ($^1/20$ mol.)	2-hydroxy-3-naphthoic acid.
12.9 gm.($^1/20$ mol.)	1-amino-2-methoxy-benzene-5-sulphondiethylamide.
5.0 c.c.	pyridine.
3.0 c.c.	phosphorus trichloride.

The acid and arylamide were dissolved in pyridine at 70°C. and the phosphorus trichloride added over a period of half an hour. The mixture was then heated at 115°C. for 4 hours - during this period the mixture was frequently stirred. The reaction product was worked up in the usual manner (see page 69) for this method of procedure and a yield of arylamide equal to 94% of Theory obtained.

On recrystallisation, the arylamide was obtained in pale sulphur yellow crystals M.Pt.- 209-210°C.

On mixing the arylamide obtained by method I.and method II., the mixture melted at 209°C., thus proving that they were identical.

The 1-amino-2-methoxy-benzene-5-sulphondiethylamide of 2-hydroxy-3-naphthoic acid was readily soluble in warm aqueous caustic soda solutions, which exhibited the characteristic yellowish green fluorescence of the arylamides of β-hydroxy-naphthoic acid.-

(Found N(Micro) - 6.4%; S (micro) = 7.6%. $C_{22}H_{24}O_5N_2S$ requires N - 6.5%; S - 7.5%).

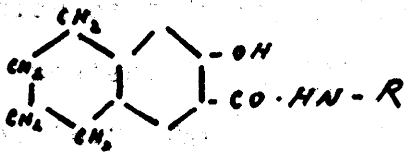
Hydrolysis with 16% alcoholic potassium hydroxide solution.

On hydrolysing the 1-amino-2-methoxy-5-sulphondiethyl-:amide of 2-hydroxy-3-naphthoic acid with 16% alcoholic caustic potash solution by boiling under a reflux condenser for six hours and working up the products of hydrolysis in the usual manner, 1-amino-2-methoxybenzene-5-sulphondiethylamide ([Fast Red ITR Base], crystals from alcohol, M.Pt.- 105°C. - Found N(micro) - 10.61%; S(micro) - 12.5%. $C_{11}H_{18}O_3N_2S$ - requires N - 10.8%; S - 12.4%) and 2-hydroxy-3-naphthoic acid were obtained.

Similar results were obtained by hydrolysing this arylamide with mono-ethanolamine and ethylenediamine under the conditions already described.

It is interesting to observe that 1-amino-2-methoxybenzene-5-sulphondiethylamide itself resisted hydrolysis with boiling 16% alcoholic potassium hydroxide. This was also the case when the ethanolamines and ethylenediamine were used as the hydrolysing agent. Furthermore, this was found to be the case in all instances, examined by the author, in which 1-amino-2-methoxybenzene-5-sulphondiethylamide formed the arylamine component of the arylamide.

Section II. Arylamides of 5:6:7:8-tetrahydro-2-hydroxy -3-naphthoic acid.



The 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid used in these experiments was supplied to the author by the I. G. Farbenindustrie A-G. and crystallised from dilute alcohol (50 parts alcohol and 50 parts water) in long narrow plates M.Pt. 178-179°C. (Found - C(micro) - 68.7%; H(micro) - 6.3%; $C_{11}H_{12}O_3$ requires C- 68.8%. H - 6.3%).

In contrast to 2-hydroxy-3-naphthoic acid which gave a blue coloration, 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid gave a violet coloration with ferric chloride solution.

On boiling with acetic anhydride the acid gave an acetyl derivative, - OAc - $C_{10}H_{10}$· CO_2H - crystals from alcohol M.Pt.147°C. (Schroeter, loc.cit. gives M.Pt.142-143°C.). (Found - C(micro) - 66.8%; H(micro) - 5.9% Calculated for $C_{13}H_{14}O_4$ - C = 66.7%; H = 6.0%).

Anilide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.

The preparation of this arylamide has been described by G. Schroeter, Annalen, 1922, 426, 83-160), and the General Aniline Works Inc. (U.S. Pat. 2,040,397). Recently the preparation of the arylamide by the hydrogenation of the anilide of 2-hydroxy-3-naphthoic acid has been described in French Pat. 814,169 granted 16/6/37 to the I. G. Farbenind. A.G. (abstracted Chem. Zentrl., 1938, 109, I, 434-435).

The author has prepared this arylamide by the "pyridine" process. The following quantities were used.-

19.2 gm. ($^1/10$ mol.)	5:6:7:8-tetrahydro-2-hydroxy -3-naphthoic acid.
9.3 gm. ($^1/10$ mol.)	Aniline.
10 c.c.	pyridine.
6 c.c.	phosphorus trichloride.

The acid and the aniline were dissolved in the pyridine and heated to 70°C., when the phosphorus trichloride was added drop by drop over a period of half an hour. The temperature was gradually raised to 115° C. and maintained at this point for a further four hours. During the addition of the phosphorus trichloride stirring was continuous; thereafter stirring was carried out at frequent intervals as the reaction mass became fairly viscous. On cooling the reaction mass, alcohol was added and the whole boiled for 10 minutes when complete solution had occurred. On allowing to stand overnight in the ice-chest 14.5 gm. of arylamide were obtained on filtering off and drying in the steam-oven. On adding water carefully to the filtrate; good stirring being necessary during the mixing, a further quantity (8.3 gm.) of arylamide was obtained on filtering off and drying. Total Yield = 22.8 gm. = 85.4% of Theory.

The arylamide recrystallised from alcohol in small white leaves M.-Pt.183°C. (Schroeter [loc.cit.] gives M.Pt. 182-184°C.; F.P.814,169 gives M.Pt. 183°C.). (Found N = I - 5.26%; II - 5.2 %. Calculated for $C_{17}H_{17}O_2N$ - N = 5.2%).

Hydrolysis with 16% alcoholic potassium hydroxide solution.

The anilide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid dissolved in 16% alcoholic caustic potash solution with a distinct blue-violet fluorescence and on boiling the solution for 6 hours under a reflux condenser on a sand-bath - aniline (acetyl derivative M.Pt.114°C.) and 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid (M.Pt.178°C. and violet ferric reaction) were obtained on working up the products of hydrolysis in the usual way.

2-Toluidide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.

The preparation of this arylamide is described in U.S. Patent 2,040,397 but no analysis is given.

The arylamide was readily prepared in the same manner as the anilide.

The following quantities were used:-

19.2 gm. ($^1/10$ mol.)	5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.
10.7 gm. ($^1/10$ mol.)	o-toluidine.
10 c.c.	pyridine.
6 c c.	phosphorus trichloride.

The yield of o-toluidide was 81% Theory.

The o-toluidide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid recrystallised from alcohol in colourless crystals M.Pt.164°C. (This agrees with the value given in U.S. Pat. 2,040,397).

(Found N - (I) - 5.10%; (II) 5.16%. Calculated for $C_{18}H_{19}O_2N$ - N = 5.00%).

Hydrolysis with 16% alcoholic potassium hydroxide solution.

On carrying out the hydrolysis by the standard method and working up the products of hydrolysis in the usual manner o-toluidine (acetyl derivative M.Pt.110°C.) and 5:6:7:8-

tetrahydro-2-hydroxy-3-naphthoic acid were obtained.

α-Naphthylamide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.

This arylamide is described in U.S. Patent 2,040,397 but no analysis is given.

The arylamide was prepared by the author in a similar manner to that described in U.S. Patent 2,040,397; the following quantities being used:-

9.6 gm. (1/20 mol.)	5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.
7.2 gm. (1/20 mol.)	α-naphthylamine.
50 c.c.	toluene.
3 c.c.	phosphorus trichloride.

The yield of α-naphthylamide obtained was 93% of Theory. On recrystallising from nitrobenzene the α-naphthylamide melted at 190° - 191°C. (U.S. Pat. gives M.Pt. 192°C.). (Found N = (I) - 4.50%; (II) - 4.53%; $C_{21}H_{19}O_2N$ requires N = 4.4%).

Hydrolysis with 16% alcoholic potassium hydroxide solution.

On dissolving the α-naphthylamide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid in 16% alcoholic caustic potash solution and boiling for 6 hours under a reflux condenser and separating the products of hydrolysis in the already described manner, α-naphthylamine (crystals from alcohol. M.Pt. 50°C.) and 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid were obtained.

β-Naphthylamide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.

This arylamide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid has already been described in U.S. Patent 2,040,397 but no analysis is given.

The author has prepared this compound by means of the "pyridine" method, the following quantities being used:-

9.6 gm. ($^{1}/20$ mol.)	5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.
7.2 gm. ($^{1}/20$ mol.)	β-naphthylamine.
7.5 c.c.	pyridine.
3 c.c.	phosphorus trichloride.

The method of procedure was the standard one and a yield of 91% of Theory of arylamide was obtained.

The β-naphthylamide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid crystallised from nitrobenzene in small white crystals (with a slight yellowish tinge) which melted at 202° C. (U.S. Patent 2,040,397 gives M.Pt. as 200°C.

Hydrolysis with 16% alcoholic potassium hydroxide solution.

Hydrolysis of the β-naphthylamide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid with 16% alcoholic caustic potash solution under the usual conditions, provided β-naphthylamine (Recrystallised from water, M.Pt.-110° C.) and 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.

2:5-Dimethoxyanilide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.

The preparation of this arylamide is described in U.S. Patent 2,040,397, but no analysis given.

The author has prepared this arylamide by the method described in this patent, viz.- the "toluene" method; the following quantities being used.-

9.6 gm. (1/20 mol.)	5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.
7.7 gm. (1/20 mol.)	2:5-dimethoxyaniline.
50 c.c.	toluene.
3 c.c.	phosphorus trichloride.

On carrying out the reaction in the customary manner for this method a yield of 2:5-dimethoxyanilide equal to 92% of Theory was obtained.

The 2:5-dimethoxyanilide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid recrystallised from alcohol in colourless crystals of melting-point 147-148°C. (U.S. Patent gives M.Pt. = 147°C.)

(Found:- N = (I) - 4.49%; (II) - 4.34%. $C_{19}H_{21}O_4N$ requires N. - 4.3%).

Hydrolysis with 16% alcoholic potassium hydroxide solution.

On hydrolysing this arylamide with 16% alcoholic caustic potash solution by the standard method and working up the products of hydrolysis in the usual way, 2:5-dimethoxyaniline (crystals from water M.Pt. 81°C.) and 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid were obtained.

Similar results were obtained when the 2:5-dimethoxyanilide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid was hydrolysed with monoethanolamine by the method already described by the author.

2-Chloro-4-anisidide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid. (HN:Cl:OCH_3 = 1: 2: 4.).

So far as could be found from an examination of the literature, this arylamide has not been previously described.

The 2-chloro-4-anisidide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid was prepared by the "pyridine" method: the following quantities being used:-

9.6 gm. ($^1/20$ mol.)	5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.
7.9 gm. ($^1/20$ mol.)	2-chloro-4-anisidine.
5 c.c.	pyridine.
3 c.c.	phosphorus trichloride.

The method of procedure adopted was the standard one for this process. - The yield of arylamide obtained was equal to 95% of Theory.

The 2-chloro-4-anisidide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid crystallised out from alcohol solution in colourless plates melting at 182°C. (Found:- N = (I) 4.29%; (II) 4.38%. $C_{18}H_{18}O_3NCl$ requires N - 4.2%.).

Hydrolysis with 16% alcoholic potassium hydroxide solution.

The 2-chloro-4-anisidide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid on hydrolysis with 16% alcoholic potassium hydroxide solution under the usual conditions gave , 2-chloro-4-anisidine (crystals from water - M.Pt. 62°C.) and 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.

Similar results were obtained by hydrolysis with monoethanolamine and ethylene diamine under the conditions employed by the author for these substances.

2:5-Dimethoxy-4-chloroanilide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.

No reference to the preparation or properties of this arylamide could be found in the literature.

The 2:5-dimethoxy-4-chloroanilide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid was prepared readily by the "pyridine" process in the usual manner. The following quantities of materials were used.-

9.6 gm. ($^1/20$ mol.)	5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid.
9.4 gm. ($^1/20$ mol.)	2-5-dimethoxy-4-chloroaniline.
7.5 c.c.	pyridine.
3 c.c.	phosphorus trichloride.

The yield of the arylamide obtained was equal to 96% of that theoretically possible.

The 2:5-dimethoxy-4-chloroanilide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid recrystallised from benzene in colourless crystals which melted at 192° C. (Found:- N = (I) - 3.94%; (II) 3.98%. Calculated for $C_{19}H_{20}O_4NCl$, N - 3.9%.).

Hydrolysis with 16% alcoholic potassium hydroxide solution.

On hydrolysing the 2:5-dimethoxy-4-chloroanilide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid with 16%

alcoholic caustic potash solution in the usual way - 2:5-dimethoxy-4-chloro-aniline (crystals from water M.Pt. 118°C.) and 5:6:7:8-tetra-hydro-2-hydroxy-3-naphthoic acid were obtained.

The arylamide behaved in like manner when the hydrolysing agents were di-ethanelamine and tri-ethanolamine; the conditions of hydrolysis being that standardised for these compounds by the author.

1-Amino-2-methoxybenzene-5-sulphondiethylamide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.

No reference to this compound having been prepared previously could be found in the literature.

The 1-amino-2-methoxybenzene-5-sulphondiethylamide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid was prepared by the "pyridine" process. The following quantities of materials were used:-

9.6 gm. (^{1}/20 mol.)	5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.
12.9 gm.(^{1}/20 mol.)	1-amino-2-methoxybenzene-5-sulphondiethylamide.
5 c.c.	pyridine.
3 c.c.	phosphorus trichloride.

The yield of arylamide obtained was equivalent to 94% of Theory.

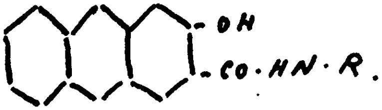
The 1-amino-2-methoxybenzene-5-sulphondiethylamide of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid crystallised from alcohol-benzene (20:1) in colourless crystals which melted at 183-184° C.

(Found:- N - (I) - 6.53%; (II) - 6.57% S = $\overset{\text{I.}}{7.51}$%; $\overset{\text{II.}}{7.48}$%.
$C_{22}H_{28}O_5N_2S$ requires N - 6.5% and S - 7.4%.).

Hydrolysis with 16% alcoholic potassium hydroxide.

Hydrolysis of this arylamide with 16% alcoholic caustic potash solution in the usual way gave - 1-amino-2-methoxybenzene-5-sulphondiethylamide (crystals from alcohol M.Pt.105° C.) and 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.

Section III. Arylamides of 2-hydroxyanthracene-3-carboxylic acid.



The 2-hydroxyanthracene-3-carboxylic acid used in these experiments was very kindly gifted to the author by the I. G. Farbenindustrie A-G.

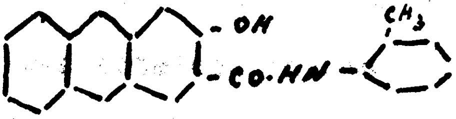
The acid crystallised from nitrobenzene or monochlorobenzene in small yellow crystals which melted at 298° C. (indefinite) with decomposition.

(Found:- C(micro) - 75.7%; H(micro) - 4.3%.
$C_{15}H_{10}O_3$ requires C - 75.7% and H - 4.2%.).

Naphtol AS-GR.

As mentioned in the theoretical section the outstanding characteristic of this Naphtol is its property of combining with certain "Fast Bases" to produce green shades on cellulosic fibres.

Naphtol AS-GR crystallised from nitrobenzene in yellow coloured crystals which melted at 270° C. (Found:- C(micro) - 80.1%; H(micro) - 5.1%, N(micro) - 4.3%.



$C_{22}H_{17}O_2N$ requires C - 80.7%; H - 5.2% and N - 4.3%).

Hydrolysis of Naphtol AS-GR with 16% alcoholic potassium hydroxide solution (boiling for 7 hours) and working up in the usual manner gave as the amino-component, o-toluidine (acetyl derivative, M.Pt.- 110° C.) and as the acid component 2-hydroxy-anthracene-3-carboxylic acid (crystallised from mono-chlorobenzene M.Pt. 298° C. (with decomp.) and gave no depression of the melting point of an authentic sample of the acid on mixing. From the above hydrolysis experiment Naphtol AS-GR appeared to be the o-toluidide of 2-hydroxy-anthracene-3-carboxylic acid. This was confirmed by heating equimolecular proportions of 2-hydroxy-anthracene-3-carboxylic acid (11.9 gm. = $^1/20$ mol.) and o-toluidine (5.4 gm./

gm. = 1/20 mol.) in xylene solution with phosphorus trichloride (3 c.c.). The phosphorus trichloride was added drop by drop at around 70° C. over a period of ½ an hour. After the addition of phosphorus trichloride, the mixture was heated at the boil for 6 hours after which time the evolution of H Cl had ceased. The product which separated out on cooling was filtered off at the pump and then boiled up with sodium carbonate solution. Finally the product was filtered off and well washed with water and dried. The dry product was crystallised from nitrobenzene and was obtained in small yellow crystals which melted at 270° C. These crystals did not depress the melting-point of Naphtol AS-GR (recrystallised from nitrobenzene) on admixture.

2:5-Dimethoxyanilide of 2-hydroxyanthracene-3-carboxylic acid.

No reference to this compound could be found in the literature.

The author has prepared this arylamide by heating equimolecular proportions of 2-hydroxyanthracene-3-carboxylic acid and 2:5-dimethoxyaniline in pyridine solution with phosphorus trichloride. The following quantities of materials were used:-

11.9 gm. ($^1/20$ mol.) ... 2-hydroxyanthracene-3-carboxylic acid.

7.7 gm. ($^1/20$ mol.) ... 2:5-dimethoxyaniline.

10 c.c. .... pyridine.

3 c.c. .... phosphorus trichloride.

The usual procedure, which has been adopted by the author in preparing arylamides of hydroxycarboxylic acids where pyridine is used as the diluent, was used. A yield equivalent to 94% of Theory was obtained.

The arylamide crystallised from nitrobenzene in small yellowish-orange coloured plates which melted at 285° C. (Found:- N = (I) 3.85%; (II) 3.90%. $C_{23}H_{19}O_4N$ requires N = 3.8%).

Hydrolysis with 16% alcoholic potassium hydroxide solution.

The/

The 2:5-dimethoxyanilide of 2-hydroxyanthracene-3- carboxylic acid dissolved readily in 16% alcoholic caustic potash solution giving an orange colour to the solution. On boiling the solution for 6 hours in a flask fitted with a reflux condenser and working up the products of hydrolysis in the customary manner, 2:5-dimethoxyaniline (M. Pt. 81°C.) and 2-hydroxyanthracene-3-carboxylic acid were obtained.

Similarly on dissolving the arylamide in mono-ethanolamine and boiling the solution for 6 hours, 2:5-dimethoxyaniline and 2-hydroxyanthracene-3-carboxylic acid were obtained.

2:5-Dimethoxy-4-chloroanilide of 2-hydroxyanthracene-3-carboxylic acid.

According to the literature this compound had not been previously prepared.

The arylamide was readily formed when equimolecular quantities of 2-hydroxyanthracene-3-carboxylic acid and 2:5-dimethoxy-4-chloroaniline were dissolved in pyridine and heated with phosphorus trichloride at 115° C. for 4½ hours.

The following quantities of materials were used:-

11.9 gm. (1/20 mol.) ...	2-hydroxyanthracene-3-carboxylic acid.
9.4 gm. (1/20 mol.) ...	2:5-dimethoxy-4-chloroaniline.
10 c.c.	pyridine.
3 c.c.	phosphorus trichloride.

The procedure for adding the phosphorus trichloride and the general working up of the arylamide was the standard one used by the author when pyridine was the diluent. Yield equal to 95% Theory.

The 2:5-dimethoxy-4-chloroanilide of 2 hydroxyanthracene-3-carboxylic acid was recrystallised from nitrobenzene and obtained in small mustard yellow coloured crystals melting at 237° C.

(Found:- N = (I) 3.44%; (II) 3.41%. $C_{23}H_{18}O_4NCl$ requires N = 3.4%).

Hydrolysis with 16% alcoholic potassium hydroxide solution.

The arylamide dissolved in 16% alcoholic potassium hydroxide solution with an orange colour and on boiling for 6 hours under a reflux condenser and working up in the usual way, 2:5-dimethoxy-4-chloroaniline (crystals from water M. Pt. 118°C.) and 2-hydroxyanthracene-3-carboxylic acid were obtained.

2:4-Dimethoxy-5-chloroanilide of 2-hydroxyanthracene-3-carboxylic acid.

No reference to the preparation or properties of this arylamide of 2-hydroxyanthracene-3-carboxylic acid could be found in the literature.

The 2:4-dimethoxy-5-chloroanilide of 2-hydroxyanthracene-3-carboxylic acid was prepared in exactly the same way as the 2:5-dimethoxy-4-chloroanilide referred to in the preceding page.

For the preparation the following quantities were used:-

11.9 gm. (1/20 mol.) ...	2-hydroxyanthracene-3-carboxylic acid.
9.4 gm. (1/20 mol.) ...	2:4-dimethoxy-5-chloroaniline.
10 c.c.	pyridine.
3 c.c.	phosphorus trichloride.

The 2:4-dimethoxy-5-chloroanilide was obtained in a yield equivalent to 92% of Theory. It was recrystallised from nitrobenzene and was obtained in small deep yellow coloured needles which melted at 272° C.

(<u>Found:-</u> N = (I) 3.45%; (II) 3.43%. $C_{23}H_{18}O_4NCl$ requires N - 3.4%).

Hydrolysis/

Hydrolysis with Monoethanolamine.

On dissolving the 2:4-dimethoxy-5-chloro-anilide of 2-hydroxy-anthracene-3-carboxylic acid in monoethanolamine and boiling the solution for 6 hours on a sand bath, hydrolysis took place and on working up the products of hydrolysis in the usual way, 2:4-dimethoxy-5-chloro-aniline (crystals from water M. Pt. 91° C.) and 2-hydroxy-anthracene-3-carboxylic acid were obtained.

5-chloro-2-toluidide of 2-hydroxyanthracene-3-carboxylic acid. (HN : CH_3 : Cl = 2 : 1 : 5).

The melting point of this arylamide as well as a general method of preparing arylamides of 2-hydroxyanthracene-3-carboxylic acid is given in D.R.P. 554,786 (I. G. Farbenind. A-G.). No analysis of the 5-chloro-2-toluidide is given in this patent, however.

The author has prepared 2-hydroxyanthracene-3-carboxylic acid-5-chloro-2-toluidide by the method described in the above mentioned patent. The following quantities were used:-

11.9 gm.	(1/20 mol.) ...	2-hydroxyanthracene-3-carboxylic acid.
7.1 gm.	(1/20 mol.) ...	5-chloro-2-toluidine.
75 c.c.	....	toluene.
3 c.c.	....	phosphorus trichloride.

The amine and acid were dissolved in the toluene by heating at 70° C. When dissolved the phosphorus trichloride was added over a period of half an hour - stirring being continuous during the addition. The mixture was then boiled for 5 hours (evolution of H Cl had ceased at this stage). On cooling the arylamide settled out, and was then filtered at the pump, washed and dried. It was then boiled up with sodium carbonate solution, filtered, washed and dried. The

The arylamide crystallised from nitrobenzenein yellow coloured crystals M. Pt. 284° C. (D.R.P. 554,786 gives M. Pt. 282° C.).

(Found:- N = (I) 4.01%; (II) 4.06%. $C_{22}H_{16}O_{2}NCl$ requires N = 3.9%).

Hydrolysis with 16% alcoholic potassium hydroxide solution.

Hydrolysis of the 5-chloro-2-toluidide of 2-hydroxyanthracene-3-carboxylic acid with 16% alcoholic caustic potash solution by boiling for 6 hours, gave 5-chloro-2-toluidine (M.Pt. 30° C.) and 2-hydroxyanthracene-3-carboxylic acid.

5-Methoxy-2-toluidide of 2-hydroxy-anthracene-3-carboxylic acid.

This arylamide is described in D.R.P. 554,786 but no analysis is given.

The author has been able to prepare this arylamide in good yield by means of the standard "pyridine" method.

The following quantities were used:-

11.9 gm. ($^1/20$ mol.) ... 2-hydroxy-anthracene-3-carboxylic acid.
7.0 gm. ($^1/20$ mol.) ... 5-methoxy-2-toluidine.
10 c.c. .... pyridine.
3 c.c. .... phosphorus trichloride.

The arylamide was obtained in a yield equivalent to 94% of Theory.

The 5-methoxy-2-toluidide of 2-hydroxy-anthracene-3-carboxylic acid was crystallised from nitrobenzene and obtained in small mustard-yellow plates melting at 243-244° C. (D.R.P. 554,786 gives M.Pt. 253° C.). (Found:- N = (I) 4.01%; (II) 3.97%. $C_{23}H_{19}O_3N$ requires N = 3.9%).

Hydrolysis with 16% alcoholic potassium hydroxide solution.

On dissolving the 5-methoxy-2-toluidide of 2-hydroxy-anthracene-3-carboxylic acid in 16% alcoholic potassium hydroxide solution and boiling for 6 hours on a sand-bath and working up the products of hydrolysis in the usual way , 5-methoxy-2-toluidine (acetyl derivative M. Pt. 134° C.), and 2-hydroxyanthracene-3-carboxylic acid were obtained.

1-Amino-2-methoxybenzene-5-sulphondiethylamide of 2-hydroxyanthracene-3-carboxylic acid.

No reference to the preparation or properties of this compound could be found in the literature.

The preparation of this arylamide was carried out by the "toluene" process described in D.R.P. 554,786.

The following quantities of materials were used:-

11.9 gm. ($^1/20$ mol.) ...	2-hydroxyanthracene-3-carboxylic acid.
12.9 gm. ($^1/20$ mol.) ...	1-amino-2-methoxybenzene-5-sulphondiethylamide.
50 c.c.	toluene.
3 c.c.	phosphorus trichloride.

A yield of arylamide equivalent to 96% of Theory was obtained.

The 1-amino-2-methoxybenzene-5-sulphondiethylamide of 2-hydroxyanthracene-3-carboxylic acid crystallised out from nitrobenzene in small gamboge-yellow coloured needles which melted at 245° C.

(Found:- N(micro) - 5.9%; S(micro) - 6.8%.

$C_{26}H_{26}O_5N_2S$ requires N - 5.9%; S - 6.7%).

Hydrolysis with Ethylene diamine.

On dissolving the arylamide in ethylene diamine and boiling the solution under a reflux condenser on a sand-bath for 6 hours hydrolysis took place and 1-amino-2-methoxy-benzene-5-sulphondiethylamide (crystals from alcohol-M.Pt.105° C.) and 2-hydroxy-anthracene-3-carboxylic acid were obtained.

Section IV. Arylamides of Aceto-acetic acid.

$CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot HN - R$

Naphtol AS-G.

As already stated in the theoretical section, Naphtol AS-G is diacetoacetic-o-tolidide (cf. Saunders, J. Soc. D. & C. 1924, 40, 49; also Rowe & Levin, Ibid., 1924, 40, 228). On boiling the Naphtol in a flask fitted with a reflux condenser with N/1 alcoholic potassium hydroxide solution for 6 hours on a sand-bath, distilling off the excess alcohol at the end of this period and then pouring in to water, a clear solution, which exhibited no sign of fluorescence, was obtained. On extracting this solution with ether in a separator, washing the ethereal layer free from alkali and finally distilling-off the ether, a solid product was obtained which on crystallising from alcohol (50 parts alcohol/50 parts water) gave a white crystalline product and which had a melting-point of 128° - 129° C. (On admixture with an authentic sample of o-tolidine no depression of the melting-point was noted).

On acidifying the aqueous layer with hydrochloric acid no precipitate was formed. When the aqueous solution was only faintly acid, however, the solution gave, with ferric chloride solution a faint reddish-violet coloration, which was indicative of the presence of the - CO. CH_2 CO. group. (Found:- /

(<u>Found:</u>- for crystallised Naphtol AS-G.
N - (I) 7.60%; (II) 7.56%. $C_{22} H_{24} O_4 N_2$ requires N - 7.4%).
Naphtol AS-G crystallised from benzene-nitrobenzene (50/50) in small fine colourless needles, which melted at 208° C.

Diacetoacetic-o-tolidide was synthesised by the author by boiling ethyl acetoacetate (2 mols.) and o-tolidine (1 mol. in monochlorobenzene solution with a trace of $^N/1$ Na OH. The following quantities were used:-

26 gm.	ethyl acetoacetate.
21.2 gm.	o-tolidine.
50 c.c.	chlorobenzene.
0.05 c.c.	$^N/1$ Na OH.

The ethyl acetoacetate was dissolved in the monochlorobenzene and the catalyst (0.05 c.c. $^N/1$ NaOH) added. The mixture was then rapidly raised to the boil and boiled for a few minutes. The o-tolidine was then added to the hot mixture, and the whole boiled for five hours. Full details of the method are given by Thomson (Thesis, Glasgow, 1935, pages 162-165). On cooling, diacetoacet-o-tolidide crystallised out and was filtered off at the pump and dried. The substance obtained was re-crystallised from benzene-nitrobenzene (50 pts. benzene/50 pts. nitrobenzene) and crystals (fine white needles) which melted at 208° C. were obtained. On admixture with Naphtol AS-G which had been crystallised from benzene-nitrobenzene no depression of the melting-point was observed.

Naphtol AS-L4G.

Naphtol AS-L4G crystallised from alcoholic solution in fine lustrous white needles which melted at 200° C.

On boiling this Naphtol with $^{N}/1$ alcoholic potassium hydroxide solution in a flask fitted with a reflux condenser for 5 hours on a sand-bath, then distilling-off the excess of alcohol and finally pouring the whole into twice its volume of cold water a clear pale yellow solution was obtained which exhibited no fluorescence. This aqueous solution was transferred to a separator and extracted with ether. The ethereal layer was washed with cold water until the last traces of alkali had been removed. On distilling-off the ether a white (with a slight pale green tinge) crystalline product was obtained. This product was recrystallised from dilute alcohol (90 pts. water - 10 pts. alcohol) and fine white needles having a slight greenish-yellow tinge were obtained. These crystals had a melting-point of 163° C. and showed no depression in melting-point when admixed with an authentic sample of 2-amino-6-ethoxybenzthiazole.

The aqueous solution (layer) from the ether extraction was placed on the water-bath and the small quantity of ether present evaporated-off. On then adding hydrochloric acid to the cold aqueous solution no precipitate was obtained.

On making the solution only faintly acid, however, ferric chloride gave a slight reddish-violet coloration thus indicating the presence of the (-CO-CH_2-CO-) group.

Naphtol AS-L4G was synthesised, however, by heating 1 part of 2-amino-6-ethoxybenzthiazole with 4 parts of ethyl acetoacetate in a flask fitted with a condenser for 15 minutes when all the alcohol, formed during the reaction, had distilled over (cf. D.R.P. 603,623). On cooling, a white crystalline product separated out. This was filtered at the pump, washed with dilute alcohol and dried. On crystallising from alcohol white needles were obtained which had M.Pt. 200° C. On admixture with crystalline Naphtol AS-L4G no depression of the melting-point was observed.

(Found for Naphtol AS-L4G (recrystallised):- C(micro) - 56.6%; H(micro) - 5.1%; N - I. 10.20%; II. 10.05%; S - I. 11.6%; II. 11.5%. $C_{13}H_{14}O_3N_2S$ requires C - 56.1%; H - 5.0% N - 10.1%; S - 11.5%).

Naphtol AS-L4G is therefore 2-acetoacetylamino-6-ethoxybenzthiazole.

Aceto-acet-p-anisidide.

This compound has been already described by Jadhav (J. Ind. Chem. Soc., 1930, 7, 669-76) and Thomson (Thesis, Glasgow, 1935, page 170); an earlier reference to aceto-acet-p-anisidide is to be found in D.R.P. 268,318 (F.Bayer & Co.).

The present author has used the following quantities which are the quantities suggested by Thomson (loc. cit.) for optimum results.-

14.3 gm.	ethyl aceto-acetate.
12.3 gm.	p-anisidine.
50 c.c.	chlorobenzene.
0.05 c.c.	$^{N}/1$ NaOH.

All the reactants were mixed in the cold, raised to the boil and boiled for 5 hours.

The aceto-acet-p-anisidide obtained had a melting-point of 116° C. the product having been crystallised from alcohol. On admixture with an authentic sample of aceto-acet-p-anisidide no depression of the melting-point was observed.

Hydrolysis with $^{N}/1$ Alcoholic potassium hydroxide solution.

On boiling aceto-acet-p-anisidide with $^{N}/1$ alcoholic potassium hydroxide solution for 5 hours in the customary manner and working up the products of hydrolysis in the usual manner - p-anisidine was obtained. No acid could be detected on acidifying the aqueous layer. The usual faintly reddish-violet ferric reaction however was obtained with the faintly acid aqueous layer.

Section V. Arylamides of Benzoylacetic acid.

$C_6H_5\cdot CO\cdot CH_2\cdot CO\cdot HN-R.$

2-Benzoylacetylamino-6-ethoxybenzthiazole.

This compound is briefly referred to in D.R.P.603,623.

2-Benzoylacetylamino-6-ethoxy-benzthiazole was prepared by heating 4 parts of the ethyl ester of benzoyl acetic acid (supplied by the Society of Chemical Industry in Basle) and 1 part of 2-amino-6-ethoxybenzthiazole in a flask fitted with a condenser at 160° C. for 15 minutes when all of the ethyl alcohol produced had distilled over. On cooling, the 2-benzoylacetylamino-6-ethoxybenzthiazole separated out, was filtered off at the pump and well washed with alcohol. On drying and recrystallising from benzene-nitrobenzene (90 benzene: 10 nitrobenzene), small fine pale sulphur yellow coloured needles melting at 208° C. (D.R.P. 603,623 gives M.Pt.- about 200° C.) were obtained.

(Found:- N - I. 8.3%; II. 8.4%; S = I. 9.71%; II. 9.77%.

$C_{18}H_{16}O_3N_2S$ requires N - 8.2% and S - 9.4%).

Hydrolysis with 2N/1 Alcoholic potassium hydroxide solution.

On boiling 2-benzoylacetylamino-6-ethoxybenzthiazole with 2N/1 alcoholic potassium hydroxide solution for 5 hours under a reflux condenser, on a sand-bath hydrolysis took place and on separating the products in the usual manner -

2-amino-6-ethoxybenzthiazole (crystals from water - alcohol (90/10) M. Pt.163° C.) was obtained. No acid, however, could be detected. A faint violet-red coloration, however, was produced when ferric chloride solution was added to the faintly acid solution of the aqueous layer.

Similar results were obtained when the hydrolysing agents were mono-ethanolamine and ethylenediamine.

Section VI. Arylamides of terephthaloyldiacetic Acid.

As already stated in the theoretical section arylamides of terephthaloyldiacetic acid were prepared by the author by boiling diethyl terephthaloyldiacetate with the arylamine for 10 minutes.

The diethyl terephthaloyldiacetate used in the following experiments was supplied to the author by the Society of Chemical Industry in Basle.

This ester crystallised from alcohol-water (50/50) in shining plates which had a melting point of 70° C. (Behrend and Herms., J. pr. Chem., 1906, [2], 74, 126 give M.Pt.70°C)

The aqueous solution of the ester gave the characteristic red-violet coloration with ferric chloride solution.

Naphtol AS-LG.

Naphtol AS-LG was insoluble in most of the commoner organic solvents. It dissolved in boiling nitrobenzene and yellow crystals separated out on cooling. These crystals melted at 253-254° C.

On boiling Naphtol AS-LG with 2N. alcoholic potassium hydroxide solution in a flask fitted with a reflux condenser on a sand-bath for 5 hours, distilling off the excess alcohol and then pouring into twice its bulk of cold water, a clear yellow solution which exhibited no signs of fluorescence was obtained. On transferring to a separator and extracting with ether, washing the ethereal layer free from alkali and distilling off the ether, a solid product was obtained. This product on crystallising from water gave a crystalline product (white) which melted at 91°C. No depression of the melting point was observed on admixture with an authentic sample of 2:4-dimethoxy-5-chloroaniline. On concentrating the aqueous layer, and then adding a slight excess of hydrochloric acid a little terephthalic acid was precipitated and was identified by conversion into its methyl ester (M. Pt. 140°C.).

(Found for crystallised Naphtol AS-LG. C - 57.6%; H - 4.4%; N - 4.8%; Cl - 12.4% - Calculated for $C_{28}H_{26}O_8N_2Cl_2$ - C - 57.0%; H - 4.4%; N - 4.8% and Cl - 12.1%).

Synthesis/

Synthesis of Naphtol AS-LG.

Analysis of Naphtol AS-LG had suggested that this Naphtol might be the di-2:4-dimethoxy-5-chloro-anilide of terephthaloyldiacetic acid - the terephthalic acid obtained in the hydrolysis experiments apparently having been formed by the alkaline hydrolysis of the terephthaloyldiacetic acid. Therefore equimolecular proportions of diethyl terephthaloyl diacetate and 2:4-di-methoxy-5-chloro-aniline were boiled in a boiling tube for 10 minutes when most of the alcohol had evaporated off. On cooling and extracting the mass with boiling alcohol a greenish-yellow amorphous looking powder settled down. This was cooled, filtered, and washed with alcohol and dried. On recrystallising from nitrobenzene a yellow crystalline product which melted at 262-263° C. was obtained but on admixture with crystallised Naphtol AS-LG did not depress the melting point of this latter.

Naphtol AS-LG is therefore the di-2:4-dimethoxy-5-chloro-anilide of terephthaloyldiacetic acid.

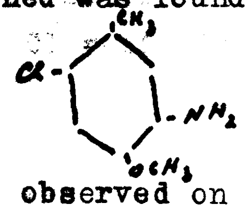
Naphtol AS-L3G.

Naphtol AS-L3G, like Naphtol AS-LG, was insoluble in most of the commoner organic solvents. It dissolved, however, in boiling nitrobenzene and yellow crystals separated out on cooling. These crystals melted at 255-256° C.

On boiling Naphtol AS-L3G with 2N. alcoholic potassium hydroxide solution in a flask fitted with a reflux condenser on a sand-bath for five hours, distilling off the excess alcohol and then pouring into twice its bulk of cold water, a clear yellow solution which did not exhibit any signs of fluorescence was obtained. On transferring this solution to a separator and extracting with ether, washing the ethereal layer free from alkali and distilling off the ether, a light brown coloured solid product was obtained. On crystallising this product from water (norit), white fine needles which melted at 105-106° C. were obtained.

Found N(micro) - 8.05%; Cl(micro) - 20.67%.

$C_6H_2 \cdot CH_3 \cdot NH_2 \cdot OCH_3 \cdot Cl = C_8H_{10}ONCl$ requires
N = 8.2% and Cl = 20.7%.

The arylamine obtained was found to be 3-amino-4-methoxy-6-chlorotoluene 

for no depression of the melting point was observed on admixture with an authentic sample of 3-amino-4-methoxy-6-chloro-toluene which was very kindly supplied to the author by the Society of Chemical Industry in Basle. 3-Amino-4-methoxy-6-chloro-toluene has been described by O. de Vries in Koninkijke Akademie van Wetenschappen te Amsterdam, 1909, 247-248; abstracted in Chem. Zentrl., 1910, I, 260 and in Rec. trav. chim. des Pays-Bas, 1909, 28, 395 - 407; abstracted in Chem. Zentrl., 1910, I, 429, who prepared it by reducing 3-nitro-4-methoxy-toluene - $C_6H_3 \cdot CH_3 \cdot NO_2 \cdot OCH_3$ ($CH_3 : NO_2 : OCH_3$ = 1 : 3 : 4) with tin and hydrochloric acid. The acetyl derivative of 3-amino-4-methoxy-6-chloro-toluene crystallised from dilute alcohol (50 pts. alcohol: 50 pts. water) in fine white needles which melted at 114-115° C.

On concentrating the aqueous layer, after ether extraction, and then acidifying with hydrochloric acid a little terephthalic acid was isolated and identified as previously.

(Found for crystallised Naphtol AS-L3G: - C(micro) - 60.44%; H(micro) - 4.60%; N(micro) - 4.81%; Cl(micro) - 12.5%. Calculated for $C_{28}H_{26}O_6N_2Cl_2$; - C = 60.3%; H = 4.7%, N = 5.0% and Cl = 12.7%).

Synthesis of Naphtol AS-L3G.

Analysis of Naphtol AS-L3G had suggested that this Naphtol was probably the di-4-methoxy-6-chloro-3-toluidide of terephthaloyldiacetic acid. Molecular proportions of diethyl terephthaloyldiacetate and 3-amino-4-methoxy-6-chlorotoluene were therefore boiled in a large boiling-tube for 10 minutes, when most of the alcohol had evaporated -off. On cooling and extracting the reaction mass with boiling alcohol, a greenish-yellow amorphous powder settled out on re-cooling. This was filtered off at the pump, washed with alcohol and dried. On crystallising from nitrobenzene a pale yellow crystalline product was obtained. These crystals melted at 258-259° C. and on admixture with crystallised Naphtol AS-L3G did not depress the melting-point of this latter.

Naphtol AS-L3G is therefore the di-4-methoxy-6-chloro-3-toluidide of terephthaloyldiacetic acid.

Di-2:5-dimethoxy-4-chloroanilide of terephthaloyldiacetic acid.

No reference to the preparation of this compound could be found in the literature.

Di-2:5-dimethoxy-4-chloroanilide of terephthaloyldiacetic acid was prepared by boiling molecular proportions of diethyl terephthaloyldiacetate and 2:5-dimethoxy-4-chloro-aniline in a boiling-tube for 10 minutes to eliminate the ethyl alcohol produced during the reaction. On cooling and extracting with boiling alcohol a bright yellow precipitate settled out on re-cooling. This latter was filtered off at the pump, washed with alcohol and dried in the steam-oven. The yield obtained amounted to 86% of Theory.

The arylamide was crystallised from nitrobenzene and was obtained in bright yellow coloured needles which melted at 255-256° C.
(Found - N - (I) - 4.90%; (II) - 4.88%. Calculated for $C_{28}H_{26}O_8N_2Cl_2$ - N - 4.8%).

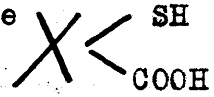
Hydrolysis with 2N. alcoholic potassium hydroxide solution.

On boiling the di-2:5-dimethoxy-4-chloroanilide of terephthaloyldiacetic acid with 2N. alcoholic caustic potash solution for 5 hours and working up in the usual manner, 2,5-dimethoxy-4-chloroaniline was obtained on evaporation of the ethereal layer. A little terephthalic acid was isolated on concentrating the aqueous layer.

Similar results were obtained when the arylamide was hydrolysed with monoethanolamine and ethylenediamine.

PART II.

The Preparation of certain Thiol-acids and arylamides of type



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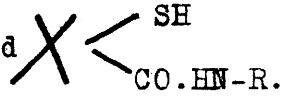


In view of the recognised importance, as dye-intermediates, of the arylamides of certain hydroxy-carboxylic acids the author considered that a study of the arylamides of certain thiol-carboxylic acids such as stated below in the same connexion, would offer a profitable field of investigation.

In the first place, an examination of the literature dealing with this aspect of these compounds revealed that comparatively little progress appeared to have been made in this direction. For example, of the thiol-carboxylic acids examined no reference to the preparation of arylamides therefrom could be found.

In this study, arylamides of o-thiolbenzoic acid, p-thiolbenzoic acid, and 2-thiol-3-naphthoic acid have been prepared and examined. The preparation of arylamides of the lactone of 1-thiol-8-naphthoic acid (i.e. the inner anhydride of the hypothetical 1-thiol-8-naphthoic acid) was also attempted but all efforts to bring about condensation of arylamines and the lactone were unsuccess-

:ful.

The thiol-carboxylic acids used were all prepared from the corresponding amino-acids by the method recommended by C. F. H. Allen and D. D. Mackay for preparing o-thiolbenzoic acid and which has been described fully by these authors in "Organic Syntheses", 1932, 12, 76. In all cases, yields of thiol-acids of over 80 per cent of the theoretical (calculated on the amino-acids) were obtained.

The preparation of the arylamides from these acids, however, presented more difficulty. Attempts to prepare these arylamides by the method most generally used for preparing arylamides of hydroxy-carboxylic acids, i.e. by treating the thiol acid and the arylamine in toluene (or xylene) solution with phosphorus trichloride and boiling until all of the hydrochloric acid had been eliminated lead generally to the production of viscuous materials from which solid products could be obtained only with difficulty. Furthermore, the yields of these products were always extremely small. By substituting phosphorus pentoxide for phosphorus trichloride as the condensing agent and working with a ratio of 3 mols. of arylamine for 1 mol. of thiol-acid much better yields (around 50-60 per cent) of arylamides were obtained. The author has found, however, that the best method of preparing arylamides of thiol-carboxylic acids is to dissolve the thiol-acid and the arylamine (usually in the ratio of 2 mols. of arylamine for every mol. of thiol-acid) in the minimum amount of pyridine and to add phosphorus trichloride to the solution at 70°C. over a period of half an hour. During the addition of the phosphorus trichloride the mixture is thoroughly stirred. After the addition of the phosphorus trichloride, the temperature of the mixture is raised to 115°C. and maintained at this temperature for four hours; the mixture being occasionally stirred during this period. On cooling the reaction mixture, alcohol is added and the whole then boiled until complete solution has occurred. On allowing to stand overnight a solid product (often crystalline) separates out. On carefully adding water to the filtrate, obtained after filtering-off this solid material at the pump, a cream coloured precipitate is obtained which also contains arylamide. By this method the author has been able to obtain yields of arylamides of over 80 per cent and in some cases of over 90 per cent of that theoretically possible. It will be remembered that this method of procedure has been successfully used by the author in preparing arylamides of hydroxy-carboxylic acids (see this Thesis, page 13,).

The arylamides of thiol-carboxylic acids prepared by these methods were all practically insoluble in most of the commoner organic solvents. They were, however, soluble in hot pyridine and in nitrobenzene and were invariably purified by crystallisation from this latter solvent. The arylamides were also practically insoluble in aqueous solutions of sodium hydroxide. They dissolved readily, however, in warm $^N/1$ alcoholic potassium hydroxide solution and these solutions, with the exception of these of the arylamides of p-thiolbenzoic acid could be diluted with a limited amount of water without re-precipitation of the arylamides. The addition of even small amounts of water to the $^N/1$alcoholic caustic potash solutions of the arylamides of p-thiolbenzoic acid immediately reprecipitated the arylamides unchanged.

On padding cotton yarn in solutions of the arylamides of o-thiol-benzoic acid and 2-thiol-3-naphthoic acid (prepared by dissolving the arylamides in the requisite amount of $^N/1$ alcoholic potassium hydroxide solution and diluting to the correct volume with water), squeezing evenly and then working the impregnated cotton yarn in solutions of the following diazotised bases.-

1)./

1). 2:5-dichloro-aniline (Fast Scarlet GG.Base - I.G.).
2). 5-chloro-2-toluidine (Fast Red TR Base - I.G.)
3). 5-nitro-2-anisidine (Fast Red B. Base - I.G.)
4). o-amino-azo-toluene (Fast Garnet GC Base - I.G.).
5). o-dianisidine (Fast Blue B. Base - I.G.).
and 6). 4'-methoxy-4-amino-diphenylamine, (Variamine Blue B. Base - I.G.).

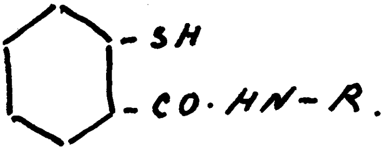
biscuit, lemon and fawn shades were obtained from the arylamides of o-thiolbenzoic acid, while the arylamides of 2-thiol-3-naphthoic acid yielded biscuit, orange and tan shades.

The dyeings, however, did not possess the allround fastness properties of the azoic combinations used commercially. It is of interest, however, to note that, by replacing the OH' group in the arylamides of 2-hydroxy-3-naphthoic acid with the SH' group, the shades with these diazotised bases were changed from reds and blues to biscuit, orange and tan shades.

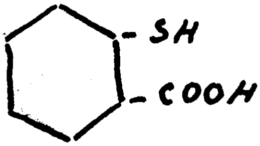
The preparation and properties of the thiol-acids and and their arylamides will now be discussed individually under the following sectional headings.-

<u>Section I.</u> - Arylamides of o-Thiolbenzoic acid.
<u>Section II.</u> - Arylamides of p-Thiolbenzoic acid.
<u>Section III.</u> Arylamides of 2-Thiol-3-naphthoic acid.
<u>Section IV.</u> Lactone of 1-thiol-8-naphthoic acid.

Section I. Arylamides of o-Thiolbenzoic acid.



o-Thiolbenzoic acid I (thiosalicylic acid, o-mercaptobenzoic acid)

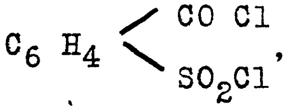
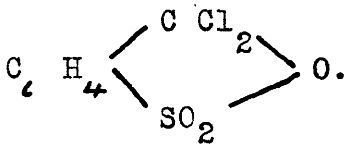
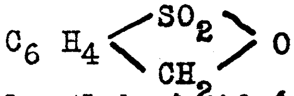


I.

forms small sulphur yellow plates or needles from glacial acetic acid or alcohol which melt at 163-164°C. o-Thiolbenzoic acid is readily soluble in hot water and its aqueous solution gives with ferric chloride solution a transient blue coloration. Commercially, o-thiolbenzoic acid is principally used for the preparation of Thioindigo.

According to C. F. H. Allen and D. D. Mackay ("Organic Syntheses", 1932, 12, 76, cf. Kalle, D. R. P. 205,450: also Meister, Lucius and Brüning, D. R. P. 69,073), o-thiolbenzoic acid is best prepared from diazotised anthranilic acid. The diazo compound of anthranilic acid is decomposed by treatment with sodium polysulphide and di-thiosalicylic acid -- $[S_2\cdot(C_6H_4\cdot CO_2H)_2]$ is formed. On reducing the di-thio acid by boiling with zinc dust and glacial acetic acid, o-thiolbenzoic acid is formed. This was the method adopted by the author for the preparation of the acid and full details of the procedure employed are given in the experimental section.

The preparation of o-thiolbenzoic acid by reduction of benzoic-sulphinic acid has been described by L. Gattermann (Ber., 1899, 32, 1149).

o-Sulphobenzoic acid on treatment with phosphorus pentachloride gives two dichlorides, melting at 40°C. and 79°C. respectively. The lower melting di-chloride is the labile form --  $C_6H_4\left<\begin{matrix}CO\,Cl\\SO_2Cl\end{matrix}\right.$, while the higher melting variety is the stable form --  $C_6H_4\left<\begin{matrix}C\,Cl_2\\SO_2\end{matrix}\right>O$. The reduction products of these two forms are interesting, for example thelabile form gives o-thiolbenzoic acid while the stable form yields sulpho-benzide --  $C_6H_4\left<\begin{matrix}SO_2\\CH_2\end{matrix}\right>O$ which is the anhydride of an o-benzylalcohol sulphonic acid (cf. Richter-Anschütz - Reindel,"Chemie der Kohlenstoffverbindun:gen", 12th. Edn., Vol. II, part 2, page 394).

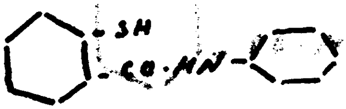
As already mentioned (page 137) in the general intro:ductory section, arylamides of thiol-carboxylic acids can only be prepared with difficulty and in low yield by the usual "Toluene" process for producing arylamides of hydroxy-carboxylic acids. This was particularly the case when attempts were made to prepare arylamides of o-thiol-benzoic acid by this method. Increasing the ratio of thiol-acid to arylamine from 1:1 to 1:3 only improved the yield of arylamide very slightly. However, by replacing phosphorus trichloride with phosphorus pentoxide and carrying out the reaction otherwise in the usual manner arylamides of o-thiolbenzoic acid were obtained in good yield (around 60% of theory).

By using pyridine as the solvent instead of toluene, and phosphorus trichloride as the condensing agent yields of the arylamides were greatly improved. In the case of the arylamides of o-thiolbenzoic acid yields equivalent to 80-85% of the theoretical were obtained; the best results being obtained when the ratio of o-thiolbenzoic acid to arylamine was 1:2.

The following arylamides of o-thiolbenzoic acid have been prepared by the author.-

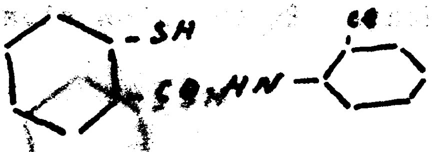
1). Anilide of o-thiolbenzoic acid (II) from o-thiolbenzoic acid and aniline.

II.



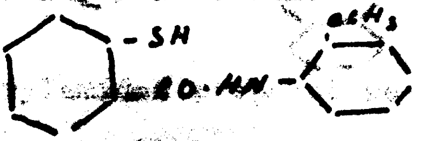
2). o-chloroanilide of o-thiolbenzoic acid (III), from o-thiolbenzoic acid and o-chloroaniline.

III.



3). o-anisidide of o-thiolbenzoic acid (IV), from o-thiolbenzoic acid and o-anisidine.

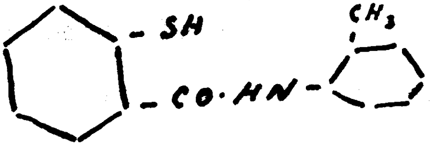
IV.



4). o-toluidide of o-thiolbenzoic acid (V), from o-thiolbenzoic acid and o-toluidine.

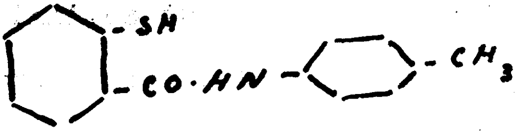
V./

V.



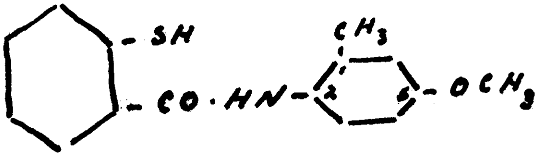
5). p-toluidide of o-thiolbenzoic acid (VI) from o-thiolbenzoic acid and p-toluidine.

VI.



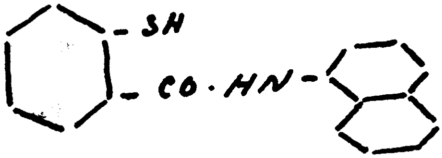
6). 5-methoxy-2-toluidide of o-thiolbenzoic acid (VII), from o-thiolbenzoic acid and 5-methoxy-2-toluidine (5-methoxy-2-aminotoluene).

VII.



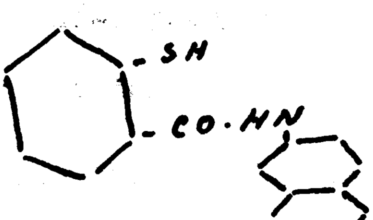
7). α-naphthylamide of o-thiolbenzoic acid (VIII) from α-naphthylamine and o-thiolbenzoic acid.

VIII.



8). β-naphthylamide of o-thiolbenzoic acid (IX) from o-thiolbenzoic acid and β-naphthylamine.

IX.



All of the arylamides prepared were white crystalline products which were insoluble in most of the commoner organic solvents. They were, however, soluble in pyridine, nitrobenzene and benzene-nitrobenzene mixtures. The arylamides were also insoluble in boiling aqueous solutions of sodium hydroxide, but were soluble in warm $^{N}/1$ alcoholic potassium hydroxide solution.

On boiling these N/1 alcoholic potassium hydroxide solutions of the arylamides in a flask under a reflux condenser for four hours hydrolysis took place and o-thiolbenzoic acid and the arylamine were obtained.

<u>Dyeings of the arylamides of o-thiolbenzoic acid.</u>

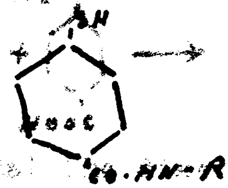
In the special "Dyeings" section, dyeings of the anilide of o-thiolbenzoic acid in combination with the following diazotised bases are shown.-

1), 2:5-dichloroaniline.
2). 5-chloro-2-toluidine.
3). 5-nitro-2-anisidine.
4). o-amino-azo-toluene.
5). o-dianisidine.
and 6). 4'-methoxy-4-aminodiphenylamine.

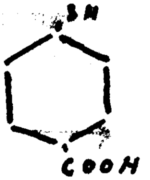
The anilide of o-thiolbenzoic acid was taken as representative of this group. To impregnate the cotton yarn with the anilide of o-thiolbenzoic acid the anilide was dissolved in the requisite amount of $^{N}/1$ alcoholic potassium hydroxide solution and this solution diluted with water to the desired volume. 30 grams of Glauber's salt per litre of padding liquor were added in order to improve the substantivity of the anilide.

The biscuit, lemon and fawn shades obtained did not possess the fastness properties associated with the azoic colours of commerce, for example, they possessed very poor fastness to washing and to sodium hypochlorite solution (made slightly acid with hydrochloric acid).

Section II. Arylamides of p-thiolbenzoic acid.

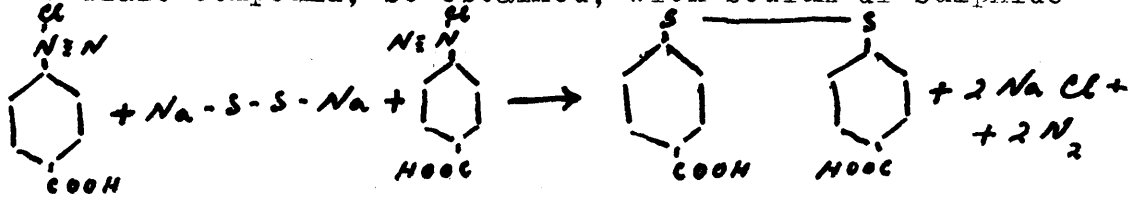


According to Smiles and Harrison (J. Chem. Soc., 1922, 121, 2022) p-thiolbenzoic acid (I).

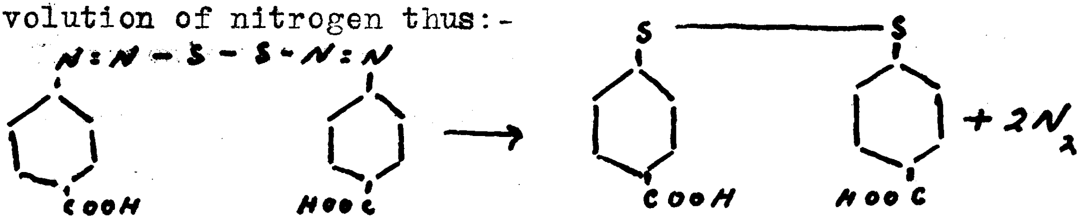


is prepared by dissolving dry p-toluene sulphonyl chloride in glacial acetic acid and adding zinc dust and concentrated hydrochloric acid at intervals in small quantities to the hot solution. When reduction is nearly complete the liquid becomes turbid and ultimately a solid separates which increases in quantity after the liquid has been cooled and kept for a few hours. Hydrochloric acid is then added to remove excess of zinc and the product collected. The p-thiolbenzoic acid thus obtained by Smiles and Harrison (loc. cit.) was stated to be a colourless micro-crystalline powder which decomposed at around 250°C. and was very sparingly soluble in all the commoner organic solvents.

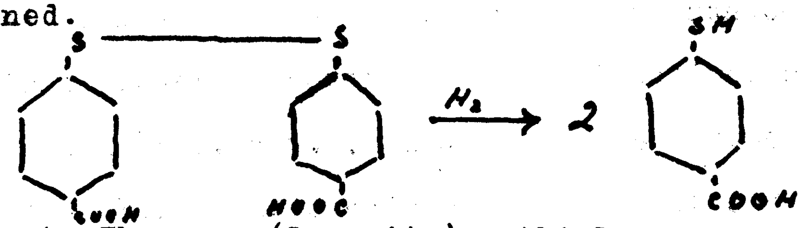
In 1925, G. Thompson (J. Soc. Chem. Ind., 1925, 44, 196T) published a method of synthesising p-thiolbenzoic acid by diazotising p-aminobenzoic acid and interacting the diazo-compound, so obtained, with sodium di-sulphide



It can be assumed that the diazo-di-sulphide is first formed and this is decomposed into the disulphide with evolution of nitrogen thus:-



The p-dithiobenzoic acid, obtained at this stage of the process, is then reduced with iron powder in concentrated sodium carbonate solution by boiling for two days. On acidification of the alkaline solution with hydrochloric acid, after all iron had been removed, p-thiolbenzoic acid is obtained.



According to Thompson (loc.cit.) p-thiolbenzoic acid is best purified by subliming under reduced pressure and crystallising the sublimed product from chloroform. In this way Thompson obtained a crystalline product which melted at 219°C. It is of interest to note at this stage that Smiles and Harrison (lot. cit.) state that p-thiolbenzoic acid decomposes at about 250°C. while Thompson (loc.cit.) gives the melting-point as 219°C. As will be shown later the author was able to confirm the melting-point given by Thompson.

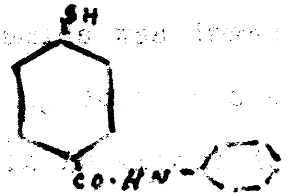
The present author has carried out the preparation of p-thiolbenzoic acid in a similar manner to that adopted by Thompson (loc. cit.) and has been able to confirm Thompson's results. Instead of reducing the p-dithio-benzoic acid in concentrated sodium carbonate solution with iron powder as suggested by Thompson the author has found that reduction of the p-dithio-benzoic acid is easily accomplished by dissolving the di-thio acid in sodium hydroxide solution and adding sodium hyposulphite ($Na_2 S_2 O_4$) at the boil. In this manner the reduction of p-dithio-benzoic acid to p-thiolbenzoic acid is completed in about 10-15 mins. As already stated reduction with iron powder, according to the directions supplied by Thompson (loc. cit.), takes two days. Attempts to reduce p-dithio-benzoic acid with zinc dust and glacial acetic acid (the method adopted by Allen and Mackay [loc. cit.] for reducing o-dithio-benzoic acid to form o-thiolbenzoic acid) and with zinc dust and a mixture of glacial acetic acid and hydrochloric acid were abortive, as products which had indefinite melting-points were always obtained. From the author's experiments in this direction it would appear that reduction of p-dithio-benzoic acid in acid media leads to the formation of compounds of indefinite melting-point and which can not be purified by sublimation and/or crystallisation. In fact in one experiment which the author carried out, p-dithiobenzoic acid remained unaffected after boiling for five hours with zinc dust and glacial acetic acid in a flask under a reflux condenser. p-dithiobenzoic acid is a white amorphous powder which melts at around 316°C.

The arylamides of p-thiolbenzoic acid were prepared in exactly the same manner as the arylamides of o-thiolbenzoic acid, i.e. the arylamine and p-thiolbenzoic acid were condensed in the minimum amount of pyridine as solvent, using phosphorus trichloride as the condensing agent. The ratio of p-thiolbenzoic acid to arylamine was usually that of 1:2.

The following arylamides of p-thiolbenzoic acid have been prepared by the author.

1). Anilide of p-thiolbenzoic acid (II) from p-thiolbenzoic acid and aniline.

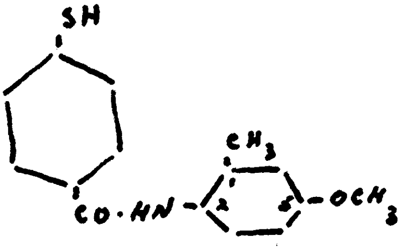
II.



2). 5-methoxy-2-toluidide of p-thiolbenzoic acid (III) from p-thiolbenzoic acid and 5-methoxy-2-toluidine (5-methoxy-2-aminotoluene).

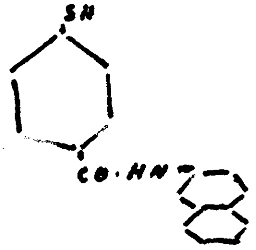
III.

III.



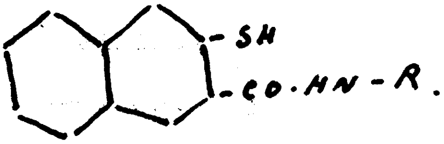
3). β-naphthylamide of p-thiolbenzoic acid (IV) from p-thiolbenzoic acid and β-naphthylamine.

IV.



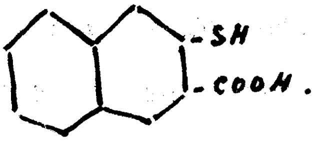
These arylamides of p-thiolbenzoic acid were all white crystalline substances. They were all insoluble in the commoner organic solvents. They were, however, soluble in hot pyridine, nitrobenzene and benzene-nitrobenzene mixtures. Like the arylamides of o-thiolbenzoic acid, the arylamides of p-thiolbenzoic acid were insoluble in boiling aqueous sodium hydroxide solutions. They were, however, soluble in warm $^N/1$ alcoholic potassium hydroxide. On addition, even of small amounts, of water to these solutions the arylamide was immediately precipitated unchanged. On boiling solutions of the arylamides of p-thiolbenzoic acid in 2N alcoholic potassium hydroxide solution for five hours in a flask under a reflux condenser, hydrolysis took place and p-thiolbenzoic acid and the arylamine were isolated on working up the products of hydrolysis in the usual manner. The p-thiolbenzoic acid was identified by subliming the acid component obtained after hydrolysis and comparing with the original acid used.

Section III. Arylamides of 2-thiol-3-naphthoic acid.

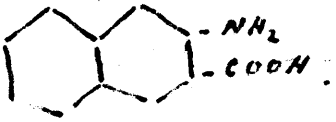


The preparation of 2-thiol-3-naphthoic acid (I) is briefly described in D.R.P.240,118 (Kalle & Co., Chem. Zentr., 1911, 82, II, 1567; Frdl., 10, 510). This patent describes the preparation of the acid from 2-amino-3-naphthoic acid (II). The 2-amino-3-naphthoic acid is diazotised and the 2-diazo-3-naphthoic acid decomposed with sodium polysulphide solution. The dithionaphthoic acid thus formed is reduced to form the 2-thiol-3-naphthoic acid. No details, however, of the decomposition of the 2-diazo-3-naphthoic acid with sodium polysulphide or the reduction of the dithionaphthoic acid to the 2-thiol-3-naphthoic acid, are given in the patent. The present author has prepared 2-thiol-3-naphthoic acid in an analogous way to the preparation of o-thiolbenzoic acid (see page 141).

I.



II.



The 2-amino-3-naphthoic acid dissolved in hot dilute alcohol with a yellow colour and crystallised out on cooling in small shining yellow leaves which melted at 214°C. The dilute alcoholic solution of the acid exhibited a green fluorescence. 2-Amino-3-naphthoic acid is insoluble in cold water and sparingly soluble in hot water. Aqueous solutions of 2-amino-3-naphthoic acid give a pale green ferric chloride reaction; on warming the solution a green precipitate is formed. The preparation of 2-amino-3-naphthoic acid was first described by R. Möhlau, (Ber., 1895, 28, 3096) who prepared it, in poor yield, by the action of aqueous ammonia on 2-hydroxy-3-naphthoic acid at 280°C. and at pressures of over 100 atmospheres (e.g. cf. the pressure curve in H.E. Fierz-David-"Grundlegende Operationen der Farbenchemie", 2nd Edition, page 180). D.R.P.488,946 (I.G., cf. also Swiss Patent 132,031 of the same company) describes the preparation of 2-amino-3-naphthoic acid by heating 100 parts of 2-hydroxy-3-naphthoic acid with 150 parts of ferrous sulphate and 600 parts of ammonia for 15 hours at 200°C. in an autoclave. A yield of 90 per cent is claimed. H. E. Fierz - David and R. Tobler,(Helv. Chim. Acta., 1922, 5, 557-560) describe a process for amidating 2-hydroxy-3-naphthoic acid by heating this compound with zinc chloride-ammonia and ammonium chloride in a current of ammonia at 180-190°C. The reaction is carried out in an autoclave fitted with a stirrer. Heating is carried out by means of an oil-bath. After cooling, the reaction product is extracted with 10% hydrochloric acid, filtered off and the residue on the filter boiled with 35% hydrochloric acid whereupon the hydrochloride of the amino-acid goes into solution while the unchanged hydroxy-acid is filtered -off. On cooling the filtrate, the hydrochloride of 2-amino-3-naphthoic acid, separates out. These authors claim yields of 2-amino-3-naphthoic acid equal to 70% of theory. In a private communication to the author Professor Fierz-David states that the mixture of zinc chloride-ammonia and ammonium chloride was prepared by mixing powdered ammonium chloride in an autoclave (a flat pan which was capable of withstanding a pressure of 2 atmospheres). By heating the mixture at about 150°C. and passing a current of ammonia through the vessel a mixture was obtained which gave satisfactory results when it was mixed (after cooling) with 2-hydroxy-3-naphthoic acid. Professor Fierz-David also states in this communication that the results were never constant and that the reaction proceeded also without ammonium chloride (not published). Finally, the I.G. Farbenindustrie A-G. claim that 2-amino-3-naphthoic acid is obtained in 70-80% yield by heating 2-hydroxy-3-naphthoic acid or its zinc salt with zinc oxide or zinc carbonate and ammonium chloride at 180-200°C. preferably in a current of dry air or ammonia gas (cf. English Patent 330,941 of 20th. June, 1930). This process has the advantage over those already mentioned by reducing the duration of the reaction to 3-4 hours, and avoiding the manufacture of zinc chloride-ammonia, which it is stated is cumbersome and costly. Uniformly good results are claimed by the Patentees. The following example taken from the patent illustrates the method of working. -- 220 parts by weight of the zinc salt of 2-hydroxy-3-naphthoic acid, 162 parts by weight of zinc carbonate and 395 parts by weight of ammonium chloride are thoroughly mixed and heated for three hours to 190°C. in a continuously rotating ball-mill provided with a heating jacket. At the same time a slow current of dry ammonia is passed through the mill. The dry mixture at first becomes a thin paste and finally solidifies to a hard greenish mass. After cooling, the mass is powdered, dissolved in 2000 parts of hot water and 565 parts by weight of hydrochloric acid (specific gravity = 1.152) and filtered from any undissolved residue. On cooling, the hydrochloride of 2-amino-3-naphthoic acid crystallises out. By dissolving in sodium carbonate solution, filtering from a little impurity and precipitating with acetic acid, the 2-amino-3-naphthoic acid is obtained in a pure state. By working in this manner it is claimed that yields amounting to 80 per cent of the theoretical are obtained.

To prepare 2-thiol-3-naphthoic acid from 2-amino-3-naphthoic acid the author made use of the general principles of Allen and Mackay's method (loc. cit.) for preparing o-thiolbenzoic acid, the success of which method the author had already confirmed during his work on that acid (see page 141).

In the preparation of 2-thiol-3-naphthoic acid, the 2-amino-3-naphthoic acid was dissolved by boiling with concentrated hydrochloric acid (200 c.c. conc. HCl per mol. of 2-amino-3-naphthoic acid) and water. The diazotisation of the 2-amino-3-naphthoic acid was easily carried out by cooling the solution to 0° - 5° C. and adding the requisite amount of sodium nitrite (dissolved in water) in small quantities at a time - care being taken that the temperature of the diazo-solution did not rise above 5°C. This temperature was easily maintained by adding crushed ice as required. The diazo-solution was then filtered in order to remove a small amount of a black insoluble material. The diazo solution was slowly run into sodium polysulphide solution prepared by dissolving sulphur in sodium sulphide solution and then adding sodium hydroxide (full details of the preparation being given in the experimental section). Thorough mixing was maintained by using a mechanical stirrer and the temperature was kept below 5°C. by adding crushed ice. The solution was at first orange in colour but on allowing to stand at laboratory temperature overnight, in order to ensure the complete evolution of nitrogen, the solution acquired an olive-yellow colour. The solution, which was faintly alkaline to Thiazole paper (Mimosa paper) and phenolphthalein paper, was then filtered and the dithio-naphthoic acid precipitated by the addition of a slight excess of concentrated hydrochloric acid (blue to Congo Red paper). The dithio-acid was filtered-off at the pump and washed once with cold water. It was then dissolved in sodium carbonate solution, the solution boiled and filtered in order to remove any excess of sulphur. The filtrate was then acidified with a slight excess of hydrochloric acid (blue to Congo Red paper) and the precipitated dithio-acid again filtered off at the pump. The dithio-naphthoic acid which was light brown in colour was then reduced to the 2-thiol-3-naphthoic acid by boiling for four hours with zinc dust and glacial acetic acid in a flask fitted with a reflux condenser. On cooling, a pale yellow amorphous looking precipitate settled down. This was filtered, washed well with cold water and then boiled with sodium hydroxide solution for 20 minutes and filtered. The pale yellow coloured filtrate was acidified with hydrochloric acid (blue to Congo Red paper) and the pale yellow precipitate filtered-off, washed free from mineral acid and dried in the steam-oven. Yields of 2-thiol-3-naphthoic acid, calculated on the 2-amino-3-naphthoic acid, equal to 85-90% of the theoretical were obtained. 2-thiol-3-naphthoic acid dissolved in boiling dilute alcohol (50 parts alcohol: 50 parts water) and crystallised out on cooling in pale yellow micro-crystals which melted at 275-276°C. (cf. Kalle & Co. D.R.P. 240,118). 2-Thiol-3-naphthoic acid is insoluble in cold water and is only sparingly soluble in boiling water. On cooling the boiling solution, the acid separated out as a flocculent precipitate which was very pale yellow in colour. The aqueous solution of 2-thiol-3-naphthoic acid gave no characteristic ferric chloride reaction.

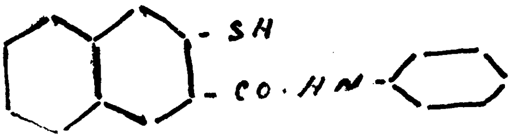
As already mentioned in the general theoretical section no reference to the preparation of arylamides of 2-thiol-3-naphthoic acid could be found in the literature. They were, however, readily prepared by the author by dissolving 2-thiol-3-naphthoic acid and the arylamine, usually in the ratio of 1 mol. of 2-thiol-3-naphthoic acid to 2 mols. of arylamine, in the minimum amount of pyridine and adding phosphorus trichloride to the solution at 70°C. The phosphorus trichloride was added over a period of half an hour. After the addition of the phosphorus trichloride the temperature was maintained at 115°C. for a further four hours. During the course of the reaction the whole was well stirred except towards the end of the reaction when the reaction mass had become fairly viscuous in consistency. On cooling the reaction product, alcohol was added and the mixture then boiled until complete solution resulted. On allowing to stand in the ice-chest overnight the arylamide settled out and was filtered-off with suction. On adding cold water to the filtrate to which a little glacial acetic acid had been added and stirring vigorously during the addition of the water, a cream coloured precipitate was obtained which contained appreciable amounts of arylamide. The yields of the arylamides produced by this means were in the region of 80 per cent and in some cases yields of around 90 per cent of the theoretical were obtained.

The following arylamides of 2-thiol-3-naphthoic acid were prepared by the author.

1). Anilide of 2-thiol-3-naphthoic acid (III), from 2-thiol-3-naphthoic acid and aniline.

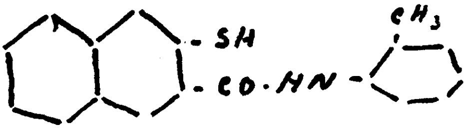
III./

III.



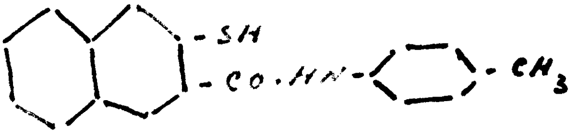
2). o-toluidide of 2-thiol-3-naphthoic acid (IV) from 2-thiol-3-naphthoic acid and o-toluidine.

IV.



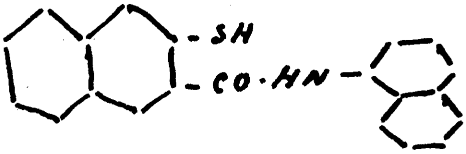
3). p-toluidide of 2-thiol-3-naphthoic acid (V), from 2-thiol-3-naphthoic acid and p-toluidine.

V.



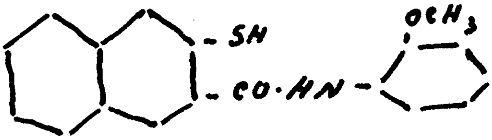
4). α-naphthylamide of 2-thiol-3-naphthoic acid (VI) from 2-thiol-3-naphthoic acid and α-naphthylamine.

VI.



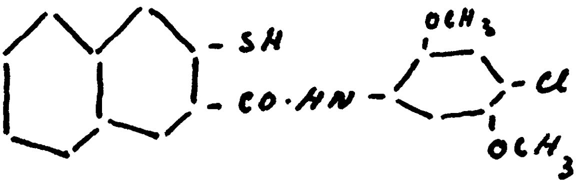
5). o-anisidide of 2-thiol-3-naphthoic acid (VII) from 2-thiol-3-naphthoic acid and o-anisidine.

VII.



6). 2:5-dimethoxy-4-chloroanilide of 2-thiol-3-naphthoic acid (VIII) from 2-thiol-3-naphthoic acid and 2:5-dimethoxy-4-chloroaniline.

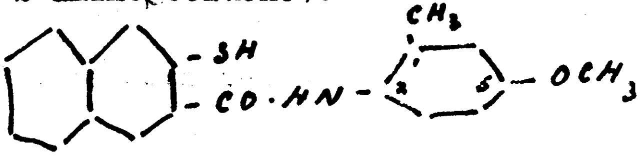
VIII.



7)./

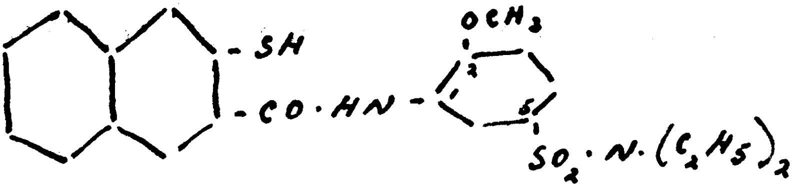
7). 5-methoxy-2-toluidide of 2-thiol-3-naphthoic acid (IX) from 2-thiol-3-naphthoic acid and 5-methoxy-2-toluidine (5-methoxy-2-aminotoluene).

IX.



8). 1-amino-2-methoxybenzene-5-sulphondiethylamide of 2-thiol-3-naphthoic acid (X) from 2-thiol-3-naphthoic acid and 1-amino-2-methoxybenzene-5-sulphondiethylamide.

X.



All of the above mentioned arylamides of 2-thiol-3-naphthoic acid were white or cream-coloured crystalline products which were insoluble in the majority of the commoner organic solvents. They were, however, soluble in pyridine, nitrobenzene and benzene-nitrobenzene mixtures. Like the arylamides of o-thiolbenzoic acid, the arylamides of 2-thiol-3-naphthoic acid were almost insoluble in boiling aqueous solutions of sodium hydroxide, but were soluble in warm $^N/1$ alcoholic potassium hydroxide solution. As already stated in the general theoretical section these $^N/1$ alcoholic potassium hydroxide solutions of the arylamides of 2-thiol-3-naphthoic acid could be diluted with a limited amount of water without precipitation of the arylamide.

On boiling the $^N/1$ alcoholic potassium hydroxide solutions of the arylamides of 2-thiol-3-naphthoic acid in a flask fitted with a reflux condenser for four hours hydrolysis took place and the arylamine and 2-thiol-3-naphthoic acid were obtained.

Dyeings of the arylamides of 2-thiol-3-naphthoic acid.

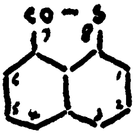
In the special "Dyeings" section, dyeings of the 5-methoxy-2-toluidide and the α-naphthylamide of 2-thiol-3-naphthoic acid in combination with the following diazotised bases are shown.-

1). 2:5-dichloroaniline.
2). 5-chloro-2-toluidine.
3). 5-nitro-2-anisidine.
4). o-amino-azo-toluene.
5). o-dianisidine.
and 6). 4'-methoxy-4-aminodiphenylamine.

The 5-methoxy-2-toluidide and the α-naphthylamide were taken as representative of the arylamides of 2-thiol-3-naphthoic acid. To impregnate cotton yarn with the arylamides of 2-thiol-3-naphthoic acid the arylamides were dissolved in the requisite amount of $^N/1$ alcoholic potassium hydroxide solution and the solutions diluted with water to the desired volume. 30 grams of Glauber's salt per litre of padding liquor were added in order to improve the substantivity of the arylamides for the cotton fibre.

The biscuit, orange and tan shades obtained did not possess the excellent fastness properties of the shades produced by the combination of the arylamides of 2-hydroxy-3-naphthoic acid (i.e. members of the Naphtol AS series of dye intermediates) and the same diazotised amines. The shades produced by the arylamides of 2-thiol-3-naphthoic acid and these diazotised amines were, however, stronger and slightly faster than the shades produced from the arylamides of o-thiolbenzoic acid and the same diazotised amines.

Section IV. Lactone of 1-thiol-8-naphthoic acid.

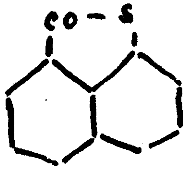


= 7-keto-8-thia-acenaphthen.

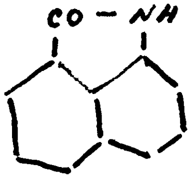
As already stated in the general theoretical section all attempts to prepare arylamides of the lactone of 1-thiol-8-naphthoic acid were unsuccessful. This was not altogether surprising owing to the fact that, as the inner anhydride of the hypothetical 1-thiol-8-naphthoic acid, the lactone of 1-thiol-8-naphthoic acid is extremely stable. For example, on dissolving the lactone of 1-thiol-8-naphthoic acid in 10 per cent sodium hydroxide solution and acidifying the solution or by passing in to the solution carbon dioxide gas the substance is recovered unchanged (cf. Friedländer, & Woroshzow, Annalen, 388, 21).

According to Friedländer, Woroshzow (loc. cit.; cf. also Höchst Farbwerke, D.R.P.198,050; Chem. Zentr. 1908, I, 1815; Frdl. 9, 591) the lactone of 1-thiol-8-naphthoic acid (I) is

I.



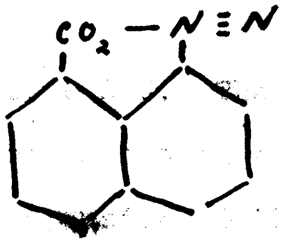
II.



prepared by diazotising the lactam of 1-amino-8-naphthoic acid, viz:- naphthostyril (II) and decomposing the resultant diazo compound (III) with potassium ethyl xanthate.

III./

III.

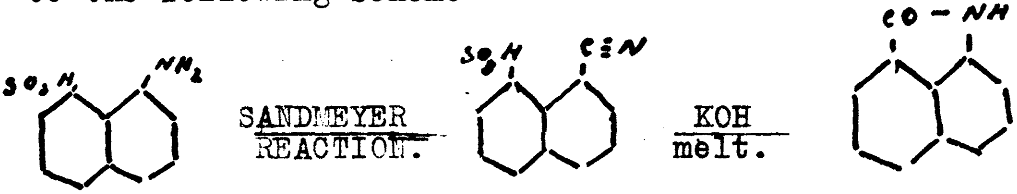


The present author has repeated Friedländer and Woroshzow's (loc. cit.) experiments by decomposing the diazo naphthostyril with potassium ethyl xanthate but obtained very poor yields (around 20%) of 1-keto-2-thio-acenaphthen. Very good yields (around 80%), however, were obtained by the author by first dissolving the naphthostyril in 10 per cent sodium hydroxide solution by boiling for about half an hour, then adding hydrochloric acid, while the whole was well stirred, until the reaction of the solution was very faintly alkaline to phenolphthalein paper. At this stage a small amount of a black product remained undissolved and this was filtered-off. The clear brown filtrate was then taken, cooled to between 0°-5°C. and the requisite amount of sodium nitrite added. This solution was then run quickly into an ice-cold solution of hydrochloric acid (0°C.), while the whole was thoroughly stirred. The amount of hydrochloric acid present in this solution was sufficient to react with the sodium nitrite to form the diazo-compound of naphthostyril and yet leave the final diazo-solution slightly but distinctly acid to Congo Red paper. The temperature of the diazo-mixture was never allowed above 5°C. The diazo-compound of naphthostyril separated out in small light brown coloured needles. The suspension of the diazo-compound was then run into the well stirred sodium polysulphide solution and the temperature during the addition maintained at under 5°C. After the addition of the diazo-solution, the resultant solution, which was then faintly alkaline to Thiazole paper and to phenolphthalein paper, was allowed to stand overnight at Laboratory temperature to remove the last traces of nitrogen. The olive-yellow solution was filtered and acidified with hydrochloric acid (blue to Congo Red paper). The cream coloured precipitate so obtained was filtered-off with suction, washed well with cold water and redissolved in sodium hydroxide solution (Norit). This solution was boiled and filtered to remove any excess of sulphur. The filtrate was then acidified with hydrochloric acid (blue to Congo Red paper) and the precipitate filtered-off at the pump, washed free from mineral acid and dried at a low temperature (50°C.). The dry product was then dissolved in alcohol and boiled with a little "Norit" and filtered. On cooling, a large amount of a pale yellow crystalline product was obtained. On recrystallising from alcohol (Norit), small sulphur yellow needles which had a melting-point of 145-146°C. (Fried-

(Friedländer and Woroshzow [loc. cit.] give the melting-point of the lactone of 1-thiol-8-naphthoic acid as 144½° - 145½° C.) were obtained and these were found to be the lactone of 1-thiol-8-naphthoic acid.

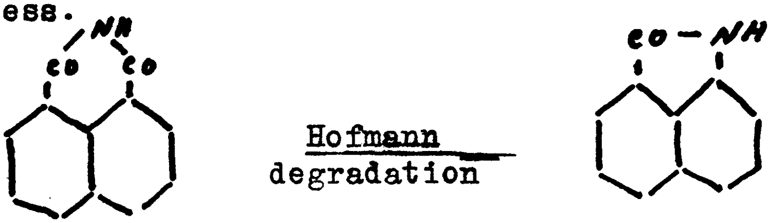
According to Friedländer and Woroshzow (loc. cit.) warming the diazo-compound of naphthostyril with sodium disulphide solution leads to the formation of a red-violet coloured by-product which interferes with the yield of the lactone of 1-thiol-8-naphthoic acid and for this reason these authors recommend the preparation of the lactone of 1-thiol-8-naphthoic acid from diazotised naphthostyril and potassium xanthate. The present author has found, however, that the production of this red-violet coloured by-product can be eliminated by having the diazo-naphthostyril suspension distinctly acid to Congo Red paper prior to mixing with the sodium polysulphide solution. It was also found that by causing the reaction of diazo-naphthostyril and sodium polysulphide to take place at temperatures not exceeding 5°C. much better yields of the lactone were obtained than when the reaction was allowed to proceed at higher temperatures.

Naphthostyril crystallises from dilute alcohol (50 parts alcohol 50 parts water) in straw-yellow needles melting at 180-181° C. Naphthostyril sublimes readily and is easily soluble in alcohol and acetone. Solutions of naphthostyril in these two solvents exhibit a greenish fluorescence. Naphthostyril is sparingly soluble in water and ether; a yellow coloured solution is obtained on dissolving in concentrated sulphuric acid. Naphthostyril is the lactam or inner anhydride of 1-amino-8-naphthoic acid which is unstable. 1-amino-8-naphthoic acid and its salts are unstable to mineral acids; by warming their solutions they are converted into the stable naphthostyril (cf. Eckstrand, J. pr. Chem. [2], 38, 160). Naphthostyril can be prepared either from 1-amino-naphthalene-8-sulphonic acid (cf. D.R.P. 441,225 I.G., Frdl. 15, 1810) according to the following scheme.



1-amino-naph-:thalene-8-sulphonic acid. 1-cyano-naph-:thalene-8-sulphonic acid. Naphthostyril.

or from naphthalimide (cf. F. Ullmann and E. Cassirer, Ber., 1910, 43, 439) by means of the Hofmann degradation process.

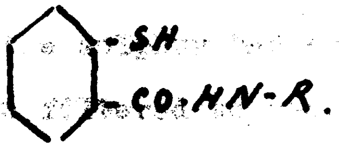


Naphthalimide Naphthostyril

At the present time, naphthostyril~~,~~ is principally used in the manufacture of anthanthrone, the halogen derivatives of which are valuable vat dyestuffs.

EXPERIMENTAL SECTION.

Section I. Arylamides of o-thiolbenzoic acid.



Preparation of o-thiolbenzoic acid.

As already stated in the theoretical section (page 141) o-thiolbenzoic acid is prepared by the method recommended by Allen and Mackay (Organic Syntheses, 1932, 12, 76).

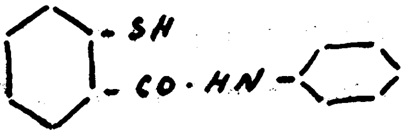
The following quantities of materials were used.-

13.7 gm.	anthranilic acid.
20.0 c.c.	conc. hydrochloric acid.
6.9 gm.	sodium nitrite.
8.5 gm.	sodium sulphide (fused).
3.4 gm.	sulphur.
6.0 gm.	sodium hydroxide sticks.

The anthranilic acid was dissolved by boiling with the hydrochloric acid and 100 c.c. of water. The solution was then cooled down to 0° C. and diazotised by adding the sodium nitrite, dissolved in 50 c.c. of boiling water and subsequently cooled to 0° C. During the diazotisation care was taken that the temperature of the diazo-solution did not rise above 5° C. During the diazotisation the whole was well stirred.

The sodium sulphide was dissolved in 100 c.c. of water by boiling and then the sulphur was added and boiling continued until the sulphur had completely dissolved. The solution was then filtered to remove a small amount of a black insoluble compound. The sodium hydroxide sticks dissolved in about 100 c.c. of water were then added to the filtrate. The sodium polysulphide solution was then cooled down to 0°C. The diazo-solution was then carefully run into the sodium polysulphide solution. Thorough mixing was maintained by using a mechanical stirrer and care was taken that the temperature of the mixture did not rise above 5°C. This was easily maintained by adding crushed ice at intervals. Towards the end of the addition of the diazo-solution frothing occurred during the evolution of nitrogen but this was easily controlled by the addition of ether from time to time. When the addition of the diazo-solution had been completed, stirring was stopped and the solution allowed to remain at laboratory temperature overnight in order to ensure complete evolution of nitrogen. The final colour of the solution was olive-yellow and reacted faintly alkaline to Thiazole paper and phenolphthalein paper. The dithiobenzoic acid was precipitated by the addition of concentrated hydrochloric acid to the solution - blue to Congo-Red paper. The dithiobenzoic acid was filtered off at the pump and washed once with cold water. To remove excess of sulphur from the di-thio-acid the residue on the filter was boiled with sodium carbonate solution (6.0 gms. anhydrous sodium carbonate in 200 c.c. water) and filtered. The di-thio-benzoic acid was reprecipitated by the addition of conc. hydrochloric acid, (until blue to Congo red paper) filtered off with suction, washed well with cold water and dried as well as possible on the filter. The di-thio-acid was then transferred to a suitable flask and boiled with 27 grams zinc dust (99.9 per cent Zn.) and 300 c.c. glacial acetic acid under a reflux condenser for four hours. The flask and contents were then allowed to cool. The solid matter was filtered-off at the pump, washed with a little 40% acetic acid and finally with water. The contents of the filter were then transferred to a beaker and boiled with an excess of sodium hydroxide solution for 20 minutes. The insoluble matter was filtered-off and washed with a little warm water. The pale yellow coloured filtrate was acidified with hydrochloric acid (blue to Congo red paper) and the o-thiolbenzoic acid was obtained as a very pale yellow flocculent precipitate, which was filtered-off at the pump, washed free from mineral acid and finally dried at 105°C. The yields of o-thiolbenzoic acid obtained in the various repeats of this preparation ranged between 80-85% of the theoretical calculated on the amount of anthranilic acid used. The o-thiolbenzoic acid was crystallised from dilute alcohol (Norit) - 1 part alcohol; 2 parts water in pale yellow plates which melted at 163-164°C. and gave in aqueous solution a transient blue ferric chloride reaction. No depression of the melting-point was observed on admixture with an authentic specimen of o-thiolbenzoic acid.

Preparation of the anilide of o-thiol-benzoic acid.



No reference to the preparation or properties of this compound could be found in the literature.

The anilide of o-thiolbenzoic acid was prepared by the author by causing o-thiolbenzoic acid and aniline to react in pyridine solution with phosphorus trichloride. The following quantities of materials were used:-

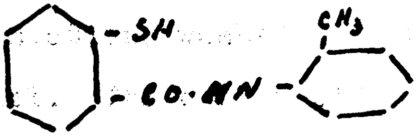
15.4 gm. (1/10 mol.)	o-thiolbenzoic acid.
20 c.c. ($^1/5$ mol.)	aniline.
10 c.c.	pyridine.
6 c.c.	phosphorus trichloride.

The thiolbenzoic acid and the aniline were dissolved in the pyridine by heating to 70° C. At this point the phosphorus trichloride was added in small quantities at a time over a period of half an hour. After the phosphorus trichloride had been added the temperature of the reaction mixture was raised to 115°C. and maintained at this temperature for a further four hours. To ensure thorough mixing the whole was well stirred during the entire course of the reaction. On completion of the reaction and on cooling down to around 70°C., 150 c.c. of alcohol were added and the whole boiled on the steam-bath until complete solution had occurred. At this point 5 c.c. of glacial acetic acid were added. On allowing to remain in the ice-chest overnight a small amount of a white crystalline solid separated out, and this was filtered-off with suction, washed with alcohol and dried. To the filtrate, half its volume of water was added carefully and with efficient stirring. In this way a flocculent white precipitate was obtained which was filtered off at the pump washed with water and dried at a low temperature. Total yield of anilide was equal to 83% of theory. On crystallising from nitrobenzene (Norit) the anilide was obtained in small fine white needles which melted at 236-37°C.

The anilide of o-thiolbenzoic acid was insoluble in aqueous solutions of sodium hydroxide but dissolved slowly in cold N/1 alcoholic potassium hydroxide solution and more rapidly on warming.
(Found N - 5.9%; S - 14.2%. $C_{13}H_{11}ONS$ requires N = 6.1% and S = 14.0%).

Hydrolysis of the anilide of o-thiolbenzoic acid with N/1 alcoholic potassium hydroxide solution (boiling under a reflux condenser for 4 hours, distilling off the excess alcohol and separating the products of hydrolysis in the usual manner see page 59.) yielded o-thiolbenzoic acid and aniline.

Preparation of the o-toluidide of o-thiolbenzoic acid.



No reference to the preparation or properties of the o-toluidide of o-thiolbenzoic acid could be found in the literature.

The author has been able to prepare this compound by the "toluene" process using phosphorus pentoxide as the condensing agent and by the "pyridine" process using phosphorus trichloride as the condensing agent.

1). "Toluene" Process.

The following quantities of materials were used:-

15.4 gm.($^1/10$ mol.) .... o-thiolbenzoic acid.
21.4 gm.($^1/5$ mol.) .... o-toluidine.
20 c.c. .... toluene.
6 gm. .... phosphorus pentoxide.

The o-thiolbenzoic acid and o-toluidine were dissolved in the toluene by heating to 70° C. The phosphorus pentoxide was added in small quantities at a time over a period of half an hour. After the addition of the phosphorus pentoxide the mixture was boiled for six hours. During the whole course of the reaction the mixture was well stirred. On completion of the reaction a little sodium carbonate solution was added and the toluene remaining, distilled-off with steam. The reaction product which separated was filtered off with suction, washed with water and finally with a little alcohol. The o-toluidide of o-thiolbenzoic acid so obtained was dried in the steam-oven. Yield - 14.4 gm. = 59% of the theoretical. The arylamide was crystallised from nitrobenzene (Norit) in white micro-crystals which melted at 217-218° C.

(Found:- C(micro) - 69.1%; H(micro) - 5.1% N - 5.80% and 5.83%; S - 13.28% and 13.20%. $C_{14}H_{13}ONS$ requires C = 69.1%; H = 5.3%; N = 5.8% and S = 13.2%).

2). "Pyridine" Process.

The following quantities of materials were used.-

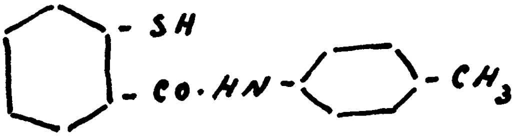
15.4 gm. ($^1/10$ mol.)	o-thiolbenzoic acid.
21.4 gm. ($^1/5$ mol.).......	o-toluidine.
10 c.c.	pyridine.
6 c.c.	phosphorus trichloride.

The o-thiolbenzoic acid and o-toluidine were dissolved in the pyridine by heating to 70° C. The phosphorus trichloride was added over a period of ½ an hour. The whole was then heated for four hours at 115° C. cooled to about 70°C. and 150 c.c. of alcohol added. The whole was then boiled until the viscous reaction mass had com-

:pletely dissolved. At this point 5 c.c. of glacial acetic acid were added. On allowing to stand in the ice-chest overnight a white solid separated out and this was collected by filtering-off at the pump, and washing with alcohol. The residue was dried at 100°C. The filtrate was treated carefully with water (½ volume of filtrate). To obtain the remainder of the arylamide as a flocculent precipitate the whole was mechanically stirred during the addition of the water and for a short time thereafter. The precipitate (cream coloured) was filtered off at the pump and washed well with water and dried. Total yield of arylamide was 18.0 gm. = 74% of theory. On crystallising from nitrobenzene (Norit) a white micro-crystalline product was obtained which melted at 217-218° C. and on admixture with the product obtained by the "Toluene" process no depression of melting point was observed.

Hydrolysis of the o-toluidide of o-thiolbenzoic acid with N/1 alcoholic potassium hydroxide solution (boiling under a reflux condenser for 4 hours), gave o-toluidine and o-thiolbenzoic acid on working up the products of hydrolysis in the manner usually adopted (see page 59).

Preparation of the p-toluidide of o-thiolbenzoic acid.



No reference to the preparation or properties of the p-toluidide of o-thiolbenzoic acid could be found in the literature.

The arylamide was prepared by the "toluene" process using phosphorus pentoxide as the condensing agent.

The following quantities of materials were used:-

15.4 gm. ($^1/10$ mol.)	o-thiolbenzoic acid.
21.4 gm. (1/5 mol.)	p-toluidine.
20 c.c.	toluene.
6 gm.	phosphorus pentoxide.

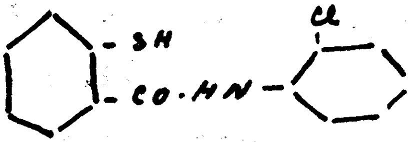
The method of working was exactly the same as that described for the preparation of the o-toluidide (see page 179).

The p-toluidide of o-thiolbenzoic acid crystallised from nitrobenzene (Norit) in white micro-crystals which had a melting-point of 230° C.

(Found:- C(micro) - 69.1%; H(micro) - 5.3%; N - 5.91% and 5.86%; S - 13.3% and 13.3%. $C_{14}H_{13}ONS$ requires C = 69.1%, H = 5.3%, N = 5.8% and S = 13.2%).

On boiling the p-toluidide of o-thiolbenzoic acid with $^N/1$ alcoholic potassium hydroxide solution for four hours hydrolysis took place and p-toluidine and o-thiolbenzoic acid were obtained on working up the products of hydrolysis in the usual manner (see page 59.).

Preparation of the o-chloroanilide of o-thiolbenzoic acid.



No reference to the preparation or properties of the o-chloroanilide of o-thiolbenzoic acid could be found in the literature.

By condensing o-thiolbenzoic acid and o-chloroaniline in pyridine solution in the presence of phosphorus trichloride and working up the condensation product in the usual manner (see page 175) the o-chloroanilide of o-thiolbenzoic acid was obtained in a yield equal to 77% of the theoretical.

The following quantities were used:-

15.4 gm. ($^1/10$ mol.)	o-thiolbenzoic acid.
25.5 gm. ($^1/5$ mol.)	o-chloroaniline.
10 c.c.	pyridine.
6 c.c.	phosphorus trichloride.

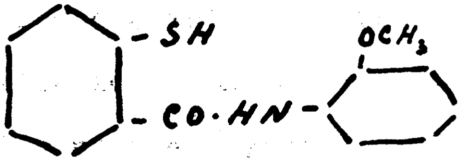
The o-chloroanilide of o-thiolbenzoic acid crystallised from Benzene-nitrobenzene (75: 25 + Norit) (~~75:-25--Norit~~) in small fine white needles which melted at 218-219°C.

The o-chloroanilide was insoluble in aqueous sodium hydroxide solutions even on boiling but dissolved slowly in cold $^N/1$ alcoholic potassium hydroxide solution.

(<u>Found:-</u> N = 5.3%; S = 12.3%. $C_{13} H_{10} O N Cl S$ requires N = 5.3% and S = 12.1%).

On boiling the o-chloroanilide of o-thiolbenzoic acid with N/1 alcoholic potassium hydroxide solution for four hours in a flask fitted with a reflux condenser, hydrolysis took place and on working up the products of hydrolysis in the usual manner o-thiolbenzoic acid and o-chloroaniline were isolated.

Preparation of the o-anisidide of o-thiolbenzoic acid.



No reference to the preparation or properties of the o-anisidide of o-thiolbenzoic acid could be found in the literature.

This arylamide was readily prepared by condensing o-thiolbenzoic acid and o-anisidine in pyridine solution with phosphorus trichloride as the condensing agent. The usual procedure for this process was adopted (see page 175).

The following quantities of materials were used:-

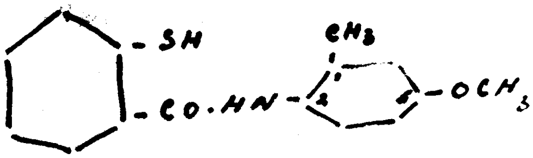
15.4 gm. (1/10 mol.)	o-thiolbenzoic acid.
25.6 gm. (1/5 mol.)	o-anisidine.
10 c.c.	pyridine.
6 c.c.	phosphorus trichloride.

The yield of o-anisidide was equal to 75% of theory. The o-anisidide of o-thiolbenzoic acid crystallised from benzene-nitrobenzene (75:25 + Norit) in small fine white needles which had a melting-point of 156-157°C., and which were insoluble in boiling aqueous solutions of sodium hydroxide but dissolved rapidly in warm N/1 alcoholic potassium hydroxide solution.

(<u>Found:</u>- N = 5.8%; S = 12.6%. $C_{14}H_{13}O_2NS$ requires N = 5.4% and S = 12.4%).

On boiling the o-anisidide with $^N/_1$ alcoholic potassium hydroxide solution for four hours in the usual manner and working up the products of hydrolysis in the customary manner, o-thiolbenzoic acid and o-anisidine were obtained.

Preparation of the 5-methoxy-2-toluidide of o-thiolbenzoic acid.



No reference to the preparation or properties of the 5-methoxy-2-toluidide of o-thiolbenzoic acid could be obtained in the literature.

This arylamide was readily prepared by the usual "Pyridine" Process, full details of which are given on page 175.

The following quantities of materials were used:-

7.7 gm. ($^1/20$ mol.)	o-thiolbenzoic acid.
8.0 gm. ($^1/20$ mol.+ excess)	5-methoxy-2-toluidine.
5 c.c.	pyridine.
3 c.c.	phosphorus trichloride.

Yield of arylamide was equivalent to 81% of that theoretically possible.

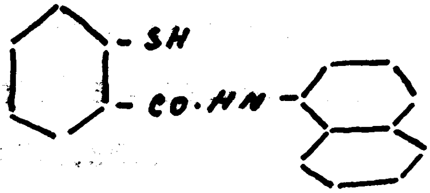
The 5-methoxy-2-toluidide of o-thiolbenzoic acid recrystallised from nitrobenzene (Norit) in small fine white needles which had a melting-point of 233-234° C. The arylamide was insoluble in boiling aqueous sodium hydroxide solutions but dissolved slowly in cold, more quickly in warm $^N/1$ alcoholic potassium hydroxide solution.

(Found:- /

(Found:- N = 5.1%; S = 11.8%. $C_{15}H_{15}O_{2}NS$ requires N = 5.1% and S = 11.7%).

On boiling the 5-methoxy-2-toluidide of o-thiolbenzoic acid with $^{N}/1$ alcoholic potassium hydroxide solution in a flask fitted with a reflux condenser for four hours, hydrolysis took place and on working up the products of hydrolysis in the usual manner, o-thiolbenzoic acid and 5-methoxy-2-toluidine were obtained.

Preparation of the α- naphthylamide of o-thiolbenzoic acid.



No reference to the preparation or properties of the α-naphthylamide of o-thiolbenzoic acid could be found in the literature.

This arylamide was readily prepared by the author by condensing o-thiolbenzoic acid and α -naphthylamine in pyridine solution using phosphorus trichloride as the condensing agent. The α -naphthylamide was worked up in the usual manner for this process.

The following quantities were used:-

15.4 gm. ($^1/10$ mol.)	o-thiolbenzoic acid.
14.3 gm. ($^1/10$ mol.)	α-naphthylamine.
10 c.c.	pyridine.
6 c.c.	phosphorus trichloride.

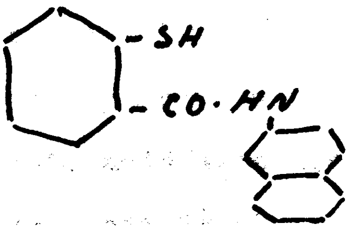
It will be noted molecular proportions were used in this preparation as it was found that in the cases of the α - and β -naphthylamides (q.v.) of o-thiolbenzoic acid the best results were obtained when equimolecular proportions were used. The yield of α -naphthylamide was 91% of that theoretically possible.

The α -naphthylamide crystallised from nitrobenzene

(Norit) in small white crystals which melted at 247-248°C. (Found:- N = 5.2%; S = 11.5%. $C_{17} H_{13} O N S$ requires N = 5.0% and S = 11.5%).

The arylamide, as usual, was insoluble in boiling aqueous caustic soda solutions but was soluble in cold $^{N}/1$ alcoholic potassium hydroxide solution. On boiling the arylamide with $^{N}/1$ alcoholic potassium hydroxide solution in a flask fitted with a reflux condenser for four hours hydrolysis took place and o-thiolbenzoic acid and α-naphthylamine were isolated on working up in the usual manner.

Preparation of the β-naphthylamide of o-thiolbenzoic acid.



No reference to the preparation or properties of the β-naphthylamide of o-thiolbenzoic acid could be found in the literature.

This arylamide, however, was readily prepared by condensing o-thiolbenzoic acid and β- naphthylamine in pyridine solution and using phosphorus trichloride as the condensing agent. The method of working up the arylamide was the usual one for this process.

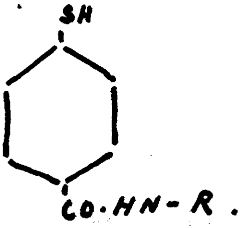
The following quantities of materials were used:-

15.4 gm. ($^1/10$ mol.)	o-thiolbenzoic acid.
14.3 gm. ($^1/10$ mol.)	β- naphthylamine.
10 c.c.	pyridine.
6 c.c.	phosphorus trichloride.

The β -naphthylamide crystallised from nitrobenzene (Norit) in small micro cream coloured plates (rectangular) which melted at 167-168° C. These crystals were insoluble in boiling aqueous sodium hydroxide solutions but were soluble in cold $^N/1$ alcoholic potassium hydroxide solution. (Found:- N = 5.1%; S = 11.6%. $C_{17}H_{13}ONS$ requires N = 5.0% and S = 11.5%).

On boiling the β-naphthylamide with $^N/1$ alcoholic potassium hydroxide solution in a flask fitted with a reflux condenser, hydrolysis took place and β-naphthylamine and o-thiolbenzoic acid were isolated by working up the products of hydrolysis in the usual manner.

Section II. Arylamides of p-thiolbenzoic acid.



Preparation of p-thiolbenzoic acid.

The method of preparation of p-thiolbenzoic acid adopted by the author was similar to that recommended by G. Thompson (J. Soc. Chem. Ind., 1925, 44, 196T); the only difference being that instead of reducing the p-dithio-benzoic acid in sodium carbonate solution with iron powder at the boil for 2 days as suggested by Thompson (loc. cit.), the author was able to bring about reduction of the p-dithio-acid in 15 minutes by dissolving the acid in sodium hydroxide solution and adding sodium hyposulphite; thereby greatly shortening the time of reduction.

The following quantities of materials were used:-

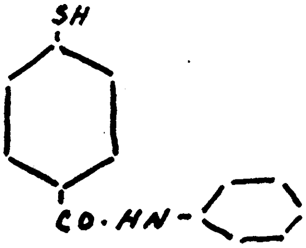
13.7 gm.	p-aminobenzoic acid.
20 c.c.	conc. hydrochloric acid.
6.9 gm.	sodium nitrite.
8.5 gm.	sodium sulphide (fused)
3.4 gm.	sulphur.
6.0 gm.	sodium hydroxide sticks.

The p-aminobenzoic acid was dissolved by boiling the acid with the hydrochloric acid and 100 c.c. of water. The solution was then cooled down to 0° C. and diazotised by adding the sodium nitrite, which had previously been dissolved in boiling water and subsequently cooled to 0°C. During the course of diazotisation care was taken that the temperature of the diazo-solution did not rise above 5° C., and this was accomplished by adding crushed ice to the solution as required and by external cooling. The diazo solution was thoroughly stirred during this time.

The sodium polysulphide solution was prepared by first dissolving the sodium sulphide in 100 c.c. of water and then adding the sulphur and boiling the whole until the sulphur had gone completely into solution. A small amount of a black insoluble compound settled out and this was filtered-off. The sodium hydroxide sticks, dissolved in about 100 c.c. of water, were then added to the filtrate. The sodium poly:sulphide solution was then cooled down to 0° C. by the addition of crushed ice. The diazo-solution was then care:fully run in to the sodium polysulphide solution. Thorough mixing of the two solutions was maintained by using a mechanical stirrer. Care was, of course, taken that the temperature of the mixture did not exceed 5° C. - crushed ice being added to the solution when necessary. It was observed that on this occasion practically no frothing o:ccurred during the evolution of the nitrogen - this was in contrast with the author's experience in preparing o-thiolbenzoic acid (q.v.). When all of the diazo-solution had been added, stirring was stopped and the solution allowed to remain at laboratory temperature overnight to ensure complete evolution of nitrogen. The colour of the solution was then olive-yellow and reacted faintly alkaline to Thiazole paper. The p-di-thiobenzoic acid was precipitated from the solution by the addition of a slight excess of conc. hydrochloric acid (blue to Congo-Red paper), and was filtered-off at the pump and washed once with water. To remove excess sulphur the di-thio-acid was then dissolved in sodium carbonate solution (6 gm. anhydrous sodium carbonate in 200 c.c. water), the solution boiled and filtered; the di-thio acid being reprecipitated from this solution by the addition of a slight excess of hydrochloric acid (blue to Congo-Red paper). The reprecipitated di-thio-acid was filtered with suction and washed free from hydrochloric acid. To reduce the p-di-thio-acid to the p-thiolbenzoic acid the former was dissolved in a slight excess of sodium hydroxide solution (5 c.c. 30% Na OH solution in 500 c.c. water), the solution brought to the boil and 10 grams of sodium hyposulphite (91% $Na_2S_2O_4$) added over a period of 10 minutes. The solution immediately changed colour from a deep brownish-yellow to a pale straw yellow. After the addition of the hyposulphite the whole was boiled for a further 5 minutes. The solution at the end of this period coloured Indanthrene Yellow G paper a cornflower blue shade in three seconds (and so indicating the presence of sufficient hyposulphite). If the solution did not react in this manner to Indanthrene Yellow G paper, more hyposulphite was added and boiling continued for a few minutes longer. This was repeated until the solution gave the cornflower blue reaction with Indanthrene Yellow G paper. The solution was then cooled and the p-thiolbenzoic acid precipitated by adding a slight excess of acetic acid. The putty coloured precipitate was filtered off at the pump and washed twice with cold water. The precipitate was redissolved in sodium hydroxide solution, the solution boiled and filtered. The p-thiolbenzoic acid was then precipitated by adding hydrochloric acid in slight excess (blue to Congo Red paper). This was filtered off with suction and washed free from mineral acid with cold water. The p-thiolbenzoic acid was then dried at 50°C. It was found most important to dry at a low temperature. The yield of p-thiolbenzoic acid, calculated on amino-acid was equal to 80% of that theoretically possible. The acid melted at 210°C. - rather indefinitely. On subliming the acid under reduced pressure, as suggested by Thompson (loc. cit.), small colourless glistening plates were

obtained which melted at 218-219°C.
(Found:- C(micro) - 54.6%; H(micro) - 4.0%. S(micro) - 20.6%. $C_7H_6O_2S$ requires C = 54.5%, H = 3.9% and S = 20.8%).

Preparation of the anilide of p-thiolbenzoic acid.



No reference to the preparation or properties of the anilide of p-thiolbenzoic acid could be found in the literature.

The anilide of p-thiolbenzoic acid was prepared by condensing p-thiolbenzoic acid and aniline in pyridine solution, and using phosphorus trichloride as the condensing agent.

The following quantities of materials were used:-

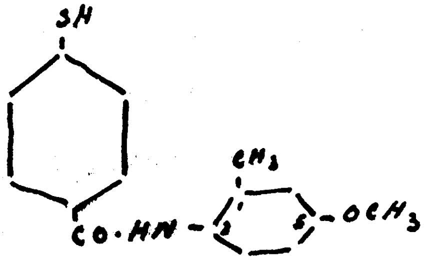
7.7 gm.	($^1/20$ mol.)	p-thiolbenzoic acid.
9.3 gm.	($^1/10$ mol.)	aniline.
5 c.c.	....	pyridine.
3 c.c.	....	phosphorus trichloride.

The p-thiolbenzoic acid and the aniline were dissolved in the pyridine by heating to 70°C. The phosphorus trichloride was added in small amounts at a time over a period of half an hour. The temperature of the mixture was then maintained at 115°C. for four hours longer. During the course of the reaction the mixture was well stirred. On cooling the reaction mixture to 70°C., 75 c.c. of alcohol were added and the whole boiled on the steam-bath until complete solution had taken place. On allowing to remain in the ice-chest over-night, the solution deposited a white crystalline product which was filtered off with suction, washed with alcohol, and dried. Water ($\frac{1}{2}$ volume of filtrate) was carefully added to the filtrate while the whole was well stirred. A white flocculent precipitate was obtained and this was filtered off at the pump, washed with water and dried. This precipitate consisted almost entirely of anilide. The total yield of anilide was equal to 83% of that theoretically possible.

The anilide of p-thiolbenzoic acid was crystallised from nitrobenzene (Norit) and obtained in fine white needles which melted at 263-264°C. The anilide was insoluble in boiling aqueous solutions of sodium hydroxide but dissolved readily in warm $^N/1$ alcoholic caustic potash solution. On addition of water, even in small amount, to the $^N/1$ alcoholic potassium hydroxide solution of the anilide, the anilide was precipitated unchanged.
(<u>Found:</u>- N - 5.8%; S - 13.5%; Calculated for $C_{13}H_{11}ONS$ - N = 6.1%; and S = 13.97%).

On boiling the $^N/1$ alcoholic potassium hydroxide solution of the anilide in a flask fitted with a reflux condenser for four hours, hydrolysis took place and p-thiolbenzoic acid and aniline were isolated in the usual manner. The p-thiolbenzoic acid was identified by subliming the acid component obtained by hydrolysis when pure p-thiolbenzoic acid was obtained.

Preparation of the 5-methoxy-2-toluidide of p-thiolbenzoic acid.



No reference to the preparation or properties of the 5-methoxy-2-toluidide of p-thiolbenzoic acid could be found in the literature.

This arylamide was prepared in exactly the same manner as the anilide of p-thiolbenzoic acid - full details of the method of preparation of which are given on page 198 .

The following quantities of materials were used:-

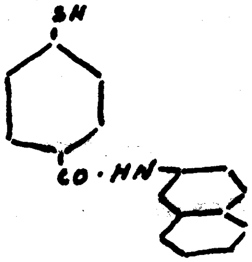
7.7 gm. (1/20 mol.)	p-thiolbenzoic acid.
8.0 gm. (1/20 mol.)	5-methoxy-2-toluidine.
5 c.c.	pyridine.
3 c.c.	phosphorus trichloride.

The yield of 5-methoxy-2-toluidide was equal to 81% of that theoretically possible. On recrystallising from nitrobenzene (Norit) the 5-methoxy-2-toluidide of p-thiolbenzoic acid was obtained in colourless fine micro-crystalline needles which had a melting point of 235-36°C.

(**Found:**- N(Micro) - 5.1%. - $C_{15} H_{15} O_2 N S$ requires N = 5.1%.

Like the other arylamides of p-thiolbenzoic acid examined the 5-methoxy-2-toluidide was insoluble in boiling aqueous solutions of sodium hydroxide, but was soluble in warm $^{N}/1$ alcoholic potassium hydroxide solution. On boiling the $^{N}/1$ alcoholic potassium hydroxide solution in a flask fitted with a reflux condenser for four hours, hydrolysis occurred and p-thiolbenzoic acid and 5-methoxy-2-toluidine were isolated.

Preparation of the β-naphthylamide of p-thiolbenzoic acid.



No reference to the preparation or properties of the β-naphthylamide could be found in the literature.

The β-naphthylamide of p-thiolbenzoic acid was prepared in exactly the same way as the anilide of this acid. Full details of the method of preparation of the anilide are given on page 198).

The following quantities of materials were used for preparing the β-naphthylamide:-

7.7 gm. (1/20 mol.)	p-thiolbenzoic acid.
7.2 gm. (1/20 mol.)	β-naphthylamine.
5 c.c.	pyridine.
3 c.c.	phosphorus trichloride.

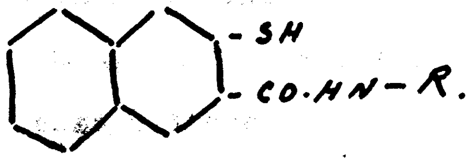
The yield of β-naphthylamide obtained was equivalent to 97% of that theoretically possible.

The β-naphthylamide of p-thiolbenzoic acid crystallised from nitrobenzene in white fine micro-crystalline needles which melted at 282-283°C.

(Found:- N(micro) - 5.1% and S - 11.0% $C_{17}H_{13}ONS$ requires N = 5.0% and S = 11.4%).

This arylamide was also insoluble in boiling aqueous sodium hydroxide solutions but soluble in warm $^{N}/1$ alcoholic potassium hydroxide solution. On boiling, for four hours, the $^{N}/1$ alcoholic potassium hydroxide solution of the β-naphthylamide in a flask fitted with a reflux condenser, hydrolysis occurred and β-naphthylamine and p-thiolbenzoic acid (identified after purification by sublimation) were obtained on working up the products of hydrolysis in the usual manner.

Section III. Arylamides of 2-thiol-3-naphthoic acid.



Preparation of 2-thiol-3-naphthoic acid.

The preparation of 2-thiol-3-naphthoic acid is briefly described in D.R.P. 240,118 (Kalle & Co.) but no experimental details or analysis of the acid are given. The author has been able to prepare the acid in exactly the same manner as o-thiolbenzoic acid was prepared (cf. page 171).

The following quantities of materials were used:-

20 gm. ..... crude 2-amino-3-naphthoic acid = 18.7 gm. (1/10 mol.) pure acid.

20 c.c. .....conc. hydrochloric acid.

7.0 gm. .....sodium nitrite.

8.5 gm. .....sodium sulphide (fused).

3.5 gm. .....sulphur.

6.0 gm. .....sodium hydroxide sticks.

The 2-amino-3-naphthoic acid was dissolved by boiling with the hydrochloric acid and 500 c.c. of water. The solution was then cooled down to 0°C. and diazotised in the usual way, care being taken that the temperature of the diazo-solution did not exceed 5°C. The diazo-solution

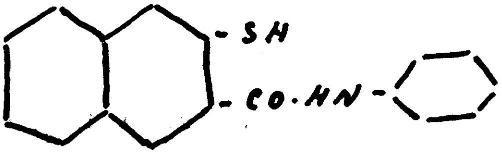
the diazo-solution did not exceed 5°C. The diazo-solution Le

was filtered to remove a small amount of a black insoluble product. The diazo-solution was then mixed with the sodium polysulphide solution which had been prepared in the usual way. During the mixing the temperature was never allowed above 5°C. and to ensure thorough mixing a mechanical stirrer was employed. Towards the end of the reaction, frothing occurred and this was prevented by the addition of a small quantity of ether. On allowing the mixture to remain standing at laboratory temperature overnight to ensure complete evolution of nitrogen.the solution acquired an olive-yellow colour. The solution was then filtered to remove a small quantity of insoluble material and the o-dithio-naphthoic acid precipitated by the addition of hydrochloric acid. The dithio-acid was filtered off at the pump, washed with water and freed from any excess sulphur by boiling with sodium carbonate solution and filtering. The dithio-acid was reprecipitated by the addition of hydrochloric acid, filtered with suction and washed free from mineral acid with water. The dithio-acid was dried as well as possible at the pump and then reduced to 2-thiol-3-naphthoic acid by boiling in a flask under a reflux condenser with zinc dust (99.9% Zn) and glacial acetic acid (28 gm. Zn, 300 c.c. $CH_3 \cdot COOH$) for four hours. On cooling, the pale yellow amorphous precipitate, which had separated, was filtered off at the pump and washed once with water; it was then boiled up in a beaker with excess sodium hydroxide solution for 20 minutes to remove zinc. The insoluble matter was filtered-off and washed with warm water. On adding hydrochloric acid to the filtrate (blue to Congo Red paper) the 2-thiol-3-naphthoic acid was precipitated as a pale yellow flocculent substance. The 2-thiol-3-naphthoic acid was filtered off at the pump and washed free from hydrochloric acid. On crystallising from dilute alcohol (50 parts alcohol: 50 parts water), 2-thiol-3-naphthoic acid was obtained as a pale yellow crystalline product which melted at 275-276° C.

In several experiments using this method of preparation yields equal to 85-90% of the theoretical were obtained.

(<u>Found</u>:- C(micro) - 65.3%. H(micro) - 4.0%. S(micro) - 15.7%. $C_{10}H_6 \cdot SH \cdot CO_2H = C_{11}H_8O_2S$ requires C = 64.7%; H = 3.92% and S = 15.7%).

Preparation of the anilide of 2-thiol-3-naphthoic acid.



No reference to the preparation or properties of the anilide of 2-thiol-3-naphthoic acid could be found in the literature.

The author has been able to prepare this arylamide by condensing 2-thiol-3-naphthoic acid and aniline (Ratio of acid: aniline = 1 mol.: 2 mols.) in pyridine solution and using phosphorus trichloride as the condensing agent.

The following quantities of materials were used:-

10.2 gm. ($^1/20$ mol.)	2-thiol-3-naphthoic acid.
9.3 gm. ($^1/10$ mol.)	aniline.
5 gm.	pyridine.
3 c.c.	phosphorus trichloride.

The 2-thiol-3-naphthoic acid and the aniline were dissolved in the pyridine by heating to 70° C. in a flask placed in an oil-bath and the phosphorus trichloride was added over a period of half an hour. After the addition of the phosphorus trichloride the mixture was heated at 115° C. for four hours. During the course of the reaction the whole was efficiently stirred. At the end of the reaction the whole was cooled down to about 70°C. and 150 c.c. of alcohol added. The mixture was then boiled on the water-bath until complete solution had occurred. On allowing to stand in the ice-chest overnight a white solid separated and this was filtered-off at the pump, washed with alcohol and dried. The filtrate was taken and water (about ½ volume of filtrate) carefully added while the whole was mechanically stirred. A flocculent cream coloured precipitate which consisted principally of anilide was formed and this was filtered-off at the pump, well washed with water and dried. The yield of anilide amounted to 66% of that theoretically possible.

The anilide of 2-thiol-3-naphthoic acid crystallised from nitrobenzene in small white crystals which melted at 285-286°C (<u>Found:-</u> C(micro) - 73.1%; H(micro) - 4.81%. N(micro) - 4.9%; S(micro) - 11.5%. $C_{17}H_{13}ONS$ requires C = 73.1%; H = 4.7%; N = 5.0% and S = 11.5%).

The anilide of 2-thiol-3-naphthoic acid was insoluble in boiling aqueous solutions of sodium hydroxide but was soluble in warm N/1 alcoholic potassium hydroxide solution. On boiling the 2N. alcoholic potassium hydroxide solution of the anilide for five hours in a flask fitted with a reflux condenser, hydrolysis occurred and 2-thiol-3-naphthoic acid and aniline were isolated on working up the products of

Hydroclysis in the usual way.

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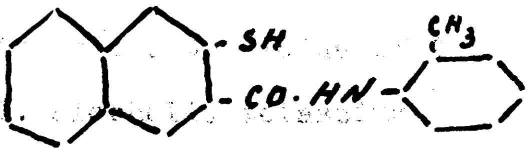
Preparation of the o-toluidide of 2-thiol-3-naphthoic acid.



No reference to the preparation or properties of the o-toluidide of 2-thiol-3-naphthoic acid could be found in the literature.

The o-toluidide of 2-thiol-3-naphthoic acid was prepared by the author in a similar manner to the anilide, the preparation of which has been fully described in the preceding page.

The following quantities of materials were used:-

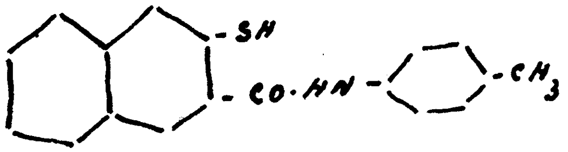
10.2 gm. (1/20 mol.)	2-thiol-3-naphthoic acid.
10.7 gm. (1/10 mol.)	o-toluidine.
5 c.c.	pyridine.
3 c.c.	phosphorus trichloride.

The yield of o-toluidide was 10.0 gm. which was equal to 70% of that theoretically possible. The o-toluidide crystallised from nitrobenzene in colourless crystals which had a melting-point of 279-280° C., and which did not dissolve in aqueous solutions of sodium hydroxide even at the boil. The o-toluidide was readily soluble in warm N/1 alcoholic potassium hydroxide solution.

(Found:- N = $\overset{\text{I.}}{4.8}$% and $\overset{\text{II.}}{4.7}$%. $C_{18}H_{15}ONS$ requires N = 4.78%.)

On boiling the o-toluidide of 2-thiol-3-naphthoic acid with 2 N. alcoholic potassium hydroxide for five hours in a flask fitted with a reflux condenser, hydrolysis took place and 2-thiol-3-naphthoic acid and o-toluidine were detected on working up the products of hydrolysis in the usual way.

Preparation of the p-toluidide of 2-thiol-3-naphthoic acid.



No reference to the preparation or properties of the p-toluidide of 2-thiol-3-naphthoic acid could be found in the literature.

The preparation of the p-toluidide of 2-thiol-3-naphthoic acid was carried out in the same manner as the anilide (see page 208).

The following quantities of materials were used:-

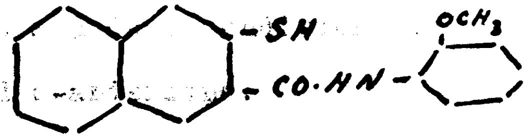
10.2 gm. ($^1/20$ mol.) ..... 2-thiol-3-naphthoic acid.
10.7 gm. ($^1/10$ mol.) ..... p-toluidine.
5 c.c. .... pyridine.
3 c.c. .... phosphorus trichloride.

The yield of p-toluidide was 10.5 gm. which was equal to 73. % of theory.

The p-toluidide of 2-thiol-3-naphthoic acid crystallised from nitrobenzene in white crystals which melted at 276-277°C. and was insoluble in boiling aqueous solutions of sodium hydroxide. The p-toluidide was readily soluble in warm $^N/1$ alcoholic potassium hydroxide solution. (<u>Found</u>:- N = 4.8%. $C_{18}H_{15}ONS$ requires N = 4.78%).

Hydrolysis of the p-toluidide of 2-thiol-3-naphthoic acid with 2N alcoholic potassium hydroxide solution in the standard manner gave 2-thiol-3-naphthoic acid and p-toluidine.

Preparation of the o-anisidide of 2-thiol-3-naphthoic acid.



No reference to the preparation or properties of the o-anisidide of 2-thiol-3-naphthoic acid could be found in the literature.

This arylamide was prepared from o-anisidine and 2-thiol-3-naphthoic acid in the same manner as the anilide, the preparation of which has been fully described (see page 208).

The following quantities of materials were used:-

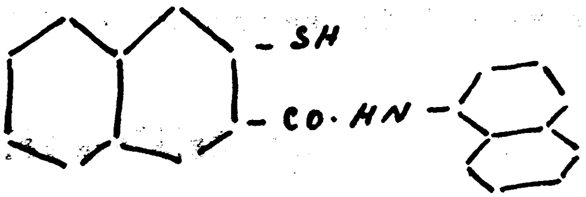
10.2 gm. ($^{1}/20$ mol.) ..... 2-thiol-3-naphthoic acid.
12.3 gm. ($^{1}/10$ mol.) ..... o-anisidine.
5 c.c. .... pyridine.
3 c.c. .... phosphorus trichloride.

The yield of o-anisidide obtained was 11.5 gm. which was equivalent to 74% of that theoretically possible.

The o-anisidide of 2-thiol-3-naphthoic acid crystallised from nitrobenzene in small white crystals which had a melting-point of 220-221° C. Like the other arylamides of 2-thiol-3-naphthoic acid, the o-anisidide was insoluble in boiling aqueous solutions of sodium hydroxide, but was soluble in warm $^{N}/1$ alcoholic potassium hydroxide solution. (Found:- N = 4.7%; S = 10.7%. $C_{18}H_{15}O_2NS$ requires N = 4.5% and S = 10.4%).

Hydrolysis with 2N. alcoholic potassium hydroxide solution under the standard conditions yielded 2-thiol-3-naphthoic acid and o-anisidine.

Preparation of the α-naphthylamide of 2-thiol-3-naphthoic acid.



No reference to the preparation or properties of the α-naphthylamide of 2-thiol-3-naphthoic acid could be found in the literature.

The author has prepared this arylamide by the standard "pyridine" method which is fully described on page 208.

The following quantities of materials were used:-

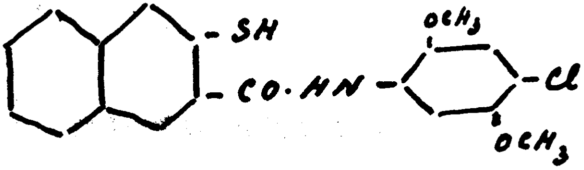
10.2 gm. (1/20 mol.)	2-thiol-3-naphthoic acid.
14.4 gm. (1/10 mol.)	α-naphthylamine.
5 c.c.	pyridine.
3 c.c.	phosphorus trichloride.

The yield of α-naphthylamide was 12.0 gm. which was equivalent to 73.% of that theoretically possible. The α-naphthylamide of 2-thiol-3-naphthoic acid crystallised from nitrobenzene in white crystals which melted at 306-307°C. The α-naphthylamide was insoluble in boiling aqueous solutions of sodium hydroxide but was soluble in warm N/1 alcoholic potassium hydroxide solution, imparting like the other arylamides of 2-thiol-3-naphthoic acid an orange colour to the solution. This solution was not fluorescent.

(Found:- N = $\overset{I.}{4.3}$% and $\overset{II.}{4.3}$%. $C_{21}H_{15}ONS$ requires N = 4.3%).

Hydrolysis of the α-naphthylamide with 2N.alcoholic potassium hydroxide solution yielded 2-thiol-3-naphthoic acid and α-naphthylamine; the usual procedure being adopted.

Preparation of the 4-chloro-2:5-dimethoxyanilide of 2-thiol-3-naphthoic acid.



No reference to the preparation or properties of the 4-chloro-2:5-dimethoxyanilide of 2-thiol-3-naphthoic acid could be found in the literature.

This arylamide was readily prepared by the standard "Pyridine" process described fully on page 208.

The following quantities of materials were used:-

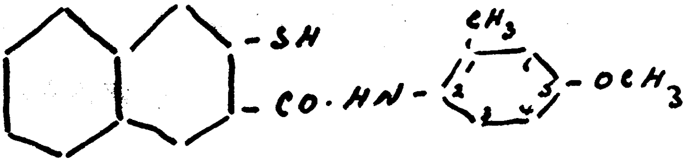
10.2 gm. ($^1/20$ mol.)	2-thiol-3-naphthoic acid.
10.0 gm. ($^1/20$ mol.)	4-chloro-2:5-dimethoxyaniline.
5 c.c.	pyridine.
3 c.c.	phosphorus trichloride.

Slightly more than the equimolar proportion of arylamine was used - 9.38 gm. of 4-chloro-2:5-dimethoxyaniline would have been $^1/20$ mol. The arylamide was obtained in 80% yield. The 4-chloro-2:5-dimethoxyanilide crystallised from benzene-nitrobenzene (45 pts. benzene and 55 parts nitrobenzene) in fine white micro crystals which had a melting-point of 255-256°C. The arylamide was insoluble in boiling aqueous sodium hydroxide solutions, but soluble in warm $^N/1$ alcoholic potassium hydroxide solution.

(Found:- N - 3.8%; Cl - 9.1% $C_{19}H_{16}O_{3}NClS$ requires N = 3.7% and Cl. 9.5%).

On boiling the arylamide with 2N. alcoholic potassium hydroxide solution for five hours in a flask fitted with a reflux condenser, hydrolysis took place and 2-thiol-3-naphthoic acid and 4-chloro-2:5-dimethoxy-aniline were isolated on working up the products of hydrolysis in the usual manner.

Preparation of the 5-methoxy-2-toluidide of 2-thiol-3-naphthoic acid.



No reference to the preparation or properties of the 5-methoxy-2-toluidide of 2-thiol-3-naphthoic acid could be found in the literature.

This arylamide was prepared by the standard "Pyridine" process which is fully described on page 208.

The following quantities of materials were used:-

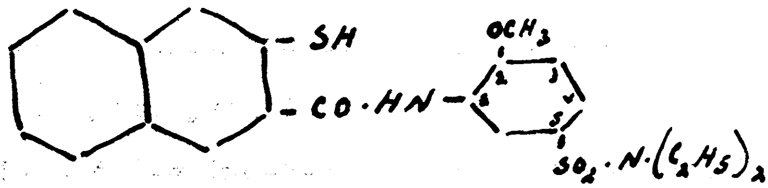
10.2 gm. (1/20 mol.)	2-thiol-3-naphthoic acid.
7.0 gm. (1/20 mol.)	5-methoxy-2-toluidine.
5 c.c.	pyridine.
3 c.c.	phosphorus trichloride.

The yield of 5-methoxy-2-toluidide was equivalent to 85% of theory. The arylamide crystallised from nitrobenzene-benzene (75 pts. nitrobenzene: 25 pts. benzene) in cream coloured crystals which melted at 264-265° C. The 5-methoxy-2-toluidide was insoluble in boiling aqueous solutions of sodium hydroxide, but was soluble in N/1 alcoholic potassium hydroxide solution.

(Found:- N = 4.3% $C_{19}H_{17}O_2NS$ requires N = 4.33%).

Hydrolysis with 2N. alcoholic potassium hydroxide solution gave 2-thiol-3-naphthoic acid and 5-methoxy-2-toluidine - the usual procedure for isolating the products of hydrolysis being adopted.

Preparation of the 1-amino-2-methoxybenzene-5-sulphon-:diethylamide of 2-thiol-3-naphthoic acid.



No reference to the preparation or properties of the 1-amino-2-methoxybenzene-5-sulphondiethylamide of 2-thiol-3-naphthoic acid could be found in the literature.

The standard "Pyridine" process was again adopted for the preparation of this arylamide.

The following quantities of materials were used:-

10.2 gm. (^{1}/20 mol.)	2-thiol-3-naphthoic acid.
25.8 gm. (^{1}/10 mol.)	1-amino-2-methoxybenzene-5-sulphondiethylamide.
5 c.c.	pyridine.
3 c.c.	phosphorus trichloride.

Yield of arylamide was 15.2 gm. which was equivalent to approximately 70% of that theoretically possible.

The arylamide was crystallised from benzene-nitrobenzene (75 pts. benzene: 25 pts. nitrobenzene) and was obtained in white micro-crystals which melted at 214-215° C.

(<u>Found:-</u> C(micro) - 59.2%; H(micro) - 5.3%; N(micro) - 6.26% and S(micro) - 13.9% $C_{22} H_{24} O_4 N_2 S_2$ - Requires C = 59.5%; H = 5.4%, N = 6.3% and S = 14.4%).

On boiling the arylamide with 2N. alcoholic potassium hydroxide solution for five hours in a flask fitted with a reflux condenser, hydrolysis took place and on working up the products of hydrolysis in the usual way, 2-thiol-3-naphthoic acid and 1-amino-2-methoxy-benzene-5-sulphondiethylamide were isolated. Under the conditions no hydrolysis of the sulphondiethylamide occurred.

The [illegible] were used.

[illegible] gm. [illegible] gm. pure.

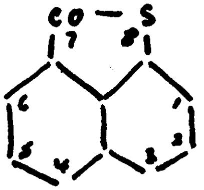
[illegible] gm. [illegible]

[illegible]

[illegible] ethyl-[illegible]

The [illegible] was dissolved in 150 c.c. of a 10% solution of [illegible] by boiling the solution for ½ an hour. The solution was [illegible] made slightly alkaline to phenolphthalein paper by the [illegible] addition of hydrochloric acid. At this stage the [illegible] was boiled for a [illegible] minutes and then filtered [illegible]

Section IV. Lactone of 1-thiol-8-naphthoic acid.



= 7-keto-8-thia-acenaphthen.

Friedländer and Woroshzow's method for preparing the lactone of 1-thiol-8-naphthoic acid (Annalen, 388. 21) was repeated.

The following quantities of materials were used.-

19 gm. ... Naphthostyril (crude) = 16.9 gm. pure.
6.9 gm. .. sodium nitrite.
25 c.c. .. conc. hydrochloric acid.
10 gm. ... potassium ethyl-xanthate.

The naphthostyril was dissolved in 150 c.c. of a 10% solution of sodium hydroxide by boiling the solution for ½ an hour. The solution was ~~was~~ made slightly alkaline to phenolphthalein paper by the careful addition of hydrochloric acid. At this stage the whole was boiled for a few minutes and then filtered so as to remove a small amount of a black insoluble product. The filtrate, which was very faintly alkaline to phenolphthalein paper was then treated with the sodium nitrite dissolved in 20 c.c. of water, and finally cooled down to 0°C. The ice-cold solution was then added as quickly as possible to 200 c.c. of ice cold water containing 25 c.c. of concentrated hydrochloric acid. To ensure thorough mixing of the two solutions the mixture was mechanically stirred. The temperature of the mixture was maintained at 0° - 5° C. by the addition of crushed ice. The diazo-solution was distinctly acid to Congo-Red paper and gave an instantaneous blue reaction with starch-iodide paper. The diazonium chloride of naphthostyril separated out as a light brown crystalline precipitate. The diazo-suspension was then added, while the whole was mechanically stirred, to the potassium ethyl-xanthate dissolved in 400 c.c. of water. The temperature of the potassium ethyl-xanthate solution was 10° C. when the diazo-suspension was added. The temperature of the mixture was slowly raised to 50° C. while the whole was well stirred. The temperature was then brought rapidly to the boil and boiling continued for half an hour. A black oil floated on the surface of the liquid and this solidified on cooling. The solid was filtered off, air-dried, and extracted with alcohol (Norit). On filtering and cooling pale yellow crystals separated out. These crystals had a melting-point of 140° C. On recrystallising from light petroleum (B.P.40/60°C.) pale sulphur yellow needles which melted at 144-145°C. were obtained. The yield of the lactone of 1-thiol-8-naphthoic acid was 4.0 gm. which was equal to

21.5% of that theoretically possible.

Much better yields of the lactone of 1-thiol-8-naphthoic acid were obtained when the diazo-naphthostyril was decomposed by means of sodium disulphide solution. The following quantities of materials were used:-

19.0 gm.	naphthostyril.
6.9 gm.	sodium nitrite.
25 c.c.	conc. hydrochloric acid.
8.5 gm.	sodium sulphide (fused).
3.5 gm.	sulphur.
6.0 gm.	sodium hydroxide sticks.

The method of diazotising the naphthostyril was exactly the same as that described in the previous experiment. The ice cold suspension of the diazo-naphthostyril was then carefully added to the ice-cold sodium polysulphide solution, prepared by dissolving the sodium sulphide in water (100 c.c.) and boiling the solution with sulphur until complete solution had occurred; filtering-off a little black insoluble matter, adding the sodium hydroxide (dissolved in 50 c.c. of water) and cooling the mixture to 0° C. During the addition of the diazo-solution to the polysulphide solution the mixture was efficiently stirred and the temperature kept below 5°C. Practically no frothing occurred during the mixing. When all of the diazo-

solution/

solution had been added the mixture was allowed to remain at laboratory temperature overnight to ensure the complete evolution of nitrogen. The solution was then filtered and the filtrate acidified with a slight excess of hydrochloric acid. The cream coloured precipitate was filtered off at the pump, washed twice with water, transferred to a beaker and boiled with an excess of sodium hydroxide solution containing a little Norit. This solution was filtered and acidified with hydrochloric acid. The cream coloured precipitate was filtered off at the pump and washed free from hydrochloric acid. The precipitate was dried as well as possible on the filter and then dried at around 50°C. The dry substance was dissolved by boiling in alcohol (Norit). On filtering-off the Norit and on cooling the lactone of 1-thiol-8-naphthoic acid separated out in fine sulphur yellow needles, which were purified by recrystallising from alcohol or light petroleum(B.P.40/60°C.). The lactone of 1-thiol-8-naphthoic acid crystallised from these solvents in sulphur yellow needles which had a melting-point of 145-146°C.

The yield of lactone of 1-thiol-8-naphthoic acid was 14.8 gm. and was equal to approximately 80% of that theoretically possible.

The lactone of 1-thiol-8-naphthoic acid was insoluble in sodium carbonate solutions but was soluble in aqueous sodium hydroxide solutions from which it was precipitated unchanged by mineral acids. It was also soluble in mono-ethanolamine and ethylenediamine.

(**Found:-** C(micro) - 71.4%; H - 3.2% and S(micro) - 17.5% $C_{11}H_6OS$ requires C = 71.0%, H = 3.2% and S = 17.2%

DYEING SECTION.

The shades produced on cotton yarn by some of the arylamides, prepared by the author during this study, in combination with certain diazotised amines are shown in the pages which follow.

A description of the methods employed by the author in producing these dyeings is now given.

I. IMPREGNATION OF THE COTTON YARN WITH THE ARYLAMIDES.

a). Arylamides of 2-hydroxy-3-naphthoic acid.

As representatives of this group of arylamides the following members were chosen:-

1). The 5-chloro-2:4-dimethoxy-anilide.
2). The 4-chloro-2:5-dimethoxy-anilide.
3). The 5-methoxy-2-toluidide.
4). The 2:4-dimethoxy-anilide.
and 5). The 1-amino-2-methoxy-benzene-5-sulphondiethylamide.

In each case, 4 grams of the arylamide was pasted up with 8 c.c. Turkey Red Oil solution ("Total oil" content of solution 25%) and 4.c.c. of caustic soda solution (26% NaOH). The paste was warmed a little and then 100 c.c. boiling water added. The whole was boiled until complete solution had occurred and the bulk then finally made up to 1 litre by the addition of cold water and 1 c.c. of formaldehyde solution (40% H.CHO). When the temperature of the liquor was 30°C., the bleached cotton yarn was entered and worked in the solution, which was maintained at 30°C, for half an hour. The impregnated yarn was then removed, squeezed thoroughly in order to remove completely that part of the arylamide solution mechanically adhering to it, and thus limiting as much as possible formation of dyestuff (i.e. on subsequent coupling with the diazotised amine) on the surface of the fibre. As is well known, failure to do this causes the colouring matter ~~lake~~ formed on the fibre to rub-off and thus affect the fastness of the dyeing. After squeezing, the impregnated yarn was ready for entering into the solutions of the diazotised amines.

b). Arylamides of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid.

As representatives of this group of arylamides the following members were chosen:-

1). The 4-chloro-2:5-dimethoxyanilide.

and 2). The 1-amino-2-methoxybenzene-5-sulphondiethylamide.

The amount of arylamide used was, in each instance, at the rate of 4 grams per litre of liquor. The method of preparing the arylamide solutions was exactly the same as that used in preparing the 2-hydroxy-3-naphthoic arylamide solutions (q.v.); the duration and the temperature of impregnation also being the same. After impregnation, the yarn was thoroughly squeezed and was then ready for entering into the solutions of the various diazotised amines.

c). Arylamides of 2-hydroxyanthracene-3-carboxylic acid.

As representatives of this group of arylamides the following members were chosen:-

1). The o-toluidide.

2). The 2:5-dimethoxyanilide.

and 3). The 4-chloro-2:5-dimethoxyanilide.

In each case, 3 grams of the arylamide was pasted up with 8 c.c. of Turkey Red oil solution (25% "total oil" content) and 3 c.c. caustic soda solution (26% NaOH); otherwise the procedure adopted in applying the arylamides of 2-hydroxy-3-naphthoic acid (q.v.) to cotton yarn was used.

d). Arylamides of acetoacetic acid.

As representatives of this group of arylamides the following were selected.-

1). Diacetoacet-o-tolidide.

and 2). 2-acetoacetylamino-6-ethoxybenzthiazole.

To dissolve these acetoacetarylamides, 3 grams of the arylamide were pasted up with 8 c.c. Turkey Red oil 25% "Total oil" content) and 3 c.c. caustic soda solution (26% NaOH) and the paste dissolved by the addition of 100 c.c. of boiling water. When solution was complete the bulk was made up to 1 litre by the addition of cold water. To increase the substantivity of the acetoacetarylamides, 30 grams of Glauber's salt per litre were added to the bath in each case. No formaldehyde was added to the solutions of the acetoacetarylamides because the dyeing power of the arylamides would have been destroyed. The cotton yarn was entered into the solution at 30°C. and worked therein for half an hour - the temperature of the padding liquor being maintained at 30°C. during this period. On removing the yarn, it was thoroughly squeezed and was then ready for coupling with the diazotised amines.

e). Arylamides of Terephthaloyldiacetic acid.

As representative of this group the bis-5-chloro-2:4-dimethoxyanilide was selected.

The sodium salt solution of this arylamide was prepared in exactly the same manner as the acetoacet arylamides with this difference that no Glauber's salt was added owing to the high substantivity for the cotton fibre of this class of arylamides. The strength of the solution was 3 grams arylamide per litre. The time of working the cotton yarn in the solution was half an hour and the temperature of the bath 30°C. On removing the cotton yarn from the solution, it was thoroughly squeezed and was then ready for coupling with the solutions of the diazotised amines.

f). Arylamides of o-thiolbenzoic acid.

As representative of this group the anilide was chosen As already mentioned (see page 145).the arylamides of o-thiolbenzoic acid are insoluble in aqueous sodium hydroxide solutions, but are soluble in $^{N}/1$ alcoholic potassium hydroxide solution. To impregnate cotton yarn with the anilide of o-thiolbenzoic adid, therefore, 6 grams of the anilide were dissolved in 50 c.c. $^{N}/1$ alcoholic potassium hydroxide solution and 8 c.c. Turkey Red Oil (25% "Total oil" contant) added. Luke warm water was then added to bring the bulk to 1 litre. To increase the substantivity of the anilide 30 grams Glauber's salt were added. The cotton yarn was then entered and worked in the solution for half an hour, while the temperature of the solution was maintained at 30°C. After half an hour, the yarn was removed from the solution and thoroughly squeezed. The yarn was then ready for coupling with the solutions of the diazotised amines.

g). Arylamides of 2-thiol-3-naphthoic acid.

As representatives of this group the 5-methoxy-2-toluidide and the α-naphthylamide were chosen.

In each case, the quantity of arylamide was 6 grams per litre. The amounts of $^N/1$ alcoholic caustic potash and Turkey Red oil used were the same as in the case of the anilide of o-thiolbenzoic acid, described above. 30 grams Glauber's salt were added per litre of padding bath to increase the substantivity of these arylamides. The cotton yarn was entered into the arylamide solutions at 30°C. and worked for half an hour, while the temperature was kept constant. On removing the yarn it was thoroughly squeezed and was then ready for developing in the solutions of the diazotised amines.

II. DEVELOPMENT OF THE IMPREGNATED YARN.

After thorough squeezing, the impregnated yarn was, in each case, developed in the wet state by entering into solutions of the following diazotised amines.

1). 2:5-dichloro-aniline.
2). 5-chloro-2-toluidine.
3). 5-nitro-2-anisidine.
4). o-amino-azo-toluene.
5). o-dianisidine.
and 6). 4'-methoxy-4-amino-diphenylamine.

In the case of the yarn impregnated with the 1-amino-2-methoxybenzene-5-sulphondiethylamide of 2-hydroxy-3-naphthoic acid, this was also coupled with diazotised 1-amino-2-methoxybenzene-5-sulphondiethylamide.

The impregnated yarn was, in each instance, worked in the solutions of the diazotised amines, in the cold, for 20 minutes, after which time the colour lake had formed on the fibre. On removing the dyed yarn from the developing bath, it was squeezed lightly, to remove excess diazo liquor, and rinsed well with cold water. The dyed yarn was then soaped at about 85-90°C. for half an hour in a bath containing 1 gram soda ash and 2 grams of a good quality tallow soap (63% Fatty acids) per litre. Finally the dyed yarn was rinsed thoroughly with luke-warm water and dried.

DIAZOTISATION OF THE AMINES.

1). 2:5-Dichloroaniline.

2.3 grams of 2:5-dichloroaniline (Fast Scarlet GGS Base - I.G.) were pasted up with a mixture of 4.6 c.c. hydrochloric acid (31.5% HCl) and 10 c.c. of water. After 5 mins., 0.83 gram sodium nitrite dissolved in 5 c.c. water was run in while stirring thoroughly. The temperature during the diazotisation was maintained at between 10°-15°C. by the addition of ice. The diazo-solution was then hydrochloric acid replaced by acetic acid

filtered and neutralised by the addition of sodium acetate (5.75 grams in 15 c.c. water) and finally made up to 1 litre by the addition of ice cold water (cf. I.G."Ratgeber", 1933. page 518).

2). 5-chloro-2-toluidine.

2 grams of 5-chloro-2-toluidine (Fast Red TR Base - I.G.) were dissolved in about 40 c.c. cold water and 2 c.c. hydrochloric acid (31.5% H Cl)added, the whole stirred up well and whilst stirring 0.8 gram sodium nitrite dissolved in 5 c.c. cold water was run in. Diazotisation was complete after 30 mins. The diazo solution was neutralised with the addition of 1.5 grm. sodium acetate, dissolved in 20 c.c. cold water, and 0.5 c.c. 40% Acetic acid. The solution was then made up to 1 litre with ice cold water. Diazotisation temperature was 10°C. (cf. I.G. "Ratgeber", 1933, 523).

3). 5-nitro-2-anisidine.

1.75 grams 5-nitro-2-anisidine (Fast Red B Base I.G.) was pasted up with 3 c.c. hot water and 0.75 gm. sodium nitrite added. After complete solution of the nitrite, the paste was cooled down and stirred into 20 c.c. ice cold water containing 3 c.c. hydrochloric acid (31.5% H Cl). The whole was left to stand for half an hour, stirred at frequent intervals, then filtered and neutralised by the addition of 1.5 gm. sodium acetate, dissolved in 10 c.c., cold water, and 1 c.c. 40% acetic acid. The solution was then made up to 1 litre with the addition of ice cold water. Diazotisation temperature was 15°C. (cf. I.G. "Ratgeber", 1933, page 527).

4). o-Amino-azo-toluene.

2.8 grams of o-amino-azo-toluene (Fast Garnet GC Base - I.G.) were pasted up with 6 c.c. hot water and 2 c.c. hydrochloric acid (31.5% H Cl) and after standing for a short time stirred up with 50 c.c. ice cold water and ice. 0.8 gm. sodium nitrite dissolved in 20 c.c. cold water was then gradually stirred in. The diazo-solution was left to stand for half an hour, stirred at frequent intervals, filtered and neutralised by the addition of 1.5 gm. sodium acetate, dissolved in 20 c.c. water, and 1 c.c. acetic acid (40% $CH_3.COOH$). The solution was finally made up to 1 litre by the addition of ice cold water (cf. I.G. "Ratgeber", page 528

5). o-Dianisidine.

As the diazo solution of o-dianisidine (Fast Blue B. Base - I.G.) is only suitable for developing piece goods, the author used Fast Blue Salt B, which is recommended exclusively for development of cotton yarn by the I.G.

Farbenind. A-G. (cf. I.G. "Ratgeber", 1933, page 531). The FAST COLOUR SALTS, of the I.G. Farbenind. A-G., contain the corresponding bases in a ready diazotised form and are distinguished by excellent stability and good solubility. 1 part FAST BLUE B BASE ≡ 5 parts FAST BLUE SALT B.

To prepare the developing bath, therefore, 14 grams of FAST BLUE SALT B were pasted up with 60 c.c. of luke-warm water (30°C.) and dissolved to a clear solution by stirring in ice cold water until the bulk was 1 litre; 20 grams of common salt (NaCl) were then added.

6). 4'-methoxy-4-aminodiphenylamine.

4'-methoxy-4-aminodiphenylamine is VARIAMINE BLUE B. BASE of the I.G. Farbenind. A-G. The author used in all cases the corresponding FAST COLOUR SALT viz:- VARIAMINE BLUE SALT B. 1 part. VARIAMINE BLUE B. BASE ≡ 2 parts VARIAMINE BLUE SALT B.

To prepare the developing bath 6.0 gm. of VARIAMINE BLUE SALT B were pasted up with 60 c.c. of luke-warm water (30°C.) and dissolved by adding ice cold water until the bulk was 1 litre. 20 grams of common salt (NaCl) were then added; also 5 c.c. of 40% acetic acid. The final development of all the VARIAMINE BLUE B combinations was carried out by after-treating (i.e. subsequent to the 20 minutes treatment in the FAST COLOUR SALT solution) in a 2% sodium carbonate solution at 80°C. for 10 minutes. The dyed yarn was then rinsed in luke-warm water soaped in the customary manner, rinsed and dried.

7). 1-amino-2-methoxy-benzene-5-sulphon-diethylamide.

2.85 grams of 1-amino-2-methoxy-benzene-5-sulphon-:diethylamide (FAST RED ITR BASE - I.G.) were dissolved in 30 c.c. water containing 3 c.c. of hydrochloric acid (31.5% HCl). Into the clear solution thus obtained, 0.77 gm. sodium nitrite, dissolved in 20 c.c. ice-cold water, was added and the whole well stirred. Diazotis-:ation was complete in 15 mins. The diazo-solution was then neutralised by adding 1.6 gm. sodium acetate dis-:solved in 30 c.c. cold water and 0.5 c.c. 40% acetic acid. Finally ice cold water was stirred in until the bulk was 1 litre (cf. I.G."Ratgeber" page 524).
