THE MANUFACTURE OF DYES

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THE MANUFACTURE OF DYES

BY

JOHN CANNELL CAIN

D.Sc. (Manchester)

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PREFACE

The manuscript of this book was sent to me by Mrs. Cain shortly after the death of her husband. It is printed practically as I received it, but I have added one or two preparations which I felt that my friend would have included had he had time to prepare this, his last book, for the press. It is evident, I think, that he intended the book to be a supplement to his earlier volume, "The Manufacture of Intermediate Products for Dyes," and it is possible that he intended to introduce illustrations of plant and appliances such as those which are to be found there. After careful consideration, I have decided to make no additions of this kind, not only because I wished to leave the book as he left it, but also because the plant described in the earlier volume is of the same kind as that which would be used in the manufacture of the dyes, and duplication seemed undesirable.

J. F. Thorpe.

The Imperial College,
London,
March 1922.

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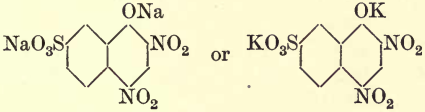
CHAPTER II

NITRO-COLOURS

NAPHTHOL YELLOW S

Naphthol yellow S (London Dye Manufacturing Co., Ltd., and most firms); Naphthol yellow FYAS (Lev.); Naphthol yellow (WDC); Citronine A (L); Sulphur yellow S (K) (AW); Acid yellow (DH) (LP); Yellow OS (P).



Caro, who discovered this dye, gives the following account of its manufacture (Badische Anilin- & Soda-Fabrik, E.P. 5305 of 1879; F.P. 134632; G.P. 10785; U.S.P. 225108).

of all About 10 parts by weight of α-naphthol are gradually mixed with about 20 parts by weight of fuming sulphuric acid (containing about 25 per cent. of sulphur trioxide), and the mixture is well stirred at 40–50° until a sample dissolves in water to a clear solution. The monosulphonic acids thus formed are then converted into a mixture of ~~their~~ higher sulphonic derivatives by gradually adding about 18 parts by weight of fuming sulphuric acid (containg about 70 per cent. of sulphur trioxide), and the (2) mixture is well agitated and kept at 40–50° until a sample, which is withdrawn from time to time, dissolved in or gently heated with an excess of nitric acid and afterwards diluted with water, remains clear, or nearly so, and the addition of potassium hydroxide solution gives an abundant precipitate of the potassium salts of the dinitronaphtholsulphonic acids.

(4) The mixture is now diluted with about 75 parts of water and gradually mixed with about 25 parts by weight of nitric acid (*d* 1·38). Stirring is continued and the temperature is not allowed to rise above 50°. After about twelve hours' standing in the cold, the dinitronaphtholmonosulphonic acid will have

crystallised out, and is filtered off and converted into its potassium, sodium, ~~or~~ ammonium salt. ~~and~~ by using Na_2CO_3 + KCl added ppt of Na salt.

The colouring matters contained in the acid filtrate may be worked up by neutralising with milk of lime, filtering, and decomposing the soluble calcium salts with, preferably, potassium carbonate.

Condn

In the French patent, in addition to the above process of sulphonation, it is stated that α-naphthol may be heated with 3 parts of sulphuric acid (*d* 1·84) for twelve to fifteen hours at 110–115°, and, on completion of the operation, the mixture is diluted with 60 parts of water.

The German patent gives the same process for sulphonation as in the English patent; 10 kilos. of α-naphthol are employed, and the mixture is diluted to 100 litres.

The American patent mentions that the time taken to sulphonate with concentrated sulphuric acid (as in the French patent) is about twelve hours, but that the use of fuming sulphuric acid is to be preferred; in the latter case, one part of α-naphthol is treated with two parts of fuming sulphuric acid in the first stage of the sulphonation, and the completion of the process takes about five hours, the mixture (from 1 part of α-naphthol) being mixed with 6 or 7 parts of water. Another process consists in nitrating the nitroso-derivative of α-naphtholdisulphonic acid (Leonhardt & Co., E.P. 11318 of 1887). The naphtholdisulphonic acid is prepared by sulphonating α-naphthol with 2 or, at most, 3 parts of sulphuric acid (65–66° Bé.), the temperature being raised to 125–130° and maintained at this point for about two hours. Into an aqueous solution, to be kept slightly acid, of the disulphonic acid (or of the calcium, barium, sodium, or potassium salt), prepared from 40 kilos. of α-naphthol, is introduced sodium nitrite, either in the solid state or in aqueous solution, as long as nitrous acid is absorbed. The nitroso-compound is oxidised by the addition of 100 kilos. of nitric acid or of a corresponding quantity of sodium nitrate and sulphuric acid at the ordinary temperature or while carefully raising the temperature to about 50°. The yellow colouring matter which precipitates, especially when potassium carbonate is added, is filtered, pressed, and dried.

In the German patent (G.P. 20716), 1 part of α-naphthol is dissolved in 2 parts of a sulphuric acid made by mixing 3 parts of fuming sulphuric acid (containing 45 per cent. of sulphur trioxide) with 2 parts of ordinary sulphuric acid (66° Bé.) at a temperature not exceeding 50°. On cooling, an equal weight of fuming sulphuric acid (containing 45 per cent. of sulphur trioxide) is added, and the whole is poured into three times its volume of ice-water. Sodium nitrite (1 equivalent to 1 equivalent of α-naphthol) is stirred in and the solution is neutralised with milk of lime, filtered, and the filtrate evaporated to obtain the calcium salt of the nitrosonaphtholsulphonic acid.

Schultz ("Chemie des Steinkohlentheers," 3rd ed., ii, 55) states that the better method of obtaining Naphthol yellow S is to heat α-naphthol with 4 parts of sulphuric acid at 120° so as to produce the disulphonic acid, to convert this into the nitroso-compound, and to oxidise this with nitric acid. In a later publication ("Farbstofftabellen," 5th ed., 6), the same author states that the above is the most usual method employed, whilst giving the following details for the direct nitration:

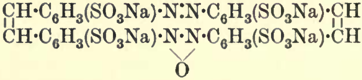
Ten kilos. of α-naphthol are dissolved in 40 kilos. of fuming sulphuric acid (containing 25 per cent. of sulphur trioxide), and the solution is heated at 125° until a sample diluted with water and heated with concentrated nitric acid gives no dinitronaphthol. The solution is then diluted to 100 litres and treated with 25 kilos. of nitric acid (42° Bé.) at a temperature not exceeding 50°. The mixture is kept at 50° for some time and then allowed to remain for twelve hours, when the greater part of the dinitronaphtholsulphonic acid will have separated out. This is filtered off and converted into the sodium salt by means of sodium carbonate; the rest is obtained from the filtrate by addition of salt.

CHAPTER III

STILBENE COLOURS

DIRECT YELLOW—SUN YELLOW—BRILLIANT YELLOW—STILBENE YELLOW—DIPHENYL CHRYSOIN—DIPHENYL FAST YELLOW

Sun yellow (G); Sun yellow G, GG (S); Curcumine S (L) (SB) (A); Direct yellow J, R (P); Direct yellow F (Sch.); Direct yellow RT (Cl. Co); Direct yellow G (J); Direct yellow R (By) (Gr. E); Azidine fast yellow G (CJ); Naphthamine yellow G (K); Diamine fast yellow A (C); Renol yellow R (t. M).



$$\begin{array}{l}\mathrm{CH{\cdot}C_6H_3(SO_3Na){\cdot}N{:}N{\cdot}C_6H_3(SO_3Na){\cdot}CH}\\ \|\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad\|\\ \mathrm{CH{\cdot}C_6H_3(SO_3Na){\cdot}\underset{\diagdown\,\diagup\atop O}{N{\cdot}N}{\cdot}C_6H_3(SO_3Na){\cdot}CH}\end{array}$$

These dyes are obtained by the action of sodium hydroxide on *p*-nitrotoluene-*o*-sulphonic acid. The shade of the product varies according to the concentration of the alkali and the temperature and time of the reaction. There are three chief types, represented by Sun yellow, Curcumine S, and Naphthamine yellow G.

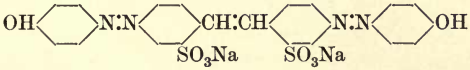
Sun yellow is prepared by Walter (*Bull. Soc. Mulhouse*, 1887, **57**, 99) as follows: Sodium *p*-nitrotoluene-*o*-sulphonate, in the form of a press-cake, is dissolved in the smallest possible amount of boiling water and heated with sodium hydroxide solution (1 kilo. NaOH for each 10 kilos. of *p*-nitrotoluene originally taken) at about 102–103° in a jacketed pan. The clear liquid becomes first magenta-coloured and finally yellow, and the dye separates out. After the formation of the dye is complete, the excess of alkali hydroxide is neutralised and the product evaporated to dryness.

Curcumine S is prepared by the use of more concentrated alkali. Fifty grams of sodium *p*-nitrotoluene-*o*-sulphonate are dissolved in 150–180 c.c. of boiling water and 100 c.c. of sodium hydroxide solution (33 per cent.; about 38° Bé.) are added gradually to the solution, which is kept boiling. The liquid becomes first deep red and then brown. A vigorous reaction sets in before all the alkali is added, which, however, is moderated on adding the remainder (60 c.c.). (Schultz, "Chemie des Steinkohlentheers," 3rd ed., ii, 58; compare also Bender and Schultz, *Ber.*, 1886, **19**, 3234.)

Naphthamine yellow G is obtained by dissolving 10 kilos. of sodium *p*-nitrotoluene-*o*-sulphonate in 100 litres of water and 20 kilos. of sodium hydroxide solution (40° Bé.), and the solution is kept at about 70° for an hour. The colour at first is an intense magenta and then becomes orange-yellow, when the sodium salt separates in orange-yellow crystals which are filtered off (Kalle & Co., E.P. 23672 of 1892; F.P. 226635). In the corresponding German patent (G.P. 79241), 10 kilos. of the sodium salt are added with stirring to 50 kilos. of sodium hydroxide solution (17° Bé.) at 80°. The mass becomes very dark, and the voluminous product is poured into 100 litres of water, filtered, pressed, and dried. The dye produces reddish-yellow shades on cotton, which are yellower and clearer than those obtained with Sun yellow.

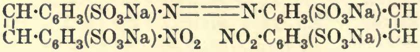
The following recipe is quoted by Schultz ("Chemie des Steinkohlentheers," 3rd ed., ii, 58). The press-cake of crude sodium *p*-nitrotoluene-*o*-sulphonate, corresponding with 117 kilos. of the pure salt and obtained from 70 kilos. of *p*-nitrotoluene, is dissolved in 1000 litres of boiling water and neutralised with a little sodium hydroxide solution. Steam is led in until the temperature of the solution is 85° and the volume 1200 litres. In the course of five minutes, 400 kilos. of sodium hydroxide solution (40° Bé.) are added and the temperature falls to 74°, but rises, in about half an hour, to 84° owing to the heat of reaction. The temperature is maintained at 80° for forty minutes by means of steam, and after shutting this off the temperature falls to about 68° in the course of half an hour. The batch is neutralised with 200 kilos. of sulphuric acid (60° Bé.), filtered, and the press-cake is pressed out in a screw or hydraulic press.

Brilliant yellow (L, By, Gr. E, SB), Brilliant yellow Y (Sch.), Renol brilliant yellow, conc. (t.M), Paper yellow 3G (B).



A solution of 20 kilos. of sodium diaminostilbenedisulphonate is diazotised by means of 7 kilos. of sodium nitrite and 25 kilos. of hydrochloric acid. The diazo-compound is precipitated, and after a little time is run into an alkaline solution of slightly more than the theoretical amount of phenol. After several hours, the dye is salted out (Leonhardt & Co., E.P. 4387^{86}; G.P. 38735; U.S.P. 350229).

> Stilbene yellow 2G, 3G, 4G, 8G (Cl. Co); Stilbene yellow 3G (By); Mikado yellow (A); Mikado yellow G, G extra (L) (SB); Mikado gold yellow 2G, 4G, 6G, 8G (L) (SB); Mikado gold yellow 8G (A); Naphthamine yellow 2G, 3G (K); Renol yellow 2G (t.M); Dianil direct yellow S (M); Formal yellow (G); Paper yellow (M).



$$\begin{array}{l}CH\cdot C_6H_3(SO_3Na)\cdot N=\!=\!=N\cdot C_6H_3(SO_3Na)\cdot CH\\ \| \hspace{22em} \|\\ CH\cdot C_6H_3(SO_3Na)\cdot NO_2 \quad NO_2\cdot C_6H_3(SO_3Na)\cdot CH\end{array}$$

Of these brands, the Stilbene yellows of the Clayton Aniline Co. are perhaps the best known. Marks 4G and 8G have the constitution given above (Green and Crosland, *Trans.*, 1906, **89**, 1608); in the former, the reduction (see below) is carried a little further than in the latter.

The process given by this firm (E.P. 21399 of 1897; G.P. 113513) is as follows:

Fifty lb. of sodium 4 : 4′-dinitrostilbene-2 : 2′-disulphonate are dissolved in 25 gallons of water, 5 gallons of sodium hydroxide solution (30 per cent.) and 15 gallons of a 10 per cent. solution of glucose are added, and the mixture is heated at 70° for three to four hours. The excess of alkali hydroxide is then neutralised by acid, and the precipitated colouring matter is filtered off and dried. It dyes yellow on cotton and dissolves in sulphuric acid, forming an orange solution. If instead of 15 gallons of 10 per cent. glucose solution 30 gallons are employed, the colour obtained dyes orange on cotton and dissolves in sulphuric acid to a violet solution. If 45 gallons of 10 per cent. glucose solution are used, the colouring matter obtained dyes a redder orange on cotton and gives a blue solution in sulphuric acid.

In the German patent, 50 kilos. of the disulphonate are dissolved in 1000 litres of water and the solution is warmed at 80–90°. Ten litres of a 10 per cent. solution of glucose are added, and then 15 litres of sodium hydroxide solution. After complete reduction, the dye is salted out, pressed, and dried.

Similar dyes are also apparently obtained by reducing sodium 4 : 4′-dinitrostilbene-2 : 2′-disulphonate with zinc dust and ammonium chloride to the corresponding hydroxylamine derivative and oxidising the latter with air or treating the solution with sodium hydroxide (Green and Meyenberg, E.P. 3393 of 1898).

A slightly different process consists in employing sodium 4 : 4′-dinitrodibenzyl-2 : 2′-disulphonate * instead of the corresponding stilbene derivative (Clayton Aniline Co., E.P. 21553 of 1897).

To a solution of 50 lb. of the above sodium salt in 100 gallons of water, 18 gallons of a 10 per cent. solution of glucose are added, together with 5 gallons of sodium hydroxide solution (30 per cent.) and the mixture is heated at about 80° for several hours. After neutralising the excess of alkali hydroxide, the dye is filtered off and dried. It is a red powder which dissolves in sulphuric acid, forming a red solution, and it dyes cotton yellowish-orange. By employing a larger quantity of glucose, products are obtained which dye reddish-orange shades on cotton and dissolve in sulphuric acid, giving a violet to blue solution.

The Mikado gold yellows are prepared (*a*) by heating 10 kilos. of Curcumine S with 100 litres of water and 9 kilos. of nitric acid (40° Bé.) under reflux for several hours. The mixture is then rendered alkaline and the dye is salted out; (*b*) by mixing 10 kilos. of Curcumine S with about 100 litres of water and adding 9 kilos. of solid commercial bleaching powder. About 17 kilos. of hydrochloric acid (21° Bé.) are added to obtain an acid reaction, the mixture is allowed to remain in the cold for some time until the oxidation is complete, then neutralised with sodium carbonate, the solution filtered, and the dye salted out (Leonhardt and Co., G.P. 42466).

One of the other brands (Naphthamine yellow 2G, 3G) is obtained from Naphthamine yellow G by mixing the paste produced from 10 kilos. of sodium *p*-nitrotoluene-*o*-sulphonate with 7·5 kilos. of dilute sulphuric acid (2 : 1) and adding to the stirred mixture 4·2 kilos. of powdered potassium dichromate at the ordinary temperature. After twelve hours, the whole is diluted with the same volume of water, filtered, the residue washed with salt solution, dissolved in ammonia, and the solution evaporated to dryness (Kalle & Co., E.P. 23672 of 1892; G.P. 79241).

* To a solution of 100 lb. of sodium *p*-nitrotoluene-*o*-sulphonate in 100 gallons of warm water, 50 gallons of sodium hydroxide solution (30 per cent.) are added, and the temperature is kept at about 40–50° while 22 gallons of sodium hypochlorite solution (containing 7 per cent. of active chlorine) are slowly run in. When all the hypochlorite has disappeared, 200 gallons of cold water are added, and the sparingly soluble sodium 4 : 4′-dinitrodibenzyl-2 : 2′-disulphonate is filtered off (Clayton Aniline Co., E.P. 5351 of 1897).

Diphenylchrysoin G (G).

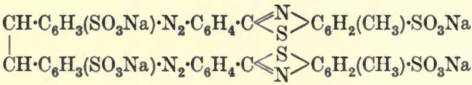
$$\begin{array}{l}\mathrm{CH\cdot C_6H_3(SO_3Na)\cdot N{:}N\cdot C_6H_4\cdot O\cdot C_2H_5}\\ \| \\ \mathrm{CH\cdot C_6H_3(SO_3Na)\cdot N{:}N\cdot C_6H_4\cdot O\cdot C_2H_5}\end{array}$$

One hundred kilos. of *p*-nitrotoluene-*o*-sulphonic acid are dissolved in 400 litres of hot water, a solution of 24 kilos. of *p*-aminophenol in 200 litres of boiling water * is added and then 300 kilos. of sodium hydroxide solution (40° Bé.) are introduced at a temperature of 70°. The mixture is stirred for about three hours while the temperature is slowly raised to about 90° (the U.S.P. gives 98°). The excess of alkali hydroxide is neutralised with hydrochloric acid and the dye † is salted out, filtered, pressed, and dried.

Thirty kilos. of this substance are dissolved in 100 litres of boiling water with the addition of 10 kilos. of sodium hydroxide solution (40° Bé.), 12 kilos. of ethyl bromide are introduced, and the whole is heated in an autoclave for about four hours at 105–110°. The ethylated dye is filtered off, pressed, and dried (Geigy & Co., E.P. 6651 of 1899; F.P. 286620; G.P. Anm. G. 13069; U.S.P. 636065). In the German patent application (G. 7525 [1892–1894]), Arnica yellow is described as being prepared by boiling a mixture of 20 kilos. of sodium *p*-nitrotoluene-*o*-sulphonate, 4·5 kilos. of *p*-aminophenol, and 50 kilos. of water with 15 kilos. of sodium hydroxide (40° Bé.) for one hour.

Diphenyl fast yellow (G).

This is produced by condensing dinitrodibenzyldisulphonic acid or dinitrostilbenedisulphonic acid with dehydrothio-*p*-toluidinesulphonic acid or primulinesulphonic acid by means of sodium hydroxide, and consists, for example, of a mixture of sodium dinitroazodistilbenetetrasulphonate (compare Stilbene yellow, p. 8) and the compound



$$\begin{array}{l}\mathrm{CH\cdot C_6H_3(SO_3Na)\cdot N_2\cdot C_6H_4\cdot C{<}{}^{N}_{S}{>}C_6H_2(CH_3)\cdot SO_3Na}\\ | \\ \mathrm{CH\cdot C_6H_3(SO_3Na)\cdot N_2\cdot C_6H_4\cdot C{<}{}^{S}_{N}{>}C_6H_2(CH_3)\cdot SO_3Na}\end{array}$$

According to Geigy & Co. (E.P. 18990 of 1897), 24 kilos. of the dye, obtained by heating sodium dinitrodibenzyldisulphonate

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* In the French patent, the water used for dissolving both materials is 500 instead of 600 litres.

† Formerly in commerce under the name of Arnica yellow.

in aqueous solution with sodium hydroxide solution (50° Bé.) for half an hour at 80°, are dissolved in 300 litres of boiling water, then 12 kilos. of dehydrothio-*p*-toluidinesulphonic acid and 50 kilos. of sodium hydroxide solution (50° Bé.) are added.

The excess of alkali hydroxide is neutralised with hydrochloric acid, and the dye filtered, pressed, and dried.

In the corresponding German patent (G.P. 100613), the above quantity of sodium dinitrodibenzyldisulphonate and 12 kilos. of sodium dehydrothio-*p*-toluidinesulphonate are dissolved in 300 litres of boiling water and the solution is treated with 80 kilos. of sodium hydroxide solution (40° Bé.).

The Clayton Aniline Co.'s process (E.P. 21553 of 1897) differs slightly from the above. Forty-seven lb. of sodium dinitrodibenzyldisulphonate and 34 lb. of sodium dehydrothio-*p*-toluidinesulphonate are dissolved in 50 gallons of water, 2·5 gallons of sodium hydroxide solution (30 per cent.) are added, and the mixture is heated for several hours at 80–90°. The excess of alkali is neutralised and the dye is filtered off and dried.*

The alternative method of the Clayton Aniline Co. (E.P. 21399 of 1897; G.P. 113514) consists in heating a solution of 100 lb. of sodium dinitrostilbenedisulphonate and 70 lb. of sodium dehydrothio-*p*-toluidinesulphonate in 100 gallons of water with 8 gallons of sodium hydroxide solution (30 per cent.) at 90–100° for about twelve hours. The dye separates out and is filtered off and dried.†

In the corresponding German patent (Leonhardt & Co., G.P. 96107), the paste produced from 24 kilos. of sodium *p*-nitrotoluene-*o*-sulphonate is stirred with 45 kilos. of concentrated sulphuric acid and 15 kilos. of powdered sodium dichromate are added. The mass foams slightly and becomes brownish-yellow. The reaction is over in a short time and the mixture is diluted with 150 litres of water and the dye filtered off, washed free from chromium with salt solution, pressed, moistened with ammonia, and dried. An amount of lead peroxide equivalent to the dichromate may also be used, in which case the oxidation is performed in a more dilute solution. The mixture is neutralised with sodium carbonate, and the filtered solution treated with salt to obtain the dye.

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* It seems obvious from the above patents that there would be no point in employing the process given in Geigy's English patent for manufacturing this dye.

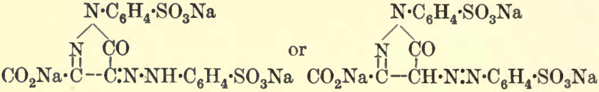
† The French patents in connexion with this dye (269466, 273018) have not yet been printed.

CHAPTER IV

PYRAZOLONE COLOURS

TARTRAZINE—FLAVAZINE S—FLAVAZINE L

Tartrazine (BD) (LBH) (Calco Chem. Co.) (Ault and Wiborg Co.) (B) (By) (J) (S), Tartrazine 94 (Nat.), Tartrazine O (M), Buffalo yellow (Sch.), Hydrazine yellow O, L (Gr. E), Fast wool yellow G (K), Wool fast yellow (J), Acid yellow AT (C), Tartrabarine (t.M), Jaune tartrique (P).



This dye, discovered by Ziegler in 1884, is prepared (1) by the action of phenylhydrazine-*p*-sulphonic acid (2 mols.) on dihydroxytartaric acid (1 mol.).

About 10 parts by weight of sodium dihydroxytartrate are mixed with about 16 parts of cold water, the mixture is heated at 40°, and about 13 parts of hydrochloric acid (*d* 1·16) are added, or as much as is required to produce a clear solution. This solution is then mixed with about 20 parts of phenylhydrazine-*p*-sulphonic acid previously dissolved in a mixture of about 60 parts of water and about 10 parts of sodium hydroxide solution (30 per cent.). The mixture is kept at about 80° for an hour or until the reaction appears to be complete, and after remaining for about twelve hours at the ordinary temperature the yellow precipitate is filtered, pressed, and finally purified by dissolving it in water at about 60° with the addition of so much sodium carbonate as is required to render the solution slightly alkaline. The solution is filtered and the dye precipitated by adding salt, filtered off, pressed, and dried (Badische Anilin- & Soda-Fabrik, E.P. 9858 of 1885; F.P. 169964; G.P. 34294; U.S.P. 324630).

Ziegler and Locher (*Ber.*, 1887, 20, 834) give a slightly different recipe. Ten grams of phenylhydrazine-*p*-sulphonic acid are dissolved in 40 c.c. of water and the necessary amount of sodium hydroxide and the solution is poured into a solution of 5 grams of sodium dihydroxytartrate in 10 c.c. of water and 10 c.c. of hydrochloric acid. A precipitate is formed which dissolves on warming; the clear solution becomes dark yellow and tartrazine separates out. The dye is collected, washed, and dried. The yield is 11·4 grams, or 97·4 per cent. of the theoretical.

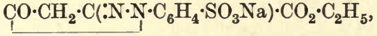
A recent paper (*Rev. Prod. chim.*, 1917, **20**, 22) describes the manufacture as follows: 33 kilos. of hydrochloric acid and 50 litres of water are mixed in a vat and 30 kilos. of sodium dihydroxytartrate are added gradually, solution being effected by warming gently, but it is important that the temperature does not rise above 30°. The solution is run into a solution of 50 kilos. of phenylhydrazine-*p*-sulphonic acid in 70 kilos. of water and 20 kilos. of sodium hydroxide (96 per cent.) and the mixture well stirred. A yellow colour is produced and the temperature is raised to 80°; after half an hour the batch is allowed to cool, the dye is precipitated with salt, filtered off, and dried.*

(2) The second method of preparation, also described by Ziegler (E.P. 5693 of 1893) consists in condensing phenylhydrazine-*p*-sulphonic acid with ethyl oxalacetate to form the hydrazone,

$$C_2H_5{\cdot}CO_2{\cdot}CH_2{\cdot}C(:N{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3Na){\cdot}CO_2{\cdot}C_2H_5,$$

which is then treated with diazotised sulphanilic acid and the product hydrolysed to tartrazine.

The process, according to the Badische Anilin- & Soda-Fabrik (E.P. 765 of 1897) gives such a small yield of colouring matter that it is useless, and this statement is confirmed by Bernthsen (*Chem. Zeit.*, 1898, **22**, 456). The modification introduced by the above firm consists in treating the hydrazone with alkalis whereby ethyl alcohol is eliminated and a pyrazolone derivative,



$$\underbrace{CO{\cdot}CH_2{\cdot}C(:N{\cdot}N}{\cdot}C_6H_4{\cdot}SO_3Na){\cdot}CO_2{\cdot}C_2H_5,$$

is produced, which is then combined with diazotised sulphanilic acid, and the ester obtained in this way is subsequently hydrolysed or the above pyrazolone derivative is hydrolysed and the product then combined with the diazo-compound.

Phenylhydrazine-*p*-sulphonic acid (9·5 parts) is suspended in

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* A modification of this process consists in mixing a solution of dinitrotartaric acid in ice-water with an emulsion of phenylhydrazine-*p*-sulphonic acid and heating until the solution turns yellow. A current of hydrogen sulphide is then passed through to destroy the nitrous fumes and the dye is obtained by neutralising with sodium carbonate and salting out (Bennert, E.P. 8504^{87}; G.P. Anm. B. 8432). The method does not appear to be of practical importance.

water (50 parts), crystallised sodium acetate (7·5 parts) is introduced, and then ethyl oxalacetate* (9·4 parts) is added. The mixture is stirred and warmed at 50° and maintained at this temperature until a clear solution is obtained, which usually occurs in about five minutes [this process for preparing the hydrazone is the same as that given by Ziegler, *loc. cit.*]. The solution is cooled to the ordinary temperature and sodium carbonate (8–10 parts) is added, care being taken that there is sufficient excess to give a distinctly alkaline reaction. The elimination of alcohol and the production of the pyrazolone derivative take place rapidly. The course of the reaction can be followed by taking samples from time to time and adding dilute sulphuric acid, when the amount of precipitate obtained indicates the progress of the change. When successive tests show no increase in the amount of precipitate the operation is complete. The product can be isolated by precipitating it with dilute sulphuric acid, filtering, and drying, in which case 167 parts of the sodium salt are dissolved in about 2000 parts of water and the solution is warmed on the water-bath for about half an hour with about 115 parts of sodium hydroxide solution (35 per cent.). The same result is produced, however, by treating the solution as obtained above directly with sodium hydroxide solution [in which case 11·5 parts of sodium hydroxide solution would be used; the quantities given for the condensation represent 1/20 mol. whilst those for the hydrolysis are ½ mol.]. The solution is now treated with the diazo-compound, and for this purpose 7·5 parts of crystallised sodium acetate [that is, for 1/20 mol.] are added to it and an amount of diazotised sulphanilic acid equivalent to 3·45 parts of sodium nitrite is introduced at 5–10°. The mixture is allowed to remain in the cold, or at a moderate warmth, for about twenty hours, when the tartrazine is salted out and collected in the usual way.

An alternative method of carrying out these operations is to dilute the solution of the pyrazolone derivative obtained in the first instance to about 200 parts and to introduce the diazotised sulphanilic acid at 5–10°, leaving the solution in the cold or at a moderate warmth for about twelve hours. The tartrazine ester is then hydrolysed by heating with alkali hydroxide on the water-bath.

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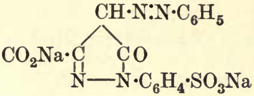
* Prepared by the interaction of ethyl oxalate and ethyl acetate in ethereal solution in the presence of sodium. The sodium salt is decomposed by sulphuric acid, when ethyl oxalacetate is obtained in an 80 per cent. yield (Wislicenus, *Annalen*, 1888, **246**, 313).

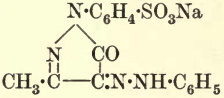
When tartrazine is treated with chlorine it is decomposed, with the formation of a diazo-compound (Schmidt, *J. pr. Chem.*, 1912, [ii], **85**, 235).

Flavazine S (M), Hydrazine yellow SO (Gr. E).



This is prepared from benzenediazonium chloride and the sodium salt of 1-*p*-sulphophenyl-5-pyrazolone-3-carboxylic acid as described under Light fast yellow (below). It gives more level dyeings than does Tartrazine but is not quite so fast to water.

Light fast yellow G, 2G, 3G (By), Flavazine L (M).



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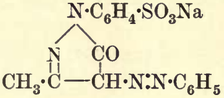

To a cold strongly alkaline solution of the sodium salt of 1-*p*-sulphophenyl-3-methyl-5-pyrazolone the calculated amount of benzenediazonium chloride is added. After remaining for some time,* the mixture is heated and about the same volume of fuming hydrochloric acid is added. An oil separates which on boiling becomes solid and crystalline. The free acid obtained in this way is collected, washed with dilute hydrochloric acid, dried, and recrystallised from glacial acetic acid with the addition of a little water. It forms small, brownish-yellow crystals, melting and decomposing at 262°, and readily soluble in water, acetic acid, or alcohol (Möllenhoff, *Ber.*, 1892, **25**, 1945).

The sodium salt dyes wool yellow.

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* The technical product can probably be salted out at this stage.

CHAPTER V

AZO-COLOURS (MONOAZO)

Containing Two Benzene Nuclei

AZO-YELLOW—AZO-FLAVINE—FAST YELLOW—ALIZARINE YELLOW GG—ALIZARINE YELLOW R—METANIL YELLOW—ORANGE IV—DIAMOND FLAVINE—CLAYTON YELLOW.

Containing One Benzene and One Naphthalene Nucleus

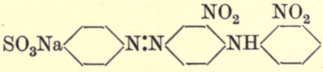
PONCEAU 4GB—PONCEAU R—ORANGE G—BRILLIANT LAKE RED—FAST RED—ORANGE II—VICTORIA VIOLET—PIGMENT FAST RED—DIAMOND BLACK—ACID ALIZARINE BLACK—AZO-ACID BLUE.

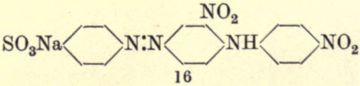
Containing Two Naphthalene Nuclei

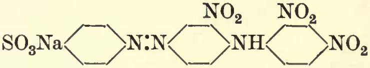
COCHINEAL RED—AMARANTH—AZO-RUBINE—ERIOCHROME BLACK A—ERIOCHROME BLACK T—ERIOCHROME BLUE BLACK—TOLYL BLUE—PALATINE CHROME BLACK.

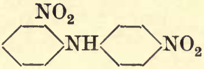
AZO-YELLOW (Sch., BK, K, S), Azo-yellow conc. (M), Azo-yellow 3G conc. (t.M), Azo-yellow M (DH), Azo-yellow O, I, (J), Azo-acid yellow (A), Azoflavine S (WDC), Azoflavine S new (B), Brilliant yellow (LP), Indian yellow G (By, C), Indian yellow extra (Mo, AW), Indian yellow 25 (LJ), Indian yellow J, JJ extra (Mo), Helianthine (G), Citronine (SB), Citronine G (L), Citronine 2AEJ (P).

This dye is obtained by the vigorous nitration of the nitrosoamine of Orange IV. The product is mainly a mixture of two dinitro- and one trinitro-derivative of Orange IV, and two dinitro- and one trinitro-derivative of diphenylamine of the following formulæ :







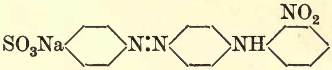


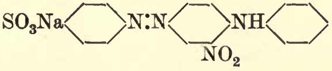
(Juillard, *Bull. Soc. chim.*, 1905, [iii], **33**, 974, 987).

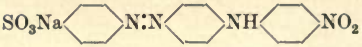
Following Fierz's preparation of Azoflavine RS, instead of 40 grams of nitric acid (60 per cent.), 90 grams are employed and the nitration is commenced at 40°. Within two hours the temperature is raised to 70° and kept at this point for two hours. To the mixture is then added 100 grams of salt, the whole is diluted to 1 litre and stirred at 70° until the dye has become bright orange and granular; this requires one to two hours. Dilution with 500 c.c. of water now follows, and the further procedure is as in the preceding case. The yield is about 95 grams (Fierz, p. 169). It will be seen that in both these cases the action of nitric acid is a two-fold one; the Azoflavine RS and Azo-yellow are nitrated in the normal manner, and they are also decomposed by the nitric acid into nitrated diphenylamines and diazosulphanilic acid (benzene diazosulphonate). Azoflavine S contains some of the nitrosoamine and consequently evolves nitrous fumes with hot water. In order to prevent this, the filtered paste is heated at 90° with four times its weight of water and after three hours 5 per cent. of sodium hydrogen sulphite is added. About 15–20 per cent. of the dye is lost by this treatment (Fierz, *loc. cit.*). Azoflavine S new has been freed from nitrous acid in this way.

Azoflavine RS (B), Azoflavine 3R conc. (t.M), Curcumeine extra (A, BK), Citronine (DH, J, Gr. E, L, S, SB), Citronine NE, Indian yellow 15 (LJ), Indian yellow R (Nw, By, C), Jasmine SF conc. (G).

This dye is prepared by the moderate nitration of the nitrosoamine of Orange IV. The product is mainly a mixture of three mononitro-derivatives of Orange IV and two dinitrodiphenylamines of the following formulæ :







(Juillard, *Bull Soc. chim.*, 1905, [iii], **33**, 974, 987).

A well-washed paste of the free acid of Orange IV (prepared from 52 grams of sulphanilic acid and 38 grams of diphenylamine) is mixed with 300 c.c. of water, cooled at 5°, and treated with 16 grams of sodium nitrite. The mixture is slowly stirred and, after two hours, 40 grams of nitric acid (60 per cent.) are added and stirring is continued for two hours, when the temperature is slowly raised to 68°. The mass foams, becomes darker, and in twenty-five minutes is all in solution. This is warmed for ten minutes at 71°, diluted with 500 c.c. of water, neutralised with 25 grams of sodium carbonate, and the dye precipitated by adding 200 grams of salt. After about twenty-four hours the precipitate is filtered off and dried at 60°. The yield is about 100 grams (Fierz, p. 168).

According to Paul (*Zeitsch. angew. Chem.*, 1896, **9**, 687), 19–21 kilos of pure Orange IV are dissolved in boiling water in a tub holding twice this volume, and next day 4–5 kilos. of sodium nitrite (as 25 per cent. solution), 18 kilos. of nitric acid, and 21 kilos. of sulphuric acid (66° Bé.) are added fairly rapidly. The whole is boiled for three hours, during which operation quantities of nitrous fumes are evolved which escape through a wooden chimney fixed to the cover of the tub. The solution of the dye is filtered through a sieve, and salted out.

A study of the nitration of Orange IV has been made by Maki (*Kōgyō-Kwagaku Zasshi* [*J. Chem. Ind. Tokyo*], 1918, **21**, 1199; 1919, **22**, 1), who found that the best product was obtained by shaking Orange IV with dilute nitric acid (*d* 1·226) at 15–17° for twenty hours.

Azoflavine RS (B), contains some of the nitrosoamine.

Azoflavine FF (B), Azoflavine H (M), is obtained by condensing aminoazobenzene with 4-chloro-1 : 3-dinitrobenzene and sulphonating the product (Nölting and Salis-Mayenfeld, F.P. 152105; G.P. 22268).*

Its constitution is represented by the formula

(Fierz, p. 173).

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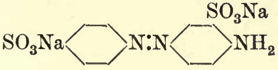
* This patent is apparently wrongly given by Friedländer, " Fortschritte der Theerfarbenfabrikation," I., p. 326, as 42276).

Fast yellow (LP, SB), Fast yellow extra (B, By), Fast yellow O (M), Fast yellow G (B, BK, DH), Fast yellow GR (t.M), Fast yellow greenish (WDC), Fast yellow S (C), Acid yellow (AW, PS, RF, Gr. E), Acid yellow G, R (A), Acid yellow T, TD, CH, G, R (L), Solid yellow BO, B, G (L), New yellow L (K), Yellow SS (P).



The dye contains also some of the monosulphonic acid.

(1) Aminoazobenzene hydrochloride is heated with 3–5 parts of strongly fuming sulphuric acid at 90–100°. On pouring into water, the monosulphonic acid, which separates, can be filtered off if necessary,* and the disulphonic acid separated from the filtrate by adding salt (Graessller, E.P. 43^{79}; F.P. 128113; G.P. 4186, 7094, 9384; U.S.P. 253598; compare also Harmsen, "Die Fabrikation der Theerfarbstoffe," 1889, 253). The solution of the sodium salt is evaporated to dryness below 90°.

(2) Aminoazobenzene hydrochloride is stirred into 4–4½ times its weight of fuming sulphuric acid containing 25 per cent. of sulphur trioxide and the temperature is maintained at 40° until a sample gives a clear solution with ammonia. The mass is poured into water or 100 parts of dilute salt solution (8° Bé.) and the precipitate is filtered and converted into the sodium salt (Schultz, "Farbstofftabellen," 1914, 51).

Alternatively, the product of the sulphonation is poured into cold water, and the sulphonic acids, when cold, are filtered off, washed, and pressed. The paste is stirred with a little water, neutralised with milk of lime, and the mixture boiled and filtered, whereby the calcium salt of the monosulphonic acid remains behind. The filtrate containing the calcium salt of the disulphonic acid is evaporated and treated with sodium carbonate. After filtering off the calcium carbonate, the sodium salt is salted out (Heumann, IV, i, 760).

(3) The disulphonic acid is also obtained by slowly adding 50 kilos. of aminoazobenzene sulphate $(C_{12}H_{11}N_3)_2,H_2SO_4$, or 47 kilos. of the hydrochloride to 230 kilos. of fuming sulphuric acid containing 14 per cent. of sulphur trioxide, with cooling,

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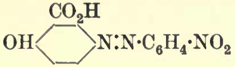
* This separation can also be effected by means of the calcium salts, the solubilities of which correspond with those of the free acids.

and then warming gradually at 60–70° until a sample is soluble in water. The product is diluted with water and neutralised with sodium hydroxide (Krügener, E.P. 5021^{79}; G.P. 16482).

The disulphonic acid, on reduction with tin and hydrochloric acid, gives sulphanilic acid and *p*-phenylenediamine sulphonic acid (Griess, *Ber.*, 1882, **15**, 2187); the fact that a sulphonic acid group is in the ortho-position with respect to the amino-group was established by Eger (*Ber.*, 1889, **22**, 847).

Alizarine yellow GG (M, J), Alizarine yellow GGW powder (M. Ault & Wiborg Co.), Alizarine yellow G, 3G (Lev.), Alizarine yellow 3G (By), Alizarine yellow G (S), Alizarine yellow A4 paste (Fab. de Thann et Mulhouse), Mordant yellow 2GT (B), Anthracene yellow GG (C), Chrome yellow R (P).



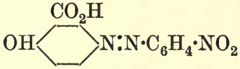
$$\mathrm{OH}\overset{\mathrm{CO_2H}}{\langle\quad\rangle}\mathrm{N{:}N\cdot C_6H_4\cdot NO_2}$$

(GG is the free acid and GGW the sodium salt; the dye is usually sold as a 20 per cent. paste.)

Ten kilos. of *m*-nitroaniline are dissolved in 40 kilos. of hydrochloric acid (20° Bé.) and 150 litres of water. The solution is cooled and 5·4 kilos. of sodium nitrite, dissolved in the necessary amount of water, are added. After a short time, the solution is run into a solution of 10 kilos. of salicylic acid and 25 kilos. of sodium carbonate in about 150 litres of water. Most of the dye separates out, and the rest is precipitated by salt. It is filtered off and made into a paste (Nietzki, transferred to Farbwerke vorm. Meister, Lucius, & Brüning. E.P. 17583^{87}; F.P. 187821 and additions; G.P. 44170; U.S.P. 424019).

The free acid melts and decomposes at 237°. It yields a crystalline barium salt (Gebek, *Annalen*, 1889, **251**, 188). When reduced with sodium hyposulphite, the sodium salt gives aminosalicylic acid and *m*-phenylenediamine (Grandmougin, *Ber.*, 1906, **39**, 3930; compare Green, "Analysis of Dyestuffs," 1915, 115), and when treated with chlorine the dye is decomposed with the production of a diazo-compound (Schmidt, *J. pr. Chem.*, 1912, [ii], **85**, 235).

Alizarine yellow R (M, By, CR), Alizarine yellow RW (M, Marden, Orth, and Hastings), Alizarine orange R, 2R (Lev.), Alizarine yellow P paste (FTM), Mordant yellow 3B (B), Mordant yellow PN (FA), Orange R (S), Chrome orange (P), Milling orange R (L), Anthracene yellow RN (C), Metachrome orange R (A), Terracotta R (G), Chromoxanthine (S).



(R is the free acid and RW the sodium salt; the dye is usually sold as a 20 per cent. paste.)

This dye was discovered by Meldola (*Trans.*, 1885, **47**, 666) by the action of a solution of diazotised *p*-nitroaniline on a well-cooled solution containing the necessary quantity of salicylic acid dissolved in excess of sodium hydroxide. On acidifying, an ochreous precipitate separated, which, after purification, crystallised from dilute acetic acid in orange-brown needles which commenced to blacken at 225° (Grandmougin, *Ber.*, 1906, **39**, 3930 gives 257°). The sodium salt, obtained by salting out the alkaline solution, is brown.

2·8 Kilos. of *p*-nitroaniline and 16 kilos. of hydrochloric acid (12° Bé.) are heated to boiling by means of direct steam and the hot solution is filtered through a woollen cloth into a tub fitted with a stirrer containing about 200 litres of water. The residue on the filter is boiled up with a little water and hydrochloric acid (2 kilos.) and the solution filtered into the tub. The contents of the latter are cooled at 5° by the addition of ice and 1·2–1·4 kilos. of sodium nitrite (as 25 per cent. solution) are added as rapidly as possible. The diazo-solution, containing a slight excess of nitrite, is stirred for two to three hours. It is then run into a solution of 2·8 kilos. of salicylic acid and 11 kilos. of sodium carbonate, and when the combination is complete 150 kilos. of salt solution are added and the dye is filtered off, giving 14·8 kilos. of paste containing 3·4 kilos. of the dry sodium salt. If the dye-acid is precipitated by adding 7 kilos. of hydrochloric acid (12° Bé.), the filtered paste weighs 11·5 kilos. (26·7 per cent.) corresponding with 3·07 kilos. of dry substance (Paul, *Zeitsch. angew. Chem.*, 1896, **9**, 683).

An alternative method of preparation consists in nitrating benzeneazosalicylic acid.

A solution of 12 kilos. of aniline in 36 kilos. of hydrochloric acid and 300 litres of water is cooled at 5° and a solution of 9 kilos. of sodium nitrite is added. The diazo-solution is poured into an alkaline solution of 17 kilos. of salicylic acid and the product is precipitated with salt or acid and filtered.

Forty-five kilos. of the dry powder are dissolved in 135 kilos. of sulphuric acid and a mixture of 20 kilos. of nitric acid and 15 kilos of sulphuric acid is added slowly. Some time afterwards the mixture is poured into water, filtered, washed, and made into a paste. When prepared in this way, the dye is known as Terracotta R (Anilinfarben- & Extract-Fabriken vorm. J. R. Geigy, E.P. 13920^{88}; F.P. 193190; U.S.P. 431297).

When Alizarine yellow R is reduced by means of sodium hyposulphite, *p*-aminosalicylic acid and *p*-phenylenediamine are formed (Grandmougin, *loc. cit.*; Grandmougin and Guisan, *Rev. gén. Mat. Col.*, 1908, **12**, 129), whilst by treatment with sodium sulphite *p*-aminobenzeneazosalicylic acid, *p*-nitroaniline, ammonia, and an aminosulphosalicylic acid

$$(CO_2H{:}OH{:}NH_2{:}SO_3H = 1:2:5:?)$$

are obtained (Lepetit and Levi, *Gazzetta*, 1911, **41**, i, 675).

Metallic lakes of the dye have been prepared by Möhlau and Maetzel (*Ber.*, 1913, **46**, 454).

Metanil yellow (Sch., Marden, Orth, and Hastings Corp., Ault & Wiborg Co., Japan Dyestuffs Co.), Metanil yellow extra (A, B, C, BK, DH, G, K, Gr. E, FA, SB, S, Sch., WDC), Metanil yellow GR extra conc. (t.M), Metanil yellow O (L), Metanil yellow PL (B), Metanil yellow 230 (AW), Yellow M (P), Victoria yellow O double conc. (M), Orange MN, MNO (J), Tropaeoline G (C).

(1) A solution of 20 kilos. of sodium metanilate and 7 kilos. of sodium nitrite in 200 litres of water, at 5°, is allowed to run slowly into a well-stirred mixture of 30 kilos. of hydrochloric acid and 200 litres of water at 5°. The diazo-compound separates in small, yellow crystals, which are filtered off and washed. The diazo-compound is added to a solution of 17 kilos. of diphenylamine in 70 litres of alcohol contained in an enamelled pan which is cooled externally. The combination is rather slow, and when it is complete the mixture is rendered alkaline with sodium hydroxide solution, the alcohol distilled off, the residue dissolved

in water, filtered from any unchanged diphenylamine, and salted out (Harmsen, "Die Fabrikation der Theerfarbstoffe," 1889, 254).

(2) A mixture of 15 kilos. of metanilic acid, 14 kilos. of hydrochloric acid, and 36 litres of water is treated at 7° with 18 kilos. of sodium nitrite solution (20° Bé.) [6·3 kilos. in 12 litres of water] and the diazo-solution is run into a solution of 10 kilos. of diphenylamine in 36 kilos. of alcohol at 14–15°. After combination is complete, the dye is isolated as sodium salt (Schultz, "Farbstofftabellen," 1914, 50).*

(3) To a concentrated solution of diazotised metanilic acid, prepared from 100 lb. of the acid, a solution of 95 lb. of diphenylamine in 85 lb. of crude carbolic acid is added, the temperature not being allowed to exceed 15°. Stirring is continued throughout the day, the temperature being gradually raised to 28°. Next day, the product is filtered on an open filter and washed with water. It is then dissolved in a concentrated solution of 60 lb. of potassium carbonate and the dye is precipitated by adding sodium hydroxide solution.

(4) A solution of metanilic acid, prepared from 20 kilos. of nitrobenzene, is divided between four casks and to each part of the solution is added a solution of 2·2 kilos. of sodium nitrite (of 100 per cent.). The end of the diazotisation is controlled by tests for free acid and nitrous acid. Above each cask stands a lead pan with bottom outlet the contents of which can be warmed by means of a lead steam-coil. In each pan is placed 20 litres of water and 4·75 kilos. of diphenylamine, and then 17 litres of sulphuric acid are added quickly. On stirring, a homogeneous solution is obtained which is stirred into the diazo-solution during about seven hours, the temperature being 18°. Stirring is continued for a further period, the product being then filtered through a wooden filter-press. The paste is stirred with 300 litres of water, again passed through the filter-press, and then stirred with 250 litres of water and potassium hydroxide or sodium hydroxide added until a sample, to which calcium chloride has been added, gives an alkaline reaction towards phenolphthalein. The whole is now heated at 60°, when all dissolves, treated with salt solution, and allowed to cool. If potassium hydroxide has been used, a mixture of the potassium and sodium salts separates which is filtered off (Heumann, IV, i, 755). *Patents*: E.P. 1226^{79}, 4966^{80} which give, however, no details of the manufacture.

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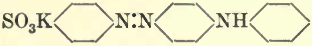
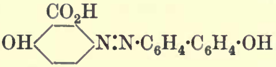
* A similar process, in which much more alcohol is used, is given by Paul (*Zeitsch. angew. Chem.*, 1896, **9**, 687).

Orange IV (B, BK, K, C, DH, G, LP, P, SB, t.M, By, RD, RF, BD, L, W, Sch., WDC, Bm), Orange No. 4 (M, P), Orange N (B, J), Orange GS (Gr. E), New yellow extra (By), Acid yellow D extra (A), Acid yellow cryst. (C), Acid yellow DMP (A), Citronine V double (DH), Tropaeoline OO (C).



This dye was discovered by Witt in 1876. A solution of 100 lb. of sulphanilic acid in sodium hydroxide is diazotised in the usual way by the addition of 72 lb. of sulphuric acid (95 per cent.), diluted with water, and 41 lb. of sodium nitrite. The whole is kept as concentrated as possible. Into the diazo-solution is run a solution of 95 lb. of diphenylamine in 85 lb. of crude carbolic acid, the temperature not being allowed to exceed 15°. Stirring is continued for a day, the temperature being gradually raised to 28°. Next day the product is filtered on an open filter and washed with water. It is dissolved in a concentrated solution of 60 lb. of potassium carbonate, and to the hot solution are added 60 lb. of sodium hydroxide, dissolved in water. On cooling, the dye is filtered off. The yield is about 180 lb.* A method of preparing this dye on the small scale is described by Fierz (p. 165). On reduction, it yields sulphanilic acid and *p*-aminodiphenylamine (Witt, *Trans.*, 1879, **35**, 189).

Diamond flavine G (By).



A solution of 10 kilos. of benzidine in 500 litres of water and 28 kilos. of hydrochloric acid (20° Bé.) is cooled and 7·5 kilos. of sodium nitrite, dissolved in 50 litres of water, are added. The diazo-solution is run into an ice-cold solution of 8·2 kilos. of salicylic acid and 15 kilos. of sodium carbonate in 500 litres of water. The formation of the intermediate compound is complete in three to four hours. The mass is acidified with dilute sulphuric acid, filtered, and the paste is mixed with 2000 litres of water to

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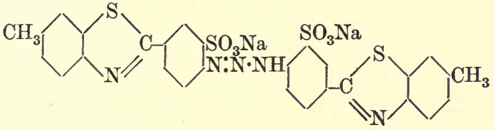
* A process for manufacturing Orange IV is also described by Paul (*Zeitsch. angew. Chem.*, 1896, **9**, 684); the diphenylamine is dissolved in sulphuric acid and the part left uncombined is distilled off in a current of steam, or the base is dissolved in alcohol and the latter recovered by distillation.

which 40 kilos. of sulphuric acid (66° Bé.) have been added. The whole is stirred and heated for several hours at the temperature of the water-bath until the evolution of nitrogen has ceased, filtered, and washed with water until free from acid. The paste is used direct for dyeing and printing (Farbenfabriken vorm. F. Bayer & Co. E.P. 11663^{91}; F.P. 214756; G.P. 60373).

Clayton yellow (Cl. Co), Thiazole yellow (A, J), Thiazole yellow G, R (By), Naphthamine pure yellow G (K), Azidine yellow 5G (CJ), Cotton yellow (BD), Oxydiamine yellow TZ (C), Titan yellow G (BD), Mimosa (G).



This is prepared either by the action of diazotised dehydrothio-*p*-toluidinesulphonic acid (or primuline) on the same base or by treating the diazo-compound with alkali. The formula given is that of the dye obtained from dehydrothio-*p*-toluidinesulphonic acid.

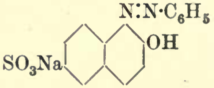
The diazo-compound prepared from 35 kilos. of dehydrothio-*p*-toluidinesulphonic acid is poured into an acetic acid solution of 25 kilos. of the same acid and the mixture is warmed at 20–30°. It is kept at this temperature for two days, then heated at 60–80°, neutralised with sodium carbonate, and the dye salted out (Clayton Aniline Co., E.P. 14207^{89} [describes combination in alkaline solution], Farbenfabriken vorm. F. Bayer & Co., E.P. 18354^{89}; F.P. 198786; G.P. 53935; U.S.P. [from which the above description is taken] 428629).

A solution of 50 kilos. of primuline in 1000 litres of water is diazotised, after the addition of 30 kilos. of hydrochloric acid (20·5° Bé.), with a solution of 7 kilos. of sodium nitrite. When the diazotisation is complete, 30 kilos. of ammonia (25° Bé.) are added. After about twelve hours, the mixture is heated to boiling and when the evolution of gas has ceased the dye is salted out (J. R. Geigy & Co., E.P. 1771^{90}; F.P. 203479; G.P. 53666, 56593; A.P. 440281).

A solution of 80 kilos. of sodium dehydrothio-*p*-toluidine-sulphonate in 1000 litres of water is cooled with ice, 80 kilos. of hydrochloric acid (20·5° Bé.) are added, and diazotisation is effected with a solution of 16 kilos. of sodium nitrite. 150 Kilos. of ammonia (25° Bé.) are added and an intense orange-red solution is formed, gas being evolved. The dye is isolated as above (*loc. cit.*).

The dye may also be prepared from the mixture of primuline and dehydrothio-*p*-sulphonic acid which is obtained by heating *p*-toluidine with sulphur and sulphonating the product (see Cain, "The Manufacture of Intermediate Products for Dyes," 2nd ed., 1920, p. 78). The mixture of acids produced from 225 lb. of the base is neutralised with ammonia and diluted to 600 gallons. A sample is titrated with sodium nitrite solution, and half the quantity calculated as corresponding with the whole batch (usually 50 lb. of nitrate) is employed. For example, to the above solution is added 25 lb. of sodium nitrite, followed after ten minutes by 15 gallons (170 lb.) of hydrochloric acid (26 per cent.) or a corresponding quantity of a different strength. After stirring for half an hour, 40 lb. of dry sodium carbonate are slowly sprinkled in and the stirring is continued for two to three hours. Fifty lb. of sodium carbonate are now added, and when dissolved the mixture is left over-night. On the following day, the whole will have set to a jelly which is difficult to stir. A further 50 lb. of sodium carbonate are added and the mixture is slowly heated by direct steam at 70°. The dye is then salted out by adding about 400 lb. of salt, filtered, pressed, and dried. The yield of dry colour is 350–400 lb.

Ponceau 4 GB (A, BK, Lev.), Rainbow orange (Brotherton), Brilliant orange G (M, C. J.), Orange GR, X (B), Orange ENL (C), Pyrotin orange (WDC), Croceine orange (By, BK, K, RF, Bm, P), Croceine orange GR (t.M), Croceine orange Y (Sch.).

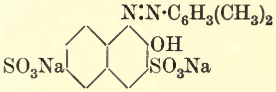


This dye was first obtained by Griess (*Ber.*, 1878, **11**, 2197) by the action of benzenediazonium nitrate on an alkaline solution of β-naphthol-6-sulphonic acid (Schaeffer's acid).

A solution of benzenediazonium chloride, prepared from 93 parts of aniline, 350 parts of concentrated hydrochloric acid, and 72 parts of sodium nitrite, in dilute solution, is added to an aqueous solution of 246 parts of Schaeffer's salt and 200 parts of sodium chloride. After stirring for some hours, the dye is filtered cold.

A chromium lake has been prepared by Möhlau and Maetzel (*Ber.*, 1913, **46**, 456).

Ponceau R, 2R (A, B, By, M, BK, Bm, CJ, Gr. E, Lev., P, RF, L, S, AW, t.M), Ponceau G (M, A, B, C, BK, Lev., Bm, t.M), Ponceau GR (M), Ponceau FR, FRR, Brilliant ponceau G (C), Brilliant ponceau R, RR (t.M), Scarlet 2R (B.D., Calco Chem. Co.).

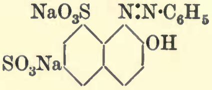


Ponceau R is prepared from *m*-xylidine and pure R-salt, 2R, from crude xylidine, G, GR, Brilliant ponceau G, from crude xylidine and crude R-salt.

Ponceau R.—A solution of 12 kilos. of xylidine in 250 litres of water and 23 kilos. of hydrochloric acid, or 15·7 kilos. of crystallised *m*-xylidine hydrochloride in 250 litres of water and 12 kilos. of hydrochloric acid, is cooled at 5° and a solution of 7 kilos. of sodium nitrite in 35 litres of water run in slowly. The diazo-solution is slowly added to a solution of 35 kilos. of R-salt in 350 litres of water and 25 kilos. of ammonia (10 per cent.) which has been cooled at 5°, the whole being well stirred. After about three hours, a concentrated and filtered solution of salt is added until a drop of the mixture, on filter-paper, shows a brownish-red rim round the paste. The dye is then filtered, pressed, dried, powdered, and standardised (Harmsen, "Die Fabrikation der Theerfarbstoffe," 1889, 246; compare Meister, Lucius, & Brüning, E.P. 1715^{78}; F.P. 124811; G.P. 3229; A.P. 210233). On reduction with sodium hyposulphite, the dye yields xylidine and 1-amino-β-naphthol-3 : 6-disulphonic acid (Grandmougin, *J. pr. Chem.*, 1907, [ii], **76**, 124; compare Green, "Analysis of Dyestuffs," 1915, 114).

In preparing Brilliant Ponceau (from crude R-salt) the mixture of R-salt, G-salt and Schaeffer's salt, formed by the sulphonation of β-naphthol, is titrated with diazotised α-naphthylamine in order to ascertain the amount of R-salt and Schaeffer's salt, and the bulk is combined with the calculated amount of diazotised xylidine. The solution containing the dye is heated to boiling, filtered (if necessary), and salted out, the dye being purified by redissolving and salting out. The filtrate containing the G-salt is used for making dyes, such as Crystal Ponceau, for which a solution of pure G-salt is necessary.

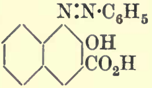
Orange G (A, B, K, M, RF, P, t.M, Gr. E, CJ, CDC, Sch.), Orange GG (BK, WDC, C, Nat), Orange GR special (C), Orange GMP (A), Patent orange (A), Crystal orange GG (WDC), Light fast orange G (By).



Five parts of aniline, dissolved in 12 parts of hydrochloric acid (20° Bé.) and 100 parts of water are diazotised and the solution is added to a solution of 20 parts of β-naphthol-6 : 8-disulphonic acid in 200 parts of water and 10 parts of ammonia solution (10 per cent.). The product is salted out (Meister, Lucius, & Brüning, E.P. 1715^{78}; F.P. 124811; G.P. 3229; U.S.P. 251162).

The calcium salt is sparingly soluble in water (Witt, *Ber.*, 1888, **21**, 3481). On reduction with stannous chloride and hydrochloric acid (Witt, *loc. cit.*) or sodium hyposulphite (Grandmougin, *J. pr. Chem.*, 1907, [ii], **76**, 129), the dye yields aniline and 1-amino-β-naphthol-6 : 8-disulphonic acid.

Brilliant lake red R (paste) (M).



Diazotised aniline is combined with 2-hydroxy-3-naphthoic acid in alkaline solution. If the solution is acidified the free acid is obtained, which crystallises from glacial acetic acid in brownish-red needles melting at 232° (Kostanecki and Kernbaum, *Ber.*, 1893, **26**, 2897).

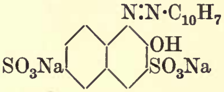
The same dye is produced by the action of diazotised aniline on methylene-bis-2-hydroxy-3-naphthoic acid,

$$CH_2[C_{10}H_5(OH)\cdot CO_2H]_2,$$

the methylene group being eliminated (Strohbach, *Ber.*, 1901, **34**, 4164).

The yield of the dye made in the ordinary way is almost theoretical (Strohbach, *loc. cit.*, obtained 29 grams from 20 grams of β-hydroxy-3-naphthoic acid).

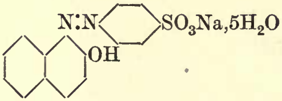
Fast red B (B, BK, L), Fast red P extra (By), Archelline 2B (Lev.), Bordeaux B (A, BK, LP, M, RF, BD, Bm. Calco Chem. Co.), Bordeaux BL (C), Bordeaux G (WDC), Bordeaux R extra (t.M), Cerasine (P), Cerasine R (DH), Azo Bordeaux (Sch.).



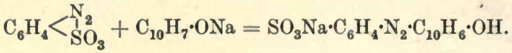
To a solution of 143 lb. of α-naphthylamine in 1 molecular proportion of hydrochloric acid and 500 gallons of water ice is added until the temperature is about 8° and then 2 molecular proportions of hydrochloric acid. A sample is now taken and if, on adding a solution of sodium nitrite, a clear brown solution is obtained diazotisation may be proceeded with, but if a precipitate is formed, more acid must be added until a diazotised solution is clear. A concentrated solution of 72 lb. of sodium nitrite is now added as quickly as possible, the temperature being at about 8°, and care must be taken that a slight excess of nitrite is present.

The clear solution is then run into a cold solution of 355 lb. of R-salt dissolved in 115 lb. of sodium hydroxide and 500 gallons of water; excess of R-salt and alkali must be present. Next day, the colouring matter is heated at 80°, salted out, and filtered. The yield of dry product is about 580 lb. (compare Meister, Lucius, & Brüning, E.P. 1715^{78}; F.P. 124811; G.P. 3229; U.S.P. 251164).

Orange II (Lev., LBH, Greengate, Brotherton, Calco, B, BK, DH, J, K, PC, RD, RF, W, VSt, CJ, AW, Bm, t.M, C), Orange No. 2 (M, P). Orange P (Gr. E), Orange extra (C), Orange A (L, Sch.), Orange G (BK, BD), Orange R extra (Mo), Orange II B (By), Orange II, P, II. PL (B), Acid orange (G), Gold orange (BK, By, WDC, t.M), Mandarin G (A, BK, By).



The following details of the manufacture of this important dye are given by Mühlhäuser * (*Dingl. Polyt. J.*, 1887, **264**, 181, 238). Its formation is represented by the equation :—



$$C_6H_4{<}\begin{matrix}N_2\\ |\\ SO_3\end{matrix} + C_{10}H_7{\cdot}ONa = SO_3Na{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH.$$

It is usual, in the manufacture of azo-dyes, to work with a slight excess of the phenol or amine which is combined with the diazo-compound, but in the case of Orange II a slight excess of β-naphthol tends to make the colour dull, and it is therefore better, after the components have been mixed, to have a slight excess of the diazo-compound present. This ensures that the whole of the naphthol is combined and the small amount of diazo-compound or its product of decomposition is harmless. A further important point is to avoid having an excess of acid present and therefore about 3 per cent. more alkali than is necessary to neutralise the acid should be taken. Excess of sodium hydroxide should be avoided, as this prevents complete precipitation of the dye owing to the formation of some of the dibasic sodium salt which remains in solution. An excess of sodium nitrite in the diazotisation of the sulphanilic acid is harmless so long as the naphthol solution is alkaline.

For dissolving, purifying, and diazotising the sulphanilic acid, the following plant is required. A cast-iron pan of 800 litres capacity having a wide manhole, which is connected to a six-chambered filter-press which retains the residue from the sulphanilic acid solution and allows the filtrate to run into a wooden tub of 800 litres capacity standing on a weighing machine. When the weight of the liquid has been ascertained, it is run down into the diazo-tub of 2000 litres capacity fitted with a stirrer. All parts of this tub with which the acid liquor comes into contact are of wood. Set above the diazo-tub is a cask of 250 litres capacity for dissolving the sodium nitrite.

The β-naphthol is dissolved in a cast-iron pan of 800 litres capacity having a wide manhole and connected to a six-chambered filter-press through which the sodium β-naphthoxide solution is filtered, the filtrate running into the combining tub of 4000 litres capacity fitted with a rapidly revolving stirrer. This tub is connected with a receiver set at a lower level, of 2000 litres capacity, which in turn communicates with two eighteen-chambered filter-presses.

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* A rough description of the manufacture is also given by Paul (*Zeitsch. angew. Chem.*, 1896, **9**, 687), but it is not necessary to reproduce the details; the solutions are measured out by buckets !

Those solutions which have to be heated are prepared the day before the combination is made so as to save ice in diazotising and coupling. The sulphanilic acid is also precipitated from solution by sulphuric acid the day before, as, when the precipitation takes place with the hot solution, the sulphanilic acid separates in the finely divided condition which is necessary for successful diazotisation. The first operation consists in dissolving 26 kilos. of solid sodium hydroxide in 400 litres of hot water in the cast-iron pan. To the boiling solution 100 kilos. of sulphanilic acid are added gradually within twenty minutes, and tests are made with litmus paper to see that the solution is alkaline, and the disappearance of the lumps of sulphanilic acid from the bottom of the pan is best ascertained by means of a stick. When all the sulphanilic acid is dissolved and the solution has a faint alkaline reaction, steam is led in for a further twenty minutes in order to expel the last traces of aniline. When this has been effected, as is ascertained by smelling the escaping steam, the latter is shut off, the pan closed, the air tap opened, and the contents of the pan are filtered through the filter-press, the plates of which are covered with cotton filter-cloth. The filtrate is collected in the tub standing on the weighing machine, weighed, and immediately analysed, the latter operation taking about five minutes.

For example, the weight of the filtrate is 560 kilos. and the specific gravity 1·095. For 10 c.c. of the liquid, 11·15 c.c. of normal sodium nitrite solution are required. The total quantity of sulphanilic acid (free acid) is therefore 98·7 kilos. which requires for diazotisation 41·3 kilos. of sodium nitrate (95 per cent.) and 82·1 kilos. of β-naphthol for coupling.

The amount of sulphuric acid taken, which corresponds exactly with 100 kilos. of pure sulphanilic acid, is always the same for each batch, as is also the quantity of sodium hydroxide used for neutralisation. For each batch, whether the sulphanilic acid solution is strong or weak, 64 kilos. of sulphuric acid are used for precipitation, and 30 kilos. of sodium hydroxide for dissolving the naphthol.

When the solution of sodium sulphanilate has been tested and the necessary amounts of nitrite and naphthol have been calculated, the hot solution is siphoned into the diazo-tub and immediately precipitated with 64 kilos. of concentrated sulphuric acid (or the equivalent amount of hydrochloric acid) which is run slowly into the stirred solution. The 41·3 kilos. of sodium nitrite are also dissolved in 200 litres of water.

On the same day, 82·1 kilos. of β-naphthol * are dissolved in the second cast-iron pan in a hot solution of 30 kilos. of sodium hydroxide in 400 litres of water. This solution is allowed to cool over-night and then filtered through the filter-press into the combining tub.

Diazotisation.—Next day ice is added to the diazo-tub to bring the temperature of the liquid to 4°. The stirrer is started, and the nitrite solution is run in within ten to fifteen minutes. More ice is added if the temperature rises above 10°. Towards the end of the addition of nitrite tests are made with starch–potassium iodide paper and the addition is stopped when a blue coloration is obtained. This usually happens when the last portion of the nitrite solution has been added. The reaction should still show faintly after five minutes' stirring.

Coupling.—The naphthol solution is cooled with ice at 4°, stirred, and the diazotised sulphanilic acid is run in within forty minutes, care being taken that the temperature in the combining tub does not exceed 12°. When the mixture is complete, the mass is tested to ascertain that it is slightly alkaline and then stirring is continued for an hour in order that the whole of the dye may separate out.

Working up.—The crystalline mass, consisting of silky, golden-yellow needles, is run into the receiver and blown into the filter-presses by means of compressed air; the faintly coloured filtrate does not contain sufficient dye to be worth recovering. Each filter-press is filled and the contents of one are blown dry with compressed air while the other is still filtering. The presses are emptied when no more liquor is being blown out, best ascertained by holding the hand in the escaping stream of air.

The press cake is collected in wooden boxes lined with lead, spread on zinc trays, and cut into small pieces with wooden spatulas. The dye is dried at 60–70° for four to five days and then ground. The average yield is 200 kilos. The following table gives figures as obtained in the factory:

Sulphanilic acid taken.	Sodium hydroxide.	Sulphanilic acid found.	Sulphuric acid.	Sodium nitrite 95 per cent.	β-Naphthol.	Sodium hydroxide.	Yield.
100	26	98·7	64	41·3	82·1	30	201
100	26	97·0	64	40·6	80·7	30	194
100	26	86·5	64	40·4	80·3	36	195

With regard to Mühlhäuser's process, it may be remarked that instead of dissolving a given weight of crude sulphanilic acid

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* Mühlhäuser's β-naphthol was 99 per cent., so by taking the theoretical amount he ensured the necessary slight deficit.

and weighing the solution, it is more convenient to dissolve more than is required and to collect the filtrate in a tub. If the tub has previously been carefully measured and a table constructed giving the contents at any given height,* the exact amount required can be run down into the diazotising tub.

It is perhaps a slight advantage to use hydrochloric acid instead of sulphuric acid for diazotising so as to form sodium chloride, which has a greater " salting-out " power than sodium sulphate.

The β-naphthol is best brought into solution by mixing it with the calculated amount of 30 per cent. sodium hydroxide solution in a small iron pan standing above the combining tub, and blowing steam into the mixture. The naphthol soon dissolves and the solution is run, without being filtered, into water contained in the combining tub. The extra alkali required for neutralisation, above that in the form of sodium β-naphthoxide, is preferably sodium carbonate, whereby the possibility of some of the dye being present as dibasic sodium salt is excluded.

If it is necessary to salt out a small amount of dye still in solution when the operation is complete, a little salt solution (filtered if necessary) is used. In Mühlhäuser's table of results, 122·3 kilos. of commercial sodium nitrite gave 590 kilos. of dye. In the author's experience, eleven batches, in each of which 100 lb. of nitrite were used, gave 5266 lb. of dye. This corresponds with 584·5 instead of 590, which is in excellent agreement with Mühlhäuser's figure. Ninety-five parts of the dye are mixed with 5 parts of dry sodium sulphate to give 100 parts of " standard " or " type."

On reduction with stannous chloride and hydrochloric acid (Liebermann, *Ber.*, 1881, **14**, 1311; Witt, *ibid.*, 1888, **21**, 3472), tin and hydrochloric acid (Grandmougin and Michel, *ibid.*, 1892, **25**, 981) or sodium hyposulphite (Grandmougin, *ibid.*, 1906, **39**, 2495; compare Green, p. 115), sulphanilic acid, and 1-amino-β-naphthol are formed.

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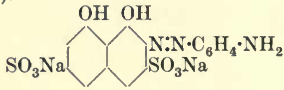
* For ordinary purposes, it is sufficient to take the mean of the diameter at the top and the bottom of the tub and the height. Then if r is the radius $\frac{\pi r^2}{27{\cdot}742}$ = lb. (of water) per inch of height. Suppose that a solution contains 10 per cent. (grams per 100 c.c.) of dissolved substance and that 150 lb. of the latter are required, and, further, that 1 vertical inch in the tub = (the volume of) 200 lb. of water; the volume of 1500 lb. of solution is obtained by running down 7½ inches. For exact purposes, the diameter of the tub at each inch is found graphically from the above measurements, and the value of each inch is calculated.

By the action of chlorine, a diazo-compound is formed (Schmidt, *J. pr. Chem.*, 1912, [ii], **85**, 235).

The free acid is obtained only by boiling the dye with a large excess of concentrated hydrochloric acid (Sisley, *Bull. Soc. chim.*, 1901, [iii], **25**, 862).

The fact that Orange II contains 5 molecules of water of crystallisation was shown by Knecht and Hibbert (*Ber.*, 1903, **36**, 1553) who analysed it by titration with titanium chloride.

Victoria violet 4BS (M, By), Victoria violet L (J), Domingo violet A (L), Ethyl acid violet S4B (B), Azo wool blue (C).*



This is prepared (1) by reducing the corresponding nitro-colouring matter (it is also formed by hydrolysing the corresponding acetyl derivative) or (2) by heating the combination of diazotised acetyl-*p*-phenylenediamine and H-acid with acids or alkalis.

(1) The dye prepared by the action of diazotised *p*-nitroaniline on chromotropic acid (Chromotrope 2B) is dissolved in fifteen to twenty times its weight of warm water and a 20 per cent. solution of sodium sulphide is gradually stirred in at 50–60° until a sample when warmed with a further quantity of sodium sulphide does not become any bluer and, on being acidified after some time, evolves hydrogen sulphide. With a little practice, the end-point is easily recognised. When the nitro-dye has been prepared from 138 parts of *p*-nitroaniline and 400 parts of sodium chromatropate, the quantity of sodium sulphide solution required for reduction is 2500 parts, corresponding with 450 parts of crystallised sodium sulphide. The reduction begins at once on adding the sulphide solution and the temperature of the mixture rises. At 60–70°, the operation is complete within an hour, whilst at a lower temperature it may take three hours.

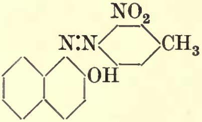
The solution is neutralised with acetic acid or a dilute mineral acid and the dye salted out (Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 8270^{92}; F.P. 221363, 226690; G.P. 70885).

(2) Acetyl-*p*-phenylenediamine (13·6 parts) is diazotised and the solution added to a solution of H-acid (37 parts) in the

* Victoria violet 8BS (M), and Victoria violet 5B (By) probably contain this dye.

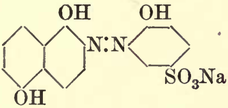
presence of sodium acetate. After stirring for one to two hours, the dye is isolated, pressed, and dried, and then heated with a mineral acid of alkali hydroxide in an autoclave or open pan at about 100° for some hours. The product is rendered neutral and the dye is precipitated in the usual way, pressed, and dried (Farbwerke vorm. Meister, Lucius, & Brüning, G.P. 73321).

Pigment fast red HL (M), Helio fast red RL (By), Lithol fast scarlet R, RPN (B), Graphitol fast red GAERR (Gr. E), Sitara fast red RL (t.M).



A solution of the diazo-compound prepared from 30 parts of *m*-nitro-*p*-toluidine is run into a solution of 35 parts of sodium β-napthoxide to which 8½ parts of Turkey red oil and 1000 parts of a paste containing 10 per cent. of aluminium hydroxide have been added, together with sufficient sodium carbonate to maintain alkalinity after all the diazo-solution has been added. The lake is filtered and worked up in the usual way (Farbenfabriken vorm. F. Bayer & Co., E.P. 19100^{05}; F.P. 357858; G.P. Anm. F. 20265).

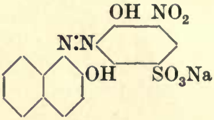
Diamond black PV (By).



A solution of 19 parts of *o*-aminophenol-*p*-sulphonic acid is diazotised and the diazo-solution run into a mixture of 16 parts of 1 : 5-dihydroxynaphthalene with ice-water. Sodium hydroxide solution is added until the whole is alkaline and the mixture stirred for some hours. The excess of alkali is then neutralised by hydrochloric acid and the dye salted out, filtered, and dried (Farbenfabriken vorm. F. Bayer & Co., E.P. 18569^{02}; G.P. 157786; U.S.P. 722715).

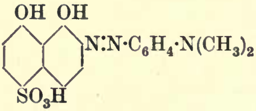
On reduction, the dye gives 2-amino-1 : 5-dihydroxynaphthalene (Fischer, *J. pr. chem.*, 1917, [ii], 95, 261), and it is remarkable that diazobenzene combines, not in the 2-position as above, but in the 4-position with 1 : 5-dihydroxynaphthalene (Fischer, *loc. cit.*).

Acid alizarine black R (M), Vigoureux black I (M).



To a solution of 3·84 kilos. of sodium 6-nitro-2-aminophenol-4-sulphonate in 100 litres of water, 3·3 litres of hydrochloric acid (30° Bé.) are added and the solution is diazotised at 10–15°. The yellow product is run into a cold solution of 0·70 kilo. of sodium hydroxide, 3·3 kilos. of sodium carbonate, and 2·2 kilos. of β-naphthol in 50 litres of water. The liquid becomes bluish-violet and it is heated at about 45° and stirred for some days. On the addition of salt, the small portion of dye still in solution is separated and the whole then filtered (Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 2772^{00}; F.P. 300011; G.P. 143892; U.S.P. 667935).

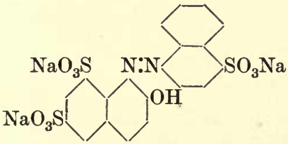
Azo-acid blue B, 3B conc., 3BO (M), Azo-acid blue 4B, 6B (By), Ethyl acid blue RR (B).



A solution of 13·6 parts of dimethyl-*p*-phenylenediamine (*p*-aminodimethylaniline) in 87 parts of hydrochloric acid (10 per cent.) is cooled and diazotised by the addition of a solution of 7 parts of sodium nitrite dissolved in water. This solution is run into a cold solution of 27 parts of sodium 1 : 8-dihydroxynaphthalene-4-sulphonate and 30 parts of sodium acetate in 500 parts of water. The combination proceeds slowly and after stirring for six to eight days most of the dye will be precipitated; it is filtered, washed with cold water, pressed, and dried (Farbenfabriken vorm. F. Bayer & Co., E.P. 5984^{91}, F.P. 212648; G.P.

77169; U.S.P. 567615; the above description is from the United States Patent).

Cochineal red A (B), Croceine scarlet 4BX (K), Brilliant scarlet (Lev. C), Brilliant scarlet S (Sch.), Rainbow scarlet 4R (Brotherton), Brilliant ponceau 4R (By, C, Bm), Brilliant ponceau 5R (By, WDC), Ponceau 4R (BK, VSt), New coccine (A, RF), New coccine O (M), Scarlet 00000 (BD), Scarlet N (FA), Special ponceau (P), Victoria scarlet 4R extra (t.M).



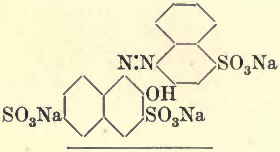
If the G salt required for the manufacture of this dye contains R salt or Schaeffer salt, or both, these must first be removed. For this purpose, it is best to dissolve as large a quantity of G salt as convenient (say 1000 lb.) in water, giving a 10–15 per cent. solution, to which is added 100 lb. of sodium carbonate. The solution is then tested with diazotised α-naphthylamine or xylidine and the amount of naphthol acid present (reckoned either as Schaeffer salt or R salt) is determined. The corresponding quantity of xylidine necessary to form an azo-dye with this is diazotised and the diazo-solution is added to the G salt solution. The mixture is salted until it has the gravity 18° Bé. and the dye filtered off. The filtrate is blown to a store tank and used from here as required.

The diazo-compound prepared from 270 lb. of commercial sodium naphthionate (70 per cent.) is filtered, mixed with a little salt solution, and run slowly into a quantity of the above G salt solution containing 320 lb. of G salt (reckoned as dipotassium salt, mol. wt. 380), and 100 lb. of sodium carbonate.

Next day the batch is heated at 70°, salt added until the gravity at 65° is 19° Bé., and the dye is filtered on the following day at 25–30°. The yield is 426 lb., which gives 450 lb. of "standard" or "type."

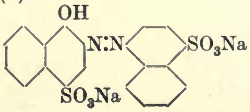
Patents: E.P. 1715^{78}, 816^{84}; F.P. 124811, 159998; G.P. 3229, 36491; U.S.P. 314938.

Amaranth (C, M, BK, F, P, RD, J, DH, t.M, Lev., CDC, Ault and Wiborg), Amaranth 107 (Nat.), Naphthol red O (M), Naphthol red S (B, BK), Naphthol red C (C), Naphthylamine red G (By), Fast red (CJ), Fast red D (B, Gr. E), Fast red NS (By), Bordeaux (FA), Bordeaux SF (A), Bordeaux S (A, RF, Lev.), Bordeaux DH (DH), Victoria rubine O (M, BK, Bm), Azo rubine S (S), Azo acid rubine 2B (BK, WDC, CJ), Cloth red (t.M), Acid crimson (BD), Wool red (Sch.), Wool red extra (K), Azo red R (VSt), Azo red N extra (L), Oenanthinine (DH), Purple (LP).



Forty-five kilos. of sodium naphthionate are dissolved in 900 litres of water, 24·75 kilos. of ordinary commercial sulphuric acid are added, and then a solution of 10 kilos. of sodium nitrite. The diazo-compound is allowed to settle and the excess of sulphuric acid siphoned off. The precipitate is stirred with water, allowed to settle, and the liquid again siphoned off. The volume of the diazo-compound is now brought to 450 litres with water and slowly run into a solution of 45 kilos. of R salt in 1650 litres of water and 25·5 kilos. of sodium hydroxide. After six hours, 225 kilos. of solid salt are added and the whole is allowed to remain until the next day, when the dye will have completely separated. The mixture is well stirred, 450 litres of water are added, and the dye is filtered off, pressed, and dried (Heumann, IV, i, 794).

Azo rubine (Lev., AW, Gr. E, CDC), Azo rubine A (C), Azo rubine S (A, Sch.), Azo rubine G extra conc. (t.M), Azo acid rubine (WDC, CJ), Azo acid rubine R (K), Azo acid fuchsine (RF), Fast red C (B, BK), Mars red G (B), Carmoisine (S), Carmoisine B (By), Brilliant Carmoisine O (M), Crimson (FA), Brilliant Crimson (Cl. Co), Nacarat (P), Rainbow red RP (Brotherton), and for after-chroming, Chrome blue R (B), Chromotrope FB (M), Azo chrome blue R (K), Omega chrome blue A (S).

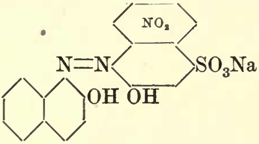


To a solution of 245 parts of sodium naphthionate in 2500 parts of water, 300 parts of hydrochloric acid (33 per cent.) are added, the temperature is brought to about 8° by means of ice, and then 73 parts of sodium nitrite, dissolved in water, are added gradually. The white naphthionic acid is gradually converted into the yellow diazo-compound (Heumann, IV, i, 787). The latter is allowed to settle, the acid liquor decanted, and the paste run into a solution of 250 parts of sodium 1-naphthol-4-sulphonate (NW acid) containing sufficient sodium carbonate to keep the mixture alkaline (in all these combinations in sodium carbonate solution one molecule of sodium carbonate is required for one equivalent of acid, so as to form sodium hydrogen carbonate, and a slight excess over this is taken). The liquid is heated at 60°, the dye salted out, and filtered when cold.

If the NW acid is not available as such, the diazotised naphthionic acid may be filtered on an open filter and the paste weighed. Four-sevenths of this is added gradually to boiling dilute sulphuric acid (in a tub fitted with a lead steam pipe), and when the decomposition is complete the liquid is rendered alkaline by adding solid sodium carbonate gradually and salt added. After settling for an hour or so, the solution is run through an open filter into the combining tub, and when cold, the remaining three-sevenths of the diazo-paste is added. Next day the batch is heated at 60°, salted until the gravity is 12° Bé., and filtered the next day at 30° (or 15° Bé.).

Patents : E.P. 2237^{83}; G.P. 26012; for employment as chrome colour, G.P. 66888, 67240.

Eriochrome black A (G).



(The position of the nitro-group is unknown.)

Twenty-four kilos. of well dried and finely powdered 1-diazo-2-naphthol-4-sulphonic acid (see under Eriochrome blue black B) are gradually stirred into 75 kilos. of concentrated sulphuric acid. A well-cooled mixture of 11 kilos. of nitric acid (60 per cent.) and 22 kilos. of sulphuric acid monohydrate is slowly run in, the temperature being kept between 0° and 5° by means of external cooling. To complete the reaction, the mixture is stirred for a further four hours and the temperature may rise to 15°. The whole is then poured on 100 kilos. of broken ice, with good stirring, and the vessel containing this must also be externally cooled to prevent overheating. The nitro-compound separates in pale yellow crystals and is filtered off (Anilinfarben- & Extract-fabriken vorm. J. R. Geigy, E.P. 15418^{04}; F.P. 349996; G.P. 164655; U.S.P. 790363).

For the combination, 15 kilos. of β-naphthol are dissolved in 200 litres of water and 14 kilos. of sodium hydroxide solution (40° Bé.) and mixed with 50 kilos. of sodium carbonate dissolved in 150 litres of water. To this is added gradually the acid paste of the nitrodiazo-compound prepared as above from 25 kilos. (*sic*) of the diazonaphtholsulphonic acid, the temperature being maintained at about 25°. The formation of the dye begins at once, but is not complete for some hours, the end-point being indicated when no more diazo-compound can be detected in the solution by means of an alkaline solution of resorcinol. The dye is then salted out, filtered, and dried (*idem*, E.P. 15982^{04}; F.P. 350071 and first addition of October 13th, 1904; G.P. 169683; U.S.P. 790363).

The idea of heating the nitration mass with a zinc salt and then combining does not appear to offer any improvement on the above (Kalle & Co., E.P. 22200; F.P. 407227; G.P. Anm. K. 39967; U.S.P. 958912).

It is also claimed that 1-amino-2-naphthol-4-sulphonic acid can be directly nitrated satisfactorily if the water formed in the reaction is removed as fast as it is formed by using an excess of fuming sulphuric acid or chlorosulphonic acid; the German patent was, however, allowed to expire after two years (Kalle and Co., G.P. 249724).

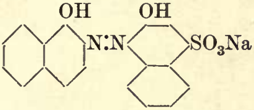
Metallic compounds of this dye have been described by Brenner (*Helv. Chim. Acta*, 1920, **3**, 90).

Eriochrome black T (G).

This is prepared like Eriochrome black A, except that α-naphthol is used instead of β-naphthol.

Metallic compounds have been prepared by Brenner (*Helv. Chim. Acta*, 1920, **3**, 90).

Eriochrome blue black B (G), and probably, Chrome fast cyanine G (J).

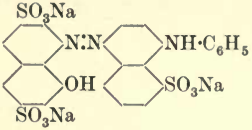


A paste of 12 kilos. of 1-amino-2-naphthol-4-sulphonic acid with 50 litres of water, cooled with ice, is mixed with a concentrated solution of 1 kilo. of copper sulphate and a concentrated solution of 3·5 kilos. of sodium nitrite is allowed to run in slowly. A clear orange-yellow solution is obtained which is filtered from any remaining undiazotised particles of the amino-acid. On adding concentrated hydrochloric acid to the filtrate, the diazo-compound is precipitated, and is filtered, washed with dilute hydrochloric acid, pressed, and dried. The diazo-compound is a greyish-yellow, non-explosive, crystalline powder (Geigy, E.P. 10235^{04}; F.P. 349989; G.P. 171024; U.S.P. 793743).

In the patents relating to the combination of this diazo-compound (Geigy, E.P. 15025^{04}; F.P. 350055; G.P. 181326), the German gives an example of the combination with β-hydroxynaphthoic acid and the English with β-naphthol. The following is a copy of the latter, substituting α-naphthol for β-naphthol.

Twenty-five kilos. of the diazo-compound are stirred into 200 litres of water and 10 kilos. of sodium carbonate are carefully added at the same time. To this is added a solution of 15 kilos. of α-naphthol in 12 kilos. of sodium hydroxide (40° Bé.) and 50 litres of water. The combination proceeds slowly and is nearly finished after twenty-four hours at 25–30°. The temperature is then raised for a short time to 60°, 10 kilos. of sodium hydrogen carbonate are added, and, when this is dissolved, sufficient salt to precipitate the dye completely. The latter is then filtered, pressed, and dried (Anilinfarben & Extract-fabriken vorm. J. R. Geigy, E.P. 15025^{04}; F.P. 350055; G.P. 181326; compare Gesellschaft für Chemische Industrie in Basel, F.P. 351125; G.P. Anm. G. 22717). It is to be noted that the combination of the diazo-compound with the α-naphthol takes place in the 2-position.

Tolyl blue SR (M), Sulphone acid blue R (By).

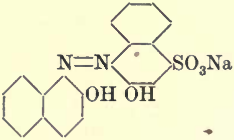


A solution of 31·9 kilos. of 1-amino-8-naphthol-3 : 6-disulphonic acid (H) is diazotised with 6·9 kilos. of sodium nitrite. The precipitated diazo-compound is filtered and the residue made into a paste with water. This is added to a solution of 30 kilos. of 1-phenylnaphthylamine-8-sulphonic acid and 40 parts of sodium acetate in 1500 litres of water and the mixture is stirred for four hours, when the formation of the dye will probably be complete. The dye separates as a dark powder with a metallic lustre, and is filtered off and dried (Farbenfabriken vorm. F. Bayer & Co., E.P. 8188^{97}; U.S.P. 611664).

If the equivalent amount of 1-*p*-tolylnaphthylamine-8-sulphonic acid is used instead of the phenylated acid, there is produced Tolyl blue SB [Sulphone acid blue B (By), Brilliant cloth blue III F (K)].

What appears to be the same dye may be prepared by phenylating the unsubstituted colouring matter in aqueous alcoholic suspension under the ordinary pressure (Farbwerke Mühlheim vorm. A. Leonhardt & Co., E.P. 24830^{98}; G.P. 108546).

Palatine chrome black 6B (B), Salicin black UL, U (K), Eriochrome blue black R (G), Acid alizarine blue black A (M), Diamond blue black EB (By), Anthracene blue black BE (C), Chrome fast black PW (J), Chrome blue N (P).



One method of diazotising 1-amino-2-naphthol-4-sulphonic acid has been given under Eriochrome blue black B (see also Cain, "The Chemistry and Technology of the Diazo-compounds," 1920, p. 18). In the following process of manufacture the 2-

sulphonic acid group in diazotised 1-naphthylamine-2 : 4-disulphonic acid is displaced by the hydroxyl group, whereby the diazo-compound from the aminonaphthol acid is obtained indirectly.

30·3 Parts of 1-naphthylamine-2 : 4-disulphonic acid * are mixed with 300 parts of water and 10 parts of sulphuric acid (66° Bé.) and diazotised by adding 7 parts of sodium nitrite dissolved in 100 parts of water. Thirty-five parts of sodium carbonate are now added, the temperature not being allowed to rise above 10–15°. Into the reddish-yellow mixture is now led a stream of chlorine, preferably diluted with air, until a faint reaction with potassium iodide–starch paper is obtained. A solution of 16–18 parts of β-naphthol in 13 parts of sodium hydroxide solution (40° Bé.) and 30 parts of water is added to the yellow diazo-compound and combination is effected with the addition of 50 parts of salt and the maintenance of the temperature at 50–55° for about three hours. The partly separated dye is completely salted out, filtered, and dried (Badische Anilin- & Soda-Fabrik, E.P. 4997^{04}; F.P. 338819 addition of December 17th, 1903; G.P. 160536; U.S.P. 770177; the use of chlorine is to prevent the formation of the diazo-sulphonic acid, the presence of which diminishes the yield when the dye is prepared without it, *idem*, E.P. 27372^{03}; F.P. 338819; G.P. 156440).

In the following process, diazotisation of 1-amino-2-naphthol-4-sulphonic acid is effected in the presence of a zinc salt. Forty-eight kilos. of 1-amino-2-naphthol-4-sulphonic acid (100 per cent.), in the form of a paste such as is obtained by reducing 1-nitroso-2-naphthol with sodium hydrogen sulphite and hydrochloric acid, filtering, and washing with water, are mixed with a solution of 28 kilos. of zinc sulphate in 70 litres of water of which a part of the zinc is previously precipitated as hydroxide by the addition of 6 kilos. of aqueous ammonia (25 per cent.). After stirring for some time, a solution of 14 kilos. of sodium nitrite in 60 litres of water is added. The mass turns yellow and the diazotisation is completed by warming for one to two hours at 40–55°. The amino-acid passes into solution, but a clear solution is not usually obtained as the diazo-compound begins to separate out. If a sample is acidified with acetic acid, no development of nitrous fumes occurs and on adding

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* This is prepared by heating α-nitronaphthalene with sodium hydrogen sulphite solution at 100° and separating the naphthionic acid simultaneously formed (Farbwerke vorm. Meister, Lucius, & Brüning, G.P. 92081).

salt the diazo-compound separates as a voluminous, crystalline mass.

When the whole has cooled to about 30°, 50 kilos of acetic acid (25 per cent.) are added, the mixture is then rendered alkaline with 60 kilos. of sodium carbonate, and a saturated solution of sodium β-naphthoxide, corresponding with 30 kilos. of β-naphthol, which is at a temperature of 60–80°, is added. The whole is warmed for some time at 40–55° or until a sample tested with resorcinol solution indicates that the combination is complete. The volume of the batch at the end is about 600–700 litres. It is now diluted with about 2000 litres of salt solution and the zinc salt of the dye (Salicine black UL) is filtered off.

The free acid is obtained by boiling the zinc salt with dilute hydrochloric acid, filtering, and washing, and this may be converted into the sodium salt (Salicine black U, Eriochrome blue black R) in the usual way (Kalle & Co., E.P. 23034^{05}; F.P. 353786; G.P. 175593, 195228; U.S.P. 807422; salts of manganese, magnesium, cobalt, and nickel can also be used instead of those of zinc, *idem*, G.P. 195322; for the diazotisation in the presence of acetic acid and combination in concentrated alkaline solution, see Kalle & Co., G.P. 188645; U.S.P. 778476; G.P. 190693 which contain, however, no example of this particular dye).

The above process has been repeated by Tomioka (*Kōgyō-Kwagaku Zasshi* [*J. Chem. Ind. Tokyo*], 1917, **20**, 577) as follows: 24 parts of the acid were dissolved in 11·3 parts of 15 per cent. ammonia solution diluted with 60 parts of water, and 58·2 parts of zinc chloride solution (40° Bé.; *d* 1·384) added; the zinc salt was cooled in ice, and 10 parts of 90 per cent. sodium nitrite in 50 parts of water were added gradually at 2–5·5°, the temperature being subsequently raised to 13° in two hours, kept at 25–30° for one hour, and at 40–45° for one hour. The diazo-solution was cooled to 30° and 30 parts of 25 per cent. acetic acid were added; after stirring for one hour, 40 parts of sodium carbonate were added gradually, the solution was warmed at 40°, and 16 parts of β-naphthol dissolved in 6 parts of sodium hydroxide and 30 parts of water at 80° were added with vigorous stirring. After stirring for five hours at 50°, the zinc salt of the dye was salted out and converted into the free acid by concentrated hydrochloric acid. The yield was 53·6 parts, corresponding with 95·8 per cent. of the theoretical.

The tendency towards the formation of an oxidation product in the ordinary process of diazotisation of 1-amino-2-naphthol-4-sulphonic acid may be overcome by first forming the acetyl derivative (1-amino-2-acetoxynaphthalene-4-sulphonic acid) thus: 23·9 kilos. of 1-amino-2-naphthol-4-sulphonic acid are dissolved in 200 litres of water with the addition of 29 kilos. of sodium hydroxide solution (30 per cent.) and acetylated by means of 11 kilos. of acetic anhydride, added at a temperature below 0° and with thorough stirring. After a half to one hour, 7 kilos. of solid sodium nitrite are added to the liquid, which should have a neutral or only very faintly alkaline reaction, and then 30 kilos. of ordinary hydrochloric acid are added all at once at 0–10° in order to acidify the mass. The diazo-compound at once separates as a yellow, crystalline mass, and no evolution of gas takes place. This is then run into a solution of 18 kilos. of sodium β-naphthoxide in excess of dilute sodium carbonate solution. A red dye is at once formed which on stirring for some time or on warming at 40–55° becomes bluish-green, and is then salted out (Gesellschaft für Chemische Industrie in Basel, E.P. 82^{05}; F.P. 351125 and addition of May 10th, 1905; G.P. 181714; U.S.P. 797441, 806415).

The diazotisation can also be effected in the presence of salt (Badische Anilin- & Soda-Fabrik, E.P. 10323^{06}; F.P. 365919; G.P. 189179; see Cain, "The Chemistry and Technology of the Diazo-compounds," 1920, p. 18) and the combination may be made in the presence of alcohol, pyridine, or aniline (Gesellschaft für Chemische Industrie in Basel, E.P. 7029^{06}; F.P. 351125, addition of June 10th, 1905; G.P. Anm. G. 21484).

AZO-COLOURS (DISAZO)

Containing Benzene Nuclei only.

RESORCIN BROWN—BISMARCK BROWN—BISMARCK BROWN R—COTTON YELLOW—PYRAMINE ORANGE—TOLUIDINE ORANGE G—TOLUIDINE ORANGE R—CHRYSAMINE.

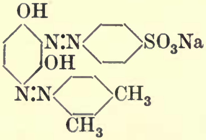
Containing Benzene and Naphthalene Nuclei.

DIAMINE FAST RED—DIAMINE SCARLET—FAST BROWN—NAPHTHOL BLUE BLACK—BRILLIANT CROCEINE—CLOTH RED—DOUBLE SCARLET—DIPHENYL BROWN—OXAMINE RED.

Containing Naphthalene Nuclei only.

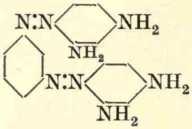
DIANOL BRILLIANT RED EXTRA—NAPHTHAMINE BLUE—DIAMINE BLUE—DIAMINE BRILLIANT BLUE—DIAMINE PURE BLUE—DIRECT BLUE—OXAMINE BLUE—BENZOAZURINE—BRILLIANT AZURINE—BENZOPURPURINE B—BENZOPURPURINE 4B—BENZOPURPURINE 10B—DIAMINE BLACK—DIAMOND BLACK—DELTAPURPURINE—NEROL B—NEROL 2B—CONGO RED—CONGO CORINTH—CONGO RUBINE—BRILLIANT CONGO—PALATINE BLACK—NAPHTHOL BLACK B—NAPHTHOL BLACK 6B—NAPHTHOL BLACK D—DIAMINOGEN.

Resorcin brown (BD, Sch., A, K, J, BK).



A diazo-solution prepared from 121 kilos. of *m*-xylidine is combined with 110 kilos. of resorcinol; the product is dissolved in sodium hydroxide solution and a diazo-solution prepared from 173 kilos. of sulphanilic acid added. The dye is salted out, filtered, and dried (Aktiengesellschaft für Anilinfabrikation, G.P. 18862; U.S.P. 269359).

Bismarck Brown.



1. A solution of 7 kilos. of sodium nitrite is added slowly to a solution of 36 kilos. of *m*-phenylenediamine hydrochloride in 1000 litres of water or to a solution of 21·6 kilos. of *m*-phenylenediamine (as obtained by the reduction of *m*-dinitrobenzene), exactly neutralised with hydrochloric acid, at 5°. The dye is salted out and purified by redissolving with the addition of 1 kilo. of chalk, and salting out the filtrate (Harmsen, "Die Fabrikation der Theerfarbstoffe," 1889, 257).

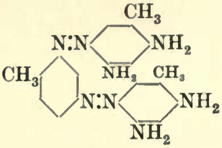
2. A dilute aqueous solution (1 : 10) of sodium nitrite (2 mols.) is run into a dilute aqueous solution (1 : 500) of *m*-phenylenediamine hydrochloride (3 mols.). The operation can be carried out in the following manner. 250 Kilos. of *m*-dinitrobenzene are mixed with 1000 litres of water and reduced with iron and 35 kilos. of hydrochloric acid. The product is filtered and diluted to 5000 litres. A solution of 42·5 kilos. of sodium nitrite and 127·5 kilos. of hydrochloric acid are allowed to act on the solution. The dye is salted out and purified by dissolving in water and again salting out (Schultz, "Chemie des Steinkohlentheers," 3rd ed., 1901, ii, 120).

Examination of the above recipe shows that if, as is stated, 2 mols. of sodium nitrite are employed for 3 mols. of *m*-phenylenediamine, the 42·5 kilos. of sodium nitrite (taking the molecular weight as 72) correspond with 95·6 kilos. of the base. This is produced, however, from 250 kilos. of *m*-dinitrobenzene and corresponds with a yield of only 59 per cent. of the theoretical, whereas it is easy to obtain a yield of more than 90 per cent.

3. Another process is the following: To a solution of 84·2 lb. of *m*-phenylenediamine (as obtained from the reduction of *m*-dinitrobenzene) a solution of 41·5 lb. of sodium nitrite is added, and then 216 lb. of hydrochloric acid are run in at 10–15°. The dye is precipitated by 600 lb. of salt. From 100 parts of *m*-dinitrobenzene 85 parts of the dye are obtained.

Patent: Dale and Caro, E.P. 3307^{63}.

Bismarck Brown R.



The preparation of this dye, from *m*-tolylenediamine, is carried out as described in the case of the preceding.

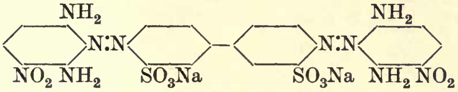
Cotton yellow G (B), Benzo fast yellow 5GL (By), Diamine fast yellow 3G (C).

A cold solution of 10 kilos. of acetyl-*p*-phenylenediamine (*p*-aminoacetanilide) in 30 kilos. of hydrochloric acid (32 per cent.) and 133 kilos. of water is cooled with ice (133 kilos.) and a solution of 4·7 kilos. of sodium nitrite in three times its weight of water is added, the mixture stirred for an hour, and the diazo-solution is run into a solution of 10 kilos. of salicylic acid in 30 kilos. of sodium carbonate, 200 kilos. of water, and 100 kilos. of ice. The azo-dye separates almost completely after twenty-four hours and is filtered off and well pressed. The paste is then added to 200 kilos. of sulphuric acid (66° Bé.) and the mixture warmed in the water-bath. After about four hours, the hydrolysis is complete. The sulphuric acid solution is then allowed to flow slowly into cold water, and the crystalline brown precipitate is collected on a filter. This aminoazo-compound is stirred with 500 litres of water and 300 kilos. of ice in a large lead-lined pan and converted into the sodium salt by the cautious addition of a solution of sodium carbonate or sodium hydroxide. The mixture is well stirred and carbonyl chloride (phosgene) is led in until an acid reaction is obtained. The brown dye-acid is filtered, pressed, mixed with the quantity of dry sodium carbonate necessary to form the sodium salt, and dried on the water-bath (Badische Anilin- & Soda-Fabrik, E.P. 15258^{88}; G.P. 46737; U.S.P. 430535).

The dye can also be obtained by tetrazotising diaminodiphenylcarbamide and combining with salicylic acid (*idem*, G.P. 47902).

The preparation, on the laboratory scale, of *p*-acetylaminobenzeneazosalicylic acid, and its hydrolysis, have been described also by Grandmougin and Guisan (*Rev. gén. Mat. Col.*, 1908, **12**, 131) and by Bülow (*Ber.*, 1911, **44**, 605).

Pyramine orange R (B).



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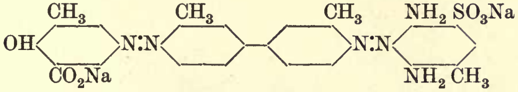
A solution of 34·3 kilos. of benzidinedisulphonic acid in the necessary amount of alkali and about 200 litres of hot water is cooled, mixed with a solution of 14 kilos. of sodium nitrite in about 200 litres of water, and the mixture run into 160 kilos. of hydrochloric acid (*d* 1·15) diluted with three times its volume of water. After five hours' stirring is added a hot solution (50–60°) of 32 kilos. of 4-nitro-*m*-phenylenediamine in 200 litres of water and 58 kilos. of hydrochloric acid (*d* 1·15), and then a solution of 112 kilos. of crystallised sodium acetate in 336 litres of water. The mixture is stirred for three hours, when a solution of 170 kilos. of sodium carbonate in 1000 litres of water is added gradually and the whole is then stirred for twenty-four hours. The dye is thereafter filtered, pressed, and dried (Badische Anilin- und Soda-Fabrik, E.P. 8564^{94}; F.P. 238340; G.P. 80973; U.S.P. 545333).

Toluylene orange G (Gr. E, By, A, L), Dianil orange N (M), Alkali orange GT (WDC), Azidine orange G (CJ), Renol orange G (t.M), Direct orange G (J, P), Direct orange Y (Sch.), Oxydiamine orange G (C), Pluto orange G (By).



A solution of 21·2 kilos. of tolidine in 500 litres of water and 48 kilos. of hydrochloric acid (20° Bé.) is cooled to 0° and a solution of 28 kilos. of sodium nitrite in 150 litres of water is added.

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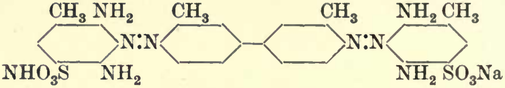
* It seems most probable that the diazo-groups combine with nitro-*m*-phenylenediamine in the ortho- position as shown.

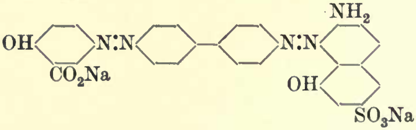
The diazo-solution is run into a solution of 15·2 kilos. of *o*-cresotic acid and 20 kilos. of sodium carbonate in 300 litres of water. The intermediate compound is gradually formed as a brown mass, and when the combination is complete a solution of 20·2 kilos. of *m*-tolylenediamine-5-sulphonic acid and 6 kilos. of sodium carbonate in 300 litres of water is added, the mixture stirred for twenty-four hours, heated to boiling, and the dye salted out, filtered, and pressed (Oehler, E.P. 7997^{88}; G.P. 47235; U.S.P. 396634).

Toluylene orange R (Gr. E, M, L, S). Alkali orange RT (WDC), Azidine orange R (CJ), Renol orange R (t.M), Direct orange R (J, Sch.), Pyramine orange RT (B), Oxydiamine orange R (C), Pluto orange R (By).



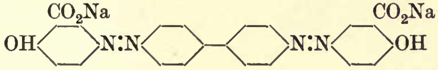
A mixture of 31 kilos. of tolidine sulphate, 500 litres of water, and 25 kilos. of hydrochloric acid (20° Bé.) is treated with a solution of 14 kilos. of sodium nitrite and the diazo-solution is run into a faintly alkaline solution of 44 kilos. of sodium *m*-tolylenediamine-5-sulphonate in 1000 litres of water. After stirring for some time the dye is salted out, filtered, and dried (Oehler, E.P. 4492^{87}; G.P. 40905).

Diamine fast red F (C), Dianol fast red F (Lev.), Dianil fast red PH (M), Naphtamine red H (K, Oe.V), Oxamine fast red F (B), Benzo fast red FC (By), Columbia fast red F (A), Triazole fast red C (Gr. E), Diphenyl fast red (G), Azidine fast red F (CJ), Hessian fast red F (L), Benzamine fast red F (WDC), Direct fast red F (J, Sch.), Erie fast red FD.



A diazotised solution of 18·4 kilos. of benzidine is run into an alkaline solution of 14 kilos. of salicylic acid, the mixture is faintly acidified with acetic acid, and a solution of 27 kilos. of the sodium salt of γ-acid is added. The combination is complete after a short time (Cassella & Co., E.P. 16699[89]; F.P. 201770; G.P. 57857).

Chrysamine G (By, A, L, Lev., BD, t.M, S. Oe.V, Barking Chemicals Co., Marden, Orth, and Hastings Corp., Calco Chem. Co.).

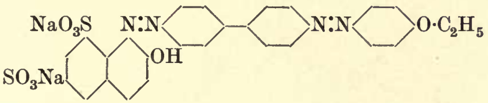


A suspension of 22 lb. of benzidine sulphate in 330 lb. of water is treated with 44 lb. of hydrochloric acid (21° Bé.) and then 11 lb. of sodium nitrite dissolved in water. The diazo-solution is run slowly with good stirring into a solution of 22 lb. of salicylic acid in 88 lb. of sodium hydroxide and 500 lb. of water. The dye separates out and is filtered off and washed with water until neutral (Farbenfabriken vorm. F. Bayer & Co., E.P. 9162[84]; G.P. 31658 *; U.S.P. 329638, 329639).

When chrysamine G is treated with sodium hydrogen sulphite, it furnishes benzidine sulphate and aminosulphosalicylic acid (Lepetit and Levi, *Gazzetta*, 1911, **41**, i, 675).

If tolidine is substituted for benzidine in the above preparation, Chrysamine R (By, A, L, Lev., t.M, S, Oe.V) is obtained (*idem*, E.P. 9606[84], other patents as above).

Diamine scarlet B (C), Dianil ponceau G (M).



A solution of 18·4 kilos. of benzidine is tetrazotised and run into a cold solution of 40 kilos. of sodium 2-naphthol-6 : 8-disulphonate. After a short time 10 kilos. of phenol are added and then the batch is heated until the dye is in solution, when it is salted out and filtered. The precipitate is dissolved in 200 litres of water, 200 kilos. of alcohol, and 4·5 kilos. of sodium hydroxide, 12 kilos. of ethyl bromide are added and the whole

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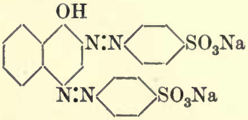
* The quantities given in the German patent are incorrect; the recipe is taken from the English patent.

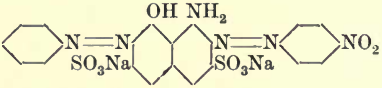
is heated in a closed vessel for twenty-four hours at 60°. On cooling, the dye separates in shining crystals (Cassella & Co., E.P. 12560^{89}; F.P. 200152; G.P. 54084; U.S.P. 426345).

Fast brown G, GR (A, RF), Acid brown (R, P, WDC), Acid brown G (t.M, BK), Acidol brown G (t.M).



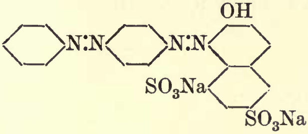
Two molecular proportions of sulphanilic acid are diazotised and the diazo-solution is run into a solution of one molecular proportion of α-naphthol in excess of sodium hydroxide solution. The combination is complete after a few hours' stirring and the mixture is evaporated to dryness as the dye cannot be salted out. It is mostly used in leather staining. On reduction with tin and hydrochloric acid, it yields 2 : 4-diamino-α-naphthol and sulphanilic acid (Krohn, *Ber.*, 1888, 21, 3241).

Naphthol blue black S (C), Naphthol blue black B (L), Blue black NB (K), Blue black NOe. (Oe.V), Acid black 16622 (L), Wool black 6G extra conc. (t.M), Acidol black 6G extra conc. (t.M), Amido black 10BO (M), Amido acid black 10B (A), Coomassie blue black (Lev.), Naphthylamine black 10B (By), Buffalo black NB (Sch.), Agalme black 10B (B), Naphthalene black 10B (P).



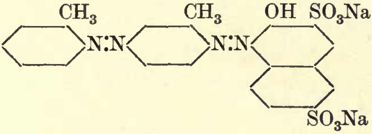
To a diazo-solution prepared from 13·8 kilos. of *p*-nitroaniline in hydrochloric acid solution is added a neutral solution of 32 kilos. of H-acid (or 34·1 kilos. of the acid sodium salt), the end reaction being strongly acid. A red solution is formed from which the monoazo-dye partly separates. When the combination is complete, it is rendered slightly alkaline with sodium carbonate, when the whole passes into solution with a blue colour. Into this solution, which is kept alkaline, the diazo-compound prepared from 9·3 kilos. of aniline is run and the finished dye is salted out, filtered, and dried (Cassella & Co., E.P. 6972[91]; F.P. 201770, fourth addition; G.P. 65651; U.S.P. 480326).

Brilliant croceine M (C, BK, Gr. E), Brilliant croceine 3B (By), Brilliant croceine bluish (M), Brilliant croceine O (K), Brilliant croceine extra conc. (t.M), Cotton scarlet (B), Ponceau BO extra (A), Croceine 3B (P), Croceine AZ (S), Paper scarlet (M), Croceine 3BN (P).



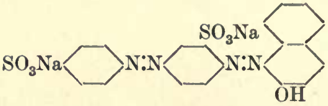
A mixture of 19·7 parts of aminoazobenzene, 25 parts of hydrochloric acid (33 per cent.), and 250 parts of water is treated with a solution of 6·9 parts of sodium nitrite in 20 parts of water, the temperature being kept below 5°. After some time, the diazo-solution is run into a solution of 38 parts of potassium 2-naphthol-6 : 8-disulphonate in 250 parts of water and 10 parts of ammonia solution (25 per cent. NH_3). The dye is salted out with 100 parts of salt and is deposited as a red powder (Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 816[84]; F.P. 159998; G.P. 36491; U.S.P. 314939).

Cloth red B (Gr. E, K), Fast Milling red B (Lev.), Cloth red O (M), Cloth red BA (A), Cloth red BB (WDC), Wool red B (C), Fast Bordeaux O (M), Acid azo Fuchsine (RF).



o-Aminoazotoluene, prepared from 85 lb. of *o*-toluidine (see Cain, "The Manufacture of Intermediate Products for Dyes," 2nd ed., p. 82) in the form of the crystalline paste of hydrochloride, is mixed with 500 lb. of water and 50 lb. of "chamber acid" (32 lb. of concentrated sulphuric acid) is added. The mixture is cooled to 3–4° and 25 lb. of sodium nitrite are added within an hour. The whole is stirred for four to six hours, ice being constantly added. The diazo-solution is filtered and the filtrate run into a solution of 100 lb. of sodium 2-naphthol-3 : 6-disulphonate (R salt) and 160 lb. of sodium carbonate in water. (The patents covering this dye are: Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 536^{80} [compare also 5003^{79}]; F.P. 133864, 134802; G.P. 16482; U.S.P. 233465.)

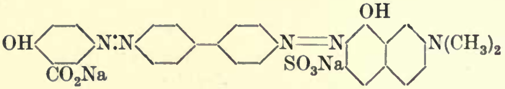
Double scarlet (K), Ponceau B extra (M), Ponceau 3RB (A, BK), Fast ponceau B, G (B), New red L (K, Oe.V), Scarlet EC (C), Scarlet B (P), Blackley scarlet (Lev.).



A solution of the sodium salt of aminobenzenedisulphonic acid prepared from 50 kilos. of aminoazobenzene sulphate (see under Fast yellow) is acidified with 50 kilos. of hydrochloric acid (30 per cent.), cooled to 3–5°, and diluted until all the crystals have dissolved; a solution of 14 kilos. of sodium nitrite (100 per cent.) in 2–3 parts of water is gradually added, the temperature not being allowed to rise. The diazo-solution is run slowly into a solution of 29 kilos. of β-naphthol in 16 kilos. of sodium hydroxide (100 per cent.) and so much water that on cooling all remains in solution, which is cooled to 3–5°. The finished dye is salted out, filtered, and pressed. It may be purified by redissolving and salting out (Krügener [Farbwerke vorm. Meister, Lucius, and Brüning], E.P. 5021^{79}, 529^{80}; F.P. 133864, 134802; G.P. 16482; U.S.P. 224928; compare also E.P. 5003^{79}).

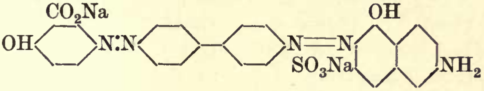
On gentle reduction of the alkaline solution with zinc dust, 1-amino-2-naphthol and aminoazobenzenedisulphonic acid are formed, whilst more energetic reduction gives phenylenediamine-sulphonic acid, sulphanilic acid, and 1-amino-2-naphthol (Nietzki, *Ber.*, 1880, **13**, 801, 1840).

Diphenyl brown BN (G).



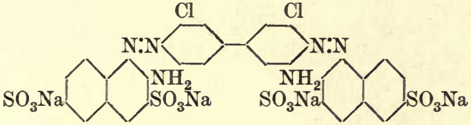
The intermediate compound, prepared by combining a diazotised solution of 18·4 kilos. of benzidine with a solution of 14 kilos. of salicylic acid and 30 kilos. of sodium carbonate, is run into a solution of 26·7 kilos. of dimethyl-γ-acid * in 300 litres of water rendered alkaline with sodium carbonate. The dye separates at once as a blackish-brown precipitate and is isolated in the usual way (J. R. Geigy & Co., E.P. 2771^{96}; F.P. 250697; G.P. 91506, 103149; U.S.P. 567413).

Oxamine red (B).



The diazo-compound prepared from 13 parts of benzidine hydrochloride, 750 parts of water, 17 parts of hydrochloric acid (30 per cent.), and 7 parts of sodium nitrite (in 10 per cent. solution) is run into a solution of 7 parts of salicylic acid in 40 parts of sodium carbonate and 250 parts of water. When the formation of the intermediate compound is complete, a solution of 12 parts of 2-amino-5-naphthol-7-sulphonic acid (J acid) and 30 parts of sodium carbonate in 250 parts of water is added. After the combination is complete, the batch is heated to boiling and the dye salted out (Badische Anilin- & Soda-Fabrik, E.P. 2614^{93}; F.P. 227892; G.P. 93276; U.S.P. 555359).

Dianol brilliant red extra (Lev.), Toluylene red (Gr. E), Azidine brilliant red 8B (CJ), Chlorantine red 8B (J), Acetopurpurine 8B (A), Diphenyl red 8G (G), Oxamine scarlet B (B).

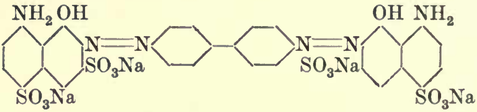


A solution of 53 lb. of dichlorobenzidine in 60 lb. of hydrochloric acid is cooled with ice, 140 lb. of hydrochloric acid are added, and then a solution of 29 lb. of sodium nitrite. The diazo-solution is run into a solution of 145 lb. of sodium 2-amino-3 : 6-disulphonate in the presence of sodium acetate (from 50 lb.

* Prepared by heating G acid with dimethylamine in an autoclave at above 200° and fusing the product with sodium hydroxide at about 210—220° or by methylating γ-acid.

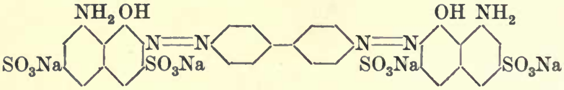
of sodium carbonate and 200 lb. of acetic acid, 30 per cent.). The amino-acid must be free from the hydroxy-acid (R salt) from which it is prepared, and the solution is therefore tested with xylenediazonium chloride and the amount of diazotised xylidine, corresponding with the amount of R salt found, is added to the solution in the presence of sodium carbonate. This red-coloured solution is then used direct. Next day the batch is rendered alkaline by the addition of 80 lb. of sodium carbonate, heated at 80°, and 100 lb. of salt are added. The dye is precipitated and is filtered off, the small amount of the dye produced in the above purification escaping in the filtrate. The yield of colouring matter is 350 lb. of "standard" or "type." (The patents relating to this dye are, Levinstein, Ltd., E.P. 25725^{96}; F.P. 265155; G.P. 94410, 97101; U.S.P. 625174.)

Naphtamine blue 2B (K).



A diazotised solution of 18·4 kilos. of benzidine is poured into a cold alkaline solution of 76 parts of 1-amino-8-naphthol-4 : 6-disulphonic acid (K acid). After some time, the mass is heated at 60–70° and the dye salted out (Kalle & Co., E.P. 515^{94}; G.P. Anm. K. 11223; U.S.P. 563385, 563386).

Diamine blue BB (C, CDC), Benzo blue BB (By), Congo blue ZBX (A), Dianol blue BB (Lev.), Dianil blue H2G (M), Naphtamine blue 2BX (K, Oe.V), Benzamine blue 2B (WDC), Azidine blue 2B (CJ), Niagara blue 2B (Sch.), Direct blue V (P).



A diazotised solution of 9·2 kilos. of benzidine is added to a solution in sodium carbonate of 34 kilos. of 1-amino-8-naphthol-3 : 6-disulphonic acid (H acid).* The dye separates in shining

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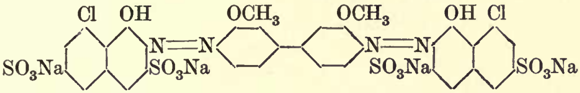
* The English patent gives 32 kilos. and the German 38 kilos. The amount given in the American patent (34 kilos.) represents the theoretical amount of H acid in the form of acid sodium salt.

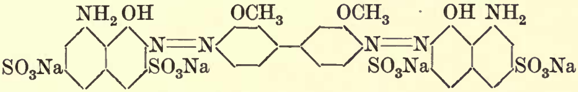
needles (Cassella & Co., E.P. 1742[91]; F.P. 210033; U.S.P. 464135).

Diamine brilliant blue G (C).



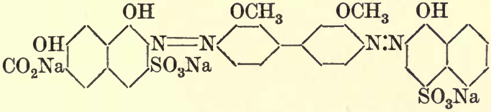
A diazo-solution prepared from 24·4 kilos. of dianisidine is added to an alkaline solution of 75 kilos. of 1-chloro-8-naphthol-3 : 6-disulphonic acid. The mixture is allowed to remain for twenty-four hours and then heated at 60°, when most of the dye separates out (Cassella & Co., E.P. 1920[94]; F.P. 235271; G.P. 82285; U.S.P. 532125).

Diamine pure blue (C), Benzo pure blue conc. (By), Congo pure blue (A), Dianol sky blue (Lev.), Dianil blue H6G (M), Naphtamine blue 7B (K), Naphtamine pure blue I (Oe.V), Renol pure blue (t.M), Oxamine pure blue 5B (B), Benzamine pure blue (WDC), Benzoin pure blue (BK), Azidine pure blue (CJ), Direct blue RBA (L), Direct pure blue (AW), Niagara blue 4B (Sch.).



A diazo-solution prepared from 12·2 kilos. of dianisidine is added to an alkaline solution of 38 kilos. of H-acid. When the combination is complete the mixture is heated at 80°, the dye salted out, and filtered off (Cassella & Co., E.P. 1742[91]; F.P. 3rd addition to 201770; G.P. 74593; U.S.P. 464135).

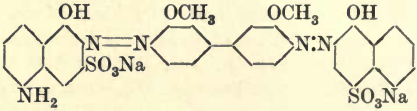
Direct blue B (J).



A diazo-solution prepared from 6·1 kilos. of dianisidine is combined in weak alkaline solution with 7·5 kilos. of sodium

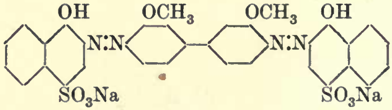
1 : 7-dihydroxy-6-carboxynaphthalene-3-sulphonate (sodium nigrotate). The intermediate compound is soon formed and then an alkaline solution of 6·2 kilos. of α-naphthol-4-sulphonic acid is added. The mixture is heated, and the dye salted out (Society of Chemical Industry in Basle, E.P. 14253⁹²; F.P. 220468; G.P. 75258; U.S.P. 493563).

Oxamine blue B (B).



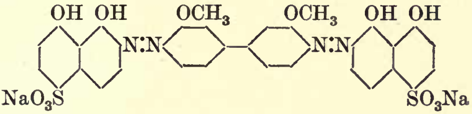
A diazo-solution prepared from 24·4 kilos. of dianisidine is rendered alkaline by adding a cold dilute solution of sodium carbonate and immediately a solution, also made alkaline with sodium carbonate, of 24 kilos. of 5-amino-α-naphthol-3-sulphonic acid is run in. The formation of the intermediate compound, which consists of a blackish precipitate, is soon complete and a solution of 25 kilos. of sodium α-naphthol-4-sulphonate is then added and the mixture stirred for twelve hours. After heating to boiling, the dye is salted out, filtered, and dried (Badische Anilin- & Soda-Fabrik, E.P. 2370⁹³; F.P. 229263; G.P. 82572; U.S.P. 558344).

Benzoazurine G (By, A, L, Lev., K, Gr. E, S, Oe.V), Dianilazurine G (M), Renol blue B (t.M), Azidine blue BA (CJ), Cotton blue 3G (J), Benzoin blue GN, 2GN, 5GN (BK), Oxamine blue A conc. (B), Direct blue G extra (Sch.), Niagara blue G conc.



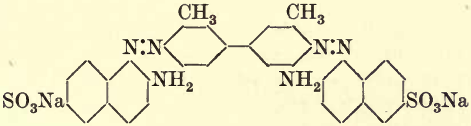
A solution of 10 kilos. of dianisidine in 150 litres of water and 20 kilos. of hydrochloric acid (*d* 1·161) is cooled with ice and a solution of 6 kilos. of sodium nitrite in water is added. The diazo-solution is poured into a solution of 22 kilos. of sodium 1-naphthol-4-sulphonate (NW acid) and 10 kilos. of sodium carbonate in 400 litres of water. The dye is salted out of the dark violet solution and, after some time, it is filtered off and dried (Farbenfabriken vorm. F. Bayer & Co., E.P. 14424[85]; F.P. 173042; G.P. 38802; U.S.P. 357273).

Brilliant azurine 5G (By, A, L).



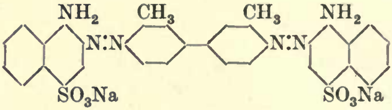
A solution of 31·7 kilos. of dianisidine hydrochloride in about thirty times its quantity of water is treated with 40 kilos. of concentrated hydrochloric acid and then a solution of 14 kilos. of sodium nitrite in 70 litres of water is added. To this diazo-solution a solution of 60 kilos. of sodium 1 : 8-dihydroxynaphthalene-4-sulphonate and 80 kilos. of sodium acetate is added, the whole being well stirred. The dye is formed at once, and separates in small, dark blue crystals which are filtered off, pressed, and dried [Farbenfabriken vorm. F. Bayer & Co., E.P. 13665[89]; F.P. 173042 (addition); G.P. 57166; U.S.P. 417294].

Benzopurpurine B (Lev., By, A, L, t.M, Gr. E, CDC), Cotton red B (J).



A diazotised solution of tolidine prepared as for Benzopurpurine 4B (see first recipe, p. 59) is run slowly into a solution of 80 kilos. of sodium β-naphthylamine-6-sulphonate containing excess of sodium carbonate solution and cooled with ice. A brownish-red precipitate is formed which dissolves after about twelve hours. On adding salt solution, a red, slimy precipitate is formed which becomes crystalline on warming and is filtered off [Aktiengesellschaft für Anilinfabrikation, E.P. 3803[85] (Bayer & Co.); F.P. 167876; G.P. 35615; U.S.P. 329633].

Benzopurpurine 4B (Lev., By, A, L, Gr. E, t.M, VSt, S, Aw, Oe.V, FA, BK, Nat. Japan Dyestuff Co.), Cotton red 4B (B, J, K), Dianil red 4B (M), Diamine red 4B (C), Direct red 4B (Sch.), Cotton red BP (P).



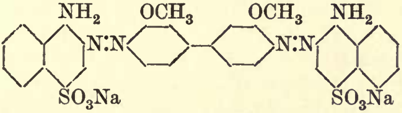
A suspension of 150 kilos. of tolidine sulphate in water is treated with 50 kilos. of hydrochloric acid (21° Bé.), cooled with ice, and a solution of 22·2 kilos. of sodium nitrite in 10 litres of water is added slowly. The diazo-solution is run into a finely divided suspension of 73 kilos. of naphthionic acid in water, the free mineral acid is neutralised by means of sodium acetate, and the mixture is stirred for several days. A reddish-brown, slimy precipitate is produced, which is converted into the sodium salt by warming and neutralising with sodium hydroxide or carbonate. On cooling, the dye separates almost quantitatively as an orange-red powder, which is filtered off [Aktiengesellschaft für Anilinfabrikation, E.P. 3803^{85} (Bayer & Co.), F.P. 167876; G.P. 35615; U.S.P. 329632].

It is usual to employ tolidine base and sodium naphthionate in this combination, and a modern recipe is as follows: 212 lb. of tolidine are stirred into 212 gallons of water, 523 lb. of hydrochloric acid (20° Bé.) are added, and the whole is stirred until a clear solution is obtained, heat being used if necessary. The solution is cooled with ice to 5° and a 25 per cent. solution of 141 lb. of sodium nitrite (98 per cent.) is run in below the surface of the liquid. The temperature must be kept at or below 5°, if necessary by the addition of ice. The clear solution is now run into a solution of 539 lb. of sodium naphthionate (100 per cent.) in 215 gallons of water to which a concentrated solution of 271 lb. of sodium carbonate (98 per cent.) has been added and the whole cooled to 15° or lower. The diazo-solution is run into the naphthionate solution at a moderate rate, and the mixture should be stirred for at least six hours. The formation of the dye is completed by heating at 60—80°, when salt is added to precipitate the colouring matter as completely as possible. It is then filtered in a filter-press and dried at 50—60° (*Colour Trade J.*, 1917, November).

The best yield of this dye is, however, obtained by employing a large excess (about three times the theoretical amount) of sodium naphthionate, adding sodium carbonate solution slowly, and gradually warming the mixture while allowing to stir for four days. The dye is then filtered, and the filtrate is collected and the excess of naphthionic acid recovered by acidifying and filtering. The paste is then dissolved by means of sodium hydroxide or carbonate and the solution used for a further batch (compare Dawson and Hirsch, E.P. 14432^{90}).

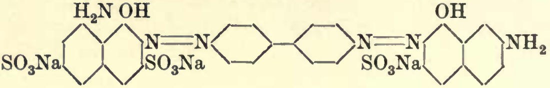
An entirely different process for preparing this dye consists in oxidising the product of combination of *o*-toluidine and sodium naphthionate. The oxidation is carried out by dissolving the monoazo-dye in concentrated sulphuric acid and treating the solution with manganese dioxide (Badische Anilin- & Soda-Fabrik, E.P. 6697^{95}; F.P. 248210; G.P. 84893), or by electrolytically oxidising this solution (*idem*, E.P. 17260^{95}; F.P. 3rd addition to 248210; G.P. 88597, but this method does not appear to be carried out on the large scale. The potassium salt of the dye crystallises with $4\frac{1}{2}H_2O$ (Knecht and Hibbert, *Ber.*, 1903, 36, 1553).

Benzopurpurine 10B (By, L, Lev., A, Gr. E, S, t.M, K, Oe.V), Dianil red 10B (M), Diamine red 10B (C), Buffalo Cardinal 7B (Sch.), Cotton red 10B (P).



Sixty lb. of dianisidine are dissolved in 2200 lb. of water and 75 lb. of concentrated hydrochloric acid. Next day, ice is added until the temperature is about 5°, then 100 lb. of concentrated hydrochloric acid, and a solution of 36 lb. of sodium nitrite. The clear diazo-solution is run into a solution of 560 lb. of sodium naphthionate (100 per cent.), and 100 lb. of sodium carbonate in 2400 lb. of water. The mixture is well stirred for forty-eight hours and then heated at 80°, and the dye is precipitated by adding 500—600 lb. of salt. The colouring matter is filtered on the following day and the filtrate is collected and acidified to precipitate the excess of naphthionic acid, which is filtered, dissolved in water with the addition of sodium hydroxide or carbonate, and the solution is used for a future batch. The yield of dry colour is 200 lb. (Patents relating to this dye are: Farbenfabriken vorm. F. Bayer & Co., E.P. 14424[85]; F.P. 173042; G.P. 38802).

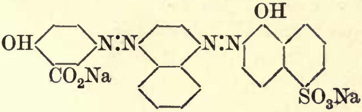
Diamine black BH (C), Dianol blue BH (Lev.), Ingrain black 2B (BD), Dianil black ES (M), Naphtamine black CE (K, Oe.V), Renolamine black BH, BHN (t.M), Azidine black BHN (CJ), Direct black HB (L), Diazo-black BHN (By), Diazine black H extra (Sch.), Oxamine black BHN (B), Direct black BD (P), Melantherin BH (J), Zambesi black BH (A).



36·8 Kilos. of benzidine are dissolved in 90 kilos. of hydrochloric acid (12° Bé.) and 900 litres of boiling water. Next day, 90 kilos. of hydrochloric acid (12° Bé.) and ice are added, and the diazo-compound is prepared by adding 224 kilos. of sodium nitrite solution (12·5 per cent). The temperature at the end of the operation should be 0–5° and the total volume 2000 litres.

To the diazo-solution is added quickly a solution of 60 kilos. of sodium carbonate in 500 litres of water (temperature 15°) and then a neutral solution of 72 kilos. of H-acid (calculated as 100 per cent.) in 11·5 kilos. of sodium carbonate, which has been cooled with ice to 0° (volume 2000 litres) is run in very rapidly. The formation of the intermediate compound takes place immediately and then 50 kilos. of sodium carbonate (in solid form) are added. The solution of γ-acid is now run in; this is prepared by dissolving 52 kilos. (reckoned as 100 per cent.) in 24 kilos. of sodium hydroxide solution (40° Bé.) and 500 litres of water at about 50°. The solution is cooled to 15°, the volume being 800 litres. After adding this to the intermediate compound, the mixture is stirred for twelve hours, and the dye is salted out by adding 300–400 kilos. of salt. The filtrate should show 7–9° Bé. The yield is about 230–250 kilos. of strong dye, which gives about 580 kilos. of "standard" or "type" (the patents relating to this dye are: Cassella & Co., E.P. 1742[91] and 6972[92]; F.P. 233032; G.P. 68462).

Diamond black F (B, By, L), Salicine black D (K, Oe.V), Era black F (Lév.), Chrome deep black (t.M), Fast chrome black B (Sch.), Chrome black J (BD), Chrome fast black FRW (J), Fast mordant black B, T (M), Acidol chrome black FF (t.M).



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p-Aminosalicyclic acid is converted in the usual way into its insoluble, grey diazo-compound and a quantity of this, corresponding with 5 kilos. of sodium nitrite, is added to a dilute hydrochloric acid solution of 10 kilos. of α-naphthylamine. Sodium acetate is added and the aminoazo-compound separates in small steel-blue metallic needles. After stirring for twenty-four hours, the batch is warmed at 50°, acidified with hydrochloric acid, and filtered. The paste is dissolved in hot water with the addition of sodium hydroxide, cooled, and a solution of 5 kilos. of sodium nitrite added. The mixture is acidified, and the diazo-compound separates out. This is filtered after three to four hours and the diazo-compound is added to an alkaline solution of 20 kilos. of 1-naphthol-5-sulphonic acid. The dye is salted out and filtered (Farbenfabriken vorm. F. Bayer & Co., E.P. 8299^{89}; F.P. 198521 and two additions; G.P. 51504; U.S.P. 438438).

Metallic compounds of this dye have been described by Brenner (*Helv. Chim. Acta*, 1920, 3, 90).

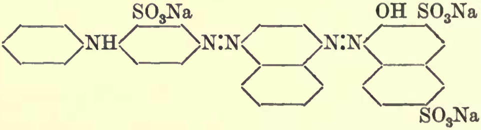
Deltapurpurine 5B (Lev., By, A, L, M, BK, K, S), Cotton purple 5B (B), Cotton red D (J).

This dye is obtained by the action of diazotised tolidine on the so-called β-naphthylamine-δ-sulphonic acid, obtained by adding 100 kilos. of β-naphthylamine sulphate to 300 kilos. of sulphuric acid (66° Bé.) heated at 160–170°, and maintaining the mixture at 160–170° for an hour. The hot solution is poured on ice, and the sulphonic acids which separate are filtered after some time. This crude acid, which may be purified by the preparation of the sodium or calcium salt (Farbenfabriken vorm. F. Bayer & Co., E.P. 5846^{86}; G.P. 41505), is a mixture of β-naphthylamine-6- and -7-sulphonic acids and is used for making

Deltapurpurine 5B as follows: 55 kilos. of tolidine sulphate, or the equivalent amount of another salt of tolidine, are suspended in water. Fifty kilos. of hydrochloric acid are added, and then a solution of 24·7 kilos. of sodium nitrite. The diazo-solution is run slowly into a suspension of 79 kilos. of β-naphthylamine-δ-sulphonic acid in water, the mineral acid is neutralised by adding sodium acetate, sodium carbonate, or ammonia, and after some time, or on warming, a red precipitate is formed which is converted into the sodium salt by means of sodium hydroxide or carbonate. On cooling, the dye is quantitatively precipitated as a red powder (Farbenfabriken vorm. F. Bayer & Co., E.P. 5846^{86}; F.P. 180728; G.P. 42021).

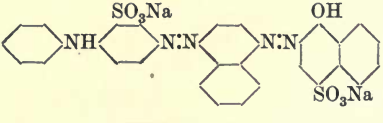
From the composition of the crude δ-acid it is clear that the dye produced from it is a mixture; it contains 50 per cent. of Diamine red B (A, RF) (Tolidine combined with one molecule of the 2 : 6- and one of the 2 : 7-acid), 25 per cent. of Diamine red 3B (A, RF) or Deltapurpurine 7B (Lev.) (Tolidine combined with two molecules of the 2 : 7-acid, and 25 per cent. of Benzopurpurine B).

Nerol B (A).



This is prepared like Nerol 2B, except that 30·4 kilos. of 2-naphthol-3 : 6-disulphonic acid (reckoned as free acid) are employed instead of 22·4 kilos. of 1-naphthol-4-sulphonic acid in the end combination.

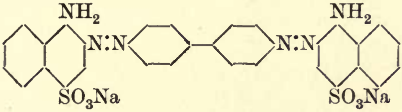
Nerol 2B (A).



A solution of 26·4 kilos. of *p*-aminodiphenylamine-*o*-sulphonic acid is diazotised with 6·9 kilos. of sodium nitrite and the necessary quantity of hydrochloric acid and the diazo-solution is added to a solution of 14·3 kilos. of α-naphthylamine in the corresponding amount of hydrochloric acid. Sodium acetate is added to neutralise the mineral acid. The combination begins at once, and is complete after about twenty-four hours' stirring. The monoazo-compound separates completely as an indigo-blue mass, which is isolated in the usual way. It is purified by conversion into the orange-yellow sodium salt.

The intermediate compound (41·8 kilos. of the free acid) in the form of its sodium salt is dissolved and mixed with a solution of 6·9 kilos. of sodium nitrite. The mixture is run into the corresponding quantity of dilute hydrochloric acid and the whole kept cold, the diazotisation being complete in a short time. The bluish-black, very sparingly soluble diazo-compound is added to a solution of 22·4 kilos. of 1-naphthol-4-sulphonic acid mixed with sufficient sodium carbonate to maintain an alkaline reaction throughout. After stirring for about thirty-six hours, the combination is complete, and the dye is isolated in the usual way (Aktiengesellschaft für Anilinfabrikation, E.P. 24527^{97}; F.P. 271609; G.P. 101274).

Congo (A), Congo red (By, L, S, Lev., BK, Oe.V, Sch., Marden, Orth, and Hastings, Japan Dyestuffs Co., RF, VSt), Congo red H (BD), Dianil red R (M), Cotton red conc. (t.M), Cotton red B (K), Cotton red C (J, P), Cotton red 4B (Gr. E), Cosmos red extra (B), Direct red C (FA, AW).



A solution of 25·7 kilos. of benzidine hydrochloride in 500 litres of water and 30 kilos. of hydrochloric acid (20° Bé.) is diazotised by adding a solution of 13·8 kilos. of sodium nitrite (100 per cent.) in 150 litres of water, and the solution of tetrazodiphenyl chloride is slowly run into a solution of 55 kilos. of sodium naphthionate and 12 kilos. of sodium acetate in 1000 litres of water, with good stirring. After twenty-four hours, the dye is filtered off, converted into the sodium or ammonium salt, and dried (Böttiger, E.P. 4415^{84}; F.P. 160722; G.P. 28753).

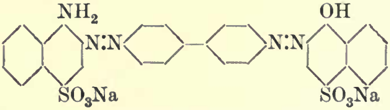
It has been found that an increased yield of the dye is obtained by using a large excess of sodium naphthionate in the following way. A diazotised solution of 104 lb. of benzidine is run into a solution of 840 lb. of sodium naphthionate (100 per cent.) at 20–30°. After stirring for an hour, a solution of 60 lb. of sodium carbonate is run in slowly, and next day, the temperature being kept at 25°, a solution of 40 lb. of sodium carbonate is similarly added.

On the third day, the temperature is still maintained at 25°, and on the fourth it is raised to 40° and 100 lb. of sodium carbonate, dissolved in water, are added in the morning. In the afternoon, the batch is heated at 80°, and next day this is filtered. The filtrate is collected and the naphthionic acid in excess precipitated by sulphuric acid (Chamber acid). This is filtered off (a brownish-red filtrate being obtained) and the paste is dissolved in water with the addition of sodium carbonate. This solution is tested and, when sufficient has been accumulated, used for further batches. From 104 lb. of benzidine about 630 lb. of standardised dye are obtained.

An alternative method of preparation, which is, however, not employed on the large scale, consists in oxidising benzeneazonaphthionic acid (prepared from diazotised aniline and sodium naphthionate) in sulphuric acid solution with manganese dioxide (Badische Anilin- & Soda-Fabrik, E.P. 6697^{95}; F.P. 248210; G.P. 84893) or electrolytically (*idem*, E.P. 17260^{95}; F.P. 3rd addition to 248210; G.P. 88597).

On reduction with zinc dust and ammonia (Witt, *Ber.*, 1886, 19, 1719), sodium hyposulphite or hydriodic acid (R. Meyer, *ibid.*, 1920, 53, [*B*], 1275) the dye furnishes benzidine and 1 : 2-diaminonaphthalene-4-sulphonic acid.

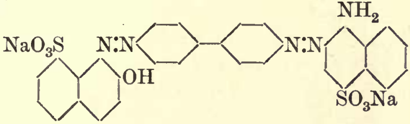
Congo Corinth G (A, By, L, Lev., S, BK), Corinth brown G (RF), Cotton Corinth G (B, Gr. E), Renol Corinth G (t.M), Dianil Bordeaux G (M), Buffalo garnet R (Sch.).



A solution of tetrazodiphenyl chloride, prepared in the usual way from 9·2 kilos. of benzidine, in 1000 litres of water, is run into a solution of 12·2 kilos. of sodium naphthionate and 32 kilos. of sodium acetate in 900 litres of water. To the intermediate compound obtained, a solution of 12·3 kilos. of sodium 1-naphthol-4-sulphonate in 100 litres of water is added, and the mixture is stirred for some time (Aktiengesellschaft für Anilinfabrikation, E.P. 15296[85], 2213[86]; F.P. 160722, 163172; G.P. 39096; U.S.P. 344971, 358865).

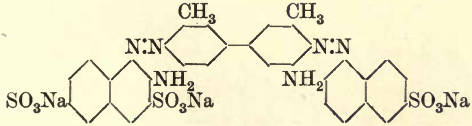
More modern practice consists in adding a tetrazo-solution prepared from 46 lb. of benzidine, the volume of the solution being 250 gallons, to a solution of 62 lb. of sodium naphthionate (calculated as 100 per cent.) and 63 lb. of sodium carbonate (total volume, 450 gallons). After stirring for half an hour, a solution of 20 lb. of sodium carbonate is added and then a solution of 67 lb. of sodium 1-naphthol-4-sulphonate. Next day, the batch is heated by direct steam at 80°, the dye salted out, filtered, and dried.

Congo rubine (A, By, L, Lev., BK, Oe.V), Congo rubine A (S), Congo rubine B (K), Cotton rubine (B), Renol rubine extra (t.M), Azidine Bordeaux (CJ), Direct crimson B (Sch.).



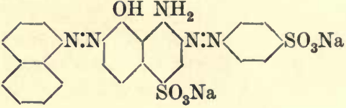
A solution of 18·4 kilos. of benzidine in 60 kilos. of concentrated hydrochloric acid and about 700 litres of water is diazotised by means of 14 kilos. of sodium nitrite. The solution is run into a solution of 25 kilos. of sodium 2-naphthol-8-sulphonate and 30 kilos. of sodium carbonate in about 1000 litres of water. When the formation of the intermediate compound is complete, a solution of 34 kilos. of crystallised sodium naphthionate (usually about 70 per cent.) is added. After about twenty-four hours, the dye is filtered, pressed, and dried (Aktiengesellschaft für Anilinfabrikation, G.P. 62659).

Brilliant Congo R (A, By, L, RF), Brilliant Dianil red R (M), Azidine scarlet R (CJ).



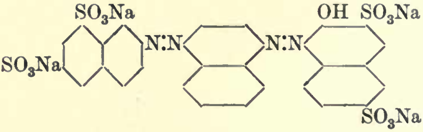
A diazo-solution prepared in the usual way from 10·6 kilos. of tolidine is added to a solution of 17·5 kilos. of sodium β-naphthylamine-3 : 6-disulphonate and 20 kilos. of sodium acetate in 500 litres of water. The intermediate compound is formed after half an hour, and to this is added a solution of 14 kilos. of sodium β-naphthylamine-6-sulphonate in 500 litres of water. After about twelve hours, the mixture is rendered alkaline by the addition of sodium carbonate, heated to boiling, and the dye salted out (Aktiengesellschaft für Anilinfabrikation, E.P. 6687^{87}; G.P. 41095).

Palatine black A (B), Wool black 4B, 6B (A), Buffalo black PY (Sch.).



A diazo-solution prepared from 12·2 kilos. of sodium sulphanilate, 19 kilos. of hydrochloric acid, and 4·3 kilos. of sodium nitrite is quickly added to a well-stirred solution of 15 kilos. of 8-amino-1-naphthol-5-sulphonic acid (S-acid) and 11·3 kilos. of sodium carbonate in 450 litres of water to which has been added 450 kilos. of ice. When the formation of the monoazo-dye is complete, a solution of 4·5 kilos. of sodium carbonate in 50 litres of water is run in and then a diazo-solution prepared from 8·9 kilos. of α-naphthylamine, 25·0 kilos. of hydrochloric acid (30 per cent.), 4·3 kilos. of sodium nitrite, and 400 kilos. of water and ice. When the diazo-compound has fully combined, the whole is heated at 80°, the dye salted out and filtered from the red-coloured liquor (Badische Anilin- & Soda-Fabrik, E.P. 9894^{93}; G.P. 91855; U.S.P. 590088, 593790).

Naphthol black B (C), Naphthol black OPAS (Lev.), Carbon black B, 3B (M), Wool black B, SG (WDC), Buffalo black 2B (Sch.), Brilliant black B (B).

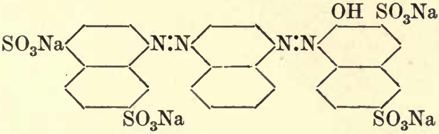


The procedure is the same as in making Naphthol black 6B, except that sodium 2-naphthylamine-6 : 8-disulphonate is diazotised (patents as under Naphthol black 6B).

A good result is obtained if the intermediate monoazo-compound, after being stirred for several hours, is heated at 40° and rendered alkaline by adding a solution of sodium hydroxide. In order to ascertain whether the coloured solution gives an alkaline reaction, a few drops are placed on a watch-glass, a crystal of ammonium chloride is added, and the watch-glass covered with another one on the concave side of which is placed a moistened red litmus paper. The bottom watch-glass is now gently warmed, and if sodium hydroxide is present ammonia will be evolved and change the colour of the test paper to blue.

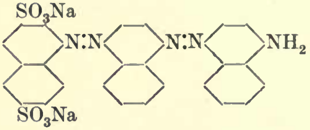
The solution is now heated at 85° for one hour and salt added. After two days (or at 25–30°), the dye is filtered (the filtrate should be 17–20° Bé.), and pressed. The cake is tested by dissolving 5 grams in 500 c.c. of water, adding 10 c.c. of hydrochloric acid, and titrating with $N/2$-sodium nitrite, which is added very slowly (three to four hours). The colour changes to brown and the test is finished when no reddish-violet colour can be seen. The amount of paste necessary for the sodium nitrite required is now dissolved in about 20 parts of cold water, acidified, and the nitrite added slowly. The mixture is stirred over-night and then the diazo-solution run into the solution of R-salt, which is kept alkaline by means of sodium carbonate. When the combination is complete, the batch is heated at 80° and the dye salted out.

Naphthol black 6B (C, K), Naphthol black (WDC), Naphthol black 2B (Lev.), Acid black 5B, BR (t.M), Acid black 6B (BD), Brilliant black BD (B), Wool black (BK), Naphthalene black 5B (P), Acidol black (t.M).



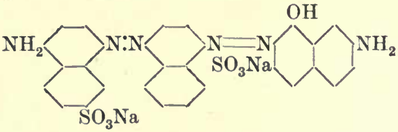
The diazoazo-compound is prepared as described under Naphthylamine black D, except that a mixture of sodium 1-naphthylamine-4 : 6- and -4 : 7-disulphonates (or preferably the latter only, as shown in the formula) is used instead of Freund's acid. It is then added to an alkaline solution of 36 kilos. of sodium 2-naphthol-3 : 6-disulphonate (R-salt) and the resulting dye is salted out (Cassella & Co., E.P. 9214[85]; F.P. 170342; G.P. 39029; U.S.P. 345901).

Naphthylamine black D (C, K), Naphthalene black R (BD), Full black D conc. (t.M), Coomassie wool black D (Lev.), Buffalo black AD (Sch.), Acid black NN (J).



A solution of 35 kilos. of sodium 1-naphthylamine-3 : 6-disulphonate in 300 litres of water is acidified with 30 kilos. of hydrochloric acid (21° Bé.) and a solution of 7 kilos. of sodium nitrite added. To the finished diazo-solution is added a solution of 18 kilos. of α-naphthylamine chloride in 500 litres of water. The dark violet product separates out at once. After twelve hours, 12 kilos. of hydrochloric acid are run in, the solution is cooled, and diazotised with 7 kilos. of sodium nitrite. Diazotisation is complete after several hours, when the diazo-solution is run into a solution of 18 kilos. of α-naphthylamine hydrochloride. After twelve hours, the precipitate is filtered off, dissolved in sodium carbonate, and the dye salted out (Cassella & Co., E.P. 9214[85]; F.P. 170342; G.P. 39029; U.S.P. 345901; and E.P. 18425[88]; F.P. 170342; G.P. 50907; U.S.P. 412440).

Diaminogen BB extra (C).

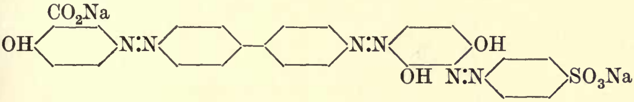


A solution of 30·2 kilos. of acetyl-1 : 4-naphthylenediamine-6-sulphonic acid is diazotised with 24 kilos. of hydrochloric acid and 7 kilos. of sodium nitrite and mixed with a solution of 14·3 kilos. of α-naphthylamine in 12 kilos. of hydrochloric acid (21° Bé.) and 250 litres of water. The combination is complete after twelve hours. The product is dissolved in 500 litres of water and 4 kilos. of sodium hydroxide, 7 kilos. of sodium nitrite are added to the solution, and this is allowed to flow into 36 kilos. of diluted hydrochloric acid, which is kept cold. The diazo-compound separates in very sparingly soluble brown flocks and when added to an alkaline solution of 27 kilos. of 7-amino-1-naphthol-3-sulphonic acid (γ-acid) formation of the dye begins at once. The sparingly soluble precipitate is filtered off, and boiled with 1000 litres of a 10 per cent. solution of sodium hydroxide until the pure blue colour of a diluted sample is no longer changed by acetic acid. On neutralising the liquid, the dye is precipitated (Cassella & Co., E.P. 15444^{93}; F.P. 232299; G.P. 78831; U.S.P. 533463).

AZO-COLOURS (TRISAZO)

CONGO BROWN—COLUMBIA BLACK—DIAMINE GREEN—ERIE DIRECT BLACK—CONGO FAST BLUE—DIRECT BLACK

CONGO BROWN G (A, Lev.), Direct brown GR (Sch.), Naphtamine brown 4G (K), Benzoin brown C (BK).



This dye may be prepared in two ways, namely (1) by treating the combination, Benzidine $<^{\text{Salicylic acid}}_{\text{Resorcinol}}$, with diazotised sulphanilic acid, or (2) by treating the monoazo-dye obtained from diazotised sulphanilic acid and resorcinol with the intermediate product obtained by combining one molecule of salicylic acid with one molecule of diazotised benzidine.

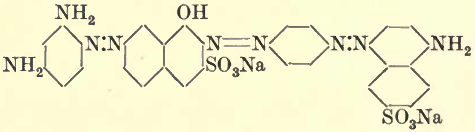
I.—A diazotised solution of 18·4 kilos. of benzidine is run into an alkaline solution of 13·8 kilos. of salicylic acid in about 500 litres of water. After some time, the intermediate product separates as a reddish-brown precipitate. This is added to an alkaline solution of 11·0 kilos. of resorcinol and after stirring for twelve hours the whole is heated to boiling and the dye is salted out, filtered, pressed, and dried (Farbenfabriken vorm. F. Bayer & Co., G.P. 44797).

Forty-seven kilos. of this compound are dissolved in 25 kilos. of sodium hydroxide solution (40° Bé.) and 4000 litres of hot water and, after cooling, 20 kilos. of diazobenzene-*p*-sulphonic acid, suspended in about 600 litres of water, are slowly added. The sparingly soluble dye is completely precipitated by means of salt solution, filtered, and dried.

II.—Thirty-six kilos. of the dye prepared from diazobenzene-*p*-sulphonic acid and resorcinol are dissolved in 1000 litres of water, and to the solution is added the intermediate compound prepared from diazotised benzidine and salicylic acid, for which are required 19·5 kilos. of benzidine, 48 kilos. of hydrochloric acid, 14·7 kilos.* of sodium nitrite, and 800 litres of water on the one hand, and 15 kilos. of salicylic acid, 14 kilos. of sodium hydroxide solution (40° Bé.), 30 kilos. of sodium carbonate, and 1200 litres of water on the other.

The mixture of the two substances is stirred for twenty-four hours and then heated to boiling and the dye salted out, filtered, pressed, and dried (Aktiengesellschaft für Anilinfabrikation, E.P. 10653^{88}; F.P. 192331; G.P. 46328, 46501; U.S.P. 399581).

Columbia black FB, FF extra (A), Dianol black FB, FF (Lev.), Azidine black FF extra (CJ), Panama black R, F (Sch.), Patent Dianil black FF extra (M).



I.—The first stage in this example consists in preparing the azo-compound, sodium *p*-aminobenzeneazo-1-naphthylamine-6-(or 7)-sulphonate, which can be done either by combining diazotised *p*-aminoacetanilide with the technical mixture of 1-naphthylamine-6- and -7-sulphonic acids (Cleve's acids) in sodium acetate solution, and subsequently hydrolysing the acetyl group by heating with sodium hydroxide solution, or by combining diazotised *p*-nitroaniline with the Cleve's acids and reducing the nitro-group with sodium sulphide in alkaline solution and salting out the diaminoazo-compound.

A solution of 3·64 kilos. of this product and 0·7 kilo. of sodium

* The German patent gives 6·9 kilos., which is an obvious mistake: the 19·5 kilos. of benzidine probably corresponds with 18·4 kilos. of the pure substance, which requires 13·8 kilos. of sodium nitrite (reckoned as 100 per cent.).

nitrite in 150 litres of water is cooled to 15° and run into 2·6 kilos. of commercial hydrochloric acid diluted with 50 litres of water and cooled to 10°. The sparingly soluble green diazo-compound (only the benzenoid amino-group is diazotised) is run into a cold alkaline solution of the chrysoidine prepared by combining the diazo-compound of 2-amino-8-naphthol-6-sulphonic acid (γ-acid) with *m*-phenylenediamine. Of this 3·58 kilos. are dissolved in 0·8 kilo. of sodium hydroxide and 1·2 kilos. of sodium carbonate and the requisite amount of water. After combination, the mixture is slowly heated at 60° and the dye salted out (Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 12804^{00}; F.P. 302499; G.P. 131987; U.S.P. 679221).

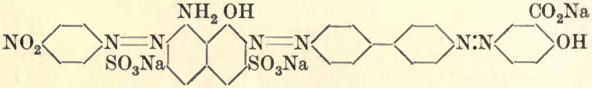
II.—The green diazo-compound mentioned above is run into a cold solution of 2·5 kilos. of γ-acid, 0·8 kilo. of sodium hydroxide, and 1·2 kilos. of sodium carbonate in the necessary quantity of water. The combination is stirred for some hours, then heated at 60–70°, and the dye salted out. Of this (as disodium salt), 0·635 kilo. is dissolved with 0·069 kilo. of sodium nitrite in 30 litres of water, the solution cooled to 10°, and run into 10 litres of cold dilute hydrochloric acid (0·14 kilo. of HCl). The insoluble diazo-compound is run into a solution of 0·125 kilo. of *m*-phenylenediamine in 5 litres of water, and after stirring for some time the whole is slowly heated at 40°, sodium carbonate added until a feebly alkaline reaction is obtained, and the dye salted out (*idem*, G.P. 131986; other patents as above).

III.—The dye may be obtained by fewer stages in the following manner. A solution of 150 lb. of *p*-aminoacetanilide in water and 140 lb. of commercial hydrochloric acid is cooled, 180 lb. of hydrochloric acid are added, and then a solution of 72 lb. of sodium nitrite. The clear diazo-solution is run quickly into a solution of 240 lb. of γ-acid in 250 lb. of sodium carbonate and 2500 lb. of water. Next day, the batch is heated at 70°, salt added, and the dye filtered off on the following day.

The whole of this azo-dye is dissolved in about 5000 lb. of water, four molecular proportions of sodium hydroxide are added, and the mixture is heated at 95° for two to two and a half hours in order to split off the acetyl group. A sample, cooled and acidified, and tested with standard sodium nitrite, should show an equivalent of sodium nitrite of about 130–135 lb. A volume of the solution, corresponding with 34 lb. of sodium nitrite, is run into a tub, cooled with ice, and to it is added 350 lb. of hydrochloric acid and a solution of 34 lb. of sodium nitrite. When the diazotisation is complete, a cold solution of 160 lb.

of sodium carbonate is added all at once, and then a solution of 47–50 lb. of Cleve's acid (calculated on a molecular weight of 245), and, ten minutes later, a solution of 25 lb. of *m*-phenylenediamine. The dye is filtered cold and the yield is about 500 lb. of "standard" or "type."

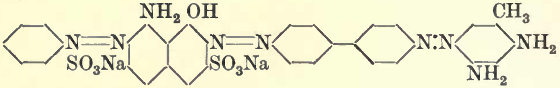
Diamine green G (C), Alkali green D (WDC), Dianol green G (Lev.), Azidine green 2G (CJ), Dianil green BBN, G (M), Benzoin dark green (BK), Erie direct green MT, BT (Sch.), Oxamine green G (B).



A neutral or acidified solution of 32 kilos. of 1-amino-8-naphthol-3 : 6-disulphonic acid is added to a diazotised solution of 13·8 kilos. of *p*-nitroaniline in hydrochloric acid. After stirring for several hours, the mixture is rendered alkaline with sodium carbonate and a diazotised solution of 18·4 kilos. of benzidine added. The intermediate compound forms a black precipitate, and to this is added a solution of 15 kilos. of sodium salicylate. After some hours, the dye is salted out (Cassella & Co., E.P. 15725^{91}; F.P. 6th addition to 201770; G.P. 66351; U.S.P. 514599).

If phenol is substituted for salicylic acid in the above combination, Diamine green B (C) [Alkali green (WDC), Dianol green B (Lev.), Azidine green 2B (CJ), Dianil green B (M), Oxamine green B (B), Direct green BN (P), Renol green B extra (t.M)] is obtained.

Erie direct black RX (Sch.), Renol black R extra (t.M), Patent Dianil black EBV extra conc. (M), Direct deep black RW extra, E extra (By), Cotton black E extra (B), Columbia black F extra (A).

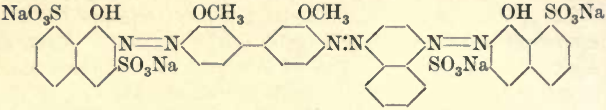


I.—A diazotised solution of 18·4 lb. of benzidine is partly neutralised with sodium acetate so that some free mineral acid remains, and a neutral solution of 32 lb. of H-acid is added. After stirring for two hours, a solution of 16 lb. of crystallised sodium acetate is slowly introduced. When the combination is complete, the violet precipitate is dissolved by adding an excess of sodium carbonate. A diazotised solution of 9·3 lb. of aniline is now added quickly and the combination is complete in one to two hours with the formation of a bluish-black precipitate. To this is added a solution of 12·5 lb. of *m*-tolylenediamine, and the resulting blackish-brown solution is heated and the dye salted out (Schoellkoff, G.P. 153557; U.S.P. 688478). When *m*-phenylenediamine is used instead of *m*-tolylenediamine, the dye is called Erie direct black GX (Sch.). [Renol black G (t.M), Patent Dianil black EB conc. (M), Direct deep black EW extra (By), Union black (By), Cotton black RW extra (B), and phenol in the last stage gives Erie direct green ET (Sch.).

II.—To a solution of 18·4 parts of benzidine diazotised by means of 90 parts of hydrochloric acid (12° Bé.) and 14 parts of sodium nitrite is added a solution of the neutral sodium salt of H-acid prepared by dissolving 32 parts of the acid in water and the theoretical amount of sodium carbonate. The mixture is stirred until the combination is complete and to the black precipitate is added a solution of 10·8 parts of *m*-phenylenediamine and the whole rendered alkaline with 45 parts of sodium carbonate. This is stirred for some hours, and then a diazo-solution prepared from 11 parts of aniline, 16 parts of hydrochloric acid, and 8·5 parts of sodium nitrite is added. After stirring for some hours, the batch is heated and the dye salted out (Aktiengesellschaft für Anilinfabrikation, E.P. 12305^{02}; G.P. Anm. A. 8974; U.S.P. 717550).

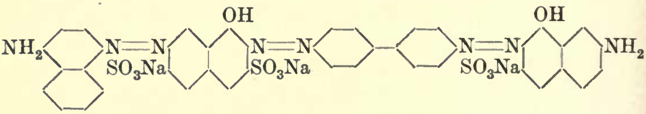
In the preparation of this dye the combination of tetrazodiphenyl with H-acid in the presence of sodium acetate is not satisfactory, as the coupling is not confined to the 2-position with respect to the amino-group, and it is best to mix the diazotised benzidine and neutral solution of H-acid as given under (II) and then add very slowly a solution of sodium carbonate until the reaction to Congo paper is weak, and to allow the mixture to remain over-night. To this is then added the diazotised aniline solution, and then, all at once, a solution of sodium carbonate so as to render the mixture faintly alkaline. When benzenediazonium chloride can no longer be detected, the *m*-phenylenediamine (or *m*-tolylenediamine) solution is added, and finally the whole is heated, rendered alkaline with sodium carbonate solution, the dye salted out, and then hydrochloric acid added until the precipitation is complete (compare details of the laboratory preparation, Fierz, "Grundlegende Operationen der Farbenchemie," 1920, p. 160).

Congo fast blue B (A), Benzo fast blue B (By).



A filtered solution of 17·1 kilos. of dianisidine sulphate in 500 litres of boiling water and 30 kilos. of hydrochloric acid is cooled and treated with a solution of 5·74 kilos. of sodium nitrite in 80 litres of water. The diazo-solution is run into a cooled solution of 6 kilos. of α-naphthylamine in 8·5 kilos. of hydrochloric acid (12° Bé.) and 1000 litres of boiling water which has been filtered. The intermediate compound, after fifteen hours, is treated with 15 kilos. of hydrochloric acid (12° Bé.), diazotised by the addition of a solution of 2·78 kilos. of sodium nitrite in 40 litres of water, and the product run into a solution of 40 kilos. of α-naphthol-3 : 8-disulphonic acid (E-acid) in 56 kilos. of sodium hydroxide solution (40° Bé.). Next day the batch is heated to boiling, and the dye salted out, filtered, and dried (Aktiengesellschaft für Anilinfabrikation, E.P. 6932^{90}; F.P. 205615; G.P. 57444; details of the manufacture on the small scale are given by Paul, *Zeitsch. angew. chem.*, 1896, 9, 558).

Direct black V (S), Diazo direct black (AW).



A suspension in about 300 litres of water of the diazo-compound from 34·2 kilos. of the acid sodium salt of 2-amino-8-naphthol-3 : 6-disulphonic acid (100 per cent.), and 6·9 kilos. of sodium nitrite is mixed with a cooled solution of 14·3 kilos. of α-naphthylamine in 12·5 kilos. of hydrochloric acid (21° Bé.) and 400 litres of water. The dye separates as a brownish-violet powder and, after twenty-four hours, is dissolved by the addition of 8 kilos. of sodium hydroxide. A solution of 30 kilos. of sodium hydroxide is added and then, at 10°, a diazo-solution prepared from 18·4 kilos. of benzidine is introduced quickly. The intermediate compound separates as a blackish-violet precipitate and to this is added a solution of 23·9 kilos. of 2-amino-8-naphthol-6-sulphonic acid (γ-acid) in 4 kilos. of sodium hydroxide and 500 litres of water. The mixture is stirred for twenty-four hours, when the combination is complete. The dye is filtered off in the cold and without the addition of salt (Chemische Fabrik vorm. Sandoz, E.P. 15294^{96}; F.P. 256950; G.P. 109161; U.S.P. 601033).

AZO-COLOURS (TETRAKISAZO)

BENZO-BROWN

Benzo brown G (By, Marden, Orth, and Hastings Corp.).

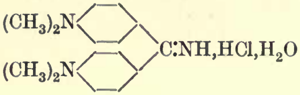
Two molecular proportions of diazotised sulphanilic acid are added to a solution of Bismarck brown which has been prepared from 3 molecular proportions of *m*-phenylenediamine and 2 of sodium nitrite. The mixture is stirred for twenty-four hours, rendered alkaline, heated, and the dye salted out (Farbenfabriken vorm. F. Bayer & Co., E.P. 16493^{87}; G.P. 46804; U.S.P. 384315; Bülow, "Chemische Technologie der Azofarbstoffe," II, 258).

CHAPTER VI

DIPHENYLMETHANE COLOUR

AURAMINE

Auramine * (B, J, G, M, S, By, t.M, A, L, BD, C, LBH, Williamsburg Chemical Co.), Pyoktanium aureum (Merck).



I.—The earlier method of manufacture consisted in heating tetramethyldiaminobenzophenone (Michler's ketone) with ammonium chloride and zinc chloride.

The operation is carried out in an enamelled pan set in an oil- or air-bath. The pan is heated at about 200° and an intimate mixture of 25 kilos. of tetramethyldiaminobenzophenone, 25 kilos. of ammonium chloride, and 25 kilos. of zinc chloride is introduced. The mixture gradually melts together and becomes deep yellow. From time to time it is stirred vigorously to assist the fusion, and if the temperature of the mixture is maintained at about 150–160° the formation of the dye is complete in four to five hours. The end of the operation is indicated when a sample of the fusion dissolves almost completely in hot water. On cooling, the solid mass is powdered and treated with cold water containing a little hydrochloric acid in order to remove most of the excess of ammonium chloride and zinc chloride. The residue is then extracted with hot water and the solution, after filtering from unchanged ketone, is treated with salt. The crystalline precipitate can be purified by recrystallisation from hot water (Badische Anilin- & Soda-Fabrik E.P. 5512^{84}, 5741^{84}; F.P. 160990; G.P. 29060; U.S.P. 301802).

In an addition to the above German patent (G.P. 38433), acetamide is employed instead of ammonium chloride and the

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* The concentrated brands are known as Auramine O, OO, OO extra conc., whilst the weaker, diluted with dextrin, are Auramine I, II, etc.

dye can also be obtained by heating aniline hydrochloride and zinc chloride with carbamide, diphenylcarbamide, and zinc chloride with ammonium chloride or tetramethyldiaminobenzophenone and zinc chloride with carbamide (Ewer and Pick, E.P. 9682^{84}; F.P. 164099; G.P. 31936) and by passing ammonia into a solution of tetramethyldiaminothiobenzophenone (Kern, E.P. 12022^{86}; F.P. 175376; G.P. 37730), but none of these processes is of practical value.

II.—In the more modern process, tetramethyldiaminodiphenylmethane is heated with sulphur, salt, and ammonium chloride. A mixture of 12·7 kilos. of tetramethyldiaminodiphenylmethane and 3·2 kilos. of sulphur is placed in a closed pan * fitted with a stirrer and set in an oil-bath, and heated until the sulphur dissolves. A mixture of 120 kilos. of salt and 7 kilos. of finely-powdered ammonium chloride, heated at 140°, is now added. The temperature of the oil-bath is raised to 175° and a fairly rapid stream of dry ammonia is passed into the mixture for seven hours under a plus pressure of about a quarter of an atmosphere. The escaping ammonia, containing some hydrogen sulphide, is freed from the latter by passing through sodium hydroxide solution, dried, and used again in the manufacture.

The product, consisting of a brownish-yellow powder, is freed from salt by means of cold water and the dye is then extracted by warm water, the solution filtered and the dye precipitated by adding the salt solution obtained as above. The yield is 110–112 per cent. of the weight of the base (Feer [patent transferred by Geigy & Co. to Badische Anilin- & Soda-Fabrik], E.P. 12549^{89}; F.P. 200613; G.P. 53614). In order to protect this process, the use of tetramethyldiaminobenzhydrol or tetramethyldiaminothiobenzhydrol, instead of tetramethyldiaminodiphenylmethane, has been patented (E.P. 16666^{90}; F.P. 200613; G.P. 58277), also the employment of chloranil or other oxidising compounds (nitro-compounds) in conjunction with these bases (G.P. 70908) and of tetramethyldiaminodiphenyldimethylmethane (obtained from dimethylaniline and acetone) instead of the above bases (E.P. 6249^{93}; G.P. 71320).

Auramine can also be obtained by heating 17 kilos. of *p*-dimethylaminobenzamide (prepared by treating the corresponding acid chloride, obtained from dimethylaniline and carbonyl

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* A pan sufficiently large to produce 80–100 kilos. of standard Auramine (that is, the pure dye reduced 8–10 per cent. with dextrose or sugar) can be charged twice in twenty-four hours (Walter, *Chem. Zeit.*, 1900, **24**, 1031).

chloride or from *p*-dimethylaminobenzoic acid and the chlorides of phosphorus, with ammonia) with 25 kilos. of dimethylaniline hydrochloride and 30 kilos. of zinc chloride for five hours in an oil-bath at 160–200°, the product being worked up as described above (Farbenfabriken vorm. F. Bayer & Co., G.P. 77329).

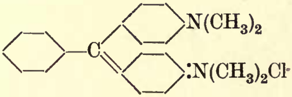
The dye is sparingly soluble in cold, but readily so in hot water. The temperature of the solution should not exceed 60–70°, otherwise the dye is decomposed into ammonia and tetramethyldiaminobenzophenone.

CHAPTER VII

TRIPHENYLMETHANE COLOURS

MALACHITE GREEN—BRILLIANT GREEN—PARAROSANILINE—MAGENTA—METHYL VIOLET—CRYSTAL VIOLET—BENZYL VIOLET—SPIRIT BLUE—ACID MAGENTA—ACID VIOLET 4BN—ACID VIOLET 6B—FAST ACID VIOLET—CYANOL—GUINEA GREEN—PATENT BLUE A—PATENT BLUE V—SOLUBLE BLUE—ALKALI BLUE—ERIOCYANINE—ERIOGLAUCINE—LIGHT GREEN

Malachite green.



The condensation of benzaldehyde and dimethylaniline was formerly effected by means of zinc chloride, but sulphuric or hydrochloric acid is now used.

The manufacture, using zinc chloride as condensing agent, is described by Mühlhäuser (" Die Technik der Rosanilinfarbstoffe," 1889, p. 84; *Dingl. Polyt. J.*, 1887, **263**, 249, 295) in great detail.

Condensation.—For a daily production of 125 kilos. of the leuco-base are required three cast-iron jacketed pans of about 500 litres capacity, each fitted with a lid carrying a stirrer and manometer; the lid also contains a manhole and connexion with compressed air, and the jacket is connected with water and steam. In addition is needed a cylindrical distilling pan with a concave bottom, fitted with direct and indirect steam coils, the still-head of which is connected with a coil set in a tub to act as condenser. Just below the run-out tap of the distilling pan is placed a steam-jacketed copper drying pan about 150 cm. in diameter.

In one of the pans is placed 100 kilos. of dimethylaniline and 40 kilos. of benzaldehyde. The stirrer is started and 40 kilos. of powdered anhydrous zinc chloride are added during two hours through the manhole. The pan is then closed and heated; on the first day at 60°, on the second at 80°, and on the third at 100°, the water in the jacket being heated to boiling. A pipe is now inserted in the pan and the warm mixture is blown into the distilling pan. After this operation, steam is blown through this pipe to free it from any adhering leuco-base.

Steam is now passed into the contents of the distilling pan in order to drive off the excess of dimethylaniline (see later) and the distillation is continued until only water passes over. The whole of the contents of the pan are now run through the tap at the bottom into the copper drying pan and allowed to cool. The aqueous zinc chloride solution is syphoned away from the solid base which floats on it, and the base is finally washed with cold water. It is then melted by turning steam into the jacket of the pan and dried. This takes about twelve hours, and the base is occasionally stirred. The dry, liquid base is transferred to zinc trays, 33 kilos. being placed on each tray, any base left over being weighed with the following batch.

From three batches the yield was 123, 125, and 126 kilos., respectively, and the corresponding amount of recovered oil was 7·5, 7·0, and 7·0 kilos.

Oxidation of the Leuco-base.—The plant required for the oxidation of the leuco-base and the isolation of the finished dye consists of tubs arranged on three stages. On the top stage is a small tub (300 litres) fitted with an open steam coil and water connexion, for dissolving the leuco-base, on the next stage are set three oxidation tubs, each about 200 cm. in diameter and 90 cm. deep (about 3000 litres capacity) fitted with rapidly rotating stirrers, and on the bottom stage, below these, are three precipitation tubs of the same size but without stirrers. Between each oxidation tub and the corresponding precipitation tub, and resting on the latter, is an open filter, and the contents of each precipitation tub can also run on to an open filter placed just above the ground. The purification of the crude dye is effected in a horizontal cylindrical pan of 3500 litres capacity. This is fitted with a dome carrying a manhole, a horizontal stirrer, a manhole at the bottom of one end for cleaning purposes, through which also passes a tap, a blow-out pipe, and steam, water, and air connexions. (This is the same kind of apparatus as is used for the purification of magenta.) Above this cylinder, and connected with the blow-out pipe, is placed a cast-iron pressure filter (the material to be filtered enters below, passes through the horizontal filter-cloth and emerges in the top half of the filter), and below the filter stand three tubs (3000 litres) without stirrers, into any of which the filtrate can run. The pure base is precipitated in these tubs, and filtered in open filters lying just below them, the filtrate from all three filters passing through a pipe running into a receiver placed below the level of the ground.

For the crystallisation, the base is dissolved in a tub of about 2000 litres capacity and below this, raised a little above the ground, are six crystallising tubs (2000 litres) fitted with floating lids cut up into sections, from which the crystals can run on open filters, the liquor from the latter being led into a receiver.

For the oxidation, a zinc tray containing 33 kilos. of the leuco-base is put into the small tub (300 litres) and turned over on top of the open steam coil. Steam is turned on, the base is melted off the tray, and the latter removed. About 200 litres of water are now run into the tub and heated to boiling. To the boiling mixture 25 kilos. of hydrochloric acid (21° Bé.) are added, a quantity which should effect complete solution of the leuco-base. Should a sample of the solution, poured into water, give a milky precipitate of the monohydrochloride, more hydrochloric acid must be added until a sample, poured into water, remains clear, showing that the dihydrochloride has been produced. The clear solution is now run into one of the oxidation tubs containing about 1000 litres of water and 31 litres of acetic acid (40 per cent.), the stirrer having been set in motion.

Preparation of Lead Peroxide.—Sixty-seven kilos. of litharge are dissolved in 125 kilos. of acetic acid (40 per cent.) and 300 litres of water in a wooden tub, the whole being stirred and heated by steam. To this solution is added a sieved paste of 81 kilos. of bleaching powder and 160 litres of water until all the lead acetate has been converted into lead peroxide. The end of the operation is recognised by testing the rim of a drop of the mixture brought on filter-paper with a little filtered bleaching powder solution. If a yellow coloration is produced, a further amount of bleaching powder is required, and this is added until a yellow coloration is no longer observed by the above test. The peroxide is now allowed to settle and the solution decanted through a filter. After twice boiling up with water and decantation the blackish-brown paste is thrown on a filter, allowed to drain, and the well-washed paste is transferred to a weighed cask and made up with water to 168 kilos. net weight. The contents of the cask are divided into three parts so that each contains 56 kilos. corresponding with 33 kilos. of the leuco-base.

Oxidation.—Into each of the three oxidation tubs the necessary amount of lead peroxide paste is introduced within five to ten minutes, the stirrers being in action. The colourless solution becomes deep green.

In order to precipitate the lead, 72 kilos. of sodium sulphate are previously dissolved in 200 litres of water in the small tub above the oxidation tubs, and the volume is brought to 300 litres. Immediately after the oxidation 100 litres of this solution are run into each of the three oxidation tubs, the volume being measured off by means of a graduated stick. The lead is then precipitated as sulphate and after twelve hours (the sulphate filters better after standing) the contents of the tubs are filtered through the open filters into the precipitation tubs and to the filtrate in each tub is added 20 kilos. of solid zinc chloride and the zinc chloride double salt is completely salted out by stirring in about 175 kilos. of salt. A sample on filter-paper should show only a slightly coloured rim round the precipitate. After remaining for twelve hours, the zinc chloride double salt is collected on an open filter and the filtrate run away.

Purification.—The paste from the three filters is added to about 2400 litres of hot water contained in the horizontal cylindrical pan, the stirrer being in motion, the mixture boiled for about ten minutes, and then about 500 litres of cold water are added to precipitate a little tarry matter. The pan is then closed and the contents are allowed to remain for ten minutes, when the tarry matter mostly settles down. The liquid is blown through the pressure filter and the filtrate runs into a tub (3000 litres), where it is allowed to cool to about 40°, and then the base is precipitated by adding 100 kilos. of ammonia. In this way, the base is precipitated in the molten condition and does not carry down with it any zinc hydroxide, and the latter is obtained in solution. The cold mixture is filtered through an open filter and the filtrate is caught in a receiver, whence it is blown to a still for the recovery of ammonia. The greyish-white base remaining on the filter is transferred to sacks and centrifuged to remove water. The yield of moist base from three batches (each corresponding with 3 × 33 kilos. of leuco-base) was 84, 85, and 82·5 kilos. respectively.

Crystallisation.—In a tub of 2000 litres capacity 120 kilos. of oxalic acid are dissolved in 1200 litres of water. The latter is heated to boiling, and when the oxalic acid is dissolved 100 kilos. of the moist base are added. This soon dissolves, and the volume is brought to 1800 litres, when 30 kilos. of ammonia (20 per cent.) are added in a thin stream with stirring. The mixture is allowed to settle for a short time and then filtered through a woollen cloth into a crystallising tub. The surface of the liquid is now covered with the floating lid, cut into sections, which follows the shape of the top of the tub. Crystallisation takes place mostly on the sides of the tub and on the lid and as soon as the temperature of the liquid has fallen to 18°, the lid is removed, the plug at the bottom of the tub is withdrawn, and the liquid allowed to run on to the open filter. If the temperature is allowed to fall below 18°, ammonium oxalate will separate out and mix with the crystals. After the liquid has run out of the tub, the crystals on the bottom are collected and placed in a separate filter. The crystals on the sides of the tub are then scraped off and placed on another filter together with those from the lid. After draining, the crystals are packed in woollen sacks and centrifuged.

The size of the crystals depends on the location of the crystallising tubs and on the thickness of the wood of which they are constructed. It is best to place the tubs in a quiet place, where they cannot be shaken by neighbouring machinery, and they should rest on the ground or on a stage outside the workshop. The wood used for the tubs should not be too thick, otherwise the crystals will be too large and possess all the disadvantages of large crystals.

The crystals are finally transferred to trays covered with cotton cloth—best through a wide-meshed sieve—spread on them uniformly, and dried at 50–60° in the stove.

In three batches 100 kilos. of moist base gave respectively 70·0, 68·0, and 67·5 kilos. of crystals.*

Working up of Residues.—About 70 kilos. of the recovered oil from the distillation of the leuco-base with steam (ten batches) are distilled with direct steam in the distilling pan, the oil is separated from the water in a cylindrical vessel, and dried with dry salt. This dimethylaniline is used again in the manufacture or for making methylene-blue, etc. The zinc chloride solution is filtered and used again for precipitating the dye, after its zinc chloride content has been brought up to 50 per cent. by the addition of solid zinc chloride. The lead residues from about ten batches are boiled with 2000 litres of water in one of the oxidation tubs, the mixture is allowed to settle, and, after cooling, filtered through an open filter into one of the precipitation tubs.

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* In the table setting out these figures the amount of oxalic acid used for 100 kilos. of moist base is given as 300 kilos., which appears to be an error, as 120 kilos. is the quantity stated in the text.

The dye in the filtrate is precipitated with salt and zinc chloride and filtered off. The residue is worked up with a following batch of dye. The lead sulphate is washed several times with much hot water containing a little sulphuric acid, filtered, and dried. It is used as such or converted into lead peroxide (compare Brockhoff and Fahlberg, G.P. 31669).

The zinc chloride double salt residue (200 kilos.) is stirred into boiling water (2000 litres) and hydrochloric acid (20 kilos.) added. After boiling for about thirty minutes, the mixture is allowed to settle and filtered into a tub, the residue being thrown away. From the filtrate, the base is precipitated by adding sodium hydroxide, and this is worked up as described below.

The liquors containing ammonia are distilled to recover the volatile alkali. The final liquors from the crystallisation are run from the filters into a receiver placed under the floor level, blown from here into a tub, heated at 80°, and rendered slightly alkaline with sodium hydroxide. The base separates as a tar containing only a small amount of oxalate. After cooling, this is filtered off, and the filtrate, containing sodium oxalate, is treated with calcium chloride solution, the calcium oxalate is filtered off, boiled several times with water, filtered through a filter-press, and sent to the oxalic acid recovery works. The tarry base is boiled with water and, after separation from the wash-water, this, or the base from the zinc chloride double salt residue (see above), is warmed with an equal weight of concentrated hydrochloric acid on the water-bath in an enamelled pan. The product is stirred into water at 50°, when tarry substances separate, whilst the green remains in solution. On cooling, and allowing to remain for about a day, this is filtered into a tub in which the base is precipitated hot with ammonia. For "liquid green," 50 kilos. of this base are dissolved in 40 kilos. of hydrochloric acid and 50 litres of water, the solution is allowed to cool, and filtered. The clear solution is, when necessary, weakly acidified and brought to standard with distilled water. The standard is a solution of 20 grams of Malachite green crystals in 80 grams of water. For "Marine blue," 50 kilos. of the base are dissolved in 40 kilos. of hydrochloric acid and 150 litres of water, and the solution is filtered when cold. The filtrate is heated and 22·5 kilos. of Violet 3B are sprinkled in and the whole stirred. The blue solution is brought to 250 litres with distilled water and filtered on cooling. This comes on the market as "liquid Indigo blue," "Marine blue," "Cotton blue," etc.

The following description of the manufacture, using hydrochloric acid, is given by Harmsen ("Die Fabrikation der Theerfarbstoffe und ihrer Rohmaterialien," 1889, p. 186). The condensation is effected in an enamelled or lead-lined jacketed pan fitted with a stirrer.

A mixture of 35 kilos. of dimethylaniline (free from monomethylaniline), 14 kilos. of benzaldehyde, and 31·5 kilos. of hydrochloric acid is stirred and heated at 100° for twenty-four hours. The oily, green mass is transferred to an iron pan, rendered alkaline with sodium hydroxide solution, and steam led in so as to distil off any unchanged benzaldehyde or dimethylaniline. The oil obtained in this way is used again in the manufacture. The contents of the pan are run into about 1000 litres of cold water, and the almost pure leuco-base separates in hard granules. It is filtered off and washed free from alkali and is then ready for the oxidation. This is the most difficult part of the manufacture, and its success depends on the careful preparation and analysis of the lead peroxide paste which is used as oxidising agent. It must be absolutely free from chlorine and bleaching powder, must have a neutral reaction, and contain no solid impurities. The latter point is determined by comparing the content of lead peroxide found by analysis with the weight of residue on drying. It is advisable not to use the commercial product (which is precipitated hot and then dried), but to prepare the lead peroxide in the cold and use it as paste. This is yellowish-brown and appears to be a hydrate. Before analysis, and also before each oxidation, the paste must be most carefully mixed; in one sample, the residue after drying at 100–105° is determined and in another the content of lead peroxide. This is best done by treating with sulphuric acid and oxalic acid and weighing the carbon dioxide evolved ($PbO_2 = CO_2$). A large sample of the leuco-base is now dried in order to ascertain its content, and from this is calculated the amount of lead peroxide and hydrochloric acid required to oxidise it (1 mol. of the leuco-base requires 1 mol. of hydrochloric acid and 1 atom of oxygen). Part of the hydrochloric acid is advantageously substituted by acetic acid.

The leuco-base is now melted in an enamelled pan by means of direct steam and the acid is added, when the former dissolves. The oxidation of this solution may be effected in different ways. In some works, a batch of the above size is diluted to 2500–3000 litres, and the lead peroxide paste, also mixed with much water, is run in with good stirring. In others, the solution of the leuco-base is not diluted, but is divided into small portions, each of which is cooled with ice, stirred very vigorously, and the corresponding amount of lead peroxide is added quickly. The reason for the latter process is stated to be that the carbinol formed from the leuco-base is easily further oxidised by lead peroxide. It is found, however, that slow oxidation of the dilute solution gives satisfactory results, provided that the dimethylaniline is entirely free from the monomethyl compound, and that exactly the theoretical amount of lead peroxide is employed. After adding the last portion of the peroxide, the mixture is stirred for a further two hours, filtered from unchanged lead peroxide (this is always coloured dark brown), the solution heated to boiling, and the lead precipitated as sulphate by adding a slight excess of sodium sulphate. After filtering from the lead sulphate and washing the residue, the filtrate is heated to boiling and the base precipitated by ammonia or sodium hydroxide solution. These operations are conveniently conducted in tubs set one above the other, using open filters.

The base forms a deep red mass which, on cooling, solidifies; it is filtered off, washed, centrifuged, and dried. It may be purified by dissolving in light petroleum, filtering the solution, and distilling off the solvent by means of indirect steam. The base then forms a brownish-red, molten mass.

This is now converted either into the zinc chloride double salt, $3(C_{23}H_{24}N_2,HCl),2ZnCl_2,2H_2O$, or the oxalate, $2C_{23}H_{24}N_2,3C_2H_2O_4$. To prepare the former, the carbinol is dissolved in the calculated amount of hydrochloric acid, exactly the theoretical amount of zinc chloride is added, and the solution, which has been kept as concentrated as possible, is allowed slowly to cool. The zinc salt forms brassy prisms.

The oxalate is obtained by melting the base in an enamelled or lead-lined pan fitted with a steam-jacket with three to four times its quantity of water, adding the theoretical amount of oxalic acid, filtering, and allowing to cool in a wooden tub containing wooden rods. The mother-liquor from the crystals is treated with sodium hydroxide solution to recover the base, which is worked up as zinc chloride double salt, and the oxalic acid is regenerated as calcium oxalate from the filtrate from the base by precipitation with milk of lime.

The yield of the oxalate of the dye is 138 per cent. of the dimethylaniline used. It should dissolve completely in hot water without any tarry residue or bronzy shimmer on the surface of the solution.

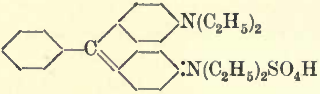
A more recent account of this process states that the mixture of benzaldehyde (1 mol.) and dimethylaniline (very little more than 2 mols.) may be heated with dry zinc chloride (equal in weight to the aldehyde employed), hydrochloric acid, sulphuric acid, anhydrous oxalic acid, or sodium hydrogen sulphate in a jacketed still at 100–110° for forty-five to forty-eight hours. After removal of the excess of benzaldehyde and dimethylaniline, 33 kilos. of the leuco-base are dissolved in 25 kilos. of ordinary hydrochloric acid and diluted with 200 litres of water; 30 kilos. of acetic acid (45–50 per cent.) are then added, and it is necessary that these two acids should be present. The solution is then oxidised in the cold (in the summer it is advisable to add some ice) with the lead peroxide paste. This must be analysed by the oxalic acid method (see above), and not by the iodometric method, as the latter gives too high results owing to the presence of crystalline peroxide, which acts neither on the leuco-base nor on oxalic acid.

The green liquid obtained by oxidation is saturated with common salt. After some time, small, glistening scales of the lead chloride double salt crystallise out and are filtered off. From the filtrate, an inferior quality of green may be obtained by adding a solution of sodium sulphate, filtering, and precipitating with zinc chloride and common salt. The crystals of the lead chloride double salt are dissolved in hot water, and the lead is precipitated by adding sodium sulphate. After filtering, ammonia is added to precipitate the base, which separates as a pink precipitate and is filtered off and washed. From it, the oxalate or zinc chloride double salt are prepared as described above. The iron double salt is occasionally prepared and the picrate is sold under the name of "spirit green" (Witt, "Triphenylmethane Colouring Matters," Thorpe's "Dictionary of Applied Chemistry," 1913, V, 533).

The earlier method of manufacturing Malachite green by condensing benzotrichloride and dimethylaniline in the presence of zinc chloride (Aktiengesellschaft für Anilinfabrikation, E.P. 828^{78}; F.P. 123187, 144169; G.P. 4322, 18959; U.S.P. 222257) and the processes of condensing benzylidene chloride with dimethylaniline in the presence of cuprous chloride (Farbenfabriken vorm. F. Bayer & Co., E.P. 1976^{78}), of oxidising the leuco-base (from benzaldehyde, dimethylaniline, and zinc chloride) with chloranil (Meister, Lucius, & Brüning, E.P. 4762^{79}; F.P. 133704; G.P. 11412), or trichloromethylsulphonyl chloride, $CCl_3 \cdot SO_2Cl$ (Espenschied, G.P. 14621) of employing potassium hydrogen sulphate as condensing agent (Aktiengesellschaft für

Anilinfabrikation, G.P. 23775) and of condensing dimethylaminobenzophenone with dimethylaniline in the presence of phosphorus trichloride (Badische Anilin- & Soda-Fabrik, E.P. 4850[84]; F.P. 160090; G.P. 27789) are of no technical interest.

Brilliant green.



Benzaldehyde and diethylaniline cannot be condensed with zinc chloride, but the condensation is effected by means of oxalic, hydrochloric, or sulphuric acid.

The manufacture, using oxalic acid, is described by Mühlhäuser ("Die Technik der Rosanilinfarbstoffe," p. 99; *Dingl. Polyt. J.*, 1887, **263**, 250). The same plant is required as is used for Malachite green (p. 81). The crystallisation is effected in two enamelled pans of 600 litres capacity, one serving for the preparation of the solution and the other for receiving the filtrate and separating the dye.

A mixture of 60 kilos. of diethylaniline and 22 kilos. of benzaldehyde is placed in the cast-iron jacketed pan, and 32 kilos. of anhydrous oxalic acid are added with stirring within one hour. The pan is then closed and heated exactly as in making Malachite green. The separation of the unattacked oil and the drying of the leuco-base are effected as described in the case of the leuco-base of Light green (p. 148). Three batches, using the above quantities, gave 76, 75, and 77 kilos., respectively, of leuco-base.

The oxidation is carried out exactly as in the case of Malachite green. The leuco-base is dissolved in hydrochloric acid, acetic acid added, and oxidation effected with lead peroxide paste. After precipitating the lead as sulphate, the mass is filtered, and the green is obtained from the filtrate as the zinc chloride double salt, which is extracted with water in the large horizontal, cylindrical pan, the base being obtained from the aqueous solution by the addition of ammonia. The yield of base from a batch (3 × 38 kilos. of leuco-base, all other quantities being as described for the leuco-base of Malachite green) was 93 kilos.

For the crystallisation, 120 kilos. of sulphuric acid and 280 litres of water are placed in an enamelled pan set in a water-bath and 100 kilos. of the colour base are stirred into the warm mixture. When the base is completely dissolved, the solution is cooled to about 20° and 130 kilos. of ammonia (16 per cent.) are introduced in a thin stream, the whole being stirred. The solution is then heated at 50–60°, at which temperature a slight separation of green is noticed; this is easily observed by spotting on filter-paper. When this slight separation has occurred, the solution is allowed to settle and then filtered through a felt filter into the second pan, in which the filtrate is rapidly heated at 85–90°. The dye then separates in golden crystals which are collected on a filter, allowed to drain, and then centrifuged. The yield of dry colour is 94 kilos. The residues from the manufacture are worked up as described in the case of Malachite green.

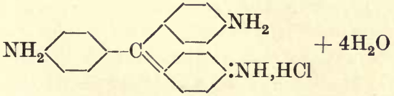
In Harmsen's process, Brilliant green is prepared by the same method as he describes for Malachite green (p. 87), 43 kilos. of pure diethylaniline being substituted for the 35 kilos. of dimethylaniline. Occasionally, the leuco-base, after the product is poured into water, separates in a tarry condition and solidification is brought about by adding acetic acid.

The dye is isolated in the form of the sulphate, and for this purpose the base is melted in an equal weight of a saturated solution of sodium sulphate in an evaporating pan and the calculated amount of sulphuric acid, previously somewhat diluted, is added with vigorous stirring. The sulphate separates in small, brassy crystals, which, after cooling, are filtered off and centrifuged. The yield is 130 per cent. of the diethylaniline (Harmsen, *loc. cit.*).

Witt (*loc. cit.*) states that the base is transformed into the sulphate by mixing it with the theoretical quantity of sulphuric acid diluted with its own weight of alcohol. The mixture forms a thick tar at first, but suddenly solidifies to a mass of well-defined crystals.

For the earlier methods of producing Brilliant green, the information given under Malachite green (end) should be consulted.

Pararosaniline.



Pararosaniline as a dye does not come on the market, but it is manufactured for the sake of the base, which is largely used for green shade spirit blues. It was formerly prepared by oxidising a mixture of *p*-toluidine and aniline with arsenic acid, or by heating a mixture of nitrobenzene, *p*-nitrotoluene, aniline, *p*-toluidine, hydrochloric acid, and iron.* Of the following processes, probably only two, namely, the *p*-nitrobenzyl chloride process and the formaldehyde process, are now used.

p-*Nitrobenzaldehyde Process.*—A mixture of 15 parts of *p*-nitrobenzaldehyde, 30 parts of aniline sulphate (or 30–32 parts of a mixture of aniline and *o*-toluidine sulphates), and 20–30 parts of zinc chloride is heated in a water- or steam-bath until the *p*-nitrobenzaldehyde has almost entirely disappeared. The reaction is greatly assisted by the addition of a small quantity of water or alcohol.

The product is dissolved in dilute hydrochloric or sulphuric acid and the nitrodiaminotriphenylmethane is precipitated by alkali and purified in a suitable way. One part of this substance is heated with two parts of solid ferrous chloride, with stirring, at 160–180° until the mass has become homogeneous and bronzy. It is boiled with dilute hydrochloric acid, and the pararosaniline in solution is isolated in the usual way, and purified (O. Fischer, E.P. 1212^{81}; G.P. 16766, 16750; U.S.P. 252202; *Ber.*, 1882, **15**, 677; Fisher and Greiff, *Ber.*, 1880, **13**, 669).

p-*Aminobenzaldehyde Process.*—Ten parts of *p*-nitrobenzaldehyde are dissolved in 50 parts of alcohol and 50 parts of hydrochloric acid added. Into this solution 12 parts of zinc powder are introduced gradually and the mass is gently warmed until the zinc is dissolved. The alcohol is then distilled off and the mass evaporated on the water-bath until it becomes pasty. A mixture of this with 17 parts of aniline hydrochloride and 10 parts of solid zinc chloride is heated at 120–140°. The paraleucaniline is isolated from the product and oxidised to pararosaniline with chloranil, manganese dioxide, or lead peroxide (O. Fischer, E.P. 1212^{81}; F.P. 141077; G.P. 16710; U.S.P. 248154).

The oxidation of the paraleucaniline is best effected as follows: A pan of about 100 litres capacity, set in a water-bath, and fitted with a stirrer and still-head leading to a condenser, is charged with 10 kilos. of paraleucaniline (dry base or paste of known contents) and 15 kilos. of acetone. The base dissolves with a few revolutions of the stirrer, which is kept in motion, and then are added to the solution 10–12 kilos. of dilute acetic

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* The addition of sodium methyl sulphate or methyl alcohol to the melt, using either arsenic acid or nitrobenzene, does not appear to be of any advantage (in the case of methyl alcohol, the operation has to be performed in an autoclave) as the patents were soon allowed to lapse (Cassella & Co., G.P. 67128, 68464).

acid, 10 litres of salt solution, and 2 kilos. of salt. The leucobase is oxidised by adding within about half an hour the calculated amount of manganese dioxide either in the form of finely-powdered pyrolusite or of Weldon mud. The cold mixture is stirred for one hour and then warmed at 60–70°, when the acetone distils. In the pan remains the pararosaniline mixed with basic manganese salts and salt solution containing acetic acid. The latter is drawn off and used for further batches or the acetic acid is recovered from it. The dye is dissolved by extracting it several times with boiling water, and the united filtrates are salted out (Farbwerke vorm. Meister, Lucius, & Brüning, G.P. 70905).

The oxidation may also be carried out using methyl or ethyl alcohol instead of acetone, in which case the condenser must be arranged so that it can be used either in the ordinary way or as a reflux condenser. The pan is charged with 10 kilos. of paraleucaniline, 15 kilos. of alcohol, 6 kilos. of salt, and 8–10 kilos. of dilute acetic acid. The mixture is heated under reflux at 60–70°, stirred rapidly, and the calculated amount of manganese dioxide is added within one hour. When the oxidation is complete, the condenser is rearranged so that most of the alcohol can be distilled off. The dye is then worked up as described above (*idem*, G.P. 72032).

p-*Nitrobenzyl Chloride Process.*—A quantitative yield of *p*-nitrobenzyl chloride cannot be obtained by the direct action of chlorine or *p*-nitrotoluene in the presence or absence of halogen carriers, as if the chlorination is carried beyond a certain point, ring-substituted chloro-derivatives and condensation products of complicated composition are formed in addition to *p*-nitrobenzyl chloride. The chlorination is stopped, therefore, when 50 per cent. of the *p*-nitrotoluene has been chlorinated, and the product consists principally of a molecular mixture of *p*-nitrotoluene and *p*-nitrobenzyl chloride. The chlorination is effected at 120–180° with or without a catalyst. When two molecular proportions of aniline are treated with one of *p*-nitrobenzyl chloride, one molecular proportion each of aniline hydrochloride and *p*-nitrobenzylaniline is produced. The operation is carried out as follows:

A large jacketed pan, of copper or cast-iron, which is fitted with a rapidly rotating stirrer and a still-head leading to a condenser and can be heated by steam, is charged with 300 kilos. of a mixture as described above, containing about 170 kilos. of *p*-nitrobenzyl chloride, and 190 kilos. of aniline. The mixture is warmed at 85–90°, when interaction takes place, as is shown by the temperature rising rapidly to 120–180° (according as to whether aniline, toluidine, or xylidine were taken). As soon as the temperature begins to fall the condensation is complete. After the mixture has cooled to about 90°, 300 litres of water are added to it and the whole is heated to boiling, when the aniline hydrochloride dissolves and can be drawn off. The insoluble residue, consisting of *p*-nitrobenzylaniline and *p*-nitrotoluene, is distilled with steam, when the latter passes over and is used again in the manufacture. The *p*-nitrobenzylaniline remains behind and can be purified, if necessary, by crystallisation from alcohol or by dissolving it in dilute acid and reprecipitating it.*

In this condensation, half of the aniline may be replaced by the carbonate or acetate of the alkali metals, or metals of the alkaline earths, or by ammonia, in which case it is advisable to add 50–100 litres of water to the batch (Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 22041^{96}; G.P. 97847).

A mixture of 250 kilos. of *p*-nitrobenzylaniline, 129 kilos. of aniline hydrochloride, and 25 kilos. of crystallised ferrous chloride (or the corresponding amount of a concentrated solution) is heated for six hours at 125–130° and finally for some time at 140°. This mass is at first grass green and contains a dye soluble in spirit with a blue colour; later, it acquires a metallic lustre and the reaction is complete when the greenish-golden mass, on cooling, becomes brittle and gives a pure magenta-red solution in spirit. This occurs usually after ten to twelve hours.

The product is extracted as in the case of ordinary magenta melts or, better, dissolved in 10 parts of water and 100 kilos. of hydrochloric acid, in which case there is almost no residue. The solution is treated with 100 kilos. of salt and allowed to cool. A small amount of dirty blue dye separates, and this is filtered off. The filtrate contains pararosaniline hydrochloride. This is precipitated by cautiously neutralising the hydrochloric acid, and recrystallised in the usual way.

The formation of the dye can be hastened by the addition of zinc chloride, and the operation can be simplified by heating a mixture of one molecular proportion of *p*-nitrobenzyl chloride and two of aniline together with a little water at 80–100° until

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* By heating *p*-nitrobenzyl chloride (1 mol.) and aniline (2 mols.) in alcoholic solution under reflux for six hours, Paal and Spenger (*Ber.*, 1897, **30**, 69) obtained *p*-nitrobenzylaniline (m. p. 72°) in 70 per cent. of the theoretical yield and, as by-product, bis-*p*-nitrobenzylaniline $(NO_2 \cdot C_6H_4 \cdot CH_2)_2N \cdot C_6H_5$ (m. p. 169°).

condensation is complete and then treating the product with ferrous chloride at 120–140° as described above (Baum, E.P. 6000^{86}; G.P. 41929).

Formaldehyde Process.

Anhydroformaldehydeaniline.—To 500 c.c. of formaldehyde solution, containing 1·838 grams of formaldehyde in 100 c.c., 25 grams of aniline are added. After one to two hours white crystals, mixed with oily lumps, separate; the latter are broken up and after some time a homogeneous mass is obtained (Wellington and Tollens, *Ber.*, 1885, **18**, 3309). The crude mass is used for the next stage.

pp′-*Diaminodiphenylmethane.*—Fifty parts of anhydroformaldehydeaniline are heated in an enamelled pan on the water-bath with 70 parts of aniline hydrochloride and excess of aniline, the whole being stirred.* The mass gradually becomes viscous, and after about twelve hours it is rendered alkaline and the excess of aniline distilled off with steam. The oil which remains solidifies to a crystalline cake of diaminodiphenylmethane.† It crystallises from benzene or water and melts at 80°.‡

The operation can be performed by introducing formaldehyde into aniline and then converting the anhydroformaldehydeaniline into diaminodiphenylmethane as above (Farbwerke vorm. Meister, Lucius, & Brüning; G.P. 53937).

Pararosaniline.—A mixture of 50 parts of anhydroformaldehydeaniline, 250 parts of aniline, 500 parts of aniline hydrochloride, 50 parts of nitrobenzene, and ferrous chloride is heated at about 170° until the melt shows a metallic lustre. The nitrobenzene and excess of aniline are removed by distillation with steam, the residue is extracted with dilute acetic acid, and the pararosaniline salted out.

In the other two examples given in this patent, the mixture containing diaminodiphenylmethane is oxidised with azobenzene

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* If a mixture of these materials is not heated, *p*-aminobenzylaniline is formed (Farbwerke vorm. Meister, Lucius, & Brüning, G.P. 87934).

† King (*Trans.*, 1920, **117**, 988) finds that crude distilled diaminodiphenylmethane is a mixture of the 4 : 4′- and 2 : 4′-derivatives in the proportions of about 9 to 1. He heated a mixture of 100 grams of solid anhydroformaldehydeaniline, 249 c.c. of aniline, 43 c.c. of water, and 130 c.c. of concentrated hydrochloric acid on the water-bath for twelve hours. The crude distilled aniline-free base boiled at 238–242°/15 mm. and amounted to 148·5 grams.

‡ The pure substance melts at 92·5°.

and arsenic acid, respectively (Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 20678^{89}; G.P. 61146).

A more recent account of this process is the following: 50 grams of aniline and 50 grams of formaldehyde solution (40 per cent.) are mixed together and when the oily mass, which soon forms, has solidified, the water is poured off and the residue rubbed with dilute acetic acid (1 : 1), the white, powdery mass collected, washed with water, and dried in the air. Fifty grams of this material are mixed with 100 grams of aniline and 70 grams of aniline hydrochloride and the whole is heated on the water-bath. The solution gradually becomes viscid and after being heated for twelve hours it is rendered alkaline with sodium hydroxide and the aniline is distilled off with steam. The oil which remains solidifies almost completely on cooling. It is dissolved in dilute hydrochloric acid and the solution fractionally precipitated with sodium carbonate solution. As soon as a colourless, instead of a dirty brown, precipitate appears, the liquid is filtered and the filtrate neutralised with sodium carbonate. The oily precipitate solidifies after some time or on stirring with a glass rod. When crystallised from dilute alcohol, the diaminodiphenylmethane melts at 80°.

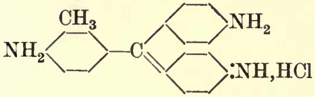
A mixture of 50 grams of aniline, 20 grams of diaminodiphenylmethane, 10 grams of aniline hydrochloride, 10 grams of nitrobenzene, and 5 grams of powdered ferrous chloride is heated first at 100° until it melts, and then with periodic stirring, for two hours at about 170°. The dark red, viscid mass is poured into 500 c.c. of water and steam passed in to drive off aniline and nitrobenzene. The residue is weakly acidified with hydrochloric acid, heated to boiling for a short time, and filtered. On cooling, small, green crystals of pararosaniline separate, which are collected. On concentrating the filtrate, a second crop is obtained, and a second extract of the residue with boiling, very dilute hydrochloric acid, and concentration of the filtrate furnishes a further amount of the dye (Möhlau and Bucherer, "Farbenchemisches Praktikum," 1908, 181).

Walter (*Bull. Soc. Mulhouse*, 1895, p. 85) prepares diaminodiphenylmethane in one operation from formaldehyde and excess of aniline; the product is boiled with hydrochloric acid, rendered alkaline, and the excess of aniline distilled off with steam. Equal molecular proportions of this, aniline hydrochloride, and nitrobenzene, in the presence of a trace of ammonium vanadate are heated at 180° to obtain pararosaniline.

Pararosaniline base is prepared in the same way as described under Magenta (below) by precipitating a solution of the dye with sodium carbonate or milk of lime.

A method for detecting pararosaniline in a mixture of rosaniline and pararosaniline consists in dissolving the substance by heating with 20 parts of 30 per cent. hydrochloric acid. If only 0·5 per cent. of pararosaniline is present the rust-coloured hydrochloride crystallises out after twelve hours, the presence of larger proportions (5–10 per cent.) is shown by immediate crystallisation on cooling. If rosaniline is dissolved in too small a volume of hydrochloric acid, the polyhydrochloride slowly separates in crystals (Lambrecht and Weil, *Ber.*, 1904, **37**, 3031).

Magenta.



The following description of the arsenic acid and nitrobenzene processes is given by Wurtz (" Progrès de l'Industrie des Matières Colorantes artificielles," 1876). His account is interesting historically, but, of course, rather out of date. Diagrams of plant are also given.

A mixture of 1000 kilos. of " aniline for red " and 1500 kilos. of a concentrated solution of arsenic acid (75 per cent.) is introduced into a still of 4000 litres capacity, set in brickwork. The still is fitted with an agitator, which is rotated during the whole time of the operation, and carries a still-head connected with a condenser. The still is heated and the temperature maintained at 190–200° for seven to eight hours, during which time oil and water distil over. When about half the aniline has passed over, the fire is drawn, the stirrer being kept in operation. The end of the process is indicated when a sample becomes brittle on cooling. Boiling water is then gradually introduced into the still to render the mass fluid. The condenser is shut off by a tap and the batch is blown into the closed extraction vessel by means of high-pressure steam. The latter vessel has a capacity of about 6000 litres, and is furnished with an agitator. About 4000 litres of water are used for the above batch and steam under 5 atmospheres pressure is blown in so that the temperature is raised to about 140°. After four to five hours the extraction is finished and the contents of the vessel are blown through a filter-press. The filtrate, on cooling to 60–70°, deposits a violet substance, and is then run to the crystallising vessels, where salt is added to it in the proportion of 120 kilos. to 100 kilos. of crude red: this converts the rosaniline arsenite and arsenate into hydrochloride and precipitates the latter, which collects on the surface of the liquid. This is collected and, after some days, the liquor is run into large reservoirs, where it deposits a further small quantity of colouring matter; the further treatment of the liquor is described below.

The rosaniline hydrochloride, precipitated as just mentioned, is now boiled with 40–50 times its weight of water. The solution is passed through a filter and allowed to cool, when magnificent crystals with an iridescent green reflex are deposited on the sides of the vat or on copper rods which dip into the solution. The mother-liquor from these crystals is precipitated by adding salt, and the rosaniline hydrochloride which separates is purified by recrystallisation as just described. The final mother-liquor which contains a yellow substance, is mixed with the filtrate from the crude hydrochloride.

The residues in the filters are taken up by boiling water and treated as crude material.

The mother-liquors from which the rosaniline hydrochloride has been salted out contain, in addition to a small amount of rosaniline, a yellow colouring matter, aniline, and sodium arsenite and arsenate. The colouring matters are precipitated by the addition of sodium carbonate and filtered off. The garnet-red precipitate contains rosaniline and chrysaniline. It is redissolved in boiling water with the addition of hydrochloric acid and reprecipitated by adding a concentrated solution of salt. The product obtained in this way is sold under the name of Garnet JOO, or yellow magenta. It is a mixture of rosaniline and chrysaniline hydrochlorides, and gives yellower shades than pure rosaniline.

In order to separate the two colouring matters, the mixture is dissolved in hot water with the addition of hydrochloric acid; on cooling, the rosaniline hydrochloride separates out and the chrysaniline salt remains in solution together with a certain amount of the former.

The filtrate from the precipitate produced by the addition of sodium carbonate contains aniline and sodium arsenite and arsenate. Excess of milk of lime is added and the liquor distilled; aniline and water pass over, and the aniline, which settles to the bottom of the cask in which the distillate is collected, is separated and the aqueous liquor, which is saturated with aniline, is used instead of water in a preceding stage of the manufacture.

The lime precipitate remaining in the still, containing the whole of the arsenic as calcium arsenite and arsenate, is stored and used in the manufacture of arsenic acids.

Rosaniline Base.—For the manufacture of aniline blue and for certain other purposes, the free base is required. The hydrochloride is dissolved in 25–30 parts of water, the solution is filtered, and a slight excess of sodium hydroxide is added. On cooling, the base separates in faintly coloured crystals. An alternative process consists in decomposing the hydrochloride with milk of lime under pressure. The crystals which deposit on cooling are treated with dilute alcohol, which dissolves the rosaniline and leaves the chrysaniline mixed with a small amount of rosaniline. The alcohol is recovered by distillation.

Treatment of the Violet Substance Precipitated on Cooling the Rosaniline Solution.—This is extracted with boiling water, which dissolves the rosaniline salt and leaves the insoluble mauvaniline. This is blue and is used in dyeing.

Treatment of the Insoluble Residues Left on Dissolving the Crude Rosaniline.—The insoluble residues left in the filter-press still contain some rosaniline, which is extracted by boiling water acidified with hydrochloric acid. The solution is filtered and precipitated by salt; the rosaniline hydrochloride which separates is purified by crystallisation as described above.

The residue, which is insoluble in acidified water, is boiled with water strongly acidified with hydrochloric acid, the solution filtered, and precipitated by milk of lime. The product is collected on a filter and is sold in paste form, under the name of Maroon; it is used for dyeing wool.

Manufacture of Rosaniline by the Nitrobenzene Process (*Coupier's Method*).—A mixture of 38 kilos. of "aniline for red," 17–20 kilos. of nitrobenzene, 18–22 kilos. of hydrochloric acid, and 2 kilos. of iron turnings is introduced into an enamelled cast-iron pan of 90 litres capacity. The condenser is an air-cooled zinc pipe, inclined at an angle of 45° and open at both ends, so that the gases can escape at the top whilst the distillate runs out at the bottom.

The mixture is heated gradually at 180° and maintained at this temperature for about five hours; towards the end it becomes thick and the temperature rises to 184–195°. When the melt is finished the still-head is removed and the contents of the pan are scooped out on to sheet-iron trays.

The crude rosaniline obtained in this way contains about 25 per cent. of aniline, which is removed by dissolving the substance in water, neutralising with milk of lime, and distilling. The calcium chloride formed precipitates rosaniline hydrochloride, which is dissolved in water, the solution filtered, and allowed to cool when the substance crystallises out.

The crude hydrochloride can also be dissolved in water, reprecipitated by salt and the aniline recovered from the filtrate by distillation with milk of lime.

The manufacture of magenta by the arsenic acid process is described by Mühlhäuser (" Die Technik der Rosanilinfarbstoffe," 1889, p. 191) as follows: The " aniline for red " used in the arsenic acid process consists of 2 parts of toluidine and 1 part of aniline, and has a specific gravity of 1·008 at 15°. As ordinary toluidine contains 36 per cent. of the para-compound, the composition of the mixture is

Aniline	33·3 per cent.
p-Toluidine	24 ,,
o-Toluidine	42·7 ,,

Three hundred and forty kilos. of this and 570 kilos. of arsenic acid solution (74° Bé. = 67·5 per cent. of As_2O_5) are placed in a cast-iron pan (2000 litres capacity), at the bottom of which is a side outlet, 18 cm. in diameter, to allow the product to be run off quickly. The lid of the pan contains a man-hole for charging and a small hole for sampling, and carries a still-head leading to a condenser, a thermometer tube, and stirring gear. It is set in brick-work and heated by gas. A second similar pan is also connected with the condenser and held in reserve. When the pan is charged it is heated slowly at 120°, the stirrer set in motion, and the heating increased as there is no fear of the contents boiling over once distillation has begun. After seven hours' heating, the temperature will have risen to 180°. Heating is continued very gently so that, after a further two hours, the temperature is 185–189°. As a rule, the melt is finished at this point. When the temperature reaches 184°, samples are taken from time to time to determine the end-point. The correct recognition of the end-point can only be learned by experience. If the batch is run out prematurely, that is, while it is still liquid, the yield of magenta will be small, whilst if it is heated for too long a time, it becomes too hard and solidifies in the pan. In the latter event, the lid must be removed and the mass chipped out, a process which is very dangerous owing to the arsenic-laden dust. As a rule, the workmen contract arsenic poisoning, which, however, can be quickly cured by means of ferrous sulphate and magnesia. It may be mentioned that during thirty years' working of the arsenic process no case has been known of the death of a workman by poisoning. At the same time, open ulcers and sores appear on the hands, and when these occur it is best to transfer the workman to another part of the works.

The course of the melt is observed by the temperature and the rate of distillation; if the latter is too quick the gas is lowered or shut off and the fire-doors are opened (if the heating is carried out by coal or coke the fire is moderated by covering it with ashes), so that the pan may be cooled by a current of cold air.

As the same quantities are always used for the melt, the same amount of distillate, consisting of water and red oil, should always be obtained, and consequently if a mark is made in the receiver to indicate the amount of distillate obtained, the operation is finished when that mark is reached; at the same time, the end of the reaction must always be checked by taking samples of the melt.

The following table shows the gradual rise in temperature of five batches. The last readings of time and temperature were made just as the sample indicated that the batch was finished and the quantity of distillate was about 330 litres.

Time.	I.	II.	III.	IV.	V.
7.30 a.m.	—	—	—	115°	—
8.0 ,,	—	115°	—	119	—
8.30 ,,	114°	120	—	121	116°
9.0 ,,	118	121	115°	126	121
9.30 ,,	121	124	119	132	125
10.0 ,,	127	130	121	140	130
10.30 ,,	132	139	125	148	138
11.0 ,,	136	150	130	153	147
11.30 ,,	144	160	138	161	158
12.0 ,,	154	168	148	167	167
12.30 p.m.	163	176	158	170	172
1.0 ,,	170	180	167	175	176
1.30 ,,	174	182	173	178	178
2.0 ,,	178	182	175	180	180
2.30 ,,	180	183	177	182	181
3.0 ,,	180	185	180	182	182
3.30 ,,	187	189	180	185	183
4.0 ,,	—	—	182	189	187
4.30 ,,	—	—	184	—	—
5.0 ,,	—	—	187	—	—
5.10 ,,	—	—	187	—	—

The dissolved and suspended oil in the aqueous distillate, called "echappé," is separated by adding 50 kilos. of salt, and rectified from a small still: 135–140 kilos. are obtained, which are used for a second melt. The echappé from this contains, however, so small an amount of *p*-toluidine that it cannot be used again for making magenta. It is therefore used for making azo-dyes or safranine, or sold for the purpose of making aniline-black.

The melt, which has been run out on to an enclosed part of the floor about 2·5 metres long, 1·8 metres wide, surrounded by a low wall about 25 cm. high, after cooling, is broken up by hand into pieces the size of one's fist and is then ready for extraction. It weighs about 575 kilos.

Extraction of the Melt.—This is effected in a horizontal cylinder, made of boiler-plate, of about 4000 litres capacity and fitted with a stirrer. Above this is fixed a pressure-filter for filtering the extract, the clear liquor from which runs into one of four rectangular iron crystallising tanks each of 4000 litres capacity, which are set on a stage 1·5 metres above the ground. A similar iron tank set on a stage above the pressure filter serves to contain the wash-water of the residue, which is run down into the horizontal cylinder and used to extract the next batch instead of pure water.

Two "crude cerise" tanks (4000 litres each), placed on the ground below the crystallising tanks, receive the filtrate from the crude magenta. After the crude cerise has been precipitated, it is skimmed off, and the liquor is run into a receiver set below the ground level, and blown through a small filter-press, set on a stage, in which the small amount of cerise still suspended in the liquor is collected. The filtrate, containing aniline, runs direct into a horizontal still (4000 litres), in which the aniline is driven over with steam.

In the first batch, the crude melt is boiled with water, but in the succeeding ones with the liquor resulting from the second extraction of the melt with water. This liquor is run into the horizontal cylinder, and, if necessary, brought to the volume of 2400 litres with water. Steam is led in until the liquid boils, the agitator is set in motion, and the crude melt is added through the man-hole. The vessel is then closed, steam led in until the pressure is 1·5 atmospheres, and stirring continued for an hour at this pressure. The steam is now shut off and the agitator stopped; the pressure falls in about one and a half hours to 0·3 atmosphere, and this is equalised by opening a tap on the man-hole lid. A blow-out pipe is now inserted, reaching to about 10 cm. above the residue in the vessel, and the liquor blown through the pressure-filter by means of steam pressure.

At the end of the filtration the blow-out pipe is replaced by another one reaching to the bottom of the vessel and the rest is filtered. In this way, stoppage of filtration, through the tarry matter settling on the filtering surface at the beginning of the operation, is avoided. The filtrate runs into one of the crystallising tanks, and at the end of the filtration the filter is opened, the cloth removed and cleaned, and the filter put in order for the next operation.

The residue in the extraction vessel still contains some dye and is therefore submitted to a second extraction. The agitator is revolved by hand to free it from any tar that may hold it to the bottom of the pan, and 2000 litres of water are run into the vessel and heated to boiling with the addition of 10 kilos. of arsenic acid. The vessel is closed, the agitator started, and the contents are heated at a pressure of 1 atmosphere for an hour. At the end of this time the agitator is stopped, the steam shut off, and the pressure in the vessel allowed to drop to 0·3 atmosphere during an hour. After equalising the pressure, the contents of the vessel are filtered as before, and the filtrate is collected in the iron tank set above it. The residue in the vessel is removed and either thrown away or worked up for the recovery of arsenic acid, or (in America) sold to farmers for destroying the potato-bug.

To the liquor in the crystallising tank is added 10 kilos. of hydrochloric acid (21° Bé.) and then 50 kilos. of salt are stirred in gradually. After three days, the crude magenta will have settled out on the sides and bottom of the tank. When the liquor is quite cold, it is run in one of the two " crude cerise " tanks where the crude cerise is obtained from it.

The crude magenta remaining in the crystallising tank is loosened and stored in a cask or transferred to the " dissolving " cylinder (see later). The mother-liquor is treated with milk of lime and sodium carbonate in order to neutralise the free acid and to precipitate the colouring matter. For this purpose, it is heated at 40° by means of direct steam and milk of lime, from 30 kilos. of quicklime, is mixed with it; afterwards, 20–25 kilos. of sodium carbonate are sprinkled in, when the crude cerise separates and collects on the top of the liquid, from which it is removed by means of perforated scoops. The liquor runs into the receiver, and is blown through the small filter-press whence it runs into the horizontal still. After ensuring that it has an alkaline reaction it is heated to boiling by means of gas and then the aniline distilled in a current of steam. Salt is added to the distillate and the aniline (6–8 kilos.) separated. The residue in the still is run away.

Crystallisation.—The plant necessary for this is analogous to that described for working up the melt. A horizontal cylinder with stirrer serves to boil the crude magenta under slight pressure, and a pressure-filter, set above it, is used to filter the solution, which then runs to one of 6 crystallising tubs, each of 3000 litres capacity. A vessel set in the ground below the tubs receives the cold mother-liquor, which is blown to a third horizontal cylinder, where it is used instead of water for extracting the crude cerise. For the first batch the cylinder is charged with 2500 litres of water, for the succeeding batches, however, with the same volume of the filtrate from rosaniline base (see p. 106); the water is boiled by means of direct steam, the agitator started, and the crude magenta added through the man-hole. Instead of the crude magenta obtained from a melt as described above, the corresponding amount of crude magenta obtained in working up the crude cerise, etc., can be used.

After the addition, the mixture is boiled for half an hour, the man-hole being left open, and at the end of this time 10 kilos. of sodium carbonate are sprinkled in slowly. The vessel is now closed and heated for about one and a half hours under a pressure of 0·5 atmosphere. The agitator is then stopped, the pressure allowed to fall to 0·3 atmosphere, and the pressure equalised with the atmosphere. The blow-out pipe is now fixed and the whole contents of the vessel are blown through the pressure filter into one of the crystallising tubs. When about one-third of the liquor has run into the tub, 18 kilos. of hydrochloric acid (21° Bé.) are added and the liquor is stirred until the whole of the filtrate has run in.

To the hot solution of rosaniline hydrochloride, 25 kilos. of salt are added within ten minutes and the solution is covered with a floating top made of eight boards cut in such a manner that a space of 2 cm. is left between the circular top and the side of the tub. Crystallisation proceeds over-night and during the two following days. The greater part of the crystals separates on the side and the lid of the tub, and the rest on the bottom. As it is desirable to have as little as possible settling on the bottom, the tubs are made rather deep, the depth being equal to the diameter. After cooling, a very pure product is obtained from the side and lid, whilst that which settles in the bottom is not quite so pure and is not of such fine appearance. When all the magenta has crystallised out and the liquor has attained the room temperature, the boards are lifted off and allowed to drain. The mother-liquor is run out of the tub into the receiver set in the ground, from which it is blown to the third horizontal cylinder, where it is used instead of water for extracting the crude cerise.

When the tub is drained, the crystals which have settled on the bottom are collected together and laid on zinc trays. The crystals on the side of the tub are then carefully loosened and also placed on zinc trays. The crystals from the lid are dried separately. The latter are sold as "Diamond magenta" or "Magenta OO," those from the side of the tub as "Magenta O" and those from the bottom as "Magenta B."

The zinc trays containing the three qualities are dried at 50–60° in about two to three days.

The average yield is, Magenta OO, 12 kilos., Magenta O, 35 kilos, and Magenta B, 16 kilos. The two former are placed on the market, whilst the last is converted into rosaniline base. For producing large crystals, the thickness of the wood of which the tubs are made should be about 3·5 cm. for a capacity of 3000 litres, the diameter and height being about the same. In four batches, such as are described above, the yields were 59, 61, 62, and 60 kilos. respectively, 30 kilos. of salt, instead of 25 kilos., having been used in the last batch.*

Rosaniline Base.—For the preparation of the base, 2000 litres of water are run into the fourth horizontal cylinder, which is identical with that used for extracting the melt, and heated to boiling with direct steam. The agitator is started and 44 kilos. of Magenta B are added during twenty minutes. When it is dissolved, 4 kilos. of sodium carbonate are added during fifteen minutes to precipitate traces of mauvaniline and chrysaniline (this residue is worked up for cerise), the whole is boiled for ten minutes longer, and the steam and agitator are stopped. In the meantime, 5 kilos. of sodium hydroxide have been dissolved in 100 litres of hot water in an open iron pan (3000 litres) fitted with a stirrer, set on a platform about 2·2 metres high. The magenta solution is now blown by steam pressure through a pressure filter set above the iron pan into the latter, the agitator in which is revolving. The red solution is decolorised and a pale red powder separates out. When filtration is complete, the contents of the pan are run down into a tub (3000 litres) and allowed to

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* From 340 kilos. of aniline, less 140 kilos. recovered, that is, 200 kilos. of aniline, 63 kilos. of Magenta would be 31·5 per cent. of the weight of the aniline entering into the reaction. Harmsen states that the yield is never more than 35 per cent.

cool for two to three days. When cold, the agitator is started and the batch is run into a receiver set in the ground, the rosaniline which has crystallised on the bottom and side of the tub is scraped off and washed into the receiver with water, and the whole is blown into a filter-press set on a platform about 4 metres above the ground (the frames of which are covered with stout cotton cloth), the filtrate running into a reservoir consisting of a rectangular iron tank (3000 litres). After blowing the press dry with compressed air, the base is washed in the press with water, and when this shows only a faint alkaline reaction, the contents of the press are again blown dry. The press-cake is spread on zinc trays and dried at 50–60°. The yield of base is 36–38 kilos.

As mentioned above, the filtrate from the base, contained in the reservoir, is conveniently used for crystallising the crude magenta, and the plant just described is arranged so that this reservoir stands on a platform just above and at the side of the cylinder used for dissolving the crude magenta. The filtrate is run into the cylinder to the overflow tap (2500 litres), heated to boiling, and the crude magenta added. As the liquor already contains 4 kilos. of sodium carbonate, only 6 kilos. are now sprinkled in and the vessel is closed and heated for two and a half hours under 0·5 atmosphere pressure. After proceeding as before, 20 kilos. of hydrochloric acid (instead of 18) are added to the filtrate, succeeded by 25 kilos. of salt and the solution is left to crystallise.

The following table shows the yields actually obtained.

Source of Crude Magenta.	Na_2CO_3. Kilos.	HCl. 21° Bé. Kilos.	NaCl. Kilos.	Yield. Kilos.
From a melt	6	20	25	63
From cerise	6	20	25	65
From the crystal residue ...	6	20	25	59
From a melt	6	20	25	62

The residue left in the cylinder and the filter is known as the "crystal residue" and is worked up as described below for "maroon," crude cerise and crude magenta being obtained as by-products (below).

Manufacture of Cerise RR.

The mother-liquor from the crystallisation of magenta, which has been run into the receiver (p. 102) is blown to the third horizontal cylinder, which is a duplicate of that used for extracting the melt and is made up, if necessary, with water to 2500 litres. This is heated to boiling, the agitator started, and the crude cerise from 3 melts added. After the addition of 40 kilos. of hydrochloric acid, the vessel is closed, steam passed in until the pressure is 1 atmosphere, and this pressure maintained for an hour. At the end of this time the steam is shut off, the pressure allowed to drop, equalised with the atmosphere, and the contents of the vessel are filtered through a pressure filter into one of four rectangular iron tanks set on a platform 1·5 metres high, the two blow-out pipes being used as described in the case of working up the crude melt (p. 102). The hot filtrate is treated with 10 kilos. of hydrochloric acid, and 20 kilos. of salt are sprinkled into it. On cooling, magenta crystallises on the sides of the tank; the crystallisation is allowed to proceed until a sample of the mother-liquor gives the standard shade on dyeing, and therefore it may not be necessary to allow the liquid to cool beyond a certain point. When this point is reached, the liquor is immediately run down into one of two similar iron tanks set on the ground. The crude magenta remaining in the top iron tank is collected, and when sufficient has been accumulated, purified as already described.

The liquor in the lower tank, which is generally lukewarm, is heated by steam at 40° if necessary and the colouring matter is precipitated by stirring in 20 kilos. of sodium carbonate, and collected by means of a scoop. The liquid, which still contains some dye, is allowed to cool completely and then run into a receiver set in the ground, from which it is blown through a filter-press. The whole of the colouring matter, namely, that which has been scooped off the liquid and that contained in the press, is brought into a steam-jacketed copper pan, where it is melted and the mother-liquor removed. To the molten mass hydrochloric acid is added, with stirring, until a sample dissolves completely in distilled water. The mixture is then evaporated in the pan at a gentle heat with frequent stirring, and, when it is sufficiently thick the mass is transferred to zinc trays, on which it is spread in a thin layer, and dried at 50–60°. When it has become fairly brittle, it is broken up into small pieces, which are dried completely and then ground. This is sold as Cerise RR. In three batches, worked up as described above, the salt used was 20, 25, and 20 kilos., respectively, and the sodium carbonate, 20, 24, and 25 kilos., the two amounts of hydrochloric acid being the same in each batch, namely, 40 and 10 kilos.

Manufacture of Cerise R.

For the production of Cerise R, a larger amount of magenta is extracted from the crude cerise than in the case of Cerise RR. The crude cerise from three melts is dissolved in 2500 litres of the mother-liquor from the crystallisation of magenta, with the addition of 35 kilos. of hydrochloric acid, the solution is filtered, and treated with 10 kilos. of hydrochloric acid and 20 kilos. of salt. The crude magenta separates on cooling and the liquor is drawn off as soon as it dyes the right shade for Cerise R. The liquor is worked up as described for Cerise RR. In three batches, the sodium carbonate used was 20, 19, and 21 kilos., respectively.

Purification of the "Crystal Residue."

The same plant is used for this as is employed for working up the crude cerise.

The horizontal cylinder is charged with 2500 litres of the mother-liquor from the crystallisation of magenta, which is heated to boiling and stirred. The residues from two crystallisations are added, together with 10 kilos. of arsenic acid, and the vessel is closed and heated by steam for an hour under a pressure of 1 atmosphere. The pressure is then allowed to fall to 0·3 atmosphere, and the contents of the vessel are filtered through the pressure filter into one of the four iron tanks. The hot filtrate is treated with 25 kilos. of hydrochloric acid and then 40 kilos. of salt are added gradually. After three days, the liquid is cold and crude magenta will have separated. From the mother-liquor a very yellow, crude cerise is precipitated by adding sodium carbonate. When sufficient of these crude products has accumulated they are worked up for pure magenta and Cerise R as already described. The residue in the extractor is broken up and removed; it is the material from which maroon is produced.

Manufacture of Maroon.

The above residue is roughly powdered, mixed, and 200 kilos. are mixed with 120 kilos. of hydrochloric acid (21° Bé.) in a tub set on a platform, 600 litres of water are added, and the whole is stirred to a thin paste. Steam is now led in and the mixture heated to boiling, during which time water is slowly run in until the total volume is 2400 litres. The whole is maintained at the boiling point for three hours and 10–12 kilos. of sodium carbonate are then added. After one to two hours it is filtered through an open filter into a tub standing a little above the ground. On the next day, the filtrate is completely precipitated by sodium carbonate and the product filtered through an open filter on the ground. The material remaining on this filter is transferred to the steam-jacketed copper pan, where it is melted and the aqueous layer removed. Hydrochloric acid is stirred in until a sample dissolves in water, and then the mixture is evaporated to a thick paste, which is then dried as described for cerise. The maroon is finally ground in a mortar-mill.

The Residues.

(1) The residue left after extracting the crude melt with water contains arsenious acid mixed with organic substances. The former is recovered by burning it in an oven, whereby arsenic is produced, which burns to arsenious oxide. This is condensed in the flue. Or the residue is heated in a coke-oven, and the arsenious oxide condensed in chambers and purified by resublimation.

(2) The arsenic liquors, containing sodium arsenite and arsenate, are evaporated (in a neutral condition) until a skin forms on the top of the liquid, mixed with powdered limestone and small coal, and the mixture is stirred until it is cold. The friable product is then dried in a muffle and finally heated to redness. The arsenic, which is evolved in a gaseous state, can be condensed, or air can be admitted to burn it to arsenious oxide, which is also condensed. The residue is lixiviated to extract the sodium carbonate, the solution being used in the magenta manufacture, and the remaining calcium carbonate can be utilised in cases where the admixture of coal ash has no disadvantage.

(3) The calcium arsenite and arsenate, precipitated by treating the liquors with milk of lime, can be dried, powdered, mixed with coal, and the mixture heated to redness, the arsenic being collected. Or the material may be mixed with the sodium carbonate necessary to convert the calcium salts into sodium salts, and the product mixed with coal and heated to redness to obtain the arsenic. Another process consists in heating the calcium salts with coal and sand, whereby the arsenic volatilises and calcium silicate remains in the retort.

(4) The organic residue, left after working up the "crystal residue" for cerise and maroon, is distilled in a horizontal retort. The aromatic bases which are condensed are separated from

water and redistilled, best in a current of steam. They consist of aniline, toluidine, xylidine, and an oil of high boiling point containing naphthylamine, acridine, and diphenylamine. The mixture is separated by fractional extraction with hydrochloric acid.

A slightly different process for the manufacture of magenta by the arsenic acid process has been given by Schoop (*Dingl. Polyt. J.*, 1885, **258**, 276), who gives the following composition of two specimens of "aniline for red":

	I.	II.
Aniline	22	16·3 per cent.
p-Toluidine	19·6	23·3 „
o-Toluidine	58·4	68·4 „

Harmsen points out that the relation of *p*- to *o*-toluidine differs greatly from that obtaining in Mühlhäuser's mixture, probably owing to Schoop's erroneous method of estimating *p*-toluidine, which depended on the insolubility of aceto-*p*-toluidide in water (*Chem. Zeit.*, 1887, **11**, 1223). Both samples also contain too little aniline for the production of a good quality of magenta.

Schoop controlled the course of the melt, not by the thermometer, but by the quantity of distillate obtained in a given time. The melt pan used by him had no outlet but had to be emptied by means of copper ladles, whilst vertical cast-iron cylinders were employed for extracting the melt under pressure, instead of horizontal, wrought-iron vessels.

From 500 kilos. of "aniline for red," 220 kilos. were recovered, a net weight of 280 kilos. yielding 100 kilos. of crystals, or a yield of about 35 per cent. of the weight of the oil used.

The following description of the nitrobenzene process is given by Harmsen ("Die Fabrikation der Theerfarbstoffe und ihrer Rohmaterialien," 1889):

In the arsenic acid process, the "aniline for red" is always of the same composition (*d* 1·008) but in the nitrobenzene process various mixtures have been proposed. The following are chiefly used:

	Parts.			Parts.	
Aniline	20	*d* 1·004	Aniline	45	*d* 1·0125
Toluidine	80		Toluidine ...	55	
Nitrobenzene ...	55		Nitrotoluene ...	62	

One of the German works uses the mixture of nitrobenzene and nitrotoluene produced by nitrating the intermediate fraction of the distillation of crude benzene. When this mixture is used, care must be taken that the nitro-compound has always the same composition, that is, the intermediate fraction should always be collected within the same range of temperature.

The size of the charge varies between 300 and 1200 kilos. of "aniline for red," according as to whether enamelled or cast-iron melt pans are used. There is no advantage in employing the former. The toluidine is mixed with the aniline and the density determined. Then two-thirds of the mixture is neutralised with the calculated quantity of hydrochloric acid either in an earthenware vessel or in an enamelled pan, and the solution is evaporated until the temperature is at least 130°. When an earthenware vessel is used, this is effected by means of a lead steam-coil resting on the bottom, whilst in the case of an enamelled pan the heating is effected by means of a steam jacket. The remaining one-third of the "aniline for red" together with the nitro-hydrocarbon is placed in the melt pan and then the evaporated hydrochloride is added from buckets. The pan is heated and when the thermometer stands at 100° the metallic iron or a solution of it in hydrochloric acid is added and the lid screwed down. The quantity of iron varies considerably. A large South German works uses 8 kilos. of iron to 400 kilos. of "aniline for red" in the nitrobenzene process and 120 kilos. of ferrous chloride in the nitrotoluene process. Another recipe employs 3 per cent. of iron filings, whilst the author finds that 2 per cent. of iron, dissolved in the calculated quantity of hydrochloric acid, is amply sufficient.

The melt pan is protected from the flame by means of an arch. Distillation begins at 110–115°, and the greater the degree of evaporation of the water from the hydrochlorides the greater is the speed of the operation [compare Witt, who evaporates the ferrous chloride as well, before starting the melt]. The vapours rise into the still-head, which is about 1·5 metres high, so that when the temperature has risen to 180° the oil which distils along with the water can condense and run back into the pan. As soon as the distillate runs in a thin stream from the end of the condenser, the stirrer is started and the temperature raised to 160°. The gas is now shut off (or the fire is drawn), as the heat in the brickwork should be sufficient to bring the temperature to 180°. The thermometer and rate of distillation are carefully watched. As the amount of water in the evaporated hydrochlorides always varies, the reaction cannot be controlled by observing the quantity of distillate. As a rule, the temperature rises from 160° to 180° in an hour. Water is now run on to the top of the pan and escapes through a hole in the upturned edge, which is 4 cm. high. If the reaction proceeds too vigorously, the fire-doors are opened. On the other hand, care must be taken that the batch is not cooled down too far. With a little practice, it is easy to control the operation without having to start heating again, and to keep the temperature within the right limits, for example, at 175–182°. The mixture turns violet at 120°, magenta being formed at 160°. Early tests show that the melt is a dull brown oil. This gradually, however, becomes bronzy and brighter and greener from hour to hour and, on cooling, viscid. After about five hours, tests are made with a long iron rod. As soon as the right consistency is reached (eight to ten hours) and the sample, after cooling, can be broken but is still not brittle, steam is led in through the hollow axis of the stirrer and the excess of "aniline for red" and nitrobenzene is distilled over and collected in a reservoir. This oil (called "melt oil") is drawn off from the bottom of the reservoir and the supernatant aqueous solution of aniline and toluidine is treated with 200 kilos. of salt and the oil collected. When only a small amount of oil distils (it is very difficult to drive it all off), the steam is turned off, the agitator stopped, and the run-out pipe (20 cm. diam.) opened, the hollow stopper being withdrawn. The melt should have the consistency of a viscid syrup and possess a yellow, metallic lustre. On cooling, it should be quite brittle; if it is still soft, either steam has been introduced too soon or the oil has not been completely driven over. In the former case, the yield of magenta will be poor, and in the latter too little "echappé" will be obtained.

The melt still contains the hydrochlorides of aniline and toluidine, ammonium chloride, and ferroso-ferric chloride. In order to remove these, the melt is run into 2000 litres of boiling water (when 400 kilos. of "aniline for red" have been employed), which is vigorously stirred, and 50 kilos. of hydrochloric acid and 100 kilos. of salt are slowly added simultaneously. The whole is allowed to cool in a copper pan and the aqueous liquor is pumped to an iron still, where the free acid is neutralised, and distilled with steam. About 10 per cent. of the original "aniline for red," free from nitro-compound, is recovered in this way, and is termed "liquor oil." The yield of "melt oil" should be 37 per cent.; it consists of a mixture of "aniline for red" containing little *p*-toluidine, and nitrobenzene (or nitrotoluene). It is either reduced in an ordinary reduction pan such as is used for making aniline, or it is used for further melts. In the latter case, 100 c.c. are mixed with 100 c.c. of hydrochloric acid (21°

Bé.) and 300 c.c. of water in a 500 c.c. measuring cylinder. From the volume of nitro-compound remaining undissolved, the specific gravity of which was known, the amount of nitro-compound in the " melt oil " is calculated. The hydrochloric acid solution is neutralised and the bases are distilled in a current of steam and the specific gravity of the oil is determined. By comparing this with the specific gravity of mixtures of known composition, the content of aniline is ascertained. The toluidine is assumed to contain 10 per cent. of *p*-toluidine, and a calculation can now be made as to how much aniline, toluidine, and nitrobenzene or nitrotoluene has to be added in order to make another charge. The following is an example of this :

Original charge :

26	kilos. of	aniline
107	,,	toluidine (36 per cent. of *p*.)
54	,,	aniline } evaporated with 287 kilos. of hydrochloric
213	,,	toluidine } acid (21° Bé.)
400	,,	" aniline for red " (*d* 1·004)
220	,,	nitrobenzene.

Recovered :

142	kilos. of	" melt oil " containing 30 per cent. of nitrobenzene. Aniline in bases = 22 per cent.
38	,,	" liquor oil " containing 25 per cent. of aniline.

	Nitrobenzene.	Aniline.	*o*-Toluidine.	*p*-Toluidine.
" Melt oil "	42	22	70	8
" Liquor oil "	—	10	25	3
	42	32	95	11
Charge requires ...	220	80	205	115
To be added	178	48	110	104

Ordinary toluidine contains 64 kilos. of *o*-toluidine to every 36 kilos. of *p*-toluidine, so that 110 kilos. of *o*-toluidine in ordinary toluidine are associated with 62 kilos. of *p*-toluidine, hence $104 - 62 = 42$ kilos. of *p*-toluidine must be added to that amount of ordinary toluidine which contains 110 kilos. of *o*-toluidine, namely, 172 kilos. For a charge in which the " echappé " oil is used, the following mixture is evaporated with 287 kilos. of hydrochloric acid (21° Bé.) :

Toluidine	172 kilos. (110 + 62)
Aniline	48 ,,
" Liquor oil "	6 ,,
p-Toluidine	41 ,,

whilst the pan is charged with

" Melt oil "	142 kilos.
" Liquor oil "	32 ,, (38–6)
p-Toluidine	1 ,,

As the melts "work" more quickly when much *p*-toluidine is present, it is easy, with some experience, to keep the addition of *p*-toluidine within the correct limits.

After the melt has been extracted in the manner described above, it forms a brittle mass with green lustre. It is broken up by hand into pieces the size of one's fist, and worked up exactly as described for the arsenic acid process. It is therefore unnecessary to repeat this description, but it may be noted that, for extracting a melt made from 400 kilos. of "aniline for red," 6000 litres of water and 16 kilos. of hydrochloric acid are usually required. The yield of crystallised magenta is not more than 42 per cent.

The isolation of cerise and maroon is also carried out as described in the arsenic acid process. Chrysaniline is separated from the dilute solutions containing cerise as follows: The magenta, leucaniline, and mauvaniline are precipitated with sodium carbonate, and the filtered solution is treated with sodium hydroxide solution, which precipitates the greenish-yellow base. This is converted into hydrochloride, the salt redissolved, the solution filtered, and the neutral filtrate salted out. The precipitate is dissolved in water, the solution filtered, and sodium hydroxide solution added to precipitate the crude chrysaniline. This is collected, washed, and dissolved in so much hot nitric acid (36° Bé.) that, on cooling, oily chrysaniline nitrate separates out. The solution is allowed to remain for several days, when the precipitate is filtered off and pressed in a hydraulic press. The cake is dried at 50° and ground, whilst the mother-liquor is precipitated with sodium hydroxide solution and the base is evaporated with hydrochloric acid, giving impure chrysaniline. The pure dye is sold as "Phosphine" and the impure as "Leather yellow." Witt ("Triphenylmethane Colouring Matters," Thorpe, "Dictionary of Applied Chemistry," vol. V, p. 539) gives the following account.

The following proportions were used by the author in regular factory work:

400	kilos. of	"aniline for red"
222	,,	hydrochloric acid, 20° Bé.
247	,,	*o*-nitrotoluene.

and the ferrous chloride prepared from

9	kilos. of	iron borings and
41	,,	hydrochloric acid.

Half of the aniline is dissolved in the 222 kilos. of hydrochloric acid, the solution of the ferrous chloride is added, and the whole evaporated in a stone still before being mixed with the remainder of the aniline and the nitrotoluene.

The nitrobenzene melt cannot be pushed so far as the arsenic acid melt. When finished, it should not solidify into a brittle mass on cooling. It should be still soft, owing to a proportion of uncombined aniline which it still contains. This aniline must be extracted by boiling with a small quantity of dilute hydrochloric acid. After its removal, the melt becomes brittle on cooling. It is worked up in the Leonhardt extractors in exactly the same manner as described for the arsenic acid melt.

The greatest care is required in regulating the temperature: at 190°, the action of the nitrobenzene becomes so violent that all the colouring matter is destroyed; the temperature should never be allowed to rise above 175°. Cold air flues and even arrangements for cooling with water or ice are therefore invariably provided in connexion with the melting pots. The size of the latter has been constantly increased, because it is easier to keep large vessels at a constant temperature than small ones. Enormous pots, capable of working one or two tons of melt, have been used. Excellent arrangements for stirring should be provided.

In describing the arsenic acid melt the author (Witt) says the mixture is gradually heated at 180° and this temperature strictly maintained during the whole operation. From eight to ten hours are required in order to complete the reaction. The enamelled iron pot is fitted with a condenser through which the vapours, etc., are condensed. When the melt is finished (judged by taking frequent samples) it is at once removed from the pot.

Following is the description of working up the arsenic acid melt: The crude melt is introduced into wrought-iron boilers, in which an eccentric horizontal stirrer is made to rotate. Water is added, the lid of the boiler is closed, and steam is introduced at a pressure of from 4 to 5 atmospheres. After several hours' vigorous stirring, the greater part of the rosaniline arsenite has been dissolved by the water. The liquid is then forced through felt into iron tanks, where it is allowed to cool down to 50°. A sufficient quantity of salt is then added to precipitate the whole of the colouring matter. Sodium arsenite is formed and remains in the liquid, whilst the colouring matter is precipitated in the shape of the chloride. It settles out as a thick, green tar of metallic lustre which solidifies into a brittle mass on cooling. The supernatant aqueous liquid is then drawn off, the crude fuchsin is chipped out, and introduced into another extractor similar to the one used for treating the melt. A very small quantity of soda ash or chalk (about 0·5 per cent. of the weight of the crude dyestuff) is added and a second extraction takes place. The liquid is again forced through felt into large wooden vats, in which some wooden boards are suspended. When the vats are filled, a small quantity of hydrochloric acid and clean butter-salt is added to each vat. In these vats the dyestuff separates out in the shape of fine, glistening, green crystals. The largest crystals are generally deposited near the surface of the liquid. When the crystallisation is finished, the mother-liquor is drawn off, and the crystals are collected and sorted according to their size and shape. The largest are sold under the name of "Diamond fuchsin."

By-products.—The residues of the first boiling may be subjected to a second extraction; as a rule, some hydrochloric acid is added in this case. A deeply-coloured solution is thus obtained from which an impure colouring matter may be precipitated by the addition of salt. This colouring matter is sold under various names (Magenta cake, Cerise, Grenadine, Maroon), and finds a ready market. It dyes a magenta colour, which is less brilliant than the shade obtained with the crystals. A third boiling is sometimes necessary. The colouring matter obtained from this is very impure. It is therefore dissolved in weak hydrochloric acid and some zinc dust is added, which reduces the magenta contained in the liquid. On precipitating with salt, a colouring matter of a brown shade is obtained, which is sold as "Nangking" or "Leather brown." The black, insoluble residue of the third boiling still contains some dark-blue colouring matters of the induline series, which, however, are not worth the trouble of extracting.

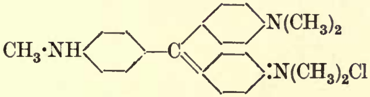
The mother-liquors from the crystals contain a yellow colouring matter of great fastness and purity. This substance, known under the name of Phosphine, belongs to another group of dyestuffs, being a salt of diaminophenylacridine. For extracting it from these mother-liquors, the latter should be acidified with hydrochloric acid, and some zinc dust added until all the fuchsin present in the liquid is reduced. The phosphine, which is not so easily reduced by zinc dust, may then be precipitated by the addition of sodium nitrate. The amount of phosphine formed varies according to the composition of the aniline oil and the temperature of the melt. It is never considerable, and very often the quantity present is so small that it is not worth while to separate it.

Witt gives the composition of " aniline for red " as the technical mixture of *o*- and *p*-toluidine (obtained by reducing the crude product of nitration of toluene : containing about 55 per cent. of *o*- and 45 per cent. of *p*-) plus half its weight of aniline. The boiling point should be 188–200° and the gravity 1·010.

Dyes belonging to the magenta group are also obtained introducing phenylglycine into the magenta melt.

A mixture of 30 kilos. of phenylglycine, 150 kilos. of *o*-toluidine hydrochloride, 45 kilos. of *o*-toluidine, 40 kilos. of *o*-nitrotoluene, and 10 kilos. of ferrous chloride are heated in the usual magenta pan at about 180–200°. The end of the reaction is indicated, as in the ordinary nitrobenzene process, when no more water passes over with the oil. The melt is boiled with water, preferably under slight pressure, freed from excess of oil by steam distillation, and the crude dye precipitated with salt. The purification is effected in the usual way by fractionally precipitating the solution with sodium carbonate or lime, and salting out. Instead of *o*-toluidine and its hydrochloride, aniline and its hydrochloride may be used (Farbwerke vorm. Meister, Lucius, & Brüning, G.P. 270930).

Methyl-violet.



The dye consists chiefly of pentamethylpararosaniline chloride, but contains also some of the tetra- and hexa-methyl derivatives.

A very detailed account of the manufacture is given by Mühlhäuser (" Die Technik der Rosanilinfarbstoffe," p. 135; *Dingl. Polyt. J.*, 1887, **264**, 37) as follows :

For a daily production of 85 kilos. of methyl-violet, five half-jacketed mixing mills (bread-kneading mills) are required, to which can be connected steam and water.

First Day.—In each mill is placed 175 kilos. of dry, finely ground salt; the agitator is started and 10 kilos. of ground and sieved copper sulphate are added. The jacket of the mill is then filled with cold water and steam introduced so as to bring it to boiling. The steam is stopped when this point is reached. In the meantime, an intimate mixture of the salt and copper sulphate has been produced by the five to ten minutes' stirring and a solution of 8 kilos. of phenol in 2 litres of water is now added to it. The liquid is immediately absorbed by the mixture, and after about ten minutes' stirring it will be homogeneous, and 20 kilos. of dimethylaniline are introduced.

When the five mills have thus been charged, the contents are raised to 55°, the man-hole is closed and the oxidation is allowed to proceed with constant agitation, the temperature being maintained at 55–60°. After about two and a half hours, or when the mass no longer gives off vapour, the lid is taken off, and the operation is continued under otherwise the same conditions for a further five and a half hours. At the end of this time, the whole of the methylaniline is converted into methyl-violet; the mass, at first fluid, and then sticky, becomes tough, and no longer adheres to the finger, that is, it no longer melts at the body-temperature, which indicates the end of the reaction.

It is best to keep the temperature at 55–60° through the whole operation, and this is effected by introducing steam or cold water into the jacket. The following variations of temperature were observed:

Temperature of mass after being stirred for ten minutes	36°
At beginning of 2nd hour	58°
,, ,, ,, 3rd ,,	59°
,, ,, ,, 4th ,,	56°
,, ,, ,, 5th ,,	55°
,, ,, ,, 6th ,,	52°
,, ,, ,, 7th ,,	57°
,, ,, ,, 8th ,,	55°

When the reaction is finished, the mass is cooled by running cold water into the jacket; the agitator is stopped and the mill revolved until the man-hole is at the bottom. On now starting the agitator, the mass drops out into a wheelbarrow placed underneath. The contents of the five mills are transferred to a flagged floor and worked into a cake about 10–12 cm. thick by means of boards laid on the top.

Second Day.—Next morning, the cake is broken up into pieces the size of one's fist, an operation which proceeds rapidly in cool weather.

For the decomposition of the copper compound, milk of lime is prepared on the evening of the same day from 40 kilos. of quicklime and 200 litres of water. After slaking, the milk of lime is passed through a sieve.

Third Day.—For decomposing the copper compound of the dye and for removing the salts soluble in water, a cylindrical iron pan, 2 metres high and 2 metres in diameter, fitted with a stirrer is required. It is fitted with two wide taps, one fixed so that the salt solution can be run off from the precipitate and the other on a flange at the bottom of the pan. An open filter, placed below the pan, serves to collect the paste which is run on to it. The pan has a capacity of 6000 litres and 3000 litres of water are run in. To this is added the milk of lime from 40 kilos. of quicklime, and then the broken-up cake gradually (a bucket at a time), the whole being vigorously stirred. Phenol and salt are dissolved whilst the violet base, calcium sulphate, and copper hydroxide are precipitated. After stirring for several hours, the dissolution of the salt and the decomposition of the copper compound are complete; this is best ascertained by exploring the bottom of the pan by means of a long rod and when no more lumps are to be perceived on the bottom the decomposition may be considered to be complete and the agitator is stopped. The contents of the pan are allowed to settle over-night, when they resolve themselves into salt solution and a muddy residue which can easily be separated by decantation.

Fourth Day.—The clear solution is run off through the higher tap, which is fixed in the side of the pan at a sufficient distance from the bottom to prevent any of the residue passing through it, into an open filter fitted with a woollen cloth. The agitator is now set going and the residue is run on to the filter, and finally the flange carrying the lower tap is taken off and the remainder of the residue is washed out of the pan by means of a hose-pipe. When no more liquid drops from the precipitate (which is frequently stirred to facilitate filtration), the paste is added to 3000 litres of water in the pan, stirred for some time, allowed to settle, and the clear liquor decanted. The residue is again brought with water to a volume of 3000 litres, mixed, and the liquor again decanted. The residue, again filtered, is allowed to drain over-night.

Fifth Day.—The conversion of the copper hydroxide, which is mixed with the violet base into copper sulphide, is brought about in a pan similar to the above and is connected with a hydrogen sulphide apparatus, the gas from which is washed before being led into the pan. An open filter serves to collect the product after treatment with hydrogen sulphide. The black residue is added to 3000 litres of water in the pan, the latter is closed, the agitator kept going, and a stream of hydrogen sulphide, prepared from crude sodium sulphide and hydrochloric acid, and washed with water, is led in. After about three hours, all copper will have been converted into sulphide; a sample, well shaken in a test-tube, should smell of hydrogen sulphide, indicating the completion of the operation.

When this point is reached, the man-hole of the pan is opened, the agitator is stopped, and the contents are allowed to settle. The liquor is decanted and the residue filtered through a filter, which is furnished with a woollen cloth. A fine paste of copper sulphide and violet base remains which is allowed to drain over-night.

Sixth Day.—The dye is extracted from this paste in a horizontal cylinder as used for extracting the magenta melt, and a filter-press, with which it is connected, serves to separate the solution of the dye from copper sulphide and tarry by-products. One of four iron tanks with disked bottoms (about 5000 litres each) receives the solution of the dye from the filter-press.

The residue of base and copper sulphide is stirred into 2500 litres of water contained in the cylinder and the mixture is treated with 50 kilos. of hydrochloric acid (*d* 1·18). Steam is led in and the whole is boiled for about ten minutes, when most of the violet dissolves. The contents of the extractor are allowed to settle and are filtered through the filter-press into the iron tank. A further extraction of the residue left in the extractor, to which is added 10 kilos. of hydrochloric acid, serves to exhaust it, but if the filtrate is deeply coloured another extraction may be necessary. The residues in the extractor and filter-press are thrown away.

The dye is precipitated from the united filtrates by adding a filtered 25 per cent. solution of salt with stirring. The salt solution is run in until a test with filter-paper shows that no more dye is in solution. The violet falls to the bottom and forms a viscid, tarry mass.

Seventh Day.—The still warm mother-liquor is run away through an open filter by means of a tap fixed a little above the surface of the crude dye. The last of the liquor is removed by inserting a funnel in the outlet from the inside of the pan and scooping the liquor through this. This operation is assisted by the fact that the pan is set up in an inclined position so that the liquor drains towards the tap. The crude violet is then collected in buckets and transferred to a tub (3000 litres) standing on a platform, in which it is dissolved. The last traces of violet are scraped out of the pan by means of a metallic scoop. The rivets in the concave bottom of the pan are sunk so that the dye is loosened without difficulty.

The crude dye is stirred into 2000 litres of boiling water contained in the tub, where it soon dissolves, any tarry admixture remaining insoluble. The liquid is allowed to settle and is filtered by means of a siphon through two open filters into one of two rectangular iron pans (5000 litres). The residue in the tub is again treated with boiling water, the quantity of which is equal to that of the residue. The second extract contains pure dye only, whilst the first always contains some salt and is therefore not so strong as the second. The residue is placed on one side and, at a convenient opportunity, is boiled out again with several other lots. About twelve to fifteen such residues are usually worked up together and the remaining insoluble matter is thrown away.

The dye is precipitated from the united filtrates by means of salt solution and allowed to settle.

Eighth Day.—The pure material, which collects as a tarry mass on the bottom of the pan, is separated from the salt solution exactly as described for the crude dye, and is transferred to a copper drying pan, where it is melted by turning steam into the jacket. Only a little steam is required and overheating of the dye is avoided by reducing the pressure of the steam to 1½ atmospheres. While the dye is being dried, it is constantly stirred with a wooden stirrer. After about six hours' heating, the mass begins to stick to the stirrer and a wrinkled skin forms on the surface, which indicates that the operation is finished. Heating is then stopped, and the dye is transferred to zinc trays by means of a copper scoop.

Ninth to Eleventh Day.—On the next day, the violet is broken up, best over the drying pan, which is now cold, and any part adhering to the trays is scraped off with a piece of hoop iron. The broken-up dye is now ground in a mortar mill and the moss-green powder transferred to about 40 drying trays, each about 0·35 sq. metre in area, which are placed in a steam-heated drying room at about 60°. After about two days, the dye is allowed to cool on the trays in a cool but dry place and (twelfth day) powdered a second time. The yield is 85–87 kilos.

When mixed with benzyl-violet it is sold as "Methyl-violet 3B" and further addition of benzyl-violet gives the marks "4B" and "5B."

A more recent account of the above process is given by Miller (*Colour Trade J.*, 1918). The first step in the process consists in drying the salt and the copper sulphate. In the present instance—a plant manufacturing approximately 250 lb.

of dye daily—the capacity of the drier should be at least 3 tons per twenty-four hours, so as to provide for unforeseen contingencies. A drying chamber, heated by steam coils and provided with blower or fan, or both, for continuous removal of moist air, is a suitable form for this purpose in spite of the labour of handling involved. The temperature of the drying chamber is maintained at 100–115° so as to ensure complete dehydration of the copper sulphate. The material is spread out on iron trays, a convenient size being 18 in. by 27 in. by 1 in.

Ordinary salt can be purchased in a finely divided state, but it will probably be found advantageous to grind the copper sulphate before incorporating it with the salt, as both the former and the latter must enter the process in a finely divided state. Any suitable type of grinder can be used which delivers the material as 20- to 40-mesh. After grinding, 700 lb. of dried salt and 35 lb. of dehydrated copper sulphate (corresponding with 54 lb. of the hydrated compound) are introduced into a 110 gallon, jacketed, heavy duty kneading machine, of which three will be required with one batch per day in each. The stirrer is started and, after half an hour, 30 lb. of molten phenol are added in a thin stream with constant stirring. The agitators, in fact, are not stopped until the end of the process. The salt, copper sulphate, and phenol are allowed to mix for fifteen minutes, the temperature is raised to 55°, and then 90 lb. of dimethylaniline are added slowly, care being taken that the temperature does not rise above 68°. After all has been added, the temperature is maintained for seven or eight hours. During this time the mass undergoes a number of colour changes, and finally assumes a characteristic glistening bronzy appearance, which is soon recognised as the end of the oxidation. Some steam is evolved at the beginning of the operation, but this eventually subsides. When oxidation has been completed, the kneading machine is turned over and the contents, while hot, are run into large iron pans about 8 ft. by 6 ft. by 6 in. placed on the floor in front of each mixer. During the reaction, the mass is of the consistency of a stiff paste, but solidifies on cooling to a hard, brittle mass, which is broken up with wooden mallets. The contents of the three mixers, representing a total of 2100 lb. of salt, 105 lb. of dehydrated copper sulphate, 270 lb. of dimethylaniline, and 90 lb. of phenol, are dissolved in about 500–600 gallons of boiling water (in a 1000 gallon wooden tank), and boiling is continued until all lumps have disappeared. To the mass are then added 126 lb. of 60 per cent. sodium sulphide and boiling is continued for about half an hour, after which 25 lb. of slaked lime and 37·5 lb. of sulphur are added. Boiling is now continued for twenty-four hours.

The mass is then filtered and washed with hot water. The filter cake consists essentially of copper sulphide and colour base, whereas the filtrate contains all the salt and phenol used, the latter probably as calcium phenoxide. The press cake is mixed with about 500 gallons of boiling water and, while boiling, sufficient hydrochloric acid is added just to obtain an acid reaction. The colour base dissolves and the copper sulphide, which is insoluble in hydrochloric acid, remains behind. The mass is allowed to settle and the supernatant solution (colour solution) is run off through a filter into an iron tank of about 2000 gallons capacity. The residue in the tank is extracted once more with boiling water (acid being added, if necessary) and the solution decanted as before. This is repeated a third time, after which the exhausted residue can be thrown away. The combined filtrates are now salted out by the addition of solid salt to the amount of 15–20 per cent. of the amount of the solution. On cooling, the methyl-violet solidifies to a bright green, glistening, resinous mass which collects along the bottom and sides of the vessel, from which it can be scraped after running off the supernatant liquor through a press. The supernatant liquor should be exhausted of colour and can therefore be run away. With proper working, the colour obtained is sufficiently pure, but, if necessary, it can be purified by redissolving and salting out. The dye is then spread out on iron trays, dried at about 60°, and ground in a ball mill.

Witt ("Triphenylmethane Colouring Matters," Thorpe, "Dictionary of Applied Chemistry," V, p. 541) remarks that the use of sodium sulphide is inconvenient in that any excess of the reagent acts as a reducing agent on the violet, transforming it into its leuco-compound, which cannot be separated from the violet, and impairs its strength, besides producing other complications. Hydrogen sulphide has no reducing action on the violet in neutral or slightly acid solutions, but the use of the gas on the large scale is extremely dangerous, and accidents, which happened repeatedly, have led to the abandonment of its use.

The following methods admit of the extraction of the violet without the use of sulphides.

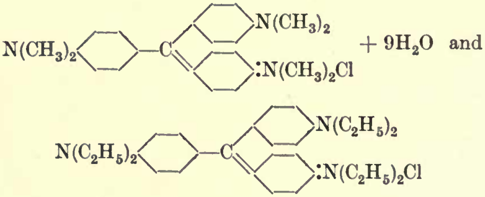
The first is based on the fact that, although the violet combines with cuprous chloride in the form of its hydrochloride, this is not the case if the two are present as sulphates. If, therefore, the crude, insoluble melt is boiled with dilute sulphuric acid, the violet dissolves together with the copper. Sodium sulphate (free from chloride) is added to precipitate the violet as sulphate, whilst the copper remains in solution. The violet sulphate is washed, redissolved, and reprecipitated as chloride by the addition of salt.

Another process, which gives equally good results, is based on the fact that the insoluble compound becomes soluble if the cuprous chloride contained in it is oxidised to cupric salt. For this purpose, the crude cake is triturated with a solution of ferric chloride. It is then filtered and washed. The violet, which has become soluble, may now be extracted with water, and precipitated by the addition of salt. It may finally be mentioned that methyl-violet is produced by heating one part of benzenesulphonyl chloride and two parts of dimethylaniline on the water-bath. In this reaction phenyl mercaptan is also formed in accordance with the equation :

$$C_6H_5{\cdot}SO_2Cl + 3C_6H_5{\cdot}N(CH_3)_2 = C_{24}H_{28}N_3Cl + 2H_2O + C_6H_5{\cdot}SH$$

(Hassenkamp, *Ber.*, 1879, 12, 1275).

Crystal violet and Ethyl purple 6B.



These dyes can be obtained (1) by condensing tetramethyldiaminobenzhydrol with dimethylaniline (for ethyl purple, the corresponding ethyl derivatives are used in this and the following process) and oxidising the resulting leuco-base with lead peroxide * (Badische Anilin- & Soda-Fabrik, E.P. 5450^{83}; F.P. 158438;

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* Details of this method of preparation of crystal violet on a small (laboratory) scale are given by Ullmann, "Organisch-Chemisches Praktikum," 1908, p. 254, and by Möhlau and Bucherer, "Farbenchemisches Praktikum," 1908, p. 183.

G.P. 27032; U.S.P. 290891, 290892, 290893); (2) by condensing leuco-auramine with dimethylaniline (Kern and Sandoz, G.P. 64270, 68144); (3) by condensing tetramethyldiaminobenzophenone and dimethylaniline in the presence of phosphorus chloride, phosphoryl chloride,* carbonyl chloride (*idem*, E.P. 4850^{84}, 5038^{84}; F.P. 160090; G.P. 27789), or trichloromethyl chloroformate (*idem*, E.P. 11159^{84}; G.P. 29962); (4) by condensing dimethylaniline with glycerol monoformate and oxidising the product with lead peroxide (Société Anonyme des Matières Colorantes et Produits chimiques de St. Denis, F.P. 213928; G.P. 61815); (5) by condensing dimethylaniline with perchloromethylmercaptan, $CCl_3{\cdot}SCl$ (Farbenfabriken vorm. F. Bayer & Co., E.P. 3149^{85}; G.P. 32829; U.S.P. 325827, 325828, 329636, 329637; Rathke, *Ber.*, 1886, **19**, 397); or (6) by condensing dimethylaniline by means of aluminium chloride with carbonyl chloride (Badische Anilin- & Soda-Fabrik, E.P. 4428^{83}; F.P. 157430; G.P. 26016; U.S.P. 290856, 290891), with chloromethyl formate or trichloromethyl chloroformate (Actien-Gesellschaft für Anilin-fabrikation, G.P. 28318, 29960 [both expired after three years]), with amyl formate (Verein Chemischer Fabriken in Mannheim, G.P. 29964 [expired after three years]), or with carbon tetrachloride (Badische Anilin- & Soda-Fabrik, E.P. 8634^{92}; G.P. 66511).

The method used at present consists in condensing dimethylaniline (or diethylaniline) with carbonyl chloride † by means of zinc chloride (Badische Anilin- & Soda-Fabrik, E.P. 11030^{84}; G.P. 29943; U.S.P. 327953), and is as follows:

Into 100 kilos. of dimethylaniline, 18–20 kilos. of carbonyl chloride are introduced at 20°, and after twenty-four hours a further 50 kilos. of dimethylaniline and 30 kilos. of powdered zinc chloride are added. The mixture is stirred and carbonyl chloride is led in at 40–50° until the weight has increased by 20 kilos.; the reaction is completed by heating for six hours at 50°. The product is rendered alkaline with sodium hydroxide and steam passed into remove dimethylaniline, and the colour base is converted into its sulphate. From the hot solution of the latter the crystalline hydrochloride of the dye can be separated by salting out.

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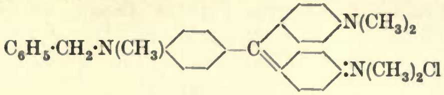
* For details on a laboratory scale see Möhlau and Bucherer, "Farbenchemisches Praktikum," 1908, p. 182.

† The use of trichloromethyl chloroformate has also been patented (Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 6311^{84}; F.P. 161522; G.P. 34607). This decomposes, on heating, in two molecular proportions of carbonyl chloride.

Benzyl-violet.



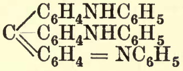
The dye consists chiefly of benzylpentamethylpararosaniline chloride, but contains also some of the benzyltetramethyl compound together with hexamethylpararosaniline chloride. The first account of its manufacture was given by Wurtz (" Progrès de l'Industrie des Matières Colorantes artificielles," 1876, p. 94). The following is a modification of this process (Mühlhäuser, " Die Technik der Rosanilinfarbstoffe," 1889, p. 146; *Dingl. Polyt. J.*, 1888, **270**, 179).

For benzylating methyl-violet, an enamelled cast-iron pan set in a water-bath is required. The lid contains a man-hole and thermometer pipe and is fitted with a reflux and an ordinary condenser. To 25 kilos. of 96 per cent. alcohol, 30 kilos. of powdered methyl-violet are added gradually, with stirring, and the mixture is heated to boiling after the ordinary condenser has been shut off. After about half an hour's heating, the dye will have dissolved and the solution is cooled to about 60°, when 18 kilos. of benzyl chloride are added. The whole is mixed for half an hour, when 24 kilos. of sodium hydroxide solution (31° Bé.) are introduced, the pan closed and heated, with constant stirring, for four hours at 80° under reflux.

When the reaction is complete, 50 litres of warm water are added and the alcohol, together with other products volatile in steam, is driven over with direct steam.

The pan is then allowed to cool a little and the contents are transferred to a tub containing warm water. The mixture is boiled by means of direct steam and the boiling mass is neutralised with 3 kilos. of hydrochloric acid (*d* 1·18). After settling for a short time, the liquid is filtered through a woollen cloth into an iron tank. The residue in the tub is boiled with water, filtered, and the united filtrate is treated with salt solution to precipitate the dye. After twelve hours, the dye will have settled on the bottom of the tank, the liquid is decanted, and the gummy dye is transferred to a tub containing hot water, which is kept boiling until the whole of the soluble portion of the crude dye has dissolved. After settling for twelve hours, the clear liquid is filtered through two thicknesses of woollen cloth into an iron container and the filtrate is salted out as described under Methyl-violet (p. 120). The dye is dried in a copper drying pan and ground in an edge runner. It forms a dull moss-green powder, the yield being 27·5 kilos.

Spirit blue.



Blue soluble in spirit is obtained by heating magenta (for the redder shades), rosaniline base (from magenta), or pararosaniline base (for the greenest shades) with excess of aniline and benzoic acid (for the greener shades), acetic acid or anhydrous sodium acetate (for the redder shades) at 180°. The shades produced depend on the degree of phenylation, whether magenta, magenta base (a mixture of rosaniline and pararosaniline), or pararosaniline is used, the purity of the aniline (for green shades, pure aniline must be employed, whilst for red shades the so-called "echappé," a mixture of aniline and *o*-toluidine, may be used), the quantity of aniline, the length of time of the operation, the temperature, and whether benzoic acid or acetic acid (sodium acetate) is employed.

The reddest shade consists of monophenylrosaniline and the greenest of triphenylpararosaniline. The shades of the various sulphonic acids prepared from this base correspond with the shades of the latter.

The patents concerned with spirit blue are: Girard and De Luire, E.P. 97^{61}; Monnet and Dury, E.P. 1939^{62}; Guinon, Marnas, and Bonnet, E.P. 2132^{62}; Collin, E.P. 2446^{62}; Eisenlohr, E.P. 3312^{62}, 541^{63}; Muller, E.P. 117^{63}; Caro and Dale, E.P. 192^{63}; Beyer, E.P. 1021^{63}; Holliday, E.P. 1148^{63}; Williams, E.P. 1173^{63}; Meister, Lucius, & Co., E.P. 1972^{63}; Smith, E.P. 2739^{63}; W. and W. H. Watson, E.P. 286^{64}; Froehling, E.P. 1199^{64}; Monnet, E.P. 1585^{65}; Schad, E.P. 2825^{65}; Phillips, E.P. 732^{66}; Nicholson, E.P. 1107^{66}, and much information on the early history of the manufacture of spirit and soluble blues is contained in the early books published on colouring matters.

The following is a detailed account of the manufacture.

The pan used for the "blue melt" is of iron and of 500 litres capacity, the diameter being 85 cm. and the height 120 cm. The plates are either cast-iron, 3 cm. in thickness, or copper, 2 mm. thick. If iron is used, it is best to line the interior of the pan with lead. The pan is set in brick-work and up to one-third of its height is surrounded by an iron jacket, 5 mm. thick, which protects it from the direct flame. The lid is bolted on, the joint being made with hemp and red lead or with a rubber ring. It carries an agitator and is furnished with a man-hole, a thermometer pipe, a hole closed by a screw plug for taking samples, a pipe leading to a condenser about 150 cm. high, 80 cm. in diameter, and containing a coil with five or six turns, a hole closed by a blind flange in which the blow-out pipe can be inserted, and a pipe connected with the compressed air supply.

On the evening before the melt is made the pan is charged successively with 250 kilos. of aniline, 25 kilos. of rosaniline base and 3 kilos. of benzoic acid. Early next morning, the agitator is started and the fire (or gas) lit. After two to three hours, the temperature should be near the boiling point of aniline. The temperature is maintained at this point so that too much aniline does not distil over.

With a properly made melt, the distillate should not exceed 10–15 per cent. of the aniline taken, that is, in the present case, 25–35 kilos. The length of the operation is eight to nine hours.

The mixture, even in the cold, is deep red, owing to the formation of the rosaniline salt and at 120° changes to reddish-violet. At 150–170°, it is bluish-violet, and at about 180° the change to blue is more gradual. It is advantageous not to put all the benzoic acid in the pan at the start, but to keep back one-seventh to one-sixth and add this at the boiling point of the mixture. The mixture boils vigorously, and much ammonia is evolved after this addition. Water and a little aniline distil up to 120°, at 140° ammonia is noticeable, and passes over, as a ten per cent. solution with more and more aniline. The distillate is transferred from time to time to a high, iron, tapering cylinder, where the aniline and water are separated by adding salt.

When the point has been reached at which two successive samples of the melt on porcelain show no difference, a more delicate test is employed. For this purpose, an alcoholic solution of spirit blue is made either from a previous good melt or from the finished colour, containing about 1 gram of spirit blue in 100 c.c. of alcohol. Of this, or, better, of a solution ten times more dilute, so much is added to 20 c.c. of alcohol in a 40 c.c. flask as will give a pale but distinct blue colour. This solution then serves as a standard for strength and shade. The determination of the strength of the blue in this case, however, is not so important as in other cases in which this method is employed.

First, the amount of blue in the melt is variable, and the latter cannot be weighed, and, secondly, in a normal melt, the maximum points of yield and brightness of the colour coincide. In order, however, always to take approximately the same amount of melt for the test, the following is the best procedure. A drop of the melt, from a long glass rod, is allowed to fall on a strip of filter-paper about 1 cm. wide and each time the same area (about half a sq. cm.) is cut off. This is boiled in a test-tube with always the same amount of alcohol, to which has been added about 0·5 per cent. of glacial acetic acid, and this solution is dropped into 20 c.c. of alcohol until it and the standard solution, held side by side, appear of equal intensity. In the case of nearly finished melts, only a very experienced eye can detect this when the solutions are being compared for strength by viewing them in a dark room in front of a gas flame. The melts must therefore never be heated until the optical test shows approximate equality in blueness, as in that case not only would a product of the desired shade not be obtained, but the yield would be low. Such a blue would be difficult to sulphonate, and would become grey on the fibre. So long as the sample shows, when viewed in front of the yellow flame, a redder shade than the standard, so long is the phenylation incomplete, but as soon as the shades are equal the reaction, if the mass is not suddenly cooled, proceeds further and the desired product is not obtained. With long contact with a large excess of aniline at 180°, triphenylrosaniline is charged into worthless products. If, however, the eye has been practised by making small experiments in the laboratory, and then work on the large scale is carried out with the same materials and apparatus, the process requires only the ordinary supervision.

The fire under the pan is at once drawn (or the gas turned off) when the final test indicates that the reaction will be completed without further heating. After about one and a half hours, the mass will be at about 150–160°, and a fresh colorimetric test, in addition to which a dyeing test on wool can be made, will show a distinct advance in the blueness. In the meantime, the quantity of the aniline distillate will have been estimated. If this has, for example, been found to be 30 kilos., this together with the amount of aniline used for the phenylation is subtracted from the original amount.

From the equation :

$$C_{20}H_{21}ON_3 + 3C_6H_5{\cdot}NH_2 = 3NH_3 + C_{20}H_{18}ON_3(C_6H_5)_3$$

the amount of aniline used is about 22 kilos. There are therefore

198 kilos. left in the pan, and for the separation of the spirit blue this and the dye base have to be converted into the hydrochlorides. Spirit blue of red shades are prepared by phenylating magenta, using sodium acetate instead of benzoic acid, exactly as described above. The following are three typical mixtures: one part of magenta, 0·25 part of sodium acetate and 5 parts of aniline (b. p. 180–183°); the same amount of magenta and sodium acetate with 3 parts of aniline (b. p. 180–185°), and the same amount of magenta and sodium acetate with 5 parts of aniline (b. p. 180–210°), the last mixture giving the reddest shade and the first the bluest.

Purification of the Greenish-blue Melt.—The melt is purified by means of hydrochloric acid (32 per cent.). As only a slight excess of this is desirable, the amount required for each base is calculated. The equivalent of an acid of the above strength is 114, so that for the aniline $\frac{198 \times 114}{93} = 242{\cdot}7$ and for the blue base $\frac{25 \times 114}{319} = 8{\cdot}9$ kilos. are required. In all, this comes to 251·6 kilos., and 260 kilos. are employed. On pouring the still warm blue solution into the hydrochloric acid, most of the blue separates in a finely divided condition. For working up the melt are required a tub for precipitating the dye and a filter for collecting it.

The tub (800 litres capacity) is lead lined and is furnished with an efficient stirrer and a lead coil lying on the bottom by which the solution can be heated. Below the tub, which is set on a platform 3 metres high, is an arrangement similar to a laboratory hot-water funnel. This large lead funnel, widened out at the upper part, has a perforated bottom fixed so that the upper part of the funnel is surrounded with warm water. A strong woollen cloth is laid on the funnel and secured on the top with a lead ring. The mixture to be separated is run on the filter, the bottom of which is connected, through a lead-lined receiver, with a vacuum pump.

When the precipitation has been carefully carried out, the blue remaining on the filter forms an extremely fine paste which may still retain its own weight of mother-liquor. This is removed by pressing. The press cakes are placed in the tub, stirred with an equal weight of hydrochloric acid, allowed to digest for a time, diluted with water, again filtered, and washed with water until the filtrate is free from hydrochloric acid and aniline. The moist mass is then laid on trays and dried at 60°. The dried material is a dusty green meal. The powdery condition is a certain guarantee of the purity, but it is so important for the later treatment that the greatest care must be taken in the precipitation to obtain this.

The melt is transferred to the tub through a pipe from the melt pan by means of compressed air. The pipe ends in a tap above the tub, so that the flow of the melt into the hydrochloric acid can be regulated and the agitator in the tub should revolve rapidly so as to break up any lumps that may be formed.

The finely powdered blue can only be obtained when it is dissolved in a large excess of aniline as in the present case, where the proportion is about 1 : 7. In other cases, and also in the preparation of reddish-blues, when less aniline is used, more lumpy precipitates are obtained which cannot be obtained in the desired state of a light powder either by repeated boiling with hydrochloric acid or by grinding when dry. It can, however, be obtained in a finely divided condition in the following way. The melt, cooled to 50°, is run into an equal weight of 95 per cent. alcohol, the blue precipitated with hydrochloric acid, cooled, filtered on the suction filter, and washed with alcohol and hydrochloric acid, finally with water. In this way, a blue is obtained in no way inferior to the above, but some blue is lost in the alcoholic solution, and loss of alcohol also occurs.

When the melt is purified without alcohol, a yield of "fine blue" of 40–43 instead of the theoretical 44·3 kilos. is obtained in addition to 2–4 kilos. of a blue of low quality.

The aqueous mother-liquors are worked up as follows:

The united filtrate and wash waters, which occupy a volume of about 800 litres, deposit some blue and benzoic acid on cooling. After collecting these, the liquid is transferred to a horizontal distilling vessel (400 cm. long and 150 cm. in diameter), which is fitted with an open steam pipe and can be heated by direct fire. Before the liquor is run into the still, milk of lime sufficient to neutralise the hydrochloric acid and liberate the aniline is introduced.

If 260 kilos. of acid have been used for the precipitation and, say, 100 kilos. for washing, these 360 kilos. of acid will require 95 kilos. of lime containing 85 per cent. of CaO.

Instead of this, 100 kilos. are taken, slaked with water, diluted to a thin cream, and transferred to the still through a sieve. When the acid liquors have been neutralised, they are heated to boiling and steam is passed in, whereby all the aniline is distilled over in seven to eight hours. The distillate is transferred to a large iron separator and salt is added to make a 15 per cent. salt solution. The aniline collects as a yellow oil and is drawn off on the following day. Table I shows the figures obtained in the above process.

TABLE I.

Rosaniline.	Aniline.	Benzoic acid.	Times.			Hydrochloric acid I.	Hydrochloric acid II.	Alcohol 95 % for precipitating.	Alcohol 85 % for washing.	Yield.		Aniline distilled from melt.	Aniline and water from melt.	Lime.	Aniline distillate.	Total aniline recovered.
			Start.	180°.	Fire drawn.					Pure.	Inferior.					
K.	K.	K.				K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.
25	250	3	6.30	10.30	12.45	260	100	—	—	40	2	30	—	—	—	—
25	250	3	6.30	10.30	12.45	260	—	250	300	40	2	30	51	70	190	220

Purification of the Reddish-blue Melt.—Although the blue from the reddish-blue melts is not obtained, as, a rule, in such a finely divided condition as the greenish-blue, it is comparatively easily sulphonated to a bright shade. Table II gives the figures obtained in this process.

TABLE II.

Magenta.	Aniline.	B. p. of aniline.	Sodium acetate.	Times.			Hydrochloric acid.	Yield.	Inferior blue.	Aniline distilled from melt.	Aniline and water from melt.	Lime.	Aniline distillate.	Total aniline recovered.
				Start.	180°.	Fire drawn.								
K.	K.		K.				K.	K.	K.	K.	K.	K.	K.	K.
25	125	180–185°	6.25	6.30	10.0	12.0	130	38	2	13	27	35	87	100·0
25	75	180–185°	6.25	6.30	9.45	11.30	75	37	1·5	7	12	20	44·5	51·5
25	75	180–210°	6.25	6.30	9.30	11.20	80	38	—	5	11·5	22	45	50·0

(C. Erhardt, *Dingl. Polyt. J.*, 1878, 230, 162, 241).

Harmsen gives an account of the process, which differs only in a few minor points from the above. As examples of the charge are mentioned the following :

For	Rosaniline base.	Magenta.	Aniline.	Recovered oil (echappé).	Benzoic acid.	Sodium acetate.
	K.	K.	K.	K.	K.	K.
Cotton blue f.f.	25	—	300	—	3	—
Alkali blue ...	50	—	500	—	5	—
Water blue G	50	—	300	—	5	—
Water blue R	—	100	300	—	—	25
Parme	—	100	—	200	—	25

[It should be noted that pararosaniline base must be used for the greenest shade blues, in which case about 4 parts of aniline may be employed.]

The melt pan is seldom of wrought iron or copper (compare Erhardt), but generally of cast-iron 25 mm. thick. At the lowest point is an outlet (50 mm. wide) fitted with a tap so that the melt can be quickly run out. The pan is heated as described by Erhardt, but for very red shades, in which less aniline is employed, the use of an oil-bath is advisable.

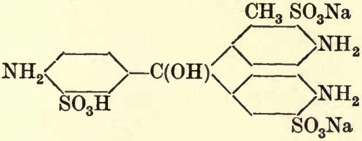
Only two-thirds of the benzoic acid is added at the beginning of the operation, the rest being introduced when the temperature has reached 180°. The yield of spirit blue is given as about 90 per cent. of the theoretical, about 82 per cent. consisting of fine blue and 8 per cent. of blue of inferior quality.

Diphenylpararosaniline is formed by heating *p*-nitrobenzaldehyde with diphenylamine and zinc chloride and reducing the nitro-compound obtained to diphenylparaleucaniline, which is also obtained by condensing *p*-aminobenzaldehyde with diphenylamine. This is then oxidised to diphenylpararosaniline. The diphenylparaleucaniline, on phenylation, gives triphenylparaleucaniline, which on oxidation furnishes triphenylpararosaniline (O. Fischer, E.P. 94^{81}, 1212^{81}; F.P. 141077; G.P. 16707, 16710; U.S.P. 248153, 252203).

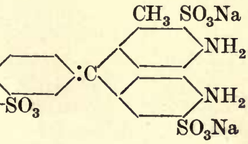
A process of obtaining triphenylpararosaniline starting from the product of interaction of formaldehyde and diphenylamine, namely, diphenyldiaminodiphenylmethane, and heating this with diphenylamine, diphenylamine hydrochloride, *o*-nitrotoluene, and ferrous chloride is of no technical interest, as the reaction does not proceed sufficiently smoothly (Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 20678^{89}; G.P. 67013).

Acid magenta.

This is a mixture of the di- and tri-sulphonic acids of rosaniline and pararosaniline, for example, the acid sodium salt of rosanilinetrisulphonic acid has the constitution



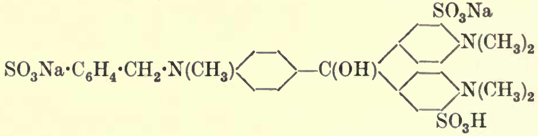
and the dye itself is



Ten kilos. of magenta dried at 110° are gradually stirred into 40 kilos. of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide), the temperature not being allowed to fall below 120° or rise above 170°. The sulphonation is finished when the viscid mass dissolves easily in water and, on being neutralised with alkali, gives no precipitate but a clear yellow solution. When this point has been reached the mass is poured into water and the solution rendered alkaline with milk of lime. The readily soluble calcium salt of the sulphonic acid is separated from calcium sulphate by filtration, converted into the corresponding sodium salt by means of sodium carbonate, and the solution evaporated to dryness. As the neutral sodium salt is hygroscopic and deliquescent, it is preferable to isolate the dye in the form of the acid sodium salt, and for this purpose the solution of the sodium salt is treated with hydrochloric acid until it is deep red, and then evaporated to dryness (Badische Anilin- & Soda-Fabrik, E.P. 3731^{77}; F.P. 122721; G.P. 2096; U.S.P. 250201).

A modification of the above process, in which only 1 kilo. of magenta is sulphonated at a time, is described by Schoop (*Chem. Zeit.*, 1887, **11**, 572), and other sulphonating agents that have been proposed are chlorosulphonic acid (Jacobsen, E.P. 2828^{79}; G.P. 8764), sulphuric acid monohydrate and sodium pyrosulphate (Farbwerke vorm. Meister, Lucius, & Brüning), and a few others of no technical interest.

Acid violet 4BN,



This is prepared either by reducing Methyl-violet to the leuco-compound, benzylating, sulphonating the product, and finally oxidising or by reducing Benzyl-violet, sulphonating the leuco-compound, and finally oxidising.

As Methyl-violet is a mixture, the product of these operations is also a mixture, the chief component of which is represented by the above formula.

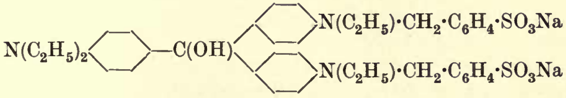
The reduction of either Methyl-violet or Benzyl-violet is carried out as follows: A solution of 10 kilos. of the dye in 40 kilos. of acetic acid (50 per cent.) is warmed at 40° and 1 kilo.

of zinc dust is gradually added to the stirred solution. The violet colour disappears completely, and the solution is filtered, diluted with 200 litres of water and the leuco-base precipitated by adding 15 kilos. of sodium carbonate. It is purified by dissolving it in dilute hydrochloric acid, filtering the solution, and reprecipitating the base with sodium hydroxide or ammonia. In the case of Methyl-violet, 10 kilos. of the dry leuco-base are mixed in an autoclave fitted with a stirrer with 3·5, 7, or 10·5 kilos. of benzyl chloride, according as to whether it is desired to introduce one, two, or three benzyl groups, and the equivalent amount of sodium hydroxide (1·1, 2·2, or 3·3 kilos. respectively) which is previously dissolved in five times its weight of water, and the mixture is heated in an oil-bath for some hours at 120–150°. The product is treated with a current of steam for several hours or dissolved in dilute hydrochloric acid, the solution filtered, the base precipitated with ammonia, and dried.

For the sulphonation, 10 kilos. of the dry base (in whichever manner prepared) are dissolved in 30 kilos. of concentrated sulphuric acid,* the solution is well cooled and so much fuming sulphuric acid is added gradually as will leave a trace of free sulphur trioxide present. The sulphonation is then finished. The sulphonated product is worked up in the usual manner and it is oxidised with lead peroxide, pyrolusite, or similar oxidising agents in acid or alkaline solution (Farbenfabriken vorm. F. Bayer & Co., E.P. 7645^{84}; F.P. 161967; G.P. 31509, A.P. 331964, 331965).

The dye is also prepared by condensing benzylmethylaniline with tetramethyldiaminobenzophenone by means of phosphoryl chloride and sulphonating the product, but no details of this preparation are given in the patent (Badische Anilin- & Soda-Fabrik, E.P. 4850^{84}, 5038^{84}; F.P. 160090; G.P. 27789; U.S.P. 297415; this describes the condensation of tetramethyldiaminobenzophenone with dibenzylaniline).

Acid violet 6B.



(1) A mixture of 22 kilos. of benzylethylaniline and 88 kilos.

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* The patent gives 66 per cent., which appears to be an error, instead of 66° Bé.

of sulphuric acid monohydrate (that is, 100 per cent.) is heated at 180° until a sample is completely soluble in water. The mass is poured into 500 litres of water, the solution neutralised with 95 kilos. of sodium carbonate, and again acidified with 20 kilos. of concentrated hydrochloric acid. There are now added 5 kilos. of formaldehyde (30 per cent.), and the mixture is boiled for half an hour. On cooling, dibenzyldiethyldiaminodiphenylmethanedisulphonic acid settles out as a viscous mass. On adding 15 kilos. of sodium carbonate, this is dissolved and the total volume of the liquid is made up to 1000 litres by adding water.

Of this solution, 200 litres are diluted with 400 litres of water in a tub fitted with a stirrer and 5·3 kilos. of lead peroxide paste (45 per cent.) are added with good stirring. A mixture of 6 kilos. of concentrated hydrochloric acid and 100 litres of water is then run in slowly, and after an hour oxidation to the hydrol is complete.

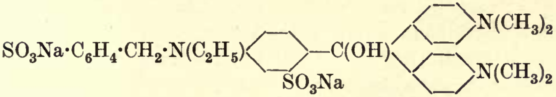
To this is immediately added 1·5 kilos. of diethylaniline (or 1·2 kilos. of dimethylaniline). The condensation of this base with the hydroldisulphonic acid proceeds fairly rapidly and is assisted by gentle warming. The end of the reaction is indicated by the change of the green colour of the solution to violet.

When this point is reached, 5·3 kilos. of lead peroxide paste (45 per cent.) are added rapidly and the solution is heated at 80°. It is then filtered, the dye salted out of the filtrate, and dried. The dye forms a bluish-violet, bronzy powder (Geigy & Co., E.P. 21284^{90}; G.P. 59811).

(2) A solution of 3 kilos. of formaldehyde (reckoned as 100 per cent.) in 50 litres of water is poured on 58 kilos. of benzylethylanilinesulphonic acid and the mixture is well stirred and warmed on the water-bath until the whole is dissolved. On standing, the liquid separates into two layers, of which the top, aqueous layer is drawn off, leaving dibenzyldiethyldiaminodiphenylmethanedisulphonic acid.

Of this, 60 kilos. are dissolved in 2000 litres of water and 12 kilos. of dimethylaniline [or the corresponding amount of diethylaniline] are added. The clear solution is treated at 40° with 20 kilos. of potassium dichromate and kept at this temperature for twenty-four hours. The deep violet liquid is filtered from the chromium precipitate and the dye is salted out (Cassella & Co., E.P. 857^{91}; F.P. 211026; G.P. 62339; U.S.P. 464538).

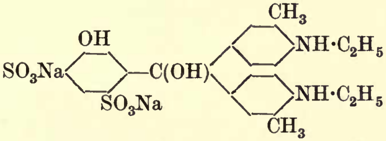
Fast acid violet 10B,



According to Schultz ("Farbstofftabellen," 1914, p. 175), this dye is obtained by condensing tetramethyldiaminobenzhydrol with benzylethylanilinedisulphonic acid and oxidising the product, whilst Georgievics and Grandmougin ("A Text-book of Dye Chemistry," Eng. translation by F. A. Mason, 1920, p. 201) state that benzylmethylanilinedisulphonic acid is employed. The latter is mentioned in the following example contained in the patent.

To a solution of 27 kilos. of tetramethyldiaminobenzhydrol in 400 kilos. of 5 per cent. sulphuric acid 40 kilos. of dry sodium benzylmethylanilinedisulphonate are added and the mixture is heated on the water-bath until the hydrol has disappeared. The acid is neutralised with sodium carbonate and the leuco-acid is precipitated by adding sodium sulphate. This is dissolved in 200 kilos. of acetic acid (50 per cent.), the solution stirred, and 48 kilos. of lead peroxide paste (50 per cent.) are added. The oxidation is complete after a short time. The lead is precipitated as sulphate by means of sulphuric acid, the solution of the dye filtered from it, and the dye precipitated by adding sodium sulphate. The dye separates in small, brass-yellow crystals. The colouring matter obtained by using benzylethylanilinedisulphonic acid shows less tendency to crystallise (Farbenfabriken vorm. F. Bayer & Co., E.P. 19062^{91}; F.P. 217020; G.P. 68291; U.S.P. 501069).

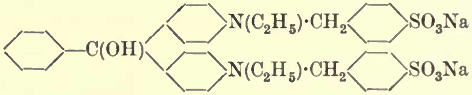
Cyanol FF.



To a mixture of 11·2 kilos. of monoethyl-*o*-toluidine and 9 kilos. of hydrochloric acid, 5 kilos. of *m*-hydroxybenzaldehyde (m. p. 103°) are added, and the whole is warmed on the water-bath for three days. The product is rendered slightly alkaline and steam passed in to remove unchanged oil. The leuco-compound is collected, washed, and dried, 14 kilos. of *m*-hydroxyphenyldiethyldiaminoditolylmethane being obtained. This compound is usually tinged green and is readily soluble in sodium hydroxide solution or hydrochloric acid.

The powdered base is added to 56 kilos. of sulphuric acid monohydrate (100 per cent.) and the mixture warmed on the water-bath until a sample dissolves in sodium carbonate solution, which takes about four hours. It is then diluted by adding ice, neutralised with milk of lime, filtered, and the solution of the calcium salt evaporated considerably. The leuco-sulphonic acid is oxidised by adding 20 kilos. of acetic acid and then 9·5 kilos. of lead peroxide, in the form of paste. The lead is precipitated by sodium sulphate and the dye is salted out by a further amount of sodium sulphate. It forms a coppery mass which is readily soluble in water to a blue solution (Cassella & Co., E.P. 15143[91]; F.P. 215835; G.P. 73717; U.S.P. 472091).

Guinea green B (A), Acid green 2BG extra conc. (t.M), New acid green 3BX (By), Sulpho green BB (P).



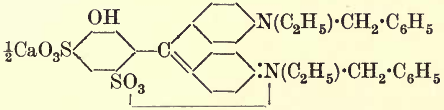
A mixture of 80 kilos. of benzylethylanilinesulphonic acid, 34 kilos. of benzaldehyde, and 30 litres of water are digested for seventy-eight hours at 110° in a pan fitted with a reflux condenser and a stirrer. The crude leuco-sulphonic acid, which is insoluble in water or alcohol but forms salts almost all of which are readily soluble in water but very sparingly so in alcohol, is neutralised with dilute sodium hydroxide solution, and water is added to bring the volume to 1000 litres. After cooling to 30°, the solution is filtered and hydrochloric acid is added until an acid reaction is obtained. The precipitated leuco-sulphonic acid is filtered off, pressed, and dried.

Of this, 100 kilos. are dissolved in 400 litres of water and 31 kilos. of sodium hydroxide solution (40° Bé.). This is cooled to below 20° and run with good stirring into a well-mixed suspension of 120 kilos. of lead peroxide (containing 34 per cent. of PbO_2) in 1500 litres of water, and then a cold (20°) solution of 45 kilos. of sulphuric acid (66° Bé.) in 300 litres of water is added rapidly.

Stirring is continued for some time and then the oxidation product is neutralised with a solution of 30 kilos. of sodium carbonate in 200 litres of water. The lead precipitate is allowed to settle, the solution is filtered, and the dye is separated from the filtrate by adding solid salt. The precipitated dye is filtered off, dissolved in 1000 litres of cold water, precipitated with salt solution, and then filtered, pressed, and dried.

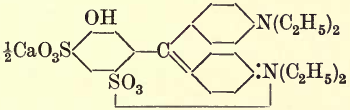
The dye is very readily soluble in water, but more sparingly so in alcohol. Weak acids precipitate the dye-acid, whilst strong acids turn the aqueous solution yellow, which changes to green on dilution. Alkali hydroxides nearly decolorise the aqueous solution (Aktien-Gesellschaft für Anilin-fabrikation, E.P. 7550^{89}; F.P. 198415; G.P. 50782).

Patent blue A,



This is prepared in an analogous manner to Patent blue V, benzylethylaniline being used instead of diethylaniline (Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 12796^{88}; F.P. 192743; G.P. 46384).

Patent blue V,



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m-Nitrobenzaldehyde is condensed with diethylaniline (2 mols.), the product is reduced, and the amino-compound converted into the hydroxy-compound by the diazo-reaction. The product, *m*-hydroxytetraethyldiaminetriphenylmethane, which can also be obtained by condensing *m*-hydroxybenzaldehyde with diethylaniline, is sulphonated and the product oxidised.

The following description of the manufacture, taken from the patent, gives no details of the first two steps in the process; these will be found, however, in the second, more recent, account.

A solution of 50 kilos. of *m*-aminotetraethyldiaminotriphenylmethane in 35 kilos. of hydrochloric acid (33 per cent.) and

5000 litres of water is cooled to 0° and a cold solution of 8·9 kilos. of sodium nitrite (96·5 per cent.) is added slowly with good stirring. The diazo-solution is slowly warmed and maintained at 60° for some time until the evolution of nitrogen becomes slight and then boiled until no more nitrogen is given off. The acid solution is rendered slightly alkaline with sodium hydroxide solution and the *m*-hydroxy-compound separates as a crystalline powder which is collected, boiled with water, and dried.

The *m*-hydroxy-compound is also obtained by heating a mixture of 20 kilos. of diethylaniline, 8 kilos. of concentrated sulphuric acid, and 9 kilos. of *m*-hydroxybenzaldehyde in a lead-lined pan fitted with a stirrer for three days (" three times twenty-four hours ") at 130°. The product is neutralised with sodium hydroxide solution and the excess of diethylaniline removed by a current of steam. The residue is boiled several times with water and then dried. The base is very readily soluble in ether, benzene, or toluene, rather more sparingly in alcohol, and insoluble in water or dilute alkali hydroxide.

A solution of 30 kilos. of *m*-hydroxytetraethyldiaminotriphenylmethane in 150 kilos. of fuming sulphuric acid (containing 10 per cent. of sulphur trioxide) is allowed to remain at the ordinary temperature until a sample gives a clear solution in dilute ammonia. The mixture is then poured into water and the solution is treated with milk of lime and the calcium salt, which is very readily soluble in water or spirit, worked up in the usual way. For the oxidation, 10 kilos. of the calcium salt just mentioned are dissolved in about 300 litres of water, the solution is treated with the calculated amount of dilute sulphuric acid and lead peroxide filtered from lead sulphate, and evaporated to dryness.

The processes of sulphonation and oxidation may be reversed as follows: To a solution of 10 kilos. of *m*-hydroxytetraethyldiaminotriphenylmethane in 8·8 kilos. of hydrochloric acid (30·8 per cent.) is added the calculated amount of manganese dioxide or lead peroxide, made into a paste, the solution being filtered and the dye salted out. Of this, 10 kilos. are dissolved in 60 kilos. of sulphuric acid monohydrate (100 per cent.) and the solution is heated at 50–60° until a sample gives a blue solution in dilute ammonia. The product is worked up in the usual way to the calcium or sodium salt (Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 12796^{88}; F.P. 192807; G.P. 46384; U.S.P. 412613, 412615; re-issue 11077).

A more recent account of this process is the following. A mixture of 140 parts of crude *m*-nitrobenzaldehyde, 308 parts of diethylaniline, and 224 grams of hydrochloric acid (33 per cent.) is well stirred and heated on the water-bath for twenty-four hours. The mixture is then rendered alkaline with sodium carbonate and steam passed through until no more oil is carried over. After cooling, the greenish-black product is separated and ground up.

The crude nitro-compound is dissolved in 10 parts of water with the aid of 1·8 parts of sulphuric acid (96 per cent.), and reduced by adding granulated zinc at about 40–60° with vigorous agitation until a sample gives a pure white precipitate on warming with a little ammonia (*d* 0·880).

The weight of zinc used varies from one-half the weight of the nitro-compound to an equal weight, and granulated zinc is to be preferred to zinc dust. Care must be taken, when a larger amount of zinc than half the weight is employed, that sufficient sulphuric acid is present. The solution is then cooled to 0° and diazotised at 0–5° with sodium nitrite (about one-sixth part). Excess of sulphuric acid must be present. The diazo-solution is allowed to remain for an hour in the cold, and then warmed gradually with continual stirring at 60°, and when the evolution of nitrogen slackens, at 100°, at which temperature it is kept for half an hour. After cooling, the solution is poured into a warm solution of sodium hydroxide and the oil which separates is washed with warm water; it solidifies on cooling and the mass is then powdered and dried.

The crude, finely powdered *m*-hydroxy-compound is gradually added to 5 parts of fuming sulphuric acid (containing 10 per cent. of sulphur trioxide) with stirring. The solid dissolves within sixteen to twenty hours and the mixture is kept at the ordinary temperature for two days. The solution is then run into 16 parts of water and allowed to remain in the cold for one or two days until no further separation of crystals occurs. The crystalline disulphonic acid is collected, washed with a little cold water, and dried in the air. The yield is about 55 per cent. of the theoretical, calculated from the crude *m*-nitrobenzaldehyde.*

The air-dried disulphonic acid, which contains $4H_2O$ (11 per cent.), is ground with half a part of calcium carbonate and boiled with 80 parts of water until effervescence ceases. After cooling, half a part of sulphuric acid (96 per cent.) diluted with 5 parts

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* Probably a further amount of the disulphonic acid, in a less pure form, could be obtained by salting out the filtrate.

of water is added, and the solution is well stirred while 0·378 part of freshly precipitated lead peroxide, mixed to a paste with 15 parts of water, is slowly added in the cold. When about 95 per cent. of the lead peroxide has been added, successive additions should be followed by small dye-trials to avoid over-oxidation. This is done by neutralising a small portion with calcium carbonate in the cold, filtering cold, and dyeing wool from an acid bath in the usual manner.

The stirring is continued for half an hour and 2 parts of calcium carbonate are added. After remaining in the cold, the liquid is filtered and evaporated carefully to dryness.

In this process, occasionally a green by-product is obtained and if it has not been removed by the treatment with calcium carbonate in the cold, the solution of Patent blue is acidified with sulphuric acid and calcium carbonate added in the cold, to precipitate the green material along with the calcium sulphate.

The constitution of Patent blue (in the form of its magnesium salt, which contains $3H_2O$) has been established by E. Erdmann and H. Erdmann (*Annalen*, 1897, **294**, 376).

Soluble blue.

It is evident that starting with ordinary rosaniline base from magenta (containing both rosaniline and pararosaniline bases) and pararosaniline base, phenylating these to mono-, di-, and tri-phenyl derivatives, and sulphonating the products (often mixtures) to mono-, di-, and tri-sulphonic acids,* or mixtures of these, a multitude of soluble blues can be obtained. Whilst the monosulphonic acids form the sharply defined class of Alkali blues, the others may be classified as follows :

Methyl Blue for Silk, Silk Blue.—Mixture of mono- and di-sulphonic acids of triphenylpararosaniline.

Methyl Blue for Cotton.—Mixture of di- and tri-sulphonic acids of triphenylpararosaniline. In this division comes also *Helvetia blue*, which is the trisulphonic acid and is prepared by an entirely different process (see p. 144).

Water Blue.—Disulphonic acids of triphenylpararosaniline and diphenylrosaniline (rosaniline from magenta variously phenylated).

Cotton Blue.—Trisulphonic acids of the preceding.

The following is a detailed account of the preparation of soluble blue. The di- and tri-sulphonic acids are more easily prepared

* The sulphonic acids of pararosaniline have been described by Bulk (*Ber.*, 1872, **5**, 419).

than the monosulphonic acid. Less sulphuric acid is required, and fuming acid only when the spirit blue is "hard" or consists of phenylrosanilines containing full amino-groups. The degree of solubility which must be reached is that the blue is soluble in neutral water. This excludes the presence of the monosulphonic acid. This point is indicated by complete solubility in 0·5 per cent. ammonia solution (see under Alkali blue). It is usual, however, to proceed either by prolonging the time of the reaction or by raising the temperature until the dye dissolves completely in strongly acid water, as results when 2–3 drops of the sulphuric acid solution are mixed with about 15 c.c. of water. In the former case, the disulphonic acid is present, and in the latter the trisulphonic acid. In most cases, 4 or even 3 parts of sulphuric acid are sufficient for 1 part of spirit blue. The latter is stirred into the sulphuric acid with the same precautions as in the case of Alkali blue, to avoid the formation of lumps, and when solution has been achieved, the temperature is raised rapidly to 60° and then slowly to 100° or 110°. The progress of the reaction (solubility) is tested from time to time. Sulphur dioxide is developed only by overheating, and its production must therefore be avoided. A spirit blue which develops sulphur dioxide in the preliminary laboratory test is best sulphonated with a mixture of ordinary and fuming sulphuric acids, the latter being added to the solution of the spirit blue in ordinary acid. One part of spirit blue is usually stirred into 3 parts of concentrated sulphuric acid, one to three parts of fuming acid are added, and the mixture is heated at 60–70°. This temperature is generally sufficiently high.

For 10 kilos. of spirit blue of good quality, using 40 kilos. of sulphuric acid, in general the temperature of sulphonation should be 90–100°, the time of sulphonation three to four hours, and the time of the whole operation one working day.

When the product consists mainly of disulphonic acid, the sulphonation mixture is added to six to eight times the quantity of water, the precipitate collected on a woollen filter, pressed, and the operation repeated.

In case the trisulphonic acid predominates and some tetrasulphonic acid is present, the mixture is added to three to four times its quantity of water.

The press cake is mixed with a little water to a paste and then dissolved in forty to fifty times the quantity of boiling water. In order to remove the sulphuric acid still present, the necessary amount of milk of lime is added. To the filtrate ammonium carbonate is added, the calcium carbonate filtered off, and the clear solution evaporated in large pans, with the addition of ammonia. In this way, the blue is obtained as a porous mass, which, when kept in a dry place, falls to a powder.

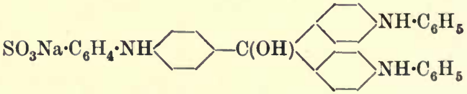
The yield is 130–140 per cent. of the spirit blue taken (C. Erhardt, *Dingl. Polyt. J.*, 1878, **230**, 342).

For the disulphonic acid (Water blue), 4 parts of sulphuric acid are used and the mixture is heated at 60–65°, whilst for the trisulphonic acid (Cotton blue) 1 part of spirit blue is added to 3 parts of sulphuric acid at 40–50° and the mixture is heated for two hours at 100°.

Patent.—Nicholson, E.P. 1857^{62}.

Helvetia Blue.—A mixture of 180 litres of a solution of sodium diphenylaminesulphonate (prepared by sulphonating the base, Merz and Weith, *Ber.*, 1873, **6**, 1512; the position of the sulphonic group has not been proved, but it is most probably in the para-position) containing 8·1 kilos. of the anhydrous salt (3 mols.), 10 litres of hydrochloric acid, and 0·75 kilo. of 40 per cent. formaldehyde solution (1 mol.), is boiled for half an hour in a pan provided with a reflux condenser. To the mixture, which is kept boiling, is added slowly during the course of an hour a mixture of 16 kilos. of a solution of ferric chloride (47 per cent.) and 100 litres of water. On cooling, the dye is filtered off, washed with a little water, dissolved by means of sodium carbonate, filtered from iron hydroxide, and the filtrate precipitated with hydrochloric acid (Geigy & Co., E.P. 12720^{92}; F.P. 223032; G.P. 73092).

Alkali blue,



When prepared from ordinary rosaniline base from magenta, the dye contains also some of the methyl derivative.

As the sulphonation of spirit blue to the monosulphonic acid is more difficult than to the polysulphonic acids, it is necessary, in the manufacture of Alkali blue, to modify the amount of sulphuric acid, the temperature, and length of treatment according to the kind of spirit blue which is employed. For sulphonation, ordinary concentrated sulphuric acid, or a mixture of this with fuming acid, is used.

All spirit blues, when in a finely divided condition, dissolve easily in excess of sulphuric acid to a brownish-red to brownish-yellow solution. The slower the introduction of the powder and the more carefully the mixture is stirred, the easier is the solution obtained. Otherwise, small lumps are formed and the temperature may easily rise above the required limit.

The spirit blue is best dissolved in an earthenware vessel or in a lead-lined iron pan, set in a water-bath.* The pan must be large enough to avoid any foaming over of the mixture. The hydrogen chloride which is evolved is removed by means of a chimney with a good draught.

In all cases the spirit blue is stirred into five to six times its weight of concentrated sulphuric acid, and occasionally this must be cooled so that the temperature does not exceed 35° in the case of fine blues and 45° in the case of inferior kinds.

When the solution is complete, four to five times the weight of sulphuric acid, or of a mixture of equal parts of sulphuric acid and fuming sulphuric acid, is added and sulphonation allowed to proceed at a moderate temperature.

All spirit blues cannot be sulphonated with the same ease, some of them, for example, the red shades, being "harder," and it is best to sulphonate by gradually raising the temperature or by adding fuming sulphuric acid, rather than to allow the reaction to proceed for a long time at a low temperature.

Laboratory experiments with quantities of 5 grams will indicate how high the sulphonation mixture may be heated without running the risk of forming higher sulphonic acids. With increase of sulphuric acid, the temperature-limit rises, but falls by the use of fuming acid. This limit depends, however, in all cases on the relative "hardness" of the spirit blue.

As a general rule, when 1 part of spirit blue is sulphonated with 10 parts of ordinary sulphuric acid, the operation satisfactorily proceeds with fine blue (from base) at 30–35°, with fine blue (from magenta) at 30–40°, very seldom at 40–45°, and with other spirit blues at 50°.

The addition of fuming sulphuric acid to the solution of spirit blue in sulphuric acid, although not absolutely necessary, greatly assists the sulphonation, and ensures that all the blue is attacked. If the fuming acid is mixed with the sulphuric acid before adding the blue, however, polysulphonic acids are formed. If it is found that these are present, it is generally better to add more spirit blue and convert the whole into Water blue. That the

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* Modern practice is to use a jacketed, enamelled pan.

stage of monosulphonation has been exceeded is shown when a sample is precipitated by water and the precipitate, on being washed, begins to dissolve.

The progress and end-point of the process can be observed by the following test. Solutions of ammonia are prepared of 8, 5, 2·5, 2, 1, and 0·5 per cent. strength. A drop of the sulphuric acid solution, from a thin glass rod, is brought into a test-tube, water is added in just sufficient amount to precipitate the blue, the precipitate is rubbed with a glass rod, about 5 c.c. of the 8 per cent. ammonia solution are added, and the mixture is heated to boiling. Most blues will completely dissolve. In the next quarter or half hour the solution in 8 per cent. ammonia will be complete and partial in the 5 per cent. solution, and so on. When the solution in the 2·5 per cent. ammonia is complete, the end-point is near; it is reached when the 2 per cent. ammonia effects solution, and exceeded when solution is obtained in the 1 per cent. ammonia, as can be seen by applying the water test mentioned above.

After reaching the end-point, the water-bath is emptied and the sulphonation mixture can now be safely left to remain for some time.

The sulphonic acid is isolated by pouring the sulphonation mixture gradually into 10 parts of water and the precipitate is collected on a woollen filter. It is transferred once or twice to the tub, in which it is stirred with water and filtered. After the last filtration, the water is allowed to drain away completely.

The sulphonic acid is converted into the sodium salt either by means of (*a*) sodium hydroxide or of (*b*) sodium carbonate.

(*a*).—The residue on the filter, consisting of about 8 parts of water to 1 part of dye, is transferred to an evaporating pan, stirred with a little more than the theoretical amount of sodium hydroxide solution, gently warmed, and the excess of sodium hydroxide removed by adding an equivalent amount of ammonium chloride. The mass is then evaporated slowly and carefully until it is pasty, when it is spread on trays and dried at about 50°.

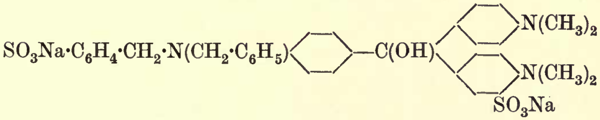
(*b*).—The residue on the filter is suspended in a tub in fifteen to twenty times its quantity of boiling water, and sodium carbonate solution is added until all has dissolved and no specks are apparent on a strip of filter-paper when some of the solution is dropped on it. One part of spirit blue requires 0·2 part of sodium carbonate (anhydrous) or 0·54 part of crystallised carbonate.

It is not advisable to evaporate such a solution, as Alkali blue is spoiled by long boiling. The dye is therefore precipitated by adding saturated salt solution. As Alkali blue is almost insoluble in a 13 per cent. salt solution, if 10 kilos. of spirit blue have been used, and brought to a volume of 200 litres, 26 kilos. of salt will be required, or the same volume of a saturated salt solution. The blue separates as a compact, bluish-black mass from which, after cooling, the supernatant liquor can be drawn off. After filtering and pressing, the dye is placed on enamelled trays and kept in the drying room at a moderate temperature until it begins to be friable. It is then extracted several times with cold water, without stirring, in order to remove the salt. The dye is then filtered again, allowed to drain, and dried at 50°. When dry, Alkali blue forms bluish-black lumps which occasionally effloresce and, especially when precipitated with salt, fall to a light blue powder. After being ground in a ball-mill, the greener it dyes and the more alkali it contains, the lighter is the powder.

The yield of Alkali blue is 125–130 per cent. of the spirit blue. The various brands (R–5R, B–5B) are obtained by mixing a few different shades of Alkali blue, 5B being the bluest shade and 5R the reddest (C. Erhardt, *Dingl. Polyt. J.*, 1878, **230**, 342).

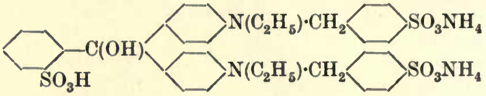
Patents: Nicholson, E.P. 1857^{62}; Monnet and Dury, E.P. 1939^{62}.

Eriocyanine A,



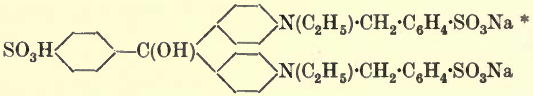
Eleven kilos. of sodium tetramethyldiaminodiphenylmethane-monosulphonate are dissolved in 1000 litres of water in a tub fitted with a stirrer and the solution is acidified with 28·5 kilos. of acetic acid. The solution is stirred vigorously and 22·8 kilos of lead peroxide paste (31·55 per cent.) are added rapidly. The oxidation is complete after half an hour. A solution of 11·5 kilos. of sodium dibenzylanilinemonosulphonate in 300 litres of water is added and the mixture heated at 80°. After about an hour, the blue colour of the liquid will have disappeared and the condensation is complete. When the solution is cold, 22·8 kilos. of lead peroxide paste (31·55 per cent.) are added, with good stirring, and when the oxidation is finished the whole is filtered and the dye salted out. In this example, the sodium dibenzylanilinemonosulphonate can be substituted by the equivalent amount of sodium dibenzylanilinedisulphonate (Geigy & Co., G.P. 88085).

Erioglaucine A (G), Acid blue EG (L), Neptune green BR (B), Alphazurine FG,



A mixture of 186 kilos. of a 10 per cent. solution of benzaldehyde-*o*-sulphonic acid and 60 kilos. of benzylethylanilinesulphonic acid is boiled under reflux for fifteen hours. The product is diluted with water to 5000 litres, acidified with hydrochloric acid, and oxidised by adding 100 kilos. of lead peroxide paste (30 per cent.). The solution is rendered alkaline with ammonia, filtered, and evaporated to dryness. The dye is a coppery powder which dissolves in water to a blue solution (Geigy & Co., E.P. 5068^{96}; F.P. 254742; G.P. 89397; U.S.P. 564801).

Light green SF yellowish,



Light green is obtained by the oxidation of dibenzyldiethyldiaminotriphenylcarbinoltrisulphonic acid. Its preparation from benzylethylaniline involves the following steps: preparation of the leuco-base, sulphonation, oxidation of the sulphonic acid, and isolation of the dye.

For a daily production of 95 kilos. of the leuco-base (Mühlhäuser, *loc. cit.*, p. 96; *Dingl. Polyt. J.*, 1887, **263**, 520), four cast-iron jacketed pans (as used for Malachite green, p. 81) are required. The speed of the stirrer is about 20 revolutions per minute. The oil remaining unchanged in the process is recovered by means of a still connected with a lead condenser, and the contents of the still can be run out into an iron-jacketed copper pan just as described under Malachite green (p. 81).

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* The calcium salt comes on the market as Acid green D (M).

Twenty-one kilos. of benzaldehyde and 80 kilos. of benzylethylaniline are placed in a pan, the stirrer is set in motion, and 34 kilos. of finely-sieved, dry, anhydrous oxalic acid are added gradually within one hour. After closing the pan, the water in the jacket is raised to 60°, and this temperature is maintained for one day. On the next two days, the water is kept at 80°, and on the fourth day it is kept boiling. In this way, the reaction proceeds very smoothly and the leuco-base is obtained as a soft green paste which contains benzaldehyde and benzoic acid. In order to neutralise the acids, the man-hole lid is taken off and 100 kilos. of sodium hydroxide solution (36° Bé.) are stirred in. The pan is closed again, the blow-out pipe inserted, and the contents are blown into the still, where the excess of benzaldehyde is distilled over by means of steam. For this purpose, the still is closed and the contents are heated to boiling with indirect steam. Direct steam is now introduced, and the benzaldehyde passes over. Distillation is carried on until nothing but water emerges from the condenser. The contents of the still are then run into the copper pan through the tap at the bottom of the still. When cold, the weakly alkaline liquor is siphoned off and the leuco-base washed with water. The alkaline liquor and the first washing are worked up for the recovery of oxalic acid. The leuco-base remaining in the copper pan is melted and stirred and kept warm for about a day until it is quite dry. When cold, it is broken up and powdered with a wooden hammer. The following table shows the yields obtained:

Benzylethylaniline.	Benzaldehyde.	Oxalic acid.	Sodium hydroxide solution.	Yield.
K.	K.	K.	K.	K.
80	21	34	100	95
80	21	34	105	92
80	21	34	98	93

Sulphonation of the Leuco-base.—For a daily production of 85 kilos. of Light green are required two cast-iron sulphonation pans similar to the condensing pans, two tubs (3000 litres) with rapid agitators, two receivers, two filter-presses, and a rectangular iron evaporating tank (about 8000 litres) fitted with a copper steam coil.

For the sulphonation, 200 kilos. of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide) are placed in a sulphonating pan (standing on the ground) and 50 kilos. of the leuco-base are added gradually with stirring, the temperature not being allowed to rise above 45°; this is easily effected by means of a rapid stream of water through the jacket. The base soon dissolves completely, some carbon dioxide and sulphur dioxide being evolved. The latter gas was contained in the fuming sulphuric acid and is expelled by the former, which owes its origin to the presence of a little oxalic acid in the base. After the base is dissolved, the mass is warmed at 80–85° and kept at this temperature for about two hours or until a sample, diluted with distilled water, is soluble in ammonia.

When the sulphonation is complete, the mass is allowed to cool, and on the next day it is blown into a wooden tub (3000 litres) standing on the ground and containing 1000 litres of water. The solution is rendered slightly alkaline with milk of lime prepared from 150 kilos. of lime, and is boiled by means of direct steam. In order to bring the calcium sulphate into an easily filterable form, about 500 litres of water are added with stirring so that the temperature falls to 60–65°. The mixture is then run into a receiver set below the ground level and filtered through a filter-press standing on the top stage (third stage). The filtrate runs into the large rectangular tank set on the second stage. The cakes left in the filter-press are allowed to fall by means of a shoot into the liming tub, boiled up with 1000 litres of water, and filtered again as described above. The calcium sulphate residue is thrown away. The united filtrates are evaporated to a volume of 1200 litres and filtered through an open filter into the oxidising tub set on the first stage, where the liquid is allowed to cool to 19–20°.

Oxidation of the Sulphonic Acid to the Dye.—The quantities of materials used for the preparation of the necessary lead peroxide are 22 kilos. of litharge, 40 kilos. of acetic acid (40 per cent.), and 27 kilos. of bleaching powder (see under Malachite green, p. 81). The blackish-brown paste is made up with water to a weight of 56 kilos.

The oxidation is carried on below 20°. The stirrer in the oxidising tub is set going rapidly and the liquid is acidified by adding 10 kilos. of sulphuric acid (67° Bé.). The lead peroxide paste is now added as rapidly as possible, when the colourless solution changes to green. After ten minutes' stirring calcium and lead are precipitated by sprinkling in about 25 kilos. of sodium carbonate. The addition of this is stopped as soon as a filtered sample gives no precipitate on dilution with water and addition of sodium carbonate solution. The mass is then heated at about 70°, run down into a receiver set below the ground, and blown through a filter-press set on the same level as the evaporating tank (second stage) which is fitted with double filter-cloths. The filtrate runs into an iron evaporating tank of 4000 litres capacity (set on the first stage) which contains a steam-coil, and is evaporated to a volume of about 600 litres; it now flows into a jacketed copper pan (of which three are required) set on the ground floor and fitted with a stirrer the arms of which are bent at the bottom in the direction in which they are revolving, and evaporated to dryness. The residue in the pan is transferred to zinc trays and completely dried in a well-ventilated drying chamber for two to three days. The dried dye is ground and is now ready for sale.

The following table gives the results of three batches, the weights being in kilos.

Leuco-base.	Fuming sulphuric acid. (20% SO_3).	Lime.	Sulphuric acid.	Litharge.	Acetic acid, 40%.	Bleaching powder.	Sodium carbonate.	Acid green.
50	200	150	10	22·3	40	27	25	85·5
50	200	160	10	22·3	40	27	20	87·0
50	200	150	10	22·3	40	27	23	88·5

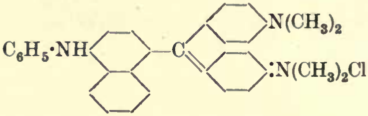
According to Harmsen (*loc. cit.*, p. 203), a mixture of 12 kilos. of benzaldehyde, 42 kilos. of benzylethylaniline, and sulphuric or anhydrous oxalic acid is heated for twenty-four hours at 110°, the slight excess of benzaldehyde is distilled off with steam, and the completely dry and finely powdered leuco-base is added to strongly fuming sulphuric acid. After heating for some time at 100°, the disulphonic acid, easily soluble in cold water, is formed. The sodium salt is prepared by neutralising with lime and treating the filtrate with sodium carbonate. The leuco-sulphonic acid is then oxidised with lead peroxide and hydrochloric acid. The dye is obtained by evaporation of the solution at a low temperature in a vacuum apparatus.

CHAPTER VIII

DIPHENYLNAPHTHYLMETHANE COLOURS

VICTORIA BLUE B—VICTORIA BLUE R—NAPHTHALENE GREEN—WOOL GREEN—ACID BLUE

Victoria blue B,



(1) To a mixture of 10 kilos. of tetramethyldiaminobenzophenone and 9 kilos. of phenyl-α-naphthylamine, 7 kilos. of phosphoryl chloride are added.* The operation is conducted in a shallow enamelled pan fitted with a stirrer and jacketed so that it can be heated or cooled. The mixture is stirred and the reaction allowed to proceed in the cold. When the semi-liquid mass shows signs of solidifying, it is warmed gradually, and the temperature is finally maintained at 110° for about fifteen minutes. On cooling, the solid product is powdered, washed with cold water, and then dissolved in about 1000 litres of boiling water. The clear liquid, after being allowed to settle and skimming, is filtered, 1 litre of hydrochloric acid added, and the dye precipitated by adding salt. It can be purified by redissolving in water and salting out (Badische Anilin- & Soda-Fabrik, E.P. 4850^{84}, 5038^{84}; F.P. 160090; G.P. 27789; U.S.P. 297414).

On being heated in a sealed tube with concentrated hydrochloric acid for six hours at 230–250°, Victoria blue B decomposes, with the production of methyl chloride, dimethylaniline, and a ketone which has probably the formula $NH_2\cdot C_6H_4\cdot CO\cdot C_{10}H_6\cdot NH\cdot C_6H_5$. When distilled by itself or mixed with soda-lime or with zinc dust, it furnishes dimethylaniline and phenyl-α-naphthylamine (Nathanson and Müller, *Ber.*, 1889, **22**, 1875).

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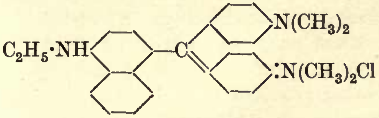
* Carbonyl chloride can also be used.

Victoria blue R,



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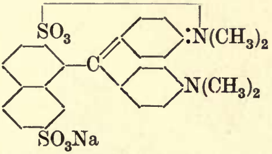
(1) To a mixture of 10 kilos. of tetramethyldiaminobenzhydrol, 6 kilos. of hydrochloric acid (*d* 1·18), and 50 litres of water, 10 kilos. of ethyl-α-naphthylamine are added and the whole is heated on the water-bath for five to six hours. The solution is rendered alkaline and excess of ethyl-α-naphthylamine is removed by a current of steam. The residual leuco-base is oxidised in dilute hydrochloric acid solution with lead peroxide as in the preparation of Malachite green (Badische Anilin- & Soda-Fabrik, E.P. 5450^{83}; F.P. 158438; G.P. 27032).

(2) To a mixture of 10 kilos. of tetramethyldiaminobenzophenone and 25 kilos. of ethyl-α-naphthylamine, 7·5 kilos. of phosphoryl chloride are added; the reaction begins in the cold and is completed on the water-bath. The deep blue, coppery product is dissolved in water, rendered alkaline with sodium hydroxide solution, and excess of ethyl-α-naphthylamine removed by a current of steam. The residue is dissolved in dilute hydrochloric acid, the solution filtered, and the dye salted out (*idem*, E.P. 4850^{84}, 5038^{84}; F.P. 160090; G.P. 27789).

Naphthalene green V.

The constitution of this dye has not been published, and it is not certain how it is prepared. It appears probable, however, that it is obtained by condensing tetramethyldiaminobenzhydrol with naphthalene-2 : 7-disulphonic acid and oxidising the product. In that case, its probable constitution is



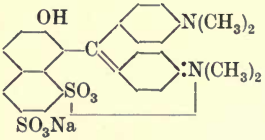
(1) A mixture of 27·0 kilos. of tetramethyldiaminobenzhydrol and 39·0 kilos. of sodium naphthalene-2 : 7-disulphonate (85 per cent.) is added to 200 kilos. of sulphuric acid (100 per cent.) with good stirring. The mass is heated in a boiling water-bath until a sample dissolves in dilute ammonia, that is, until the

hydrol has disappeared. This takes usually five to six hours. The mixture is then poured into water and the product worked up to the calcium or sodium salt in the usual way. For the oxidation, a solution of 5·0 kilos. of the leuco-salt in about 40 litres of water is mixed with the calculated amount of sulphuric acid and the mixture is added to 2·04 kilos. of lead peroxide, which has been made into a paste with water, with good stirring. The solution is filtered from lead sulphate and evaporated to dryness (Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 21839⁹⁸; F.P. 282271; G.P. 110086; compare also E.P. 21596⁹⁸; F.P. 282128 and addition of May 20, 1899; G.P. 108129; describing the condensation of the hydrol with naphthalene, sulphonation, and subsequent oxidation).

(2) 14·9 Kilos. of *p*-dimethylaminobenzaldehyde, 16 kilos. of dimethylaniline and 39·6 kilos. of sodium naphthalene-2 : 7-disulphonate (83·9 per cent.) are stirred in 100 kilos. of sulphuric acid (100 per cent.) for about seventy-two hours at 110°, the product is poured into water, neutralised with lime, filtered, the alkaline filtrate acidified with sulphuric acid, filtered, and the filtrate made up to 1200 litres. This is oxidised with the necessary amount of acid and lead peroxide, and the solution, filtered from lead sulphate, evaporated to dryness (Anilinfarben- & Extrakt-Fabriken vorm. J. R. Geigy, G.P. 169929).

Wool green S and Wool green BS.

Wool green S is probably prepared by condensing tetramethyldiaminobenzhydrol with β-naphthol, sulphonating the product, and finally oxidising,* and Wool green BS by condensing the hydrol with β-naphthol-6 : 8-disulphonic acid and oxidising. The latter possibly has the constitution



Wool Green S.—8·1 Kilos. of tetramethyldiaminobenzhydrol are dissolved in 50 kilos. of concentrated sulphuric acid, with

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* The condensation of tetramethyldiaminobenzophenone with β-naphthol in the presence of phosphoryl chloride and zinc chloride, and sulphonation of the product, apparently yields a blue dye (Ewer and Pick, G.P. 31321).

stirring. After the warm mass has cooled, 4·4 kilos. of β-naphthol are gradually added, with stirring, the temperature not being allowed to exceed 20°. When the reaction is complete, the mass is poured on ice, diluted to 350 litres, and a concentrated solution of sodium hydroxide added until only a weakly acid reaction is indicated. The leuco-base is then precipitated by adding sodium acetate, and dried. Of this base, 11·9 kilos. are gradually added, with cooling, to 60 kilos. of fuming sulphuric acid (containing 20 per cent. of sulphur dioxide), the mixture allowed to remain for twenty-four hours, and the sulphonation completed by warming at 60–70°. The operation is finished when a sample dissolves in excess of ammonia.

The mixture is poured on ice, nearly neutralised with sodium hydroxide solution, and the leuco-sulphonic acid precipitated by adding sodium acetate. The precipitate is suspended in 100 litres of water, 3·5 kilos. of concentrated sulphuric acid are added, the liquid is cooled, and oxidised by the addition of 35 kilos. of lead peroxide paste (20 per cent.). The filtrate from lead sulphate is exactly neutralised with sodium hydroxide solution, and the dye separates as a deep green precipitate (Farbenfabriken vorm. F. Bayer & Co., E.P. 14621^{90}; F.P. 208330; G.P. 58483).

Wool Green BS.—An intimate mixture of 8·1 kilos. of tetramethyldiaminobenzhydrol and 11·4 kilos. of β-naphthol-6 : 8-disulphonic acid (G) is added with stirring to 70 kilos. of concentrated sulphuric acid (66° Bé.). The mass becomes warm and acquires a dark brown colour. When the reaction is complete, it is poured into 300 litres of water, and if the clear brown solution is allowed to remain for some time, white crystals of the leuco-sulphonic acid separate. Only about 60 per cent. of this is obtained, the rest remaining in solution. On filtration and washing, the leuco-sulphonic acid forms a white crystalline powder. The rest of the leuco-sulphonic acid is obtained from the filtrate through the calcium salt, the concentrated aqueous solution of which, on acidification with hydrochloric acid, furnishes the sulphonic acid.*

For the oxidation, 10 kilos. of the leuco-sulphonic acid are dissolved in 200 litres of hot water, 1·8 kilos. of concentrated sulphuric acid added, and the solution is cooled until the leuco-sulphonic acid just begins to crystallise out. There are then added 21 kilos. of lead peroxide paste (20 per cent.) and after

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* Instead of allowing the leuco-sulphonic acid to crystallise out, it would appear simpler to convert the whole into the calcium salt and proceed as above.

the oxidation is complete, the lead sulphate is filtered off and the filtrate evaporated (*idem*, *ibid.*).

Acid blue B,

$$\underset{OH}{C}\begin{cases} C_6H_4N(CH_3)_2 \\ C_6H_4N(CH_3)_2 \\ C_{10}H_6N(CH_3)\cdot C_6H_5 \end{cases}.$$

(Unsulphonated base.)

This is probably obtained by condensing phenylmethyl-β-naphthylamine with tetramethyldiaminobenzophenone and sulphonating the product. A mixture of 20 kilos. of tetramethyldiaminobenzophenone and 60 kilos. of phenylmethyl-β-naphthylamine is melted in a jacketed pan and 13·5 kilos. of phosphoryl chloride are added at about 30°. After some time, more quickly on gently warming the reaction begins, and the temperature is allowed to rise to 115–120°, the operation being controlled by cooling or heating. After remaining for an hour at this temperature, the mass is cooled, powdered, dissolved in 1000 litres of hot water, and salted out hot. The dye separates as a coppery tar and is again washed to remove acid, and then the excess of phenylmethyl-β-naphthylamine is extracted with hot toluene and the remaining cake purified by dissolving it in about 1000 litres of boiling water. The product forms small green or bronzy needles which are readily soluble in hot water, sparingly so in cold water, and insoluble in weakly acidified water.

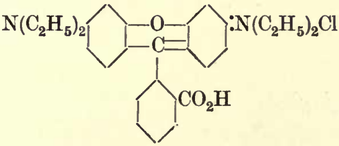
For the sulphonation, 20 kilos. of this product are dissolved in 60 kilos. of sulphuric acid (100 per cent.) at 20–30° and the solution is cooled. There is now added to it slowly at a temperature not exceeding 20°, with good stirring, fuming sulphuric acid (containing 54 per cent. of sulphur dioxide) (about 40 kilos.) until a sample dissolves in warm dilute sodium hydroxide solution. The mixture is then poured into much ice-water, the dye acid filtered off, dissolved in about 1000 litres of water and the necessary amount of sodium hydroxide solution, the solution neutralised with acetic acid, and the dye salted out (Chemische Fabrik vorm. Sandoz, E.P. 30015^{96}; G.P. 96402; U.S.P. 603016).

CHAPTER IX

XANTHONE COLOURS

RHODAMINE B—RHODAMINE 6G—FAST ACID VIOLET—FLUORESCEIN—EOSINE—EOSINE S—EOSINE BN—ERYTHROSINE—GALLEINE—CŒRULEINE.

Rhodamine B,



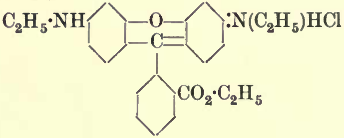
A mixture of 10 kilos. of diethyl-*m*-aminophenol and 12 kilos. of phthalic anhydride is heated for four to five hours at 170–175° until the mass solidifies. The phthalate of tetraethylrhodamine, which is formed, is finely powdered and digested for several hours with dilute ammonia (10 kilos. of 18 per cent. and 160 litres of water) at the ordinary temperature and the base is extracted by repeated shaking with benzene. The colourless benzene solutions are treated with hot, very dilute hydrochloric acid until the dye-base has been completely extracted, and on cooling the aqueous solution, after separation from the benzene layer, the hydrochloride of tetraethylrhodamine separates in small, green, bronzy crystals.

The working up of the fusion can be varied in several ways; thus alkalis other than ammonia can be employed, other solvents can be used instead of benzene, and the base may be converted into the sulphate or oxalate. Further, the phthalate can be decomposed by digestion with hot, concentrated sodium carbonate solution and the residual base converted into its salts by treatment with the corresponding acid without the use of an organic solvent (Badische Anilin- & Soda-Fabrik, E.P. 15374^{87}; F.P. 186697; G.P. 44002; U.S.P. 377350).

Another method of preparation consists in heating in an autoclave 5 parts of fluorescein chloride,[*] 4 parts of diethylamine hydrochloride, 5 parts of crystallised sodium acetate, and 8 parts of alcohol for twelve hours at 200–220°. If the heating has been continued for a sufficiently long time, no unchanged fluorescein chloride will be contained in the product. This is dissolved in alcohol to which about 10 per cent. of concentrated hydrochloric acid is added, the mixture boiled for about five hours under reflux, the alcohol distilled off, and the residue extracted with water containing hydrochloric acid. The dye is precipitated from the filtrate by means of salt (Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 9600^{88}; F.P. 192589; G.P. 48367).

Finally, the dye is formed by heating *o*-2 : 4-dihydroxybenzoylbenzoic acid (from fluorescein and sodium hydroxide solution) with diethyl-*m*-aminophenol and treating the chloride of the product with diethylamine (Badische Anilin- & Soda-Fabrik, G.P. 54684).

Rhodamine 6G,



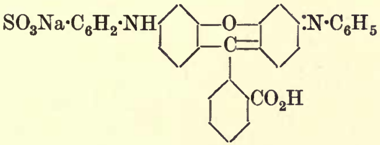
A mixture of 11·1 kilos. of monoethyl-*m*-aminophenol, 10 kilos. of phthalic anhydride, and 5 kilos. of zinc chloride is melted in an enamelled pan fitted with a stirrer at 170–180° until the mass shows an indication of solidifying. The operation is conducted with the exclusion of air so far as is possible. The product, which has a metallic lustre, is cooled, finely powdered, and freed from zinc chloride as far as possible by washing with water. It is then mixed with about 200 litres of water, 50 kilos. of ammonia (*d* 0·92) are added, and the whole is allowed to digest for twenty-four hours, first at the ordinary temperature and then, towards the end, it is warmed. The colour base separates in a crystalline form. It is filtered off, washed, and dried. It is dissolved in very dilute boiling hydrochloric acid and the dye is allowed to crystallise from the filtered solution (Badische Anilin- & Soda-Fabrik, G.P. 48731).

[*] Obtained by heating 1 mol. of fluorescein with 2 mols. of phosphorus pentachloride for one to two hours at 100° (Baeyer, *Annalen*, 1876, **183**, 18), or by heating phthalic anhydride and *m*-chlorophenol with zinc chloride (Badische Anilin- & Soda-Fabrik, E.P. 9675^{04}; F.P. 342518; G.P. 156333; U.S.P. 785003. See also under Fast acid violet B, p. 159).

For the esterification, 5 kilos. of the diethylrhodamine (as hydrochloride) are dissolved in 25 kilos. of ethyl alcohol (96 per cent.) and the solution is saturated with dry hydrogen chloride. The formation of the ester begins in the cold, but it is best to heat the solution to boiling in the water-bath under reflux for four to five hours or until a sample, dissolved in hot water, is not precipitated by the addition of sodium acetate. A slow stream of dry hydrogen chloride is passed through the solution during the operation. The alcohol and hydrochloric acid are now distilled off from the water-bath and the residue is dissolved in hot water. The solution, which contains hydrochloric acid, is filtered, if necessary, and, on cooling, the dye crystallises out. The separation of the dye can be completed, if necessary, by adding a little hydrochloric acid or salt. It is filtered off, pressed, and dried at a low temperature.

The esterification can also be effected by heating diethylrhodamine (base or sulphate) with 2 parts of ethyl alcohol and 1·5 parts of sulphuric acid in the water-bath as described above, or by heating the hydrochloride or sulphate with alcohol in an autoclave for ten hours at 150°, or by heating the base with a solution of ethyl chloride in ethyl alcohol in an autoclave (Badische Anilin- & Soda-Fabrik, E.P. 9633^{92}; F.P. 225341; G.P. 73573, 73880; U.S.P. 516584).

Fast acid violet B,



The diphenylrhodamine, sulphonation of which furnishes this dye, may be obtained by two methods.

(1) A mixture of 15 kilos. of *m*-hydroxydiphenylamine,* 10 kilos. of phthalic anhydride, and 10 kilos. of zinc chloride is heated, with exclusion of air so far as possible, in an enamelled pan fitted with a stirrer, for four to five hours at 160–170°. The deep violet produced is allowed to cool, powdered, freed from zinc chloride and phthalic anhydride by prolonged digestion

* Prepared by heating resorcinol with aniline and calcium chloride at 260–280° (Merz and Weith, *Ber.*, 1881, **14**, 2345; Calm, *Ber.*, 1883, **16**, 2786) or *m*-aminophenol with aniline and aniline hydrochloride at 210–215° (Badische Anilin- & Soda-Fabrik, G.P. 46869).

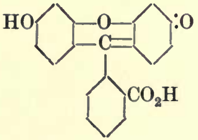
with warm dilute ammonia, filtered off, and dried. The base is insoluble in cold or hot water and sparingly soluble in ether or benzene, but more readily so in warm alcohol (Badische Anilin- & Soda-Fabrik, G.P. 45263).

(2) A mixture of 3·7 parts of fluorescein chloride (1 mol.), 1·9 parts of aniline (2 mols.), and 3 parts of zinc chloride is heated for one to two hours at 210–220°. The product is dissolved in spirit (about 8 parts) which has been acidified with hydrochloric acid or in 6–8 parts of concentrated sulphuric acid at about 50°. The solution is poured into water, preferably containing salt, and the dye separates (Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 9600^{88}; F.P. 201660; G.P. 49057).

For the sulphonation, 1 kilo. of the above *s*-diphenylrhodamine is added to 3–4 kilos. of fuming sulphuric acid (containing 20–30 per cent. of sulphur trioxide), the temperature not being allowed to rise, and the mixture kept at 20–30° until a sample dissolves completely in alkaline water. The mixture is poured into water, the solution neutralised with milk of lime, filtered, and the sodium salt prepared in the usual way (Badische Anilin- & Soda-Fabrik, G.P. 46807).

The process has recently been repeated by Sakai (*J. Chem. Ind. Tokyo*, 1920, **23**, 242). Fluorescein chloride was prepared from 1 part of fluorescein and 2 parts of phosphorus pentachloride, this mixture being heated in an oil-bath at 70–80° for one to two hours and then at 100–110° for one to two hours. The yield of the chloride, after being washed with hot water and reprecipitated from toluene, was 93 per cent. When condensed with aniline (using 10–20 per cent. more than the calculated amount) in the presence of zinc chloride by heating for two hours at 220°, diphenylrhodamine was obtained in a yield of 150 per cent. of the weight of fluorescein chloride used. The base was treated with 4 parts of sulphuric acid (100 per cent.) at 20° and the yield of the dye was about 116 per cent. (theoretical, 117 per cent.).

Fluorescein,



The following account of the manufacture of this dye is given by Mühlhäuser (*Dingl. Polyt. J.*, 1887, **263**, 49).

The condensation of phthalic anhydride and resorcinol is effected in an enamelled pan set in an oil-bath, into which 25 kilos. of resorcinol are placed and melted by heating the oil-bath at about 160°. To this are added, with stirring, 17·5 kilos. of phthalic anhydride, which soon dissolves in the resorcinol. The pan is then covered with a wooden hood, through which a small amount of sublimed phthalic anhydride and the water produced during the reaction escape to a chimney. The reaction begins when the liquid has been heated at 180° for about one and a half hours and is shown by the violent boiling. During the reaction, which lasts about forty minutes, stirring is discontinued, as this may lead to the contents of the pan foaming over. The mass, which gradually thickens, becomes like porridge, and from this point it is stirred from time to time with an iron spatula until the paste has become completely dry, which occurs when the mixture has been heated for twenty-four to thirty hours at 200–205°. The end of the reaction is indicated when a lump, broken by a hammer, is brittle.

The chief requirements for a successful fusion are the use of pure materials and the maintenance of the temperature of 180° during the reaction, whereby the latter proceeds smoothly. The temperature is regulated either by drawing the fire or by covering it with ashes. If the mass rises in the pan during the reaction and is in danger of coming over, it is cooled by blowing air into it with a bellows. The yield of crude fluorescein is 37·5 kilos.

Purification.—The crude product is dissolved by boiling it with 500 litres of water and 50 kilos. of sodium hydroxide (36° Bé.) in a tub and the volume of the solution is brought to 1000 litres. It is filtered into a tub placed at a lower level, and the reddish-yellow filtrate is precipitated with 90 kilos. of hydrochloric acid. The fluorescein falls to the bottom and the fluorescent liquor is decanted. After boiling up the residue with 500 litres of water, a turbid, reddish-yellow liquid is obtained from which the fluorescein usually separates completely only by the addition of hydrochloric acid. It is allowed to settle, the liquid decanted, the whole of the fluorescein brought on the filter, drained, and dried.

The paste is dried on shallow enamelled trays, about 80 cm. square; four such trays are placed on a water-bath so that a temperature of about 98° is attained. At this temperature, the paste, spread on the trays in a layer about 5 mm. deep, dries quickly and falls to an extremely fine powder, which is then sieved. The yield is 36 kilos.

The following table gives figures for the manufacture as obtained in actual work :

Resorcinol.	Phthalic anhydride.	Crude fluorescein.	Sodium hydroxide (36° Bé.).	Hydrochloric acid.	Yield.
25	17·5	37·5	50	90	36·0
25	17·5	37·0	50	90	36·5
25	17·5	36·9	50	90	36·3

If powdered anhydrous zinc chloride is used in the condensation, the reaction is complete in a shorter time. The resorcinol (25 kilos.) is melted as before and 17·0 kilos. of phthalic anhydride (a little less is taken than in the previous case as, in the shorter time, less is volatilised) are added. As soon as the latter is dissolved and the temperature has reached 185°, 8 kilos. of powdered zinc chloride are added rapidly and the pan is closed by a lid through a hole in which an iron spatula can be inserted. The mixture is stirred for about five minutes, when the reaction sets in; it is ended in a few minutes and further stirring is impossible, as the mass becomes quite thick. Heating is continued at 190–200° for about ten hours and the mass allowed to cool. The brittle product, which is black on the surface but brown in the interior, is broken out, and the crude material weighs 45·8 kilos.

The purification is effected by dissolving the mass in dilute sodium hydroxide solution, filtering, precipitating with hydrochloric acid, and removing the mineral acid by boiling with water and decanting several times. The yield of fluorescein is 36·5 kilos.

Resorcinol.	Phthalic anhydride.	Zinc chloride.	Crude fluorescein.	Sodium hydroxide (36° Bé.).	Hydrochloric acid.	Yield.
25	17	8·0	45·8	60	100	36·4
25	17	8·0	45·0	60	100	36·5
25	17	8·0	45·5	60	100	36·6

In a later paper, Mühlhäuser (*Dingl. Polyt. J.*, 1892, **283**, 182) describes the plant used in the above manufacture. The enamelled pan used for the fusion is set in another which forms an oil-bath, and this is set in brick-work so that it can be heated. The crude melt is dissolved, not in a tub as stated above, but in a cylindrical iron pan set a little below the level of the ground. This is fitted with a lid which is screwed to the pan and the joint is made tight with an india-rubber ring. The lid has a large man-hole, connexion with the compressed air supply, and a blow-out pipe which leads to an open filter resting on a tub which stands a little above the ground. Above the man-hole of the lid is a water tap and a steam connexion to which can be fitted a pipe passing through the man-hole to the bottom of the pan.

From the tub the fluorescein is run on an open filter standing on the ground.

The drying arrangement consists of a long rectangular sheet-iron chamber on the bottom of which is a steam coil. It is filled about two-thirds full of water and the four enamelled iron trays are set in the top.

Lefèvre ("Traité des Matières Colorantes," 1896, p. 1201) states that 150 kilos. of resorcinol are condensed with 100 kilos. of phthalic anhydride, in the manner described by Mühlhäuser, and that the length of the operation depends on the temperature, varying between twelve and twenty-four hours.

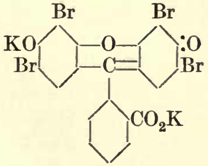
The crude product is powdered and boiled for two hours under reflux with 1½ parts of alcohol in a steam-jacketed pan. When cold, the mixture is filtered on a vacuum filter and the residue treated with very dilute hydrochloric acid and filtered again, washed, and dried.

The alcoholic solution is distilled to recover the alcohol, and the residue, consisting of impure fluorescein, is melted with sodium hydroxide. The product is dissolved in water acidified with hydrochloric acid, and the solution is extracted with ether to recover the resorcinol, which, after purification, is used again in the manufacture. The yield of purified fluorescein is 80–85 per cent. of the theoretical.

Witt (Thorpe's "Dictionary of Applied Chemistry," 1913, V, 553) gives the temperature of the melt as 190°, and states that purification with alcohol is invariably used. The impure fluorescein, obtained by evaporating the alcoholic extract, is used for making the low-class qualities of the dyes which are derived from fluorescein.

According to Schultz ("Farbstofftabellen," 1914, 196), 24 kilos. of resorcinol and 16·5 kilos. of phthalic anhydride are melted together at 300° within four hours, until the fusion has become hard. The product is powdered and extracted with 3 parts of alcohol under a reflux condenser. The residue consists of pure fluorescein.

Eosine,



According to Mühlhäuser (*Dingl. Polyt. J.*, 1887, **263**, 49;

1892, **284**, 21, 46), the bromination of fluorescein may be effected in either aqueous or alcoholic solution.

Bromination in Aqueous Solution.—In a cast-iron jacketed pan, 60 kilos. of sodium hydroxide solution (36° Bé.) are mixed with 150 litres of water, the solution is stirred, and 32 kilos. of bromine are added by means of a siphon directly from the bottles in which it is sold. A mixture of sodium bromide, sodium bromate, and sodium hypobromide is formed, the latter of which is transformed into sodium bromide by boiling for fifteen minutes. This operation is necessary, otherwise the product obtained in the subsequent decomposition with hydrochloric acid will be too yellow.

In the meantime, 16 kilos. of fluorescein have been dissolved, in a jacketed pan set alongside the other, in 25 kilos. of sodium hydroxide solution (36° Bé.) and 150 litres of water by boiling for half an hour. When both solutions are cold, they are siphoned into a wooden tub standing below their level, the mixture is well stirred, diluted, if necessary, with water, and 140 kilos. of hydrochloric acid are added from a cask standing on the same platform as the pans. A yellow precipitate separates and steam is passed in until the mixture boils. At this point the tub is filled up with cold water, the precipitate allowed to settle, the liquor run through an open filter resting on a second tub which is set below, the residue twice boiled up with fresh water, and finally filtered. The filtrate is allowed to remain for twelve hours and then filtered through an open filter and the small amount of Eosine remaining is mixed with the next batch. The Eosine acid, completely free from mineral acid, is dried on trays as in the case of fluorescein.

In three batches, taking the above quantities, the yields were 30·0, 29·3, and 28·5 kilos. respectively.

The tetrabromofluorescein may be rendered soluble by dissolving in sodium hydroxide solution, filtering, and evaporating the filtrate to dryness, but a purer product is obtained as follows :

Two batches (60 kilos. of Eosine acid) are rendered soluble with alcoholic sodium hydroxide and the Eosine B allowed to crystallise from the solution.

In order to carry out this operation, a test must first be made to ascertain how much sodium hydroxide is required to form the neutral Eosine salt. For this purpose, an average sample of 50 grams of Eosine acid is placed in a litre flask with 175 grams of 96 per cent. alcohol and heated to boiling. In the meantime, a sample of the works solution of sodium hydroxide (prepared from 1 part of the solid and 2 parts of water; about 40° Bé.) has been fetched and about 40 grams are placed in a small flask. The latter, together with the solution weighs, for example, 134·7 grams. The solution is now added drop by drop to the boiling alcoholic solution of Eosine acid. At first the red acid salt of Eosine is precipitated amd this acts as an indicator in that the addition of the alkali solution is continued, the alcoholic solution being kept hot and shaken, until the acid salt has dissolved, that is, has been converted into the neutral salt. As soon as the last trace of acid salt has disappeared, the addition of the alkali is stopped. The liquid is now yellowish-red, but if too much alkali has been added it will be blackish-red. The operation is also controlled by allowing a glass rod, dipped into the Eosine solution, to dry in the air, and then bringing it into distilled water. If sufficient alkali has been added, the Eosine will dissolve to a clear solution, but if too little, a cloud will form round the glass rod owing to the separation of the acid salt. If the neutralisation has been exact, a drop of the solution in water will show a yellowish-green dichroism, but if too much alkali has been added the solution is dirty green with a brownish-green dichroism. The Eosine solution is poured into a basin, when the edge of the solution should appear yellowish-red and not brown. In the former case, the test is correct, but in the latter too much alkali has been added. On allowing the contents of the basin to crystallise over-night, the cake, separated from the liquor, should show no signs of the acid salt on the bottom. If the small flask containing the sodium hydroxide solution is now weighed, this is found, for example, to be 114·46 grams, so that 20·24 grams have been used to neutralise 50 grams of Eosine acid, and this figure is employed for calculating the amount of sodium hydroxide solution to be used on the large scale.

Crystallisation.—To 210 kilos. of alcohol contained in a copper pan set in a water-bath, 60 kilos. of Eosine acid are gradually added. This quantity of alcohol is the amount which is necessary to keep the sodium salt in solution. The water-bath is now heated to boiling and the contents of the pan are raised to a temperature of 60°. When this point is reached, $\frac{20{\cdot}4 \times 60}{50} =$ 24·5 * kilos. of sodium hydroxide solution are run in during ten

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* Considering the meticulous care with which the author obtains the sodium hydroxide titre, one would have expected to find this quantity given as $\frac{20{\cdot}24 \times 60}{50} = 24{\cdot}3$ kilos.

minutes. The acid dissolves with the previous formation of the acid salt. The solution is now run into three tubs each of 120 litres capacity (6 in all are necessary), and thick wooden lids are laid on the surface of the liquid, dipping into it about 1–2 cm. so as, on the one hand, to provide as much surface as possible for crystallisation, and, on the other, to diminish the amount of crystals forming on the bottom of the tubs. The crystals formed on the lids and sides of the tubs are invariably purer and have a better appearance than those found on the bottom. After the tubs have been kept in a cool place for two to three days, the crystallisation is complete. The lids are raised, the liquor siphoned off into a receiver placed in the ground, from which it is blown to the alcohol still, and the crystals from the lids and sides are placed on one filter (cotton cloth) and those from the bottom on a separate one, the crystals having been loosened by means of a knife. The crystals, after draining, are dried on trays at about 60°, which takes three days, and are then ground. The yield is 57 kilos. The reddish-brown powder comes on the market as Eosine B.

Eosine.	Alcohol.	Sodium hydroxide solution.	Eosine B.
60	210	24·5	57·5
59	206	24·0	57·5
55	193	22·0	55·0

The alcoholic liquor from the crystals is returned to the distillation plant and worked up to 96 per cent. spirit. The dye dissolved in it is useless.

Bromination in Alcoholic Solution.—The bromination is effected in three enamelled pans (twelve of which are required) in each of which is placed 10 kilos. of fluorescein and 80 kilos. of alcohol (96 per cent.). This is drawn from an alcohol-rectifying apparatus, consisting of a still connecting with a column, dephlegmator condenser, and three wrought-iron receivers. The first runnings are collected in the first receiver, the last runnings in the third, and the 96–97 per cent. spirit in the second. The alcohol is run from this by gravity into a small closed measuring vessel in which the correct charge is collected and thence blown into one of the enamelled pans. A slow stream of bromine (24 kilos.) is run from a bottle with a tap at the bottom into each pan and the tube through which the bromine runs is allowed to dip a little under the surface of the alcohol, the mixture being stirred during the addition. The alcohol becomes hot, and external cooling is necessary in summer. The bromination takes about fifteen minutes, and when it is finished stirring is continued for some time and then the lids are placed on the pans. These are allowed to remain for four days and are stirred three times a day in order that the Eosine acid may separate completely. It will be observed that when half the bromine has been added the liquid, which is at first reddish-brown, becomes blackish-brown; this is due to the dibromo-compound, which is readily soluble in alcohol. On further addition of bromine, the tetrabromo-compound separates as a brick-red, crystalline mass. At the end of the four days, the acid alcohol is siphoned off into an enamelled pan set at a slightly lower level than the bottom of the enamelled pan, and partly in the ground, and the red precipitate is washed twice with alcohol. For this purpose, 40 kilos. of alcohol are added to each pan, the mixture is well stirred, allowed to settle for one day, and the alcohol siphoned off. A second washing is performed in the same manner. The alcohol washings are collected in the above pan when it is empty and blown to a larger enamelled receiver set in the ground. The red precipitate is then collected on a wool filter and, after draining, pressed. The press cake is dried on trays with a cotton bottom and wooden frame, and the drying takes two days. The yield of Eosine acid is 50 kilos.

The conversion of this into Eosine A extra is carried out as described above. The dry crystals are, however, not ground, but broken with a piece of wood into lumps the size of a nut and come in this form on the market. From 50 kilos. of Eosine acid, 20 kilos. of sodium hydroxide solution (of the same strength as above) and 175 kilos. of alcohol, 50 kilos. of Eosine A extra are obtained.

For the preparation of Eosine B with a red appearance, 30 kilos. of finely sieved tetrabromofluorescein, made by the alcohol process, are employed. The process of rendering this soluble is effected in a tall wooden chest which can be tightly closed by a door. In the inside of this chest is a rack holding thirty trays, each 3 cm. high, the bottom of which consists of cotton cloth 80 cm. square; these stand one above another at a distance of 3 cm. On each tray is spread about 1 kilo. of Eosine acid as uniformly as possible, and the door is closed. The chest is connected with an ammonia generator consisting of an iron pan fitted with a man-hole and an exit pipe, and set in brickwork, in which the gas is liberated by heating sal ammoniac with milk of lime, and a drying tower filled with lumps of sodium hydroxide. The gas is introduced at the bottom of the chest by means of a perforated pipe and passes through the layer of Eosine from the bottom to the top. It is rapidly absorbed and in about two hours the whole of the Eosine acid is converted into the neutral ammonium salt. The end of the absorption is checked by taking samples with a small, long-handled scoop which can be inserted through holes, closed by plugs, running from top to bottom of the door. When a sample, taken from different trays, gives a clear solution in water, the process is stopped. The slight excess of ammonia is led away through an iron pipe at the top of the chest to the chimney. (For a sketch of the arrangement, see Mühlhäuser, *Dingl. Polyt. J.*, 1892, **283**, 234.) The yield is 31·8 kilos. of Eosine B :

Eosine acid.	Ammonium chloride.	Lime.	Eosine B.
30	15	30	31·8
29·5	15	30	31·4

Working Up of the Alcohol.—The alcohol from a bromination, contained in the pan (see above) is stirred, and about one-third of its volume of water is added in a thin stream. If more is added, tar separates in addition to Eosine, which is to be avoided. The mixture is blown through a filter-press set on a low platform, and the acid aqueous alcohol is run by gravity into the receiver. The residue in the press is washed with water, the cakes are pressed in a hand or hydraulic press, and dried. Instead of using a filter-press, the Eosine may be allowed to settle, the acid aqueous alcohol drawn off, the residue brought on a filter, and then washed twice with water in a cask. If in the second washing the Eosine remains suspended for a longer time, this is an indication that all the acid has been washed away, as, in water containing acid, the Eosine settles more quickly and without turbidity. If the washed and filtered residue is sandy, it is allowed to drain and then pressed and dried, but if it is tarry, it must be washed with alcohol to remove the tar. The " residue " Eosine obtained in this way is accumulated until about 60 kilos. have been collected and in working this up it is washed once or twice with alcohol (2 parts by weight) according to the purity of the product. In this operation the Eosine must be stirred into the alcohol; if the whole mass is added at once, it balls together and then cannot be obtained in a sandy state by washing. The Eosine after being washed with alcohol is fairly pure, and is filtered, pressed, and dried. On crystallisation, a pure product can be obtained. The necessary amount of sodium hydroxide for solution is estimated and the dye is crystallised from alcohol as described above.

In this operation, much impure material dissolves in the alcohol. By dissolving in water the crystals of poor appearance obtained in this way, precipitating with hydrochloric acid, filtering, drying, and recrystallising, a product is usually obtained which is equal to Eosine B.

The acid alcohol from the bromination (after dilution to recover the second quality Eosine) and that from the washing of the Eosine, are, as indicated above, collected in the pan. The acid is neutralised with milk of lime and the mixture is blown to the alcohol still, where it is worked up to 96–97 per cent. spirit. When the alcohol has been driven off, the calcium bromide liquor is run into a receiver set in the ground and blown to the department for regenerating bromine.

The alcoholic liquors from Eosine A extra are distilled and the residue is dried. In this case also, the residues are kept until about 60 kilos. have been accumulated, and then they are dissolved in water and the Eosine acid precipitated with hydrochloric acid. The dried Eosine acid is washed and recrystallised with alcoholic sodium hydroxide as described above.

In the above process, only half the bromine is introduced into the molecule, and in order to economise the bromine the operation is effected in the presence of a chlorate in accordance with the equation :

$$3C_{20}H_{12}O_5 + 12Br + 2KClO_3 = 3C_{20}H_8O_5Br_4 + 2KCl + 6H_2O.$$

The bromination is carried out in a jacketed enamelled pan furnished with an agitator and a reflux condenser. It is charged with 200 kilos. of alcohol and 40 kilos. of purified fluorescein and 40 kilos. of bromine are added, the temperature being kept at 20°. When all the bromine has been introduced, 12 kilos. of potassium chlorate (or the corresponding amount of sodium chlorate) are added gradually and the mixture is heated to boiling for four hours and then allowed to cool. The insoluble Eosine is filtered off, washed with acidified water and finally with water, and then dissolved in the amount of sodium carbonate necessary to form the neutral salt, determined by a preliminary test. The acid salt is first precipitated and this dissolves with more alkali. At this point, the addition is stopped. The solution is tested in the manner described above.

Crystallisation from alcohol is effected by stirring the Eosine acid into five to six times its weight of alcohol at 60° and adding the necessary amount of sodium carbonate. The solution is allowed to crystallise as described above.

The alcoholic mother-liquor, after distillation of the alcohol, leaves some dye, which is precipitated by hydrochloric acid, washed, dissolved in sodium carbonate, and crystallised. For the bromination in aqueous solution a mixture of sodium bromide and hypobromite is prepared by adding 32 kilos. of bromine to a mixture of 60 kilos. of sodium hydroxide (36° Bé.) and 150 kilos. of water. On the other hand, 32 kilos. of fluorescein are dissolved by warming with 50 kilos. of sodium hydroxide (36° Bé.) and 150 kilos. of water. When this solution is cold, both solutions are run into a tub, stirred, 280 kilos. of hydrochloric acid are added, and the quantity of potassium chlorate necessary to liberate the bromine in accordance with the equation :

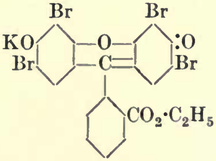
$$3C_{20}H_{12}O_5 + 6NaOBr + 6NaBr + 12HCl + 2KClO_3 = 3C_{20}H_8O_5Br_4 + 12NaCl + 12H_2O + 2KCl.$$

The Eosine is precipitated and the mixture heated to boiling, water added, the whole allowed to settle, and the liquor decanted. Fresh water is then added, the mixture boiled, settled, and the liquor decanted. When free from acid, the precipitate is filtered off, drained, dried, dissolved in sodium carbonate, and crystallised (Lefèvre, " Traité des Matières Colorantes," 1896, p. 1201).

Witt (Thorpe, " Dictionary of Applied Chemistry," 1913, V, 555) states that the bromination proceeds better in alcoholic than in aqueous solution, and that, when only 2 molecules of bromine are employed, the best chlorate to use is cupric chlorate, as it is soluble in spirit. It is prepared by mixing concentrated aqueous solutions of sodium chlorate and cupric chloride or sulphate. The solution obtained is added to the operation in progress.

When Eosine is heated for a short time with eight parts of 50 per cent. sodium hydroxide solution at 140°, and the diluted alkaline liquor is acidified, 3 : 5-dibromo-2 : 4-dihydroxy-*o*-benzoylbenzoic acid, $C_6HBr_2(OH)_2{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$, m. p. 224°, is obtained (Heller, *Ber.*, 1895, **28**, 316).

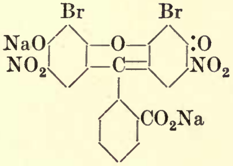
Eosine S,



This is formed (1) by heating Eosine with alcohol and potassium ethyl sulphate at 140-150° (Baeyer, *Annalen*, 1876, **183**, 46),

(2) by simultaneously brominating and ethylating fluorescein in alcoholic solution (this process of brominating fluorescein in hot alcohol is very fully described by Mühlhäuser, *Dingl. Polyt. J.*, 1887, **263**, 100; 1892, **283**, 210, where a sketch of the plant is given), and (3) by ethylating tetrabromofluorescein with alcohol and sulphuric acid. The latter process appears to be very much more preferable to the others, and is conducted as follows: A mixture of 5 kilos. of tetrabromofluorescein, 10 litres of alcohol, and 9 kilos. of sulphuric acid (66° Bé.) is boiled on the water-bath for four hours and then poured into cold water, the precipitate filtered off, washed, and converted into the potassium salt by boiling with potassium carbonate solution. The product is sparingly soluble in water or pure alcohol, but readily so in hot 50 per cent. alcohol and crystallises with $1H_2O$ (Bindschedler and Busch, *Chem. News*, 1878, **38**, 226).

Eosine BN,



This is prepared (1) by treating an alcoholic solution of fluorescein with nitric acid and then with bromine, (2) by treating an acetic acid solution of Eosine with sodium nitrate, and (3) by brominating fluorescein in aqueous solution and treating the product with nitric acid. Details of the manufacture are given by Mühlhäuser (*Dingl. Polyt. J.*, 1887, **263**, 103; a sketch of the plant required for process (2) is given in *Dingl. Polyt. J.*, 1892, **284**, 95).

(1) In each of 5 enamelled pans, 7 kilos. of fluorescein are stirred into 60 kilos. of alcohol (96 per cent.). To each mixture is added gradually 7 kilos. of nitric acid (40° Bé.) and then, immediately, 7·25 kilos. of bromine, which is siphoned out of the flasks. The dibromodinitrofluorescein, which is sparingly soluble in alcohol, separates out. Next day, the black liquor is siphoned off and the precipitate washed once with 30 kilos. of alcohol. The precipitate is brought on a filter, drained, boiled with water in a wooden tub, allowed to settle, the liquor decanted, and this treatment is repeated until the wash-water begins to be slightly coloured. This is a sign that all the acid has been

washed away. The fine paste, in thin layers, is dried on enamelled trays on the water-bath. The yield of three batches (each from 35 kilos. of fluorescein) was 63·0, 62·2, and 60·5 kilos. respectively.

(2) Thirty kilos. of Eosine (that prepared by bromination in alcoholic solution gives the finer product) are placed in an enamelled pan set in a water-bath, 25 kilos. of glacial acetic acid are added, and the whole is stirred to a uniform paste. With this is incorporated 4 kilos. of finely ground sodium nitrate by vigorous stirring. The pan is then covered and the water-bath heated to boiling. The reaction begins at about 70–80°, and a little nitrous acid and acetic acid is given off. By frequent stirring, a uniform temperature is maintained. After about six to eight hours' heating the red mass will have become flesh-coloured, when the reaction is at an end. The course of the nitration is followed by tests, and it is stopped when a sample dissolved in ammonia, compared with a test colour, produces an immediate blue shade on filter-paper. The cooled mass is then boiled with 500 litres of water in a wooden tub standing below the level of the pan. After boiling for about ten minutes, the precipitate is allowed to settle and the liquor is decanted into a second tub standing below the first. The washing with boiling water is repeated until the residue is free from acid, the washings being added to the first. On the next day, any colour that has separated from them is run on an open filter, drained, and added to the next batch. The flesh-coloured paste is now run on to an open filter resting on the lower tub, drained, and dried in thin layers on enamelled trays.

Eosine.	Glacial acetic acid.	Sodium nitrate.*	Yield of free acid.
30	25	4	29·5
29·5	25	4	29·0
29·0	25	4	28·0

(3) Ten kilos. of fluorescein are dissolved in 200 litres of water and 13 kilos. of sodium hydroxide solution (36° Bé.) in a jacketed pan, and in a second pan 12 kilos. of bromine are run into a mixture of 20 kilos. of sodium hydroxide solution (36° Bé.) and 50 kilos. of water and the solution is boiled. When this is quite cold, the two solutions are run into an enamelled pan set in a water-bath and 60 kilos. of sulphuric acid (40° Bé.) are stirred in. The yellow bromo-compound separates out. Thirty kilos. of nitric acid (40° Bé.) are now slowly run in from a tap-bottle with

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* The amount of sodium nitrate is adjusted according to the shade required.

stirring, the pan being cooled during the operation. When all the nitric acid has been added, the water-bath is heated to boiling and the mass is heated for five to six hours with occasional stirring. The reddish-yellow Eosine is converted into the flesh-coloured nitro-compound. This is washed in a tub with water, and freed from acid by repeatedly decanting and washing afresh. It is finally collected on a filter and dried in thin layers on the water-bath. The yield from three batches was 19·5, 20·0, and 19·0 kilos., respectively.

Preparation of the Salts.—The ammonium salt is prepared by treating the dry, finely-sieved dibromodinitrofluorescein with gaseous ammonia as described under Eosine:

Colour acid.	Sal ammoniac.	Lime.	Yield.
30	15	30	31·9
30	15	30	31·8

As bromination in alcohol or glacial acetic acid furnishes a very pure product, it is best, in this case, to prepare the ammonium salt.

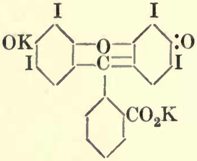
The sodium salt is prepared by mixing 30 kilos. of the colour-acid with 200 litres of water in a cast-iron pan standing on the ground, into which a steam pipe can be introduced. The mixture is heated at about 90° and a thin stream of sodium hydroxide solution is run in, but the quantity must be insufficient for complete neutralisation so as to leave the impurities formed in the nitration undissolved. The progress of the dissolution is followed by spotting a drop of the liquor on filter-paper, and the alkali is added until a drop on filter-paper gives, not a pure uniform spot, but, on the surface of the drop, a small amount of a solid, powdery residue. The purity of the product depends on the size of this. The neutralisation may, however, be taken fairly far, but the test requires some practice.

The deep red liquid, containing a little residue, is blown into a tub set on a platform, where it is allowed to settle. After two days, the clear solution is filtered through an open filter and from this run into a jacketed pan, where it is evaporated to dryness.

Colour acid.	Sodium hydroxide (36° Bé.).	Yield.
30	14·5	29·5
30	13·5	30·0

The potassium salt may be obtained in the above manner using potassium hydroxide, but usually the hot, concentrated solution of the sodium salt, contained in the evaporating pan, is treated with a concentrated solution of potassium carbonate when the dye crystallises out. The crystals are filtered off, centrifuged, and dried. The yield is 30 kilos.

Erythrosine (bluish),



According to Mühlhäuser (*Dingl. Polyt. J.*, 1887, **263**, 106; 1892, **283**, 258 (sketch of plant]), 6 kilos. of fluorescein are dissolved in a hot mixture of 8 kilos. of sodium hydroxide solution (36° Bé.) and 60 litres of water in a jacketed enamelled pan of 100 litres capacity. In an exactly similar pan standing on the same platform, 24 kilos. of unsublimed iodine are dissolved in 27–28 kilos. of sodium hydroxide solution (36° Bé.) and 60 litres of water. The solution is boiled and then run into a tub, standing below the level of the pans, into which is also run the fluorescein solution. The mixture is thoroughly stirred, and 25 kilos. of glacial acetic acid, contained in a stone jar, are introduced in a stream the thickness of a finger into the alkaline mixture with good stirring. The fluorescein and iodine separate in a finely divided condition and substitution takes place. When all the acetic acid has been added, the mixture is heated to boiling, the brown liquid is neutralised with 17 kilos. of sodium hydroxide solution (36° Bé.) and to the solution is added within three minutes a mixture of 25 litres of water and 25 kilos. of hydrochloric acid. The tub is filled up with water, the whole boiled, and allowed to settle. The hot iodine solution is separated after about an hour from the red precipitate of tetraiodofluorescein by decanting it into a tub standing below the level of the first one. The residue is brought on an open asbestos filter resting on the top of the lower tub, allowed to drain, returned to the top tub, and again boiled with about 300 litres of water and 10 kilos. of hydrochloric acid. This decantation and boiling with water is once more repeated without the addition of hydrochloric acid. The free colour-acid is finally collected on the filter, drained, and the brick-red paste is dried in a thin layer on enamelled trays set in a water-bath. When dry the red powder is sieved.

Fluorescein.	Sodium hydroxide (36° Bé.).	Iodine.	Sodium hydroxide (36° Bé.).	Acetic acid.	Sodium hydroxide (36° Bé.).	Hydrochloric acid.		Yield.
						I.	II.	
6	8	24	28	25	17	25	10	15·0
6	8	24	28	25	17	25	15	14·8
6	8	24	28	25	17	25	12	14·5

The paste may be purified in the following way. It is dissolved in a pan set partly in the ground, into which steam and water can be introduced, by adding an insufficient amount of dilute sodium hydroxide solution, the pan is closed, and the mixture blown through a small filter-press set on a platform, the filtrate running by gravity into a tub raised a little from the ground. The colour-acid is precipitated with dilute hydrochloric acid, boiled up, diluted with water, allowed to settle, the liquor decanted, and the substance, when washed free from acid, is collected on a wool filter placed just below the level of the bottom of the tub. The material is allowed to drain and then dried, in thin layers, on four enamelled trays set in a water-bath. The dry colour-acid is spread on trays and converted into the ammonium salt as described in the case of Eosine.

Tetraiodo-fluorescein.	Lime.	Sal ammoniac.	Ammonium salt.
15·0	16	8	15·3
14·8	16	8	15·2
14·5	16	8	14·7

Recovery of Iodine.—The iodine liquors, stored in the lower tub, are treated as follows. The solution is stirred and 45 kilos. of sulphuric acid (*d* 1·84) are run in and then a solution of 7 kilos. of sodium dichromate in about 42 litres of water. The iodine sinks to the bottom as a greyish-black paste. After cooling, the supernatant liquor is run off through the tap and the precipitate is run on to a filter (cotton cloth) resting on the ground, washed with water, and allowed to drain.

The paste is then pressed in a hand-press, and the iodine is used again in the manufacture. For 6 kilos. of fluorescein, 9·5 kilos. of fresh iodine are used together with the regenerated iodine, and the same effect is produced as with 24 kilos. of fresh iodine.

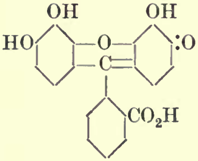
Here, as in the case of Eosine, 2 molecules of iodine may be rendered sufficient for the tetraiodination by the use of a chlorate. According to Lefevre ("Traité des Matières Colorantes," 1896, p. 1203), 35 kilos. of fluorescein, 500 kilos. of alcohol, and 65–70 kilos. of iodine are introduced into a jacketed pan furnished with a stirrer and reflux condenser. The mixture is boiled for two hours, allowed to cool, and a solution of 30 kilos. of potassium chlorate in twice its weight of boiling water is added and the mixture boiled for four hours. After cooling, the liquid is filtered and the colour-acid precipitated by adding water. The precipitate is collected and the filtrate, after removal of the alcohol by distillation, is treated with sulphuric acid to regenerate the iodine from the sodium iodide.* The crude Erythrosine is suspended in water and treated with sulphur dioxide to liberate the iodine from the alkali iodine still present, and then filtered. Iodine is recovered from the filtrate and the colour-acid is dissolved in a tub with a hot solution of 50 kilos. of sodium carbonate.

The solution is allowed to settle, then filtered and precipitated with hydrochloric acid. The residue in the tub is again extracted until the liquor is grey. The precipitate is redissolved in the theoretical amount of sodium carbonate, and the filtered solution is evaporated to dryness or allowed to crystallise.

Instead of potassium or sodium chlorate, other oxidising agents may be used, such as mercuric oxide, iodic acid, cupric chlorate, etc., and the dye may also be prepared by introducing iodine monochloride into an alcoholic suspension of fluorescein (Witt, Thorpe, " Dictionary of Applied Chemistry," 1913, V, 555).

According to Witt, a mixture of Eosine and Rose Bengal gives the same shade as Erythrosine, but the pure dye must be used when it is required as a photographic sensitiser.

Gallein,



Baeyer, who discovered this colouring matter, obtained it by heating pyrogallol with phthalic anhydride at 190–200° (*Ber.*, 1871, **4**, 457, 555, 658), but the modern method is to use gallic acid instead of pyrogallol.

By Baeyer's process a mixture of phthalic anhydride and twice its weight of pyrogallol is heated at 190–200° until the molten

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* This is present owing to an excess of iodine having been used. Evidently sodium chlorate must have been employed instead of potassium chlorate.

mass becomes thick. The crude product is boiled with water to remove any pyrogallol and phthalic acid, and the residue dissolved by the aid of sodium carbonate and reprecipitated by an acid (Durand, *Bull. Soc. Ind. Mulhouse*, 1878, **48**, 326; *Mon. Sci.*, 1878, [iii], **8**, 1122).

Montlaur (*Mon. Sci.*, 1880, [iii], **10**, 1338) adds to the product, after extraction with water, one-fifteenth of the total amount of sodium carbonate required to dissolve it, and filters the mass after an hour. The residue is then dissolved by the aid of the rest of the sodium carbonate and the dye is precipitated from the solution with sulphuric acid. The product may be purified by reduction and subsequent oxidation.

The use of gallic acid is illustrated in the following examples:

A mixture of 37·6 kilos. of crystallised gallic acid, $C_6H_2(OH)_3{\cdot}CO_2H,H_2O$, and 17 kilos. of phthalic anhydride is heated in an oil-bath at 220–235° until the product becomes solid. The gallic acid can also be previously dehydrated by heating at 100°.

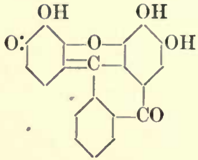
The product is powdered, extracted with water, dried, and treated with 5 parts of alcohol. The solution, containing the gallein, is distilled to recover the alcohol, leaving the dye (Gürke, G.P. 30648).

According to Lefevre ("Traité des Matières Colorantes," 1896, 1204), 20 kilos. of gallic acid are heated in an oil-bath at 180° and to the almost molten mass are added, with stirring, 6·5–7·0 kilos. of phthalic anhydride. The reaction begins at once, and the sublimation of phthalic anhydride is avoided. The mixture is stirred continuously and the temperature raised to 195°. When a sample becomes brittle on cooling, the reaction is finished. It lasts about ten hours. The product is powdered in the presence of 10 parts of water and the whole boiled by passing in steam. After settling, the water is decanted and the residue again washed with boiling water once or twice. It is then dissolved, using a slightly insufficient quantity of sodium carbonate, the solution filtered, and the dye precipitated with dilute sulphuric acid, filtered, and thoroughly washed. For dyeing, it is used in the form of a paste.

A slightly different method of working up the crude product is given by Schultz ("Chemie des Steinkohlentheers," 1901, II, 229). After the product has been washed as described above, the residue is dissolved in a hot dilute solution of sodium carbonate. For 1 kilo. of crude product, about 250 grams of sodium carbonate and 20–30 litres of water are required. For every kilo.

of crude product, 1 kilo. of solid salt is added to the hot solution and the latter filtered hot. The residue, which consists of impurities, is washed on the filter with hot 10 per cent. salt solution and the dye is precipitated from the filtrate by acid. After being washed, the material is either made into a paste of known strength or dried.

Cœrulein,



One part of dry Gallein is heated with 20 parts of sulphuric acid (66° Bé.) at 190–200°, with stirring, until a sample no longer gives with alcohol the red colour of Gallein. After cooling, the product is poured into about 10 parts of water, the precipitate filtered, and washed with water. The crude Cœrulein is suspended in water and neutralised with sodium carbonate solution, leaving only a faint alkaline reaction. The solution is heated to boiling, the sodium salt of Cœrulein precipitated by adding salt, filtered hot, and the residue washed with hot 10 per cent. salt solution until the filtrate is colourless. The last traces of Gallein are removed in this way. The sodium salt is converted into the free acid by acidifying and the Cœrulein is washed (Durand, *Bull. Soc. Ind. Mulhouse*, 1878, **48**, 326; *Mon. Sci.*, 1878, [iii], **8**, 1122; Schultz, "Chemie des Steinkohlentheers," 1901, II, 231).

According to Lefevre ("Traité des Matières Colorantes," 1896, 1204), the sulphonation takes four to five hours. On cooling to 120°, it is poured into 20–30 volumes of cold water and, after stirring and allowing to settle, the water is decanted and washing continued in this way until the product is neutral. It is then filtered and dried.

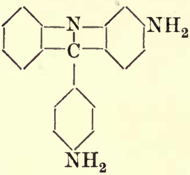
For conversion into the bisulphite compound, the paste (1 mol.) is digested with 1 (Cœrulein S) or 2 mols. (Cœrulein MS) of sodium hydrogen sulphite, and the paste is used as such or dried at a low temperature (Badische Anilin- & Soda-Fabrik, E.P. 3850^{81}).

CHAPTER X

ACRIDINE COLOURS

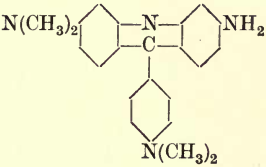
PHOSPHINE—RHEONINE

PHOSPHINE,



It has already been mentioned that Phosphine is obtained from the Magenta melt (p. 100) in the form of its nitrate. The commercial dye contains the nitrate of chrysaniline (above formula) together with some chrystoluidine. Chrysaniline has been synthesised by O. Fischer and Körner (*Ber.*, 1884, **17**, 208) by oxidising 2 : 4′ : 4″-triaminotriphenylmethane (obtained by Renouf, *Ber.*, 1883, **16**, 1304, by condensing *o*-nitrobenzaldehyde with aniline sulphate in the presence of zinc chloride) with arsenic acid at 180–200°.

Rheonine,



A mixture of 40 parts of tetramethyldiaminobenzophenone, 27 parts of *m*-phenylenediamine dihydrochloride, and 9 parts of *m*-phenylenediamine is melted in an enamelled pan fitted with a stirrer and set in an oil-bath and heated for four to six hours, the temperature of the oil-bath being kept at 195–210°. The Auramine dye, which is first formed, gradually disappears, and the formation of the new dye is followed by the behaviour of samples towards dilute hydrochloric acid. Whilst the orange-yellow solution of a sample containing only the Auramine dye, on boiling with this reagent, quickly becomes almost colourless, the brownish-yellow colour of the required product remains unchanged. When, therefore, a sample, when heated with dilute hydrochloric acid, shows no loss of colour, the reaction may be regarded as at an end.

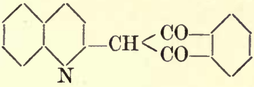
On cooling, the green metallic-looking mass is dissolved in about 400 parts of boiling water with the addition of about 20 parts of hydrochloric acid. On cooling, the liquid is filtered and the dye is precipitated by adding zinc chloride and salt. The precipitate is melted with about 20 parts of hydrochloric acid on the water-bath, the mass evaporated to dryness, and the product powdered (Badische Anilin- & Soda-Fabrik, E.P. 1352^{95}; F.P. 244660; G.P. 82989; U.S.P. 546177).

CHAPTER XI

QUINOLINE COLOURS

QUINOLINE YELLOW

Quinoline yellow, spirit soluble.



A cast-iron pan fitted with a stirrer, of about 300 litres capacity, which is contained in an oil- or phenanthrene-bath, is gently heated and charged with 40 kilos. of quinaldine and 42 kilos. of phthalic anhydride. The mixture is heated, and when the latter has dissolved, 12 kilos. of zinc chloride are added in small portions at a time. The mass remains homogeneous, and when the temperature has reached 180–190° it foams up, but this foaming soon subsides. After the temperature of this mixture has been kept at 180–190° for about five hours, the lid of the pan, together with the stirrer, is lifted off, and the molten material is poured on iron or copper trays in which it soon sets to a brown mass. This is broken up with a hammer and finely ground in a ball-mill, when the powder has a dirty brownish-yellow colour. It is then boiled with about 1200 litres of water and 90 kilos. of hydrochloric acid in a tub fitted with a stirrer, the liquid allowed to settle, and the solution decanted or filtered off. The residue is again boiled two or three times with 1200 litres of water without the addition of hydrochloric acid. On filtering, the liquor which runs away is dirty and the solid product is fairly bright. The dye is pressed or centrifuged and dried. If it is to be put on the market, it must be sieved in order that it may dissolve quickly and easily in alcohol, but if it is to be sulphonated it is sufficient to powder it with a wooden hammer and spatula. The yield is 60 kilos. (Ullmann, " Enzyklopädie der technischen Chemie," III, 363). In the melt is also formed an isomeride, *iso*quinophthalone,  $C_9H_6N{\cdot}CH{:}C{<}^{O\cdot CO}_{C_6H_4}$ (m. p.

187°), which can be converted into quinophthalone by heating at 240° or by digesting the crude melt with the necessary amount of sodium ethoxide solution on the water-bath until the mass is uniformly red. It is then filtered off and washed with alkaline alcohol until the filtrate is pale yellow. The sodium derivative of the quinophthalone is then decomposed by boiling water and the pure dye dried at 100° (Eibner, G.P. 158761. See also Eibner and Lange, *Annalen*, 1901, **315**, 303; Eibner and Merkel, *Ber.*, 1904, **37**, 3006; Eibner and Hofmann, *ibid.*, 3011, 3018; Eibner, *ibid.*, 3605).

In the patent describing the production of this dye (Jacobsen, E.P. 1362^{83}; G.P. 23188; U.S.P. 290585; compare also Traub, *Ber.*, 1883, **16**, 297, 898; Jacobsen and Reimer, *ibid.*, 513, 1082), it is stated that 1 mol. of phthalic anhydride, 2 mols. of quinaldine, and 1 mol. of zinc chloride are heated at about 250° for five to six hours, at which temperature, apparently, the *iso*quinophthalone would be converted into quinophthalone. The product is boiled with water containing hydrochloric acid or is dissolved in concentrated sulphuric acid and the solution poured into water. The dye may be purified by crystallisation from boiling glacial acetic acid.

Quinoline yellow, soluble in water.

This is the sodium salt of the disulphonic acid of quinophthalone (quinoline yellow, spirit-soluble). The position of the sulphonic acid groups is not known, but they are probably in the quinaldine nucleus as, on oxidation, the dye yields phthalic acid.

The sulphonation is effected in a jacketed pan, fitted with a stirrer, of about 200 litres capacity. It is charged with 50 kilos. of fuming sulphuric acid (containing 24 per cent. of sulphur trioxide) and 25 kilos. of dry Quinoline yellow are added very slowly with good stirring and cooling. The temperature at the beginning should be 35° and the development of heat is very great, so that the introduction of the dye should last two and a half to three hours, the temperature of the mixture being 40–47°. The Quinoline yellow, which at first clots together to lumps, gradually dissolves when the temperature is raised to 60°. The temperature is kept at 60° for two hours and then steam is turned into the jacket and the mass heated fairly rapidly at 100°. This temperature is maintained until a sample dissolves easily in cold water or alkaline water, which occurs in less than half an hour. The sulphonation proceeds very rapidly at 100° and must not be continued further than the point when a sample gives a fairly clear solution in water or dilute alkali, as otherwise polysulphonic acids are formed, which are not precipitated in the subsequent salting out and are thus lost. In addition, Quinoline yellow which has been sulphonated too far is impure, grey, and weak, so that the greatest attention must be directed to the time of sulphonation. The sulphonation at 100° is often complete in a few minutes, and is mostly finished in a quarter of an hour.

The steam is then shut off, cold water run through the jacket, and the mixture at once scooped out on to broken ice (200–300 kilos.) contained in a tub fitted with a stirrer. About 300 litres of cold water and 300 litres of salt solution are now added, the mixture is stirred well for some time, and left over-night.

On the following day, it is stirred again for an hour and filtered through a wooden filter-press fitted with woollen cloths. The more or less dark-coloured filtrate is run away. The well-pressed acid cake is dissolved in 1000 litres of hot water in a tub fitted with a stirrer and neutralised or made slightly alkaline with sodium hydroxide solution (sodium carbonate produces too much foaming). The solution is filtered through sacks into a tub standing at a lower level, salt is added to the hot solution, and, when quite cold, the dye is filtered off. By working in this way, the filtration of the dye is rendered easier.

It is dried on galvanised iron trays and finely ground in a ball-mill. The yield is 37 kilos. (Ullmann, "Enzyklopädie der technischen Chemie," III, 363). In Jacobsen's patent, to which reference has been made on p. 182, it is stated that the sulphonation is effected by means of chlorosulphonic acid at 100°, the solution being diluted with water, neutralised with sodium carbonate or milk of lime, and the dye salted out.

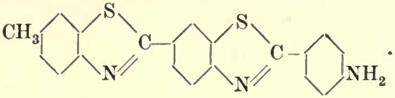
CHAPTER XII

THIOBENZENYL COLOURS

PRIMULINE—THIOFLAVINE—DIAMINE FAST YELLOW

PRIMULINE.

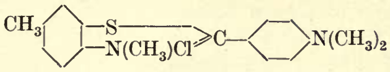
According to Green (Thorpe's "Dictionary of Applied Chemistry," 1913, IV, 386), commercial Primuline consists almost entirely of the monosulphonate of the base



By heating *p*-toluidine with sulphur in the proportions of 4½ atoms of the latter to 2 mols. of the former, a mixture of primuline base and dehydrothio-*p*-toluidine is formed. These can be separated by boiling the finely powdered and sieved crude product with alcohol when about 30 per cent. dissolves. The filtrate contains the dehydrothio-*p*-toluidine, and the residue consists of primuline base (Dahl & Co., F.P. 192305; G.P. 47102; U.S.P. 415359). The best method of separation, however, depends on the fact that the ammonium salt of dehydrothio-*p*-toluidinesulphonic acid is insoluble in water whilst that of primuline is soluble. Another method consists in dissolving the mixture of sulphonic acids in twenty times their volume of water and the necessary amount of sodium hydroxide solution at 80°, adding salt to make an 8 per cent. salt solution, and filtering at 75°. The primuline remains behind and the sodium dehydrothio-*p*-toluidinesulphonate is salted out from the filtrate.

The manufacture of Primuline has already been very fully described in the author's book, "The Manufacture of Intermediate Products for Dyes" (Macmillan & Co., London, 2nd ed., 1919, p. 78) and by Green (*loc. cit.*); (compare also Farbenfabriken vorm. F. Bayer & Co., E.P. 6319^{88}; F.P. 190535; G.P. 50525), so that the description need not be repeated here.

Thioflavine T,

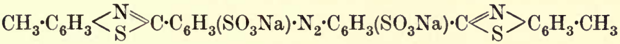


A mixture of 24 kilos. of dehydrothio-*p*-toluidine, 30 kilos. of methyl alcohol, and 11·6 kilos. of hydrochloric acid (21° Bé.) is heated in an autoclave for twelve hours at 160–170°. The product is boiled for some time with 200 litres of water and the solution filtered.* To the hot solution are added 50 kilos. of salt and, on cooling, the dye separates in glistening leaflets (Cassella & Co., E.P. 14884^{88}; F.P. 190535; G.P. 51738; U.S.P. 412978; compare Green, *Trans.*, 1889, **55**, 230).

It is also said to be obtained by heating 34·5 kilos. of sodium dehydrothio-*p*-toluidinesulphonate with 100 kilos. of methyl alcohol for ten hours at 160–170°. The contents of the autoclave consist of the sulphate of the dye, which is worked up as described above (*idem*, E.P. 14884^{88}; F.P. 190535; G.P. 55333).

Chlorophenine Y.

Diamine Fast yellow 2F.



$CH_3{\cdot}C_6H_3{<}{}^{N}_{S}{>}C{\cdot}C_6H_3(SO_3Na){\cdot}N_2{\cdot}C_6H_3(SO_3Na){\cdot}C{<}{}^{N}_{S}{>}C_6H_3{\cdot}CH_3$

A solution of 50 kilos. of dehydrothio-*p*-toluidinesulphonic acid in 1000 litres of water and 8–10 kilos. of sodium carbonate is treated at 10–15° with a solution of sodium hypochlorite prepared by decomposing 50 kilos. of bleaching powder with the calculated amount of sodium carbonate. The originally colourless liquid, which has a faint violet fluorescence, becomes first dirty grey and then a gradually deeper reddish-yellow, the reaction being at an end in twenty-four hours. The dye is salted out, filtered, washed on the filter with salt solution until no hypochlorous acid can be detected in the filtrate, and dried. The oxidation may also be effected with potassium ferricyanide or lead peroxide (Farbenfabriken vorm. F. Bayer & Co., E.P. 19061^{91}; F.P. 216954; G.P. 65402).

Five hundred lb. of ammonium dehydrothio-*p*-toluidine-

* If the crude mixture of dehydrothio-*p*-toluidine and primuline base has been methylated, the dimethylprimuline base remains behind at this point. On sulphonating this, Thioflavine S is obtained which is also formed by methylating primuline.

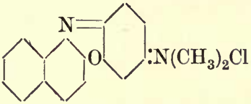
sulphonate are boiled with 500 gallons of water and a slight excess of sodium hydroxide until all the ammonia has been expelled. When cold, the solution, contained in a lead-lined vat of about 1800 gallons capacity, is diluted with 500 gallons of water, and 180 gallons of sodium hypochlorite solution (containing 13 per cent. of active chlorine) are added. After remaining over-night, the mixture is heated slowly by direct steam and finally kept at about 80° until all chlorine has disappeared. The disappearance of the chlorine should take place slowly and the product should acquire a bright orange-yellow colour. If this is not the case, more hypochlorite must be added. The dye is then salted out by adding about 900 lb. of salt, filtered, and dried. The yield is about 700 lb. When the mixed sodium sulphonates obtained from the crude primuline melt are oxidised in the above manner, the products are known as Chloramine Yellow (By), Oxyphenine (Cl. Co.), Diamine Fast Yellow B (C), and Columbia Yellow (A), and when Primuline itself is oxidised the dye is known as Thiophosphine J (Lucien Picard & Co., F.P. 209519).

CHAPTER XIII

OXAZINE AND THIAZINE COLOURS

MELDOLA'S BLUE—GALLOCYANINE—METHYLENE BLUE—METHYLENE GREEN

MELDOLA'S BLUE,

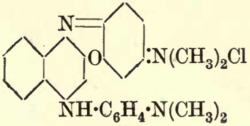


A mixture of 20 kilos. of β-naphthol, 20 kilos. of *p*-nitrosodimethylaniline hydrochloride, and 90 kilos. of alcohol contained in an enamelled pan furnished with a reflux condenser and set in a water-bath is slowly heated until a vigorous reaction sets in. The mixture is then rapidly run out of the pan and the dye precipitated by adding zinc chloride solution. The crystals are centrifuged, washed with about 35 kilos. of alcohol, and dried. The yield is 28 kilos. (Schultz, "Farbstofftabellen," 1914, p. 221).

In this reaction, Nietzki and Otto (*Ber.*, 1888, **21**, 1745) have shown that two molecular proportions of β-naphthol condense with three of *p*-nitrosodimethylaniline according to the equation

$$2C_{10}H_7{\cdot}OH + 3NO{\cdot}C_6H_4{\cdot}N(CH_3)_2,HCl = 2C_{18}H_{15}ON_2Cl + N(CH_3)_2{\cdot}C_6H_4{\cdot}NH_2,HCl + 3H_2O,$$

and Hirsch and Kalckhoff (*Ber.*, 1890, **23**, 2992) point out that, in order to use up all the naphthol the proportions indicated in the above equation must be employed. If the reaction is allowed to proceed too far, the *p*-aminodimethylaniline acts on the blue already formed with the production of New blue B,

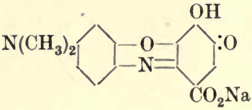


The formation of this condensation product can be almost prevented if zinc chloride is introduced at the beginning of the preparation of Meldola's blue so as to precipitate the dye as soon as it is formed and so remove it from the sphere of action.

The alcoholic filtrate, containing the *p*-aminodimethylaniline hydrochloride, may be neutralised and distilled to recover the alcohol, and the base which remains can be used for making Safranine.

Meldola's blue can also be obtained, but not so conveniently, by oxidising equimolecular proportions of *p*-aminodimethylaniline and β-naphthol in aqueous solution with chromate.

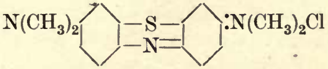
Gallocyanine,



In order to prepare pure Gallocyanine, the technical product is dissolved with the aid of sodium carbonate, the solution filtered, and dilute acetic acid added. The precipitate is washed, pressed, and dissolved in water and sodium hydrogen carbonate, the solution filtered, dilute acetic acid added, and the precipitate washed and dried. On crystallisation from xylene, green crystals with a metallic lustre are obtained which are insoluble in cold water but dissolve in boiling water to a pure blue solution. The solution in sodium hydrogen carbonate has the same colour and no doubt contains the sodium salt of the carboxylic acid. The same blue salt is present when a little sodium hydroxide is added to the aqueous solution, but on the addition of more alkali hydroxide the violet di-salt is obtained in which the phenolic hydroxyl group takes part. On warming with excess of alkali hydroxide, the dye decomposes slowly with the development of dimethylamine. With glacial acetic acid, Gallocyanine gives a violet-red acetate which is completely hydrolysed by water. The solution in concentrated hydrochloric acid (dihydrochloride) is blue and becomes red (monohydrochloride) on dilution. The latter is largely hydrolysed by water. Fuming sulphuric acid (containing 5 per cent. of sulphur trioxide) gives a red solution (trisulphate) which on adding water becomes first blue (disulphate) and then red (monosulphate) (Kehrmann and Beyer, *Ber.*, 1912, **45**, 3338).

Other salts of nitrosodimethylaniline are the persulphate, thiocyanate, naphthalene-1 : 5- and -2 : 6-disulphonates. The use of these salts is especially advantageous in the condensation of nitrosodiethylaniline and gallic acid (Farbenfabriken vorm. F. Bayer & Co., E.P. 12207^{09}; F.P. 405537; G.P. 217397).

Methylene blue,



The earlier methods of producing this dye, namely, (1) by oxidising with ferric chloride a solution of *p*-aminodimethylaniline saturated with hydrogen sulphide (Caro, E.P. 3751^{77}; F.P. 122720; G.P. 1886; U.S.P. 204796) and (2) by oxidising with ferric chloride the product of the action of zinc sulphide on a dilute sulphuric acid solution of *p*-nitrosodimethylaniline (Oehler, E.P. 4048^{82}; G.P. 24125; U.S.P. 270311; both processes are described in detail by Mühlhäuser, *Dingl. Polyt. J.*, 1886, **262**, 371) have been supplanted by the so-called "thiosulphate process," which is described below.

In the first of the series of patents concerned with this process, 12 kilos. of dimethylaniline are dissolved in 40 litres of water and 65 kilos. of concentrated hydrochloric acid and converted into *p*-aminodimethylaniline by the addition of 7·1 kilos. of sodium nitrite followed by reduction with zinc. It is convenient to use as much zinc as will leave no free hydrochloric acid present. The solution is diluted to about 500 litres, 16 kilos. of dimethylaniline hydrochloride are added, and then 50 kilos. of sodium thiosulphate. The mixture is oxidised by adding a solution of 25 kilos. of potassium dichromate, boiled for about two hours, treated with about 53 kilos. of sulphuric acid, and the sulphur dioxide expelled by further boiling. The leuco-compound present in the solution is then oxidised by adding 8 kilos. of neutral sodium chromate, and the dye is salted out (Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 43^{86}; F.P. 173137; G.P. 38573).

In a patent of addition to the above (G.P. 39757) it is claimed that, in the first oxidation, the *p*-nitrosodimethylaniline can itself act as an oxidising agent, so that less potassium dichromate is required. Thus 12 kilos. of dimethylaniline are dissolved in about 35–40 kilos. of concentrated hydrochloric acid and treated with 7·2 kilos. of sodium nitrite. The *p*-nitrosodimethylaniline hydrochloride, which separates out after some time is filtered off and dissolved in 2000 litres of water. To this solution are added 16 kilos. of dimethylaniline hydrochloride (12 kilos. of dimethylaniline in the form of its hydrochloride), 54 kilos. of zinc chloride, and 25 kilos. of sodium thiosulphate, and the whole is heated at 90° for an hour. Thereupon 10 kilos. of potassium dichromate are added, the mixture is boiled for about two hours, and 28 kilos. of sulphuric acid are added to decompose the chromium lake. After expelling the sulphur dioxide, the further oxidation is effected by means of 18 kilos.* of sodium chromate and the dye, in the form of its zinc chloride double salt, is salted out.

The use of aluminium thiosulphate instead of the sodium salt is stated, in an involved patent (Badische Anilin- & Soda-Fabrik, E.P. 10314^{88}; G.P. 45839) to be advantageous, and the process is given, in a later patent (G.P. 46805), as follows: A solution (about 250 litres) of *p*-aminodimethylaniline hydrochloride, prepared from 6 kilos. of dimethylaniline by conversion into *p*-nitrosodimethylaniline hydrochloride and reduction of the latter by zinc dust, is neutralised at 18–20° with sodium hydroxide solution until the first permanent turbidity appears. To this are added 16 kilos. of aluminium sulphate and, after half an hour's stirring, a concentrated solution of 13 kilos. of sodium thiosulphate and then, rapidly, a solution of 4·8 kilos. of potassium dichromate in 75 litres of water. The mixture is stirred for an hour to complete the formation of the *p*-aminodimethylanilinethiosulphonic acid, diluted to 600 litres, and 6 kilos. of dimethylaniline, in the form of the neutral hydrochloride, are added. For the preparation of the indamine the mixture is stirred at 10–12°, a saturated solution of 14 kilos. of potassium dichromate is run in quickly, 75 kilos. of zinc chloride solution (50° Bé.), are added and the whole is heated for half an hour at 100°. After cooling, the crystalline methylene blue, which separates, is filtered off and purified, if necessary, by dissolving and reprecipitating.

Two accounts of the manufacture of Methylene blue have recently been published in the technical literature, of which the first is as follows: Nine kilos. of dimethylaniline are introduced into a lead-lined tub fitted with an agitator and are cooled to 5° by adding 50 kilos. of ice. To this mixture are added gradually, with constant stirring, 28 kilos. of hydrochloric acid, and ice is added so as to lower the temperature as far as possible to −10°, for the two reasons that the low temperature diminishes the unpleasant odour and increases the yield of the nitroso-

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* Compare the chief patent, in which 8 kilos. are given for the final oxidation.

compound. A solution of 5·75 kilos. of sodium nitrite in 25 litres of cold water is added slowly, and when this is all in the liquor is tested with nitrite and Congo-red papers to ensure the presence of nitrous and mineral acids respectively. The batch is then allowed to remain for two hours, when a solution of 35 kilos. of hydrochloric acid in 600 litres of cold water is added and the whole is stirred until the nitroso-compound has completely dissolved. Should a little still remain undissolved, water is added in just sufficient quantity to dissolve it. There are then added 20 kilos. of zinc dust, a little every ten minutes, the whole being well stirred, and the reaction is finished when the liquid has become colourless. The temperature should not exceed 15–20°. The operation lasts about ten hours. The liquid is filtered from the zinc into another vat, where it is neutralised with sodium hydroxide solution; it must be neutral to turmeric and then is left for about an hour. A solution of sodium thiosulphate, made by dissolving 19 kilos. of the salt in 50 litres of warm water, is now run in slowly from a tap, at 15–18°, the mixture allowed to cool, and left for half an hour. There is now added rapidly a solution of 7·2 kilos. of sodium dichromate in 15 litres of cold water and the whole is stirred for three hours. At the end of this time, 7·2 kilos. of dimethylaniline and 7·2 kilos. of hydrochloric acid are added separately with constant stirring. The liquid should be slightly acid to turmeric; if it is strongly acid, the acidity is diminished by adding sodium carbonate and stirring for two hours. Then a solution of 19·2 kilos. of sodium dichromate in 35 litres of cold water is run in fairly rapidly and the mixture stirred for two hours. The dye is precipitated by adding 30 kilos. of zinc chloride (50 per cent.), the batch heated at 70–75°, and then allowed to cool to 40°. The dye is then only partly precipitated, and the precipitation is therefore completed by adding salt, the product being filtered and pressed. The zinc chloride contained in the filtrate can be recovered by concentration, and may then be used a second time. The colour-paste is stirred with 400 litres of water until it is dissolved, the solution heated at 75–90°, and filtered hot. The filtrate is allowed to cool and the dye salted out from the solution, which is kept slightly acid with hydrochloric acid. The yield of concentrated Methylene blue is 19–20 kilos. It is reduced to "standard" qualities with dextrin (Bile, *Rev. Prod. Chim.*, 1918, **21**, 195).

The second process describes the use of aluminium sulphate in the operation, which is also conducted on a much larger scale.

The preparation of the nitroso-compound is carried out in a 200-gallon tub provided with a stirrer and about 30 inches in diameter so as to compel the passage of the nitrous acid through a relatively high column of liquid, inasmuch as it is introduced at the bottom. This tub should be so situated that there is plenty of ventilation, and if covered should be provided with a wooden fume pipe leading to a hood or fan. One hundred lb. of dimethylaniline is poured into the tub, and then mixed with 440 lb. of hydrochloric acid (22° Bé.). Sufficient ice should now be added to bring the temperature to 0°, but where there is outside cooling, as from brine circulating through lead coils, it is advisable to dilute the mass with an amount of water equal at least to one volume. A solution of 72 lb. of sodium nitrite in 35–40 gallons of water is introduced into the dimethylaniline hydrochloride, with constant stirring, by means of a lead pipe leading to the bottom of the tub, approximately at the rate of half a gallon per minute. This is most conveniently done by means of air pressure, only a few pounds being required. Care must be taken that there is no development of red fumes during the reaction, nor must the temperature be allowed to exceed 5°, ice being added if necessary. The amount of dilution with water or ice will have no influence on the yield, but too high a dilution is to be avoided for practical reasons.

The nitrosodimethylaniline hydrochloride separates out as formed as a bright yellow precipitate which can receive subsequent treatment in place, or if preferred, can be filtered and separated from the liquid in which it is suspended. Filtration is to be recommended only where the dimethylaniline used contains excessive amounts (3 per cent. or more) of monomethylaniline, for the presence of this tends to influence the shade of the colour produced. Under the conditions give above, monomethylaniline does not react and would pass off in the filtrate. In any event, it is advisable to carry out the next step—reduction—in a separate container of the same size and shape so as to avoid the disturbing influence of the zinc residues which tend to form as a cake on the sides of the tub and can be removed only with difficulty.

To the aqueous suspension of the nitroso-hydrochloride are added 220 lb. of hydrochloric acid (22° Bé.) over such a period that the temperature is allowed to reach 20°. To this mass, 125–130 lb. of zinc dust are added very slowly and with constant stirring, the temperature being maintained at 29–35° (ice being added, of course, if necessary). The addition of the zinc will take two and a half to three hours. An excess of zinc must be used to ensure complete reduction, the final product yielding a water-white solution slightly acid to Congo paper. This is allowed to remain over-night, with stirring, in the presence of the excess of zinc, and is then filtered through cloth into the main reaction vessel, which consists of a 2000 gallon tub fitted with a stirrer. In this all the reactions take place which convert the *p*-aminodimethylaniline hydrochloride into the colour base which is precipitated as the zinc chloride double salt and forms the crude material from which the marketable dye is obtained by purification. Extreme care must be exercised in carrying out every step in these main reactions, as the processes are very complicated and can easily be made to yield products absolutely valueless as dyes. Three hundred lb. of dry powdered aluminium sulphate are added to the water-white solution of the diamine with constant stirring, and this is maintained for twenty minutes.

During this time, the following solutions are prepared in separate containers: 214 lb. of sodium thiosulphate in 80 gallons of water and 100 lb. of sodium dichromate in 60 gallons of water, and both are brought to a temperature at least as low as 10°. At the end of the twenty-minute period, the mass in the main reaction tub is cooled to 10–20°, and thereupon the solution of thiosulphate is added and, immediately after, the solution of sodium dichromate, both additions being made as rapidly as possible and with constant stirring. As a matter of fact, the stirrer is never stopped from the beginning to the end of the reaction. This preliminary oxidation and conversion to the thiosulphonic acid is allowed to take place over one hour, during which the temperature rises perceptibly.

In the meantime, the neutral oil is prepared by dissolving 100 lb. of dimethylaniline in sufficient hydrochloric acid to give a solution neutral to Congo paper (about 85 lb. will be required) as well as solutions of 260 lb. of sodium dichromate in 130–140 gallons of water and 600 lb. of zinc chloride in 150 gallons of water, all being cooled, as before, to about 10°. At the end of the hour, the main reaction mass is cooled to 10–14° with ice, and the neutral oil added. Fifteen minutes later, the solution of sodium dichromate is added and twenty minutes after this the last addition—the solution of zinc chloride—is made. The mass is then diluted to about 1750 gallons and boiled for one hour by means of live steam. By these operations the thiosulphonic acid is converted into an indamine, the latter is oxidised to the leuco-base of the dye, which on further oxidation yields the colour-base itself. The zinc chloride serves the double function of converting the indamine and salting out or precipitating the dye as a double chloride, in which form it is but sparingly soluble and can be recovered easily. The dye appears as the insoluble sludge admixed with insoluble chromium and aluminium hydroxides. On completion of the reaction, the mass is allowed to cool to 40° and is then filtered.

As stated above, all the dye is contained in the filter-cake, whereas the filtrate is valueless from this point of view, and can be run to the sewer except where it is practical and economical to recover the zinc. This filter-cake, known as No. 1 sludge or first precipitate, has a characteristic bronzy, glistening appearance. For further treatment, it is mixed with about 1800–2000 gallons of boiling water and extracted with constant boiling and stirring for twelve hours, after which it is filtered hot, washed with hot water, and the filtrates are collected in a wooden vessel fitted with a stirrer, and fine salt, in amount equal to 10 per cent. of the quantity of water, is added while hot and with stirring. This salts out the dye, which separates in bright red crystals. After the mass has cooled it is filtered, the filtrate, which should contain practically no colour, is run to the sewer, and the press cake of pure colour is then ready for drying. The press cake obtained from the filtration of the solution of the first precipitate still contains an appreciable amount of colour, and is usually designated as second precipitate or No. 2 sludge. In order to recover the dye, it is subjected to the same treatment as the first precipitate; that is, it is mixed with water, boiled, filtered, and the filtrate salted out. The press cake thus obtained is then combined with that of the first salting out, the filtrate being run to waste. The extracted sludge contains practically no more recoverable colour, and can be thrown away except where the location and the equipment of the plant are such that a recovery of chromium is of more than theoretical interest. The dried colour is a reddish-brown powder and the yield in the process as outlined above should be at least 200 lb. of dye of at least 80 per cent. (Miller, *Colour Trade J.*, 1918, *Chem. Trade J.*, 1918, **62**, 395; *Dyer*, 1918, p. 192).

A laboratory process similar to the above but containing certain modifications important for the large scale manufacture is described by Fierz ("Grundlegende Operationen der Farbenchemie," 1920, p. 221). A solution of 24·2 grams of dimethylaniline in 75 grams of hydrochloric acid (30 per cent.) is allowed to cool, 150 grams of ice are added, and a 20 per cent. solution of 14·7 grams of sodium nitrite is added within an hour. The production of the nitroso-compound is complete in four hours. At the end of this time 110 grams of hydrochloric acid (30 per cent.), and 200 grams of ice are added, and then, within a quarter of an hour, 35 grams of zinc dust of good quality, the whole being mechanically stirred. The temperature may rise to 25° without harm. The solution is now colourless and contains no free mineral acid; it is filtered and the zinc dust washed with a little water.

The oxidation at this stage is conducted in the presence of zinc chloride solution, which must be devoid of any reducing action. On the large scale the commercial zinc chloride solution is treated with sodium dichromate until it shows no further reducing power. For 100 kilos. of zinc chloride solution 100–250 grams of sodium dichromate are often required. The thiosulphuric acid is used in the form of aluminium thiosulphate, which is so strongly dissociated that it acts as the free acid. Before the preparation of Methylene blue is proceeded with, solutions of the necessary reagents must be prepared, as it is important that they be added quickly and at the right temperature.

Solution I = 38 grams of pure aluminium sulphate in 60 c.c. of water.

Solution II = 52·5 grams of crystallised sodium thiosulphate in 50 c.c. of water.

Solution III = 57 grams of sodium dichromate dissolved to 90 c.c.

Solution IV = 20 grams of dimethylaniline in 27 grams of concentrated hydrochloric acid.

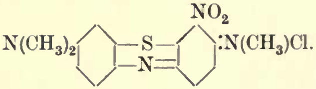
Solution V = 25 grams of most finely ground pyrolusite (MnO_2) mixed to a homogeneous paste with 30 c.c. of water.

The clear neutral solution of *p*-aminodimethylaniline is rendered acid by the addition of 4 grams of concentrated sulphuric acid and 100 grams of zinc chloride (50 per cent. neutralised as regards its reducing power) are added. Solution I is now poured in followed by solution II and immediately after two seconds one-third of solution III, corresponding with 19 grams of sodium dichromate. Dry steam is now led in, which raises the temperature to 40° in one minute, solution IV is added and the rest of solution III, and the whole heated rapidly at 70°. The solution becomes dark greenish-blue owing to the formation of the thiosulphonic acid and as soon as the temperature of 70° is reached solution V is added and the temperature raised to 85°.

The addition of the manganese dioxide serves to convert the sulphur dioxide, liberated by the ring-closure, into the harmless lead dithionate. Instead of manganese dioxide, 40 grams of copper sulphate may be used with like effect, the cupric salt being converted into insoluble cuprous sulphate. At 85°, the solution becomes bronzy and the dye precipitates. After half an hour, it is allowed to cool to 50° and 70 grams of concentrated sulphuric acid are added in order to dissolve the manganese salt, the aluminium hydroxide, and the chromium oxide. The dye is filtered off at 20° and washed with a little 10 per cent. salt solution. The crude colouring matter is dissolved in 1 litre of water at 100°, the solution filtered, and the filtrate precipitated with 50 grams of ordinary zinc chloride solution (50 per cent.) and 150 grams of salt. After twenty-four hours the zinc chloride double salt will have separated as a bronzy-red precipitate which is filtered off * and washed with a little 10 per cent. salt solution. The dye is dried at a temperature not exceeding 50°, the yield being about 44 grams.

The zinc-free dye is obtained by dissolving the ordinary product in water, precipitating the zinc with sodium carbonate, and filtering off the readily soluble Methylene blue base. This filtrate is treated with hydrochloric acid and salt whereby the Methylene blue is precipitated in a crystalline form. The crystallisation on the large scale takes several days and is hastened by cooling the solution by means of lead pipes through which cold water is allowed to circulate.

Methylene green,



I. One part of Methylene blue is dissolved in 100 parts of water and the solution acidified with 10 parts of sulphuric acid. To the cold solution is added gradually a solution of 0·8 part of sodium nitrite. The conversion of Methylene blue into the green dye proceeds slowly and is complete only after several days. When the solution has become pure green, the dye is salted out, filtered, and purified by redissolving and salting out. The reaction can be hastened by warming, but this is not advisable as the yield is thereby diminished. It can, however, be completed more rapidly by adding nitric acid (Farbwerke vorm.

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* On the large scale, the dye is generally filtered on open filters, then filled into small sacks, and centrifuged.

Meister, Lucius, & Brüning, E.P. 8992^{86}; F.P. 177131; G.P. 38979).

II. According to Gnehm (*J. pr. Chem.*, 1907, [ii], **76**, 408), a solution of 20 grams of Methylene blue in 1 litre of water is mixed with 200 c.c. of sodium nitrite solution (containing 37 grams of sodium nitrite) and cooled to 0°, whereby the Methylene blue separates almost quantitatively as a crystalline, violet blue precipitate, probably the nitrite. To this, 200 c.c. of nitric acid (36° Bé.) are added gradually, the temperature not being allowed to rise above 5–8°. The conversion to Methylene green is complete on leaving at the ordinary temperature for two days, the dye being deposited in bronzy needles. The average yield is 57–62 per cent., the dextrin content of the blue not being taken into account. With pure Methylene blue hydrochloride the yield is 80 per cent. The author adds that an earlier process (Grandmougin and Walder, *Zeitsch. Farb. Ind.*, 1906, **5**, 285), according to which Methylene blue is nitrated in acetic acid solution at 80–82°, gives a small yield and the purification of the product is difficult.

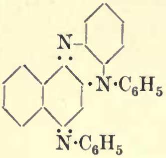
III. An amount of the zinc chloride double salt of Methylene blue equal to one-fifth of a gram-molecular weight (prepared from the nitroso-compound of 24·2 grams of dimethylaniline and equal to about 44 grams of the dry dye) in the form of paste is mixed with 50 c.c. of water and 20 grams of nitric acid (60 per cent. 40° Bé.), and a solution of 5 grams of sodium nitrite in the smallest possible quantity of water is added at 25°. The mixture is well stirred and warmed carefully and gradually at 50°, at which temperature it is kept for two hours. It is then diluted with 200 grams of saturated salt solution and filtered after twelve hours. The crude product is dissolved in a litre of water at a temperature not exceeding 60°, the solution filtered, and the dye precipitated by adding 150 grams of salt and 50 grams of zinc chloride solution. It is filtered after twelve hours and dried at 45° until the dye can be powdered. It then still contains about 20 per cent. of water. If it is completely dried. the strength of the dye becomes less and some becomes insoluble. The yield is about 38 grams (Fierz, "Grundlegende Operationen der Farbenchemie," 1920, p. 224).

CHAPTER XIV

AZINE COLOURS

AZOCARMINE—SAFRANINE—INDULINE—NIGROSINE—METHYLENE GRAY

Azocarmine G paste,



(Sodium disulphonate; the position of the sulphonic acid groups is unknown.)

A mixture of 10 kilos. of benzeneazo-α-naphthylamine hydrochloride, 10 kilos. of aniline hydrochloride, and 35 kilos. of aniline is heated in an oil-bath within an hour gradually at 100–130°. The temperature is maintained at 130° until the formation of the dye is complete or until a sample dissolves in ether with a red, and in concentrated sulphuric acid with a green, colour. The cooled product is boiled with dilute hydrochloric acid, cooled, filtered, and the residue washed with water to remove aniline hydrochloride, etc., and dried.

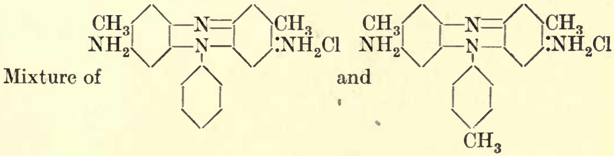
For purification, 10 kilos. of the crude dye are extracted at 100° repeatedly with 30 kilos. of toluene each time until the soluble brown impurities are removed. The undissolved residue is freed from toluene and dissolved in about 20 kilos. of alcohol. On rendering the reddish-violet alcoholic solution alkaline with sodium hydroxide solution, the colour-base separates and, after filtration, washing, and drying, can be obtained in glistening, dark reddish-brown crystals melting at 233–234° by solution in five times its weight of hot toluene.

In order to prepare the disulphonic acid, 10 kilos. of the dye are heated with 40 kilos. of fuming sulphuric acid (containing 23 per cent. of sulphur trioxide) at 90–95° until a sample, mixed with ten times its quantity of water, gives a red precipitate which dissolves in pure water on boiling. The acid mixture is then poured into 200 litres of ice-water, filtered, pressed, and the press cake is mixed with 400 litres of water and ammonia added until it is quite dissolved. The solution is boiled until a sample, on cooling, deposits the crystalline ammonium salt almost completely. The bulk is then allowed to cool, the salt filtered, pressed, and dried.

The potassium and sodium salts are obtained in a similar way (Badische Anilin- & Soda-Fabrik, E.P. 15259^88; G.P. 45370; U.S.P. 430975).

The base was prepared by O. Fischer and Hepp (*Ber.*, 1888, **21**, 2621) by adding 1 part of nitrosophenyl-α-naphthylamine to a solution, heated at 90°, of 1 part of aniline in 4 parts of glacial acetic acid and heating the mixture until it becomes deep red. This is then treated with water and dilute hydrochloric acid, the residue boiled with alcohol, and the solution, after diluting with water and filtering from a little tar, precipitated with ammonia. When crystallised from a mixture of benzene and alcohol, it melts at 235°. It is insoluble in water, rather sparingly soluble in alcohol, more readily so in benzene.

Safranine,



I. According to Harmsen ("Die Fabrikation der Theerfarbstoffe," 1889, p. 273), 21 kilos. of *o*-toluidine are mixed in a jacketed enamelled pan with 10 kilos. of hydrochloric acid, and a solution of 7 kilos. of sodium nitrite in 15 litres of water is run in slowly at exactly 40°. Then 9 kilos. of aniline (Safranine G extra) or 10 kilos. of *o*-toluidine (Safranine B) and 5 kilos. of hydrochloric acid are added and the mixture is allowed to remain at 40° for a day. For Safranine G extra, 30 kilos. of the échappé of the Magenta manufacture (free from *p*-toluidine) may be used instead of the 21 kilos. of *o*-toluidine and 9 kilos. of aniline. The product, which consists of a mixture of 1 mol. of aminoazotoluene and 1 mol. of aniline or *o*-toluidine is mixed with 500 litres of boiling water and reduced by adding zinc dust and hydrochloric acid in small portions at a time until the solution is colourless or only faintly red. About 20 kilos. of zinc dust and 30 kilos. of hydrochloric acid are required. The solution is filtered from the residue, which must be a fine powder and entirely inorganic (otherwise too little hydrochloric acid has been used), allowed to cool, diluted to about 2000 litres, treated with 10–15 kilos. of chalk and oxidised by adding a dilute solution of neutral sodium chromate. The liquid becomes intensely blue, and if a drop is brought on filter-paper the spot is blue and the rim colourless. If a drop of the sodium chromate solution is now brought into contact with the rim a green streak is formed until exactly 2 atoms of oxygen have been used up. Then exactly half the amount of sodium chromate which has been used is added and steam passed in so that the mixture boils. The blue indamine is thereby converted into Safranine. The mixture is filtered, the filtrate salted out, and the crude Safranine is redissolved in 1000 litres of water, sodium carbonate solution being added until there is a distinctly alkaline reaction. The liquid is then filtered and the dye salted out.

Instead of zinc dust, iron may be used, and instead of sodium chromate, manganese dioxide and oxalic acid. The yields are about 75 per cent. of Safranine G extra and 85 per cent. in the case of Safranine B.

II. The reduction with iron instead of zinc is described in the following process (Lefèvre, "Traité des Matières Colorantes," 1896, p. 717). Twenty-one kilos. of *o*-toluidine are mixed in a jacketed enamelled pan with 10 kilos. of hydrochloric acid; the solution is kept at 20°, and a solution of 7 kilos. of sodium nitrite in 15 litres of water is run in. Then 9 kilos. of aniline are added and the mixture is kept for a day at 40°. It is then added to a mixture of 36–40 kilos. of iron filings or turnings, and 50 litres of water contained in a cast-iron pan fitted with a lid and 60–70 kilos. of hydrochloric acid are introduced in a thin stream, the mixture being stirred and the temperature kept at 30–40°. At the end of five to six hours, the solution will have become colourless. The mixture is then blown by compressed air on to open woollen filters resting on the top of a large wooden vat on the same level as the reduction pan. The filtrate is diluted to 2000 litres and allowed to cool, when the excess of hydrochloric acid is neutralised by adding powdered chalk (about 40 kilos.) and the temperature is lowered to 10–12° by the addition of ice. Oxidation is effected in the cold by adding a solution of potassium dichromate or, more economically, sodium dichromate. The mixture is well stirred for a quarter of an hour and the liquid, at first green, becomes blue. When a filtered sample no longer turns green on adding sodium dichromate, the reaction is finished. After leaving over-night, the liquid is red. It is run into a tub standing on the stage beneath, half the amount of dichromate already employed is added, and the mixture boiled; the Safranine is formed and the liquid becomes red. When the oxidation appears to be complete, the batch is run into a receiver containing a steam-coil, standing on a lower stage, and the boiling liquid blown through a filter-press standing on the stage above. The filtrate and wash waters run into a wooden vat, where the dye is salted out. The precipitation is complete when filter-paper, dipped into the liquid, is no longer coloured. The dye is then collected in a filter-press. In order to purify it, the press cake is dissolved in 2000 litres of boiling water and the colour of the solution is examined. If it is not the required shade, 4–6 kilos. of dichromate and 4–6 kilos. of sulphuric acid are added to the boiling solution. If the shade is still not sufficiently pure, a little more dichromate is added. The liquid is then rendered alkaline with 10–12 kilos. of sodium carbonate which precipitates violet colouring matters and chromium oxide, filtered through a filter-press, and the dye salted out. It is collected in a filter-press and the cakes are pressed hydraulically, broken up, dried, and powdered. The yield of tolusafranine is 60–70 per cent. of the theoretical and that of phenosafranine 50 per cent.

III. Reduction with tin is described in a book dealing almost entirely with the manufacture of Safranine by Walter ("Aus der Praxis der Anilinfarbenfabrikation," 1903, the second edition of which is called "Erfahrungen eines Betriebsleiters," 1905). Elaborate details and drawings of plant are given, together with a plan of the Safranine plant. The process is as follows:

In an enamelled pan (150 litres capacity) fitted with a stirrer (90–95 revolutions per minute), 24 kilos. of *o*-toluidine are mixed with 14·5 kilos. of hydrochloric acid (31–31·5 per cent.) and the mixture is cooled to 18–20° externally. Then 7·8 kilos. of finely powdered sodium nitrite are added gradually, the temperature being allowed to rise to 33°. When the whole of the nitrite has been added, stirring is continued for fifteen minutes. The addition of nitrite takes two and a half to three hours (7 a.m. to 9.30 or 10). Two such pans are worked simultaneously. The contents of each pan are now filtered through sack cloth on an open filter frame resting on a wooden cask, and washed with a little water. In the afternoon, the same operations are repeated with the next batches, whilst the residues on the filters, consisting of aminoazotoluene, are transferred to wooden buckets and left there for two days.

The second operation consists in reducing the aminoazo-compound to 1 molecule of *p*-tolylenediamine and 1 mol. of *o*-toluidine. In each of two enamelled pans (each about 250 litres capacity) fitted with stirrers (65–70 revolutions per minute) are placed 30 kilos. of granulated tin which is covered with 80 kilos. of hydrochloric acid and into each is introduced slowly the contents of a bucket of aminoazotoluene (corresponding with 24 kilos. of *o*-toluidine) whereby the temperature may rise to 70°; this lasts thirty to forty minutes. When the liquid has become clear and contains no dark lumps which, when crushed, are red, cold water is added to bring the temperature to about 60° and the dissolved tin is precipitated with zinc. For this purpose, 15 kilos. of zinc dust for each reduction pan are, shortly before, stirred with about 25 litres of water in a tin and the paste is gradually added to the reduction pan, care being taken that at each withdrawal of paste from the tin the paste is well stirred up. During this operation care must be taken that the mass does not foam over and that the stirrer does not throw out foam with liquid. The addition of zinc is finished in about half an hour and the temperature rises to 80°. The precipitation of tin must be complete and in order to check this a sample is filtered into a test-tube, dilute hydrochloric acid added, and hydrogen sulphide passed through. No dark coloration should be produced, but if this does occur a little more zinc dust paste must be added and the test repeated. The contents of both pans are then filtered hot through a felt filter into a cask (600 litres capacity), when nearly all the tin remains as a heavy precipitate in the reduction pan and is washed with hot water.

The tin paste on the filter is divided roughly into two parts, which are returned to the pans. The precipitated tin is used instead of granulated for the next batches, but to each pan is added also daily 0·5–1 kilo. of fresh tin, according to the amount shown on titrating the precipitated tin residue.

In the first year in which this process was used the regenerated tin was employed so long that the addition of 3 kilos. per pan was no longer of use; later it was found advantageous to use fresh granulated tin after thirty batches.

The filtrate from the two reduction pans, together with the wash-water, is 300–320 litres, and this volume is made up with water to a fixed volume of 350 litres in order to control the course of the reduction in the laboratory and to fix the amount of aniline to be added later.

The titration of the reduction liquor is done by a laboratory boy. The workman brings him a sample of the liquor, made up to 350 litres, and of this 100 c.c. are measured out into a 2-litre porcelain basin, two handfuls of broken ice added, then 50 c.c. of 40 per cent. acetic acid and water so as to bring the volume equal to about half that of the basin, and 100 c.c. of a 10 per cent. solution of potassium dichromate are added all at once with stirring. A drop of the liquid is now brought on to filter-paper; round the blue colour of the indamine forms a pale to almost colourless rim, a little outside of which is placed a drop of dichromate solution. If not enough of the latter had been added, a blue line is formed at the junction of the two solutions. In this case, 5 c.c. more dichromate solution are added with stirring to the basin and the test made until no blue colour is obtained. The 100 c.c. of dichromate correspond with 18 kilos. of aniline and each 5 c.c. corresponds with 500 grams more, so that 120 c.c. correspond with 20 kilos. of aniline which must be added, as hydrochloride, to the boiling-pan after the formation of the indamine.

From the cask containing the filtrate the liquid is run in the afternoon (or from the afternoon reduction, on the next morning) to a larger wooden tub of about 1400–1800 litres capacity, where it is stirred (35–40 revolutions per minute) and a solution of 40 kilos. of oxalic acid in boiling water is added to it and then so much cold water and ice that, when three-quarters full, the temperature is not above 20°. In the year 1896, the oxalic acid was substituted by 95 kilos. of sodium bisulphate (5 grams required 33 c.c. of normal sodium hydroxide) added as a coarse powder while stirring, but the average yield fell by at least 1 kilo.

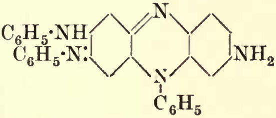
For the oxidation, the third reaction, 180 or 200 kilos. of finely-ground regenerated manganese dioxide, according to the brand of Safranine required, are ground with water, placed in a horizontal cylindrical wrought-iron pan of 8000 litres capacity, furnished with a stirrer (35 revolutions per minute), dome, and the other usual fittings, and tested to 5 atmospheres pressure, and the volume adjusted to about 1800 litres. The stirrer is started, the pan closed, and the pressure reduced by means of a steam injector fitted to the pan so as to draw in the reduced solution; the tub containing the latter is washed out (the washings also running into the pan), the lid of the pan opened, and, according to the analysis, 18–20 kilos. of aniline dissolved with 21 kilos. of hydrochloric acid in about 150 litres of water are run in and the petroleum cask which has contained the aniline solution is also washed out into the pan. The stirrer is kept going for at least an hour, when it can be stopped for the midday interval or over-night. The volume of the liquid is now about 4000 litres, and reaches to about the centre of the pan. The stirrer is now started again and the steam pipe, consisting of a perforated pipe on the lowest part of the pan, is fully opened. As soon as the liquor begins to foam, the steam valve must be regulated to avoid foaming over, and possibly the stirrer stopped for a short time. The foam is kept in the dome of the pan and the course of the reaction can be followed by its appearance, first fine and then larger bubbles; when the foam begins to drop, more steam is turned on. From this point the workman takes samples with a wooden stick and allows drops to fall on filter-paper; at first a violet rim runs out of the central dark drop, which is later red, and on the outside edge the red is encircled by a violet rim; finally, this disappears. To be quite certain, the stirrer and steam are stopped and a sample, without foam, is taken from the liquid. If this is also pure red, the stirrer is again started, the lid of the dome is closed, the steam valve opened, and the pressure in the pan increased to 1 atmosphere. The steam is then shut off and the compressed air tap opened and finally the tap leading to the two filter-presses which are simultaneously used.

The filtrate and wash waters from these, containing the Safranine, run to one of two wrought-iron reservoirs each of approximately 8000 litres capacity, and from here on the following day to a receiver (8500 litres) fitted with a stirrer containing 500 kilos. of salt: the salt is dissolved by stirring and the Safranine is precipitated and blown through a filter-press, in which the crude dye remains.

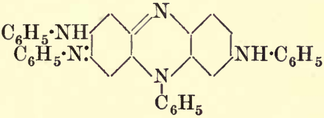
The fourth operation consists in purifying the crude product and standardising it. The paste from the filter-press is mixed to a thin paste with hot water in a tub (500 litres), from which it runs into a receiver such as is used for salting out the crude dye. The total amount of water for dissolving the paste is 2000 litres. Solution is completed in the receiver by means of steam. Now 3–14 litres (according to the brand of Safranine required) of a solution of 50 kilos. of crystallised sodium sulphide in 150 litres of water are added, the solution is filtered through a small filter-press into one of two half-cylindrical copper pans, each of 3000 litres capacity, the press washed with boiling water, and the filtrate salted out with 200 kilos. of salt; in winter, 150 kilos. are sufficient. Next day, the Safranine is filtered in a filter-press, the cake pressed in a hydraulic press, dried on copper trays, and ground. The yield of the dried product, before standardisation, is 50–55 kilos.

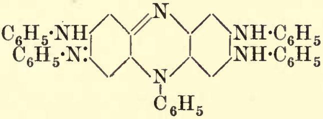
Indulines (spirit and water soluble).

The compounds formed when aminoazobenzene is heated with aniline and aniline hydrochloride vary in shade from reddish-blue to pure blue according to the amounts taken, the duration of the heating, and the temperature. In all cases they are probably mixtures of substances of which the bases have the following formulæ :



Reddest shade.



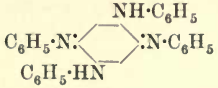


Bluest shade.

The spirit-soluble Induline gives, on sulphonation, a product which is soluble in water and probably consists of a monosulphonic acid.

In the earlier work on Indulines, separation of the components was brought about by means of alcohol, and although this is no longer done, it will be of interest to record the operation as described by Witt and Thomas (*Trans.*, 1883, **43**, 112; E.P. 1487^{81}; F.P. 142468; G.P. 17340).

A mixture of 2 parts of diazoaminobenzene, 1 part of aniline hydrochloride, and 4 parts of aniline is kept at a gentle heat for twenty-four hours in order to transfer the diazoaminobenzene into aminoazobenzene. The mixture is heated for twenty-four hours on the water-bath—at this stage it contains chiefly azophenine,



—and then the temperature is raised to 125–130° and kept at this point for twelve hours. The melt is allowed to cool very slowly, and under these conditions a crystalline deposit is formed, which may be separated by filtration and washing with spirit, in which the crystalline compound is almost insoluble.

The filtrate and spirit washings contain Induline B hydrochloride. The crystals on the filter are washed with boiling water to remove ammonium chloride and the product is called Induline 3B. It is of a sky-blue shade, and its free base dissolves with a purple coloration in spirit or aniline.

Referring again to the original mixture of diazoaminobenzene, aniline, and aniline hydrochloride, if the proportion of the latter be increased and the temperature maintained at 165–170°, only small quantities of Induline 3B will be formed and another substance will be found to crystallise out of the melt. This is Induline 6B. The best method of preparation consists in heating a mixture of 100 lb. of aminoazobenzene, 130 lb. of aniline hydrochloride, and 300 lb. of aniline for four to five hours at 110°. After that time, 65 lb. of aniline hydrochloride are added, and the mixture is then heated at 165–170° for twenty-four hours. The melt is allowed to cool, mixed with 50 gallons of methylated spirit, and allowed to drain on a filter. The insoluble residue after repeated washing with spirit consists of yellowish-brown crystals of the chloride of Induline 6B. It is washed with hot water to remove ammonium chloride, and dried.

To render it soluble, it is sulphonated by treatment with 3 parts of sulphuric acid (*d* 1·840) at 110° for about six hours. It is then precipitated by a large quantity of water, washed on a filter, dissolved in water containing sufficient sodium hydroxide, and evaporated to dryness. The filtrates contain Induline B, which is extracted, and spirit and aniline, which are recovered in the usual way.

Harmsen ("Die Fabrikation der Theerfarbstoffe," 1889, p. 279) states that Induline 6B is obtained by heating a mixture of 50 kilos. of aminoazobenzene, 50 kilos. of aniline hydrochloride, and 250 kilos. of aniline at 160° in a pan similar to that used for the Aniline blue melt. When the mass has attained the desired shade, the operation is stopped, the product is acidified with hydrochloric acid, exactly as in the case of Aniline blue, and the insoluble Induline is separated from the solution of aniline hydrochloride, from which, after neutralisation with lime, the aniline is recovered by means of steam. The Induline is dried at 70°, powdered, and sulphonated with 6 parts of sulphuric acid at 100°, as in the case of Soluble blue. The product is poured into water, the insoluble sulphonic acid filtered, washed, neutralised with sodium hydroxide, and the solution evaporated.

When a spirit-soluble Induline for lakes is required, the mixture is heated only until the aminoazobenzene (recognisable by its yellow colour) has disappeared. It is advantageous to prepare the small amount of spirit Induline that is required by extracting the blue-shade Induline with alcohol and distilling off the solvent, whereby a very pure, green Induline is obtained.

A more recent process is given by Schultz ("Chemie des Steinkohlentheers," 3rd ed., 1901, II, p. 343). A solution of 14·4 kilos. of sodium nitrite is run into a mixture of 250 kilos. of aniline and 24 kilos. of hydrochloric acid (35 per cent.). The mass is left for some time and then heated with steam at 40–50° in order to complete the change from diazoaminobenzene to aminoazobenzene. The product is mixed, in a Magenta melt pan, with 60 kilos. of dry aniline hydrochloride and heated so that at the end of the reaction, which lasts about four hours, the temperature of the melt is 175–180°. The Induline obtained in this way is easily sulphonated, and both the spirit-soluble and sulphonated products show a pure blue shade.

The following process will be found to be a useful one. To a cold mixture of 16 gallons of aniline and 29·5 lb. of hydrochloric acid 18·5 lb. of sodium nitrite are added, in the solid state, the temperature not being allowed to rise above 28°. To this mixture are then added 8 gallons of aniline and 45 lb. of hydrochloric acid and the whole is well stirred. The heat evolved is sufficient to keep the reaction in progress.

Next morning the mass is transferred to a melt pan, 4 gallons of aniline and 46·5 lb. of hydrochloric acid are added, and the whole is stirred and heated at 75–80°, and the temperature is then gradually raised to 160° and kept at this point for two days. Sodium hydroxide is added until the mixture is alkaline, and the excess of aniline is distilled off with steam. After cooling, the residue in the pan is broken up, ground, washed, and dried at a low temperature. The yield is 70 lb. of Induline 3B base, and about 19 gallons of aniline are recovered.

Sulphonation.—The Induline base is ground with a little sodium carbonate, and 150 lb. are added gradually to 450 lb. of concentrated sulphuric acid without cooling. The mixture is then heated at approximately 95° in about three hours and kept at this point until a sample, diluted with water and filtered, dissolves in sodium hydroxide solution. When cool, the mixture is poured into 200 gallons of water, filtered, the residue washed with cold water, and dissolved in 400 gallons of water with the addition of sufficient sodium hydroxide solution to make the mixture nearly neutral. The addition of 3 lb. of sodium carbonate should complete the neutralisation. The solution is evaporated on iron or copper pans to dryness. The yield is 170 lb.

Nigrosine (spirit and water soluble).

The early method of manufacturing this dye, of which the constitution is unknown, consisted in heating a mixture of 10 kilos. of aniline, 12 kilos. of nitrobenzene, and 12 kilos. of hydrochloric acid for four to six hours at 180–195°, but later the addition of iron and copper was made to produce a black or bluish-black shade. A typical mixture is 175 parts of aniline, 175 parts of nitrobenzene, 200 parts of hydrochloric acid, 16 parts of iron filings, and 2 parts of finely-divided copper, which is heated for eight hours at 160–200° until a sample is of such a consistency that it can be drawn out into a thread.

The following description of this process is given by Koons (*Colour Trade J.*, 1920, **7**, 57). The melt pan, which is heated either by direct gas or with a charcoal fire, is set in brickwork and has an outlet at the bottom of about 4 inches diameter so that the fusion can be run out while still hot into iron pans. The pan must also be fitted with a condenser and thermometer and a vent from which to take samples. The pan is charged with 180 lb. of aniline, 175 lb. of nitrobenzene, 210 lb. of hydrochloric acid (31 per cent.), 16 lb. of iron turnings, and 2 lb. of copper turnings, and this mixture is heated at 110° in about one hour. This temperature is maintained for three hours in order to distil off the water in the hydrochloric acid and then raised slowly in the course of three hours to 160°. From this point, the temperature is raised slowly to 170°, when a violent reaction takes place; aniline distils off and the temperature rises quickly to 180°. This point is maintained for seven hours, and then the temperature is raised to 190–200° and the mass allowed to cool to 170°, when it is run out into iron pans. After cooling, the brittle mass, which has a bronzy appearance, is broken up. The yield of this crude product is 350–360 lb. The aniline which distils over can be recovered and used again. The crude melt is ground to a fine powder in a ball mill and purified by boiling with water and hydrochloric acid, washing, filtering, and drying. This is Spirit Soluble Nigrosine and is blue in shade. To make jet black Spirit Soluble Nigrosine, 20 per cent. of Chrysoidine must be added to it.

Nigrosine Base.—The Spirit Soluble Nigrosine (100 lb.) is added fairly quickly to a solution of 10 lb. of sodium hydroxide in 30 gallons of water. The mixture is heated to boiling until the mass is no longer sticky while hot (free from aniline). The water is then siphoned off and the base washed three times with water, dried, and ground. The loss is about 10 per cent.

From the base, solid and liquid Oil Blacks are made as follows: The apparatus required is a steam-jacketed pan with agitator (about 60 revolutions per minute). For solid Oil Black, 1 part of dry base is heated with 1·5 parts of stearic acid until a homogeneous mass is obtained. This is run out hot into pans, allowed to solidify, and broken up.

For liquid Oil Black 1 part of dry base is similarly heated with 2·5 parts of oleic acid.

Sulphonation.—If the heating of the melt has been properly controlled, the crude material will sulphonate with three times its weight of sulphuric acid (*d* 1·84), otherwise the sulphonation must be carried out with fuming sulphuric acid (containing 20 per cent. of sulphur trioxide).

The sulphonator is charged with the sulphuric acid, which is heated at 100–110°, and then the ground Spirit Soluble Nigrosine is added slowly, care being taken that the mass does not foam over. When the addition is complete, the mixture is heated for a further four hours and a sample, poured into water, washed, and rendered slightly alkaline with sodium hydroxide solution, should dissolve. If this does not take place, the heating is continued for two hours.

The sulphonation mass is then blown into water in a wooden tub fitted with an agitator, and washed three times with water by decantation, the precipitate being allowed to settle for about four hours after each washing. The precipitate is then blown into a filter-press. The press cake is mixed in a mixer similar to a dough mixer and 30 per cent. sodium hydroxide solution carefully added until a sample is soluble in water and a slightly alkaline reaction is obtained. The mixture is then dried in a hot-air oven or vacuum drier. It appears in small, glistening lumps about the size of a pea and gives a colour with a very blue shade.

In order to produce a jet black shade, Metanil yellow is incorporated immediately after the sodium hydroxide has been added to the mixer and the whole then dried. For the production of Nigrosine by heating aniline and aniline hydrochloride with nitrophenol, Harmsen (see under "Induline") states that 50 kilos. of crude nitrophenol are heated with 50 kilos. of aniline hydrochloride and 200 kilos. of aniline exactly as in the production of Induline, whilst Schultz ("Chemie des Steinkohlentheers," 3rd ed., 1901, p. 346) gives the quantities as 50 parts of nitrophenol, 100 parts of aniline hydrochloride, and 50 parts of aniline, the mixture, with the addition of a little iron, being heated for ten hours at 180°. The cold product is powdered, freed from aniline by means of hydrochloric acid, the residue filtered, washed, and dried. This Spirit Soluble Nigrosine is sulphonated by heating with about 4 parts of fuming sulphuric acid at 80°.

A good quality of Nigrosine may be obtained by heating a mixture of 183 lb. of nitrobenzene, 183 lb. of aniline hydrochloride, 137 lb. of aniline, 12 lb. of crude nitrophenol (the crude mixture of *o*- and *p*-nitrophenol), and 3 lb. of ground iron borings gradually up to a final temperature of 215°, which takes about thirteen to fourteen hours. The end-point must be very carefully watched, as the mass must be run out of the pan before it becomes too viscid. Frequent samples are therefore taken and the consistency is observed. Should the right point be passed, the mass becomes too hard to flow, and in that case would have to be chipped out of the pan when cold. The yield is about 300 lb., and the oil which distils over is recovered and used again.

The cold melt is broken up, ground, and sulphonated by adding 120 lb. to 360 lb. of concentrated sulphuric acid, raising the temperature to 95° and keeping at this point until a sample, precipitated with water and washed, is soluble in sodium carbonate solution on boiling. The sulphonation mixture is then cooled, poured into 200 gallons of cold water, the precipitate filtered, washed free from acid, and dissolved in 300 gallons of water and about 20 lb. of sodium carbonate, or as much as will produce an alkaline reaction. After settling over-night, the clear liquid is run on to evaporating pans and evaporated to dryness. The yield is about 105 lb.

Methylene gray.

This dye, the constitution of which is unknown, is obtained by heating to boiling a solution of 10 kilos. of *p*-nitrosodimethylaniline hydrochloride in 50 kilos. of water for three hours. On cooling, the product is run into 100 litres of water and the dye is precipitated by adding zinc chloride or similar salts.

The same result is obtained if the hydrochloride is boiled with alcohol instead of water.

The dye is then filtered, pressed, and dried at 80° (Société Anonyme des Matières Colorantes et Produits chimiques de St. Denis, E.P. 5032^{89}; F.P. 195605; G.P. 49446; U.S.P. 420311). This colouring matter is also formed, together with a blue dye, by oxidising *p*-aminodimethylaniline.

A suspension of 10 kilos. of *p*-nitrosodimethylaniline hydrochloride in 700 litres of water is reduced at 40° with 10 kilos. of zinc dust. When the solution is colourless it is treated with sodium carbonate until it shows a faintly alkaline reaction towards Tropæoline OO (Orange IV). The solution is then filtered from zinc and 7 kilos. of hydrochloric acid (30 per cent.), 5·8 kilos. of sulphuric acid, or 4 kilos. of zinc chloride are added. To the boiling solution is added during an hour a solution of 5 kilos. of sodium dichromate and 4·5 kilos. of hydrochloric acid or 3·6 kilos. of sulphuric acid or 2·5 kilos. of zinc chloride in 100 litres of water. It is not so advantageous to add the 11·5 kilos. of hydrochloric acid (or 9·2 kilos. of sulphuric acid or 6·5 kilos. of zinc chloride) either to the base or to the dichromate solution.

The end of the reaction is recognised by a drop of the liquid, placed on filter-paper, being colourless and not red. If the reaction is not complete, a little more dichromate must be added carefully. The liquid is now filtered boiling hot and, after cooling, the blue dye is precipitated by adding 2·5 kilos. of zinc chloride and 100 kilos. of salt, filtered, pressed, and dried. [This dye does not appear to be on the market.] The paste left after filtration of the hot solution is suspended in 400 litres of water, 5 kilos. of hydrochloric acid are added, and the whole is boiled. From the filtered solution, the grayish-violet dye is precipitated, as above, with zinc chloride and salt. If a dye intermediate between the two is required, the liquor (above) is boiled with 5 kilos. of hydrochloric acid, and, after filtration, the dye is precipitated as described. The constitution of the blue dye is considered to be

The grayish-violet dye can be obtained in larger proportion if the addition of the oxidising agent is very rapid or if less than a molecule of hydrochloric acid to 1 molecule of *p*-aminodimethylaniline is taken (E.P. 16448^{89} [Dawson]; G.P. 61504 [Hirsch: transferred to Société Anonyme des Matières Colorantes et Produits chimiques de St. Denis]).

CHAPTER XV

SULPHUR COLOURS

IMMEDIAL YELLOW—SULPHUR BLACK—IMMEDIAL BLACK—IMMEDIAL BROWN—PYROGENE BLUE—IMMEDIAL INDONE—PYROGENE INDIGO—IMMEDIAL MAROON—KATIGENE GREEN—HYDRON BLUE G—HYDRON BLUE R

IMMEDIAL YELLOW D.

Fifty kilos. of *m*-tolylenediamine are added to 100 kilos. of molten sulphur contained in an iron pan fitted with a stirrer. The mass melts together on raising the temperature, and hydrogen sulphide is evolved. The temperature is then raised to about 190° within two hours and the operation is stopped.

One hundred kilos. of the powdered product are gradually added to a solution of 90 kilos. of sodium sulphide in 60 kilos. of water at 110° and heated at 110–120° until a sample shows that the substance has become completely soluble. The mixture is then diluted with water, filtered, and the dye precipitated by adding hydrochloric acid to the filtrate. The sparingly soluble yellow precipitate is filtered and dried (Cassella & Co., E.P. 11771^{02}; F.P. 321122; G.P. 139430; U.S.P. 714542).

Sulphur Black.

This important dye, the empirical formula of which has been given as $C_{24}H_{16}O_8N_6S_7$ or $C_{24}H_{16}O_8N_6S_8$, according to the conditions under which it is prepared (Vetter, *Diss.*, Dresden, 1910), is obtained by treating 2 : 4-dinitrophenol with sodium sulphide and sulphur, and the standard method of performing this operation now is to boil these materials together in aqueous solution.

In the earlier patents, which will be briefly reviewed, the ingredients were heated together in an iron pan, the product being used direct, but it was soon found that an improvement was effected by the boiling process. Many variations have been patented, and these will also be noted.

(1) *Fusion Methods.*—Vidal (E.P. 16449⁹⁶; F.P. 231188 and addition; G.P. 98437; U.S.P. 618152) was the first to suggest the use of dinitrophenol. He heated 1·84 kilos. of dinitrophenol with 3 kilos. of sodium sulphide at above 140° and, after reduction of the dinitrophenol had taken place, added 350 grams of sulphur. The finished product was ground and used direct. The dye was not, however, very satisfactory, and gave a better shade when mixed with 1 part of sulphur and 2½ parts of sodium sulphide and dried at 140° or heated under reflux for twenty-four hours (Aktiengesellschaft für Anilinfabrikation, G.P. 127312).

The proportions used by Cassella (Immedial Black NN, E.P. 19831⁹⁶; F.P. 259509) were 25 parts of dinitrophenol, 125 parts of sodium sulphide, and 50 parts of sulphur; the mixture was heated for one hour at 100°, then for two to three hours at 160°. In an addition to the above French patent (F.P. 267343), the same mixture is heated at 110–140° until no further formation of dye is observed, then sodium sulphide is added in order to convert the disulphide into thiosulphate, and the mass dried at 160°.

The proportion of 4 atoms of sulphur to 1 molecule of dinitrophenol in the mixture with an alkali sulphide is emphasised by Stolaroff (E.P. 2195⁰⁰; F.P. 296810; G.P. Anm. St. 6281); the mixture is heated at 115–120° until the evolution of ammonia has ceased and then further up to 200° until dry.

The chief point of the next patent is that the mixture must not be allowed to become dry before the formation of the dye is complete. The dinitrophenol (10 parts) is heated with 40 parts of sodium sulphide and 10 parts of sulphur for four to five hours at 115–120° and then dried at 140°, or the mixture is heated under 2½ atmospheres pressure at 110–115° for three to five hours. The process is shortened by raising the temperature, and the shade becomes greener. The latter effect may also be produced by the addition of copper or its salts, or about 5 per cent. of 4-chloro-1 : 3-dinitrobenzene (Thiophenol black T extra, Society of Chemical Industry in Basle, E.P. 13035⁰³; F.P. 333096).

Relatively small amounts of sodium sulphide and sulphur, so as to produce sodium tetrasulphide, Na_2S_4 (34·8 parts), are used by Kalle & Co. (Thion black, E.P. 26379⁰³; F.P. 337278; G.P. Anm. K. 24400), and this is heated with 20·6 parts of the sodium salt of dinitrophenol in the form of paste, at 135° for seven hours or at 140–160° for two to three hours. The dye may be dried and used direct, or the product is dissolved in water and the dye precipitated by acidifying.

(2) *Boiling Methods.*—The first of these methods was introduced by the Aktiengesellschaft für Anilinfabrikation (Sulphur black T extra, E.P. 1151^{00}; F.P. 299721; G.P. 127835; U.S.P. 655659), and consisted in boiling a mixture of 30 kilos. of dinitrophenol, 125 kilos. of sodium sulphide, 45 kilos. of sulphur, and 150 litres of water under reflux for twenty-five hours. The dye is obtained from the solution by acidifying or by blowing air through it.

In the following process the reaction is carried on under pressure. A mixture of a 20 per cent. paste of the sodium salt of dinitrophenol (corresponding with 80 kilos. of dinitrophenol) and a solution of 140 kilos. of crystallised sodium sulphide and 56 kilos. of sulphur in about 30 litres of water is heated at 90° in a steam-jacketed autoclave of 1000 litres capacity fitted with a stirrer. The vessel is then closed, the contents heated at 130° within thirty minutes, and this temperature is maintained for about nine hours. The pressure is about $1\frac{1}{2}$–2 atmospheres. At the end of this time, the pressure is released, the ammonia completely expelled by warming, and recovered, for example, by absorption in dilute acid, and the dye is directly filtered off, pressed, and dried. The operation may also be carried out at 150°, in which case it is completed in about half the time (Auronal black N, Chemische Fabriken vorm. Weiler-ter-Meer, E.P. 27213^{06}; F.P. 372104; G.P. 208377).

In the following patent, the reaction is carried out under reflux, but stress is laid on the maintenance of the temperature at 106–108°.

A solution of 33·5 kilos. of the sodium salt of dinitrophenol (corresponding with 30 kilos. of dinitrophenol) in 80 litres of water is heated to boiling and a solution of 40 kilos. of sodium sulphide (62 per cent.) and 30 kilos. of sulphur in 40 litres of water is added gradually. The mixture is kept at the boiling point and the temperature is raised by the addition of alkali salts, such as chlorides or sulphates, until it is 106–108°. The formation of the dye is complete after ten to fifteen hours. The product is diluted with water, the dye filtered off, and washed with water. It is free from sulphur or polysulphides (Autogen black EEB, Société Anonyme des Matières Colorantes et Produits chimiques de St. Denis, E.P. 25080^{07}; F.P. 381608; G.P, 218517; U.S.P. 904224; a German Patent application by Schenk, G.P. Anm. Sch. 26652, practically identical with the above, was withdrawn soon after publication).

(3) *Modifications of the Process.* (*a*) *Use of Sodium Thiosulphate.*—Ninety-two kilos. of dinitrophenol are dissolved in 800 parts of hot water and 61 parts of sodium hydroxide solution (33 per cent.), 400 kilos. of crystallised sodium thiosulphate are added, and the thick, yellow mass is heated in an autoclave with stirring for six hours at 160–165° (pressure about 10 atmospheres) and the dye filtered off after cooling (Thional black, Chemical Works formerly Sandoz, E.P. 26465; G.P. 136016).

(*b*) *Use of Hydrogen Sulphide.*—A current of hydrogen sulphide is passed through a boiling aqueous solution of the sodium salt of dinitrophenol in a vessel provided with a reflux condenser and agitator until the colour of the solution no longer changes. The water is then distilled off until the residue thickens. This is kept until no more colour forms and is then heated to dryness and powdered (Meyenberg and the Clayton Aniline Co., E.P. 17805^{03}).

(*c*) *Use of Azo-dyes.*—Certain azo-dyes which, when submitted to the reducing action of the mixture of sodium sulphide and sulphur, yield nitroaminophenol or diaminophenol, have been employed as starting materials, for example, the product of the combination of diazotised *p*-nitroaniline and *o*-nitrophenol (Levinstein, Ltd., E.P. 18756^{00}; F.P. 306358), and the product of the combination of diazotised aniline and *o*-nitrophenol (Kalle & Co., E.P. 26379^{03}; F.P. 337278; G.P. 186860), but such processes are evidently of little value.

A good result is obtained by adding 112 lb. of dinitrophenol to a solution of 348 lb. of crystallised sodium sulphide and 104 lb. of sulphur in 400 lb. of water, or less, contained in a lead-lined pan fitted with a reflux condenser and boiling the mixture by the aid of external heat for twelve hours. After cooling, the solution is blown into a tub and a current of air bubbled through it until the dye is precipitated. It is then blown through a filter-press, and the cake dried. The yield of dry material is about 210 lb.

Immedial black.

A mixture of 15 kilos. of 2 : 4-dinitro-4′-hydroxydiphenylamine, 75 kilos. of crystallised sodium sulphide, 30 kilos. of sulphur, and a little water is heated gradually at about 140°. The temperature is maintained at this point for some hours until the mass is almost dry. It is then heated for a short time at about 160° in order of expel the last traces of water. The dye can be used in the form obtained or the product can be dissolved in water and the dye precipitated by adding an acid (Cassella & Co., E.P. 25234^{97}; F.P. 271909; G.P. 103861; U.S.P. 610541).

Immedial brown.

A solution of 40 kilos. of 2 : 4-dinitro-4′-hydroxydiphenylamine in 80 kilos. of sodium hydroxide solution (40° Bé.) and 240 litres of water is boiled under reflux for three to four hours until ammonia is no longer evolved. The mixture is diluted with water, and the product is precipitated by acidifying with hydrochloric acid. When dry, it forms a black, amorphous powder. Of this, 25 kilos. are heated either with 50 kilos. of sodium hydroxide solution (40° Bé.) and 20 kilos. of sulphur or with 52 kilos. of sodium sulphide and 13 kilos. of sulphur, with the addition of a little water, and the temperature is gradually raised to about 160°. The mass finally becomes dry and is used direct for dyeing (Cassella & Co., E.P. 25754^{99}; F.P. 295593; G.P. 112484; U.S.P. 660058).

Pyrogen blue.

Ten parts of 4-nitro-2-amino-4′-hydroxydiphenylamine (m. p. 196–197°) or 2 : 4-dinitro-4′-hydroxydiphenylamine (m. p. 187–188°) or the brown product obtained by warming an alcoholic solution of the latter with alkali polysulphides, are heated with 50 parts of alcohol and 18 parts of dry sodium tetrasulphide (that is, in absence of water) in an iron or enamelled autoclave for three to four hours at 135–145°. The cold product is filtered, washed with alcohol, and the residue dried (Society of Chemical Industry in Basle, E.P. 5385^{00}; F.P. 298075 and additions, G.P. 132424; U.S.P. 665726).

The product may also be worked up by distilling off the alcohol and then either mixing the residue with anhydrous sodium carbonate or sulphate, whereby a magma is obtained which becomes solid, or dissolving the residue in water, filtering if necessary, and precipitating by a current of air (*idem*, E.P. 9968^{02}; F.P. 298075; G.P. 140963).

Immedial Indone (Sulphur blue).

1. Preparation of the intermediate product: *p*-aminotolyl-*p*-hydroxyphenylamine (E.P. 7025 of 1903; F.P. 330388; G.P. Application G 18017). In a vessel fitted with an agitator, 43 kilos. of ortho-toluidine are dissolved with the aid of heat in 280 kilos. of sulphuric acid, 70 per cent. The solution is cooled externally by ice and 50 kilos. of nitrosophenol are added in small quantities at a time. The temperature must not rise above 10°. After all the nitrosophenol has disappeared, the whole is poured into an aqueous solution of 250 kilos. of sodium carbonate, cooled with ice, and the product filtered off. It is nearly insoluble in water and gives a blue solution with sodium hydroxide.

The paste is stirred for about two hours with water containing 53 kilos. of sodium hydroxide solution (30 per cent.) and 50 kilos. of sodium sulphide (cryst.). The clear brown solution is acidified by adding 136 kilos. of hydrochloric acid, filtered, the residue washed, and the whole acid solution treated with sodium bicarbonate to precipitate the *p*-aminotolyl-*p*-hydroxyphenylamine. (When crystallised from alcohol this melts at 160°.)

2. Sulphur blue: E.P. 58 of 1902; G.P. 199963; U.S.P. 709151; F.P. 317219 (not yet printed).

Forty-eight kilos. of crystallised sodium sulphide are melted in an iron vessel fitted with reflux condenser, then 19 kilos. of sulphur and 11 kilos. of *p*-aminotolyl-*p*-hydroxyphenylamine are added gradually while the temperature is about 80°. The temperature is then raised to 120° and kept there for twenty hours. The solution of the dye is treated with a current of air (solution cool) and the dye filtered off. At a higher temperature the shade is greener and duller and at a lower temperature, or when alcohol is present, it is redder and brighter.

Pyrogen indigo.

To a solution of 27·6 kilos. of 4-phenylamino-4′-hydroxydiphenylamine in 150 litres of alcohol are added 55 kilos. of dry sodium pentasulphide and the mixture is boiled under reflux for twenty-four hours. The alcohol is distilled off and the residue extracted with water, which dissolves the leuco-compound of the dye. The solution is filtered and the dye isolated by means of a current of air. Alternatively, 60 kilos. of sodium sulphide and

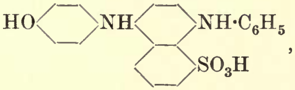
30 kilos. of sulphur are melted together and as soon as the sulphur has dissolved, 20 kilos. of 4-phenylamino-4′-hydroxydiphenylamine are added. The temperature of the mixture is raised to 140–150° and maintained at this point for two to three hours. The product is stirred into salt solution (20° Bé.) when the dye separates (Society of Chemical Industry in Basle, E.P. 16823^{02}; F.P. 323202; G.P. 150553; U.S.P. 723154).

Immedial maroon B.

Ten kilos. of 3-amino-7-hydroxyphenazine are gradually added to a mixture of 50 kilos. of crystallised sodium sulphide, 20 kilos. of sulphur, and 10 litres of water which has been heated at 90–100°. The temperature is then raised slowly to 140–150° and maintained at this point until a sample dissolves with a blackish-violet colour in water and a drop of the solution placed on filter-paper no longer gives a yellow rim. The mixture is finally heated for a short time up to 170° so that it becomes dry (Cassella & Co., E.P. 14836^{00}; F.P. 303107; G.P. 126175; U.S.P. 701435).

Katigen green.

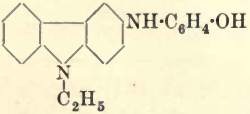
Forty kilos. of 4-*p*-hydroxyphenylamino-1-phenylnaphthylamine-8-sulphonic acid,



prepared by oxidising a mixture of 1-phenylnaphthylamine-8-sulphonic acid and *p*-aminophenol in alkaline solution with sodium hypochlorite at a temperature not exceeding 5°, and reducing the indophenolsulphonic acid with sodium sulphide in the cold, are added to a boiling solution of 40 kilos. of sulphur and 100 kilos. of crystallised sodium sulphide in 100 litres of water, the mixture is evaporated until it boils at 120° and then boiled under reflux, with stirring, for twenty hours. The product, from which the greater part of the dye has separated as a bronzy tar, is dissolved in boiling water and the dye salted out (Chemische Fabrik vorm. Sandoz, E.P. 11863^{04}; F.P. 343377; G.P. 162156; U.S.P. 776885).

Hydron blue G.

A mixture of 80 kilos. of sodium sulphide (60 per cent.), 160 kilos. of flowers of sulphur, and 400 litres of alcohol is boiled under reflux for several hours in order to form the polysulphide. To this mixture is added 40 kilos. of the base,



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prepared by condensing *p*-nitrosophenol and *N*-ethylcarbazole in the presence of concentrated sulphuric acid,* or by oxidising a mixture of *p*-aminophenol and *N*-ethylcarbazole in the same solvent, and reducing the indophenol obtained in this way,† and the whole is boiled under reflux for thirty-six to forty-eight hours. When the reaction is complete, the alcohol is distilled off, the contents of the pan are diluted with water and filtered. The press-cake is extracted with warm sodium sulphide solution and

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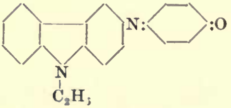
* To a solution of 19·5 kilos. of *N*-ethylcarbazole in eight to ten times its weight of cold concentrated sulphuric acid, a cold solution of 12·3 kilos. of *p*-nitrosophenol in about ten times its weight of concentrated sulphuric acid is added gradually with good stirring and external cooling, the temperature not being allowed to rise above 10°. When the interaction is complete, the product is poured on ice and the precipitate filtered and washed. It has the constitution :



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and can be used direct for making the dye (Cassella & Co., E.P. 9689^{09}; G.P. 224951; U.S.P. 966092).

† To a solution of 19·5 kilos. of *N*-ethylcarbazole in about ten times its weight of cold concentrated sulphuric acid, a solution of 10·7 kilos. of *p*-aminophenol in about 100 kilos. of sulphuric acid is added. The mixture is cooled below 0°, stirred well, and an ice-cold solution of 21 kilos. of sodium dichromate in about ten times its weight of concentrated sulphuric acid is run in slowly, the temperature not being allowed to rise above 15°. At the end of the reaction the mixture is poured on ice, filtered, and the residue washed until neutral. The dark blue paste of the indophenol can be used direct (Cassella & Co., G.P. 227323).

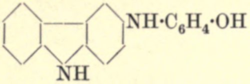
the paste standardised to 20 per cent. strength or dried (Cassella & Co., E.P. 9689^{09}; F.P. 412012; G.P. 222640; U.S.P. 966092).

Hydron blue R.

According to the first patent dealing with this dye, a solution of 800 grams of *p*-nitrosophenol in about 8 kilos. of sulphuric acid (66° Bé.) is stirred into a solution of 1 kilo. of carbazole in about 10 kilos. of the same acid, the temperature not being allowed to rise above 30°. The dark blue solution is poured on ice and the precipitate filtered and washed. After pressing, the metallic-looking paste is mixed with a little water and warmed carefully in an open pan with 1–1·5 kilos. of crystallised sodium sulphide until it is decolorised. At this point 1–1·5 kilos. of sulphur are added, the stirring being continued, the mixture is evaporated and kept fused. It can be purified by dissolution in sodium sulphide and precipitation with air or acids (Cassella & Co., E.P. 2918^{09}; F.P. 400022; G.P. 218371; U.S.P. 919572, 931598).

It was soon found that the crude product obtained in this way, when boiled with dilute sodium sulphide solution, could be separated into a portion soluble in sodium sulphide solution, which when isolated in the usual way, consisted of a dye possessing the ordinary properties of sulphide dyes, and an insoluble portion which, when reduced with sodium hyposulphite, gave a yellow " vat " from which cotton was dyed in deep blue shades. The conditions for carrying out the original operation so as to produce the maximum amount of this dye are the use of a polysulphide corresponding with the formula Na_2S_6, that is, containing to 24 kilos. of crystallised sodium sulphide, 19·2 kilos. or preferably 24–27 kilos. of sulphur, and the presence of a solvent for the starting material or its leuco-compound. The best solvent is alcohol, and if the product of the condensation of carbazole and *p*-nitrosophenol, or its leuco-compound, is boiled in alcoholic solution with a large excess of the polysulphide for forty-eight hours under reflux the dye insoluble in dilute sodium sulphide solution is almost exclusively formed. When the reaction is complete, the alcohol is distilled off, the residue washed with water to remove excess of polysulphide, and digested several times with dilute sodium sulphide solution. When dry, it forms a bluish-black powder with a metallic lustre (*idem*, E.P. 18822^{09}; F.P. 413716; G.P. 224590, 224591; U.S.P. 956348).

Indocarbon.—This is prepared by a modification of the above reaction. Forty kilos. of the base,



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are stirred with 22 kilos. of sodium hydroxide solution (20° Bé.) and a little water and then 144 kilos. of sodium sulphide, 14 kilos. of copper sulphate, and 93 kilos. of sulphur are added. The mixture is boiled until the boiling point is about 125° and then boiled under reflux for about eighteen hours. The product is diluted with salt solution and the dye filtered off. It can be purified by dissolving it in sodium sulphide solution, filtering, and precipitating by means of a stream of air (Cassella & Co., E.P. 14143^{09}; F.P. 413755; G.P. 221215).

CHAPTER XVI

ANTHRAQUINONE AND ALLIED COLOURS.

Mordant Colours.

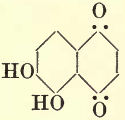
NAPHTHAZARIN—ALIZARIN—ALIZARIN ORANGE—ALIZARIN GARNET—ALIZARIN RED—ALIZARIN BLUE—ALIZARIN BLUE S—ALIZARIN GREEN S—ANTHRACENE BROWN—ANTHRAPURPURIN—FLAVOPURPURIN—ALIZARIN BORDEAUX—ALIZARIN CYANIN R—ALIZARIN CYANIN G—ANTHRACENE BLUE WR—ANTHRACENE BLUE WG—ANTHRACENE BLUE WGG.

Vat Colours.

INDANTHRENE GOLD ORANGE G—INDANTHRENE GOLD ORANGE R—INDANTHRENE SCARLET G—INDANTHRENE DARK BLUE BO—INDANTHRENE VIOLET RT—INDANTHRENE GREEN—INDANTHRENE VIOLET R (EXTRA)—INDANTHRENE VIOLET 2R (EXTRA)—INDANTHRENE VIOLET B (EXTRA).

NAPHTHAZARIN S (Alizarine Black).

This is the sodium hydrogen sulphide compound of 5 : 6-dihydroxy-α-naphthaquinone,



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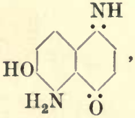
and is prepared by heating the crude mixture of 1 : 5- and 1 : 8-dinitronaphthalenes with sulphur and fuming sulphuric acid and converting the naphthazarin so obtained into its bisulphite compound.

(1) Ten kilos. of powdered 1 : 5-dinitronaphthalene are stirred into 200 kilos. of sulphuric acid (100 per cent.) and to this is added, the temperature not being allowed to rise above 40°, a solution of 5 kilos. of sulphur in 50 kilos. of fuming sulphuric

acid (containing 40 per cent. of sulphur trioxide). The reaction is complete almost at once and the end-point is reached when a sample poured into cold water gives a blue solution of 5-amino-6-hydroxy-α-naphthaquinoneimide,



which passes into naphthazarin on heating with dilute acids. The mixture is then poured into cold water, the sulphur filtered off, and the solution heated to boiling until the original blue colour changes to red. After cooling, the naphthazarin is filtered off and washed free from acid. Instead of using sulphur, a stream of hydrogen sulphide may be led through a solution of 10 kilos. of 1 : 5-dinitronaphthalene in 100 kilos. of fuming sulphuric acid (containing 40 per cent. of sulphur trioxide) or 10 kilos. of sulphur chloride or 3 kilos. of hydrogen persulphide or 13·5 kilos. of anhydrous sodium thiosulphate may be added to a mixture of 10 kilos. of 1 : 5-dinitronaphthalene and 100–200 kilos. of fuming sulphuric acid (containing 10–40 per cent. of sulphur trioxide), the product in each case being worked up as described above (Farbenfabriken vorm. F. Bayer & Co., E.P. 17673^{92}; F.P. 224739; G.P. 71386, 77330).

(2) A mixture of 10 kilos. of 1 : 8-dinitronaphthalene and 10 kilos. of aniline, α-naphthylamine, or phenylhydrazine is added to 200 kilos. of sulphuric acid (66° Bé.) and the whole heated at 125–130° until the dinitronaphthalene has disappeared, which takes about eight to ten hours. The violet-red mass is cooled, poured into ice-water, the violet-red solution filtered, and boiled until naphthazarin separates. A mixture of 10 kilos. of 1 : 8-dinitronaphthalene and 200 kilos. of sulphuric acid (66° Bé.) may also be heated at 125°, 10 kilos. of tin added slowly, and the temperature kept at 125° for ten hours. The reddish-violet product is worked up as above (for references see below).

(3) A solution of 1 part of 1 : 8-dinitronaphthalene in 20 parts of sulphuric acid (66° Bé.) is electrolysed at about 130°. The sulphuric acid solution of the dinitronaphthalene, in which is the cathode, is separated from the sulphuric acid surrounding the anode, by a suitable diaphragm. Good results are obtained with a current of 15 amperes per 100 sq. cm. of electrode surface.

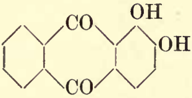
The current is stopped when no unchanged dinitronaphthalene is present.

The solution is cooled, poured into ice-water, filtered, and boiled for an hour when, on cooling, naphthazarin separates in an extremely pure state and is filtered off, and washed. A mixture of 1 : 5- and 1 : 8-dinitronaphthalenes may be used in this reduction with equally good results (Badische Anilin- & Soda-Fabrik, E.P. 3828^{94}; F.P. 236852; G.P. 76922, 79406).

The bisulphite compound is prepared as follows :

Naphthazarin in as finely divided state as possible, preferably as a 10 per cent. paste, is carefully mixed with two to three times its weight of a solution of sodium hydrogen sulphite (30–40° Bé.) and kept at 50–70° for several days. The dye gradually dissolves and the solution is filtered from a little unchanged naphthazarin which is used in a later operation. The solution obtained in this way may be used directly for dyeing or printing or the bisulphite compound can be isolated by evaporating to dryness or, better, by salting out (Badische Anilin- & Soda-Fabrik, E.P. 7833^{87}; F.P. 182962; G.P. 41518; U.S.P. 368054, 379150. A good account of the chemistry of the naphthazarin process is given by Wynne, Art. "Naphthalene," Thorpe's "Dictionary of Applied Chemistry," 1912, III, p. 656).

Alizarin,



An interesting account of the early methods of manufacturing Alizarin is given by W. H. Perkin in two lectures delivered before the Society of Arts in 1879 ("The History of Alizarin and Allied Colouring Matters, and their Production from Coal Tar," *J. Soc. Arts*, 1879, 572) and in the "Hofmann Memorial Lecture" (*Trans.*, 1896, **69**, 596; reprinted in Gardner's "The British Coal-Tar Industry," 1915, 141), and the subject is also dealt with by Auerbach ("Anthracen," translated by Crookes, 1877) who gives a very complete bibliography.

It was very soon found that in the process of melting sodium anthraquinone-2-sulphonate with sodium hydroxide (which is the only one used to-day), the addition of an alkali nitrate or chlorate gave increased yields and the modern procedure differs only in detail from the earlier one. Perkin heated a mixture of the above salt (equivalent to 100 parts of the dry salt), 400 parts of sodium hydroxide (70 per cent.) dissolved in as little water as possible, and 15 parts of potassium chlorate, in a double-riveted horizontal boiler, about 11–12 feet long and 4½ feet in diameter, fitted with a stirrer at about 170–180° for two or three days. The product was diluted, acidified, and the Alizarin well washed. A more modern description is given by Gnehm (Bolby and Kopp "Die Theerfarbstoffe," Vol. 5, Part 3, of "Handbuch der chemischen Technologie," 1895–1897, p. 1675), of which the essential points are as follows:

The melt is conducted in a horizontal cylindrical wrought-iron vessel which can be heated direct or is jacketed so as to provide an air- or oil-bath. It is fitted with a strong stirrer arranged so that the scrapers attached to the blades move very near the inside surface of the vessel. On the upper part of the latter is a dome fitted with a man-hole and side openings for a pressure gauge and a safety valve and at the lowest point is an opening to which a tap is connected, through which the finished melt is blown. The tap leads to a pipe through which the contents of the vessel may be transferred to a reservoir on a high stage. A small opening in the top of the vessel, through which passes a small pipe furnished with a tap, furnishes a means of taking samples of the melt.

The "silver salt" (sodium anthraquinone-2-sulphonate), sodium hydroxide, and chlorate are dissolved in wrought-iron pans (800–1000 litres) placed above the level of the horizontal vessel, so that the solutions can be run into the latter through the man-hole. The proportions used are 100 kilos. of "silver salt" (reckoned as pure and dry) about 28–32 kilos. of potassium chlorate and 260–280 kilos. of sodium hydroxide and so much water is used for solution as will bring the total volume to about 650–700 litres.

The duration of the fusion is forty to seventy-five hours and the pressure varies from 3·6 to 4 atmospheres.

The vessel is charged as follows. First, the solution of "silver salt" and potassium chlorate is run in, the agitator is started, and then the sodium hydroxide previously dissolved in a very little water by means of steam, is added carefully. The man-hole lid is then fixed on and the heating is begun. In order to attain the requisite pressure quickly, steam is passed into the vessel. When the pressure has been obtained, the steam is shut off and the required temperature * or pressure is maintained by careful heating, the stirrer being kept in operation continually. In order to observe the course of the process, samples are taken from time to time and tested for hydroxyanthraquinone, hydroxyanthraquinonesulphonic acid, and anthraflavic acid (2 : 6-dihydroxyanthraquinone) or *iso*anthraflavic acid (2 : 7-dihydroxyanthraquinone).

To test for hydroxyanthraquinonesulphonic acid, 10 grams of the melt are dissolved in 100 c.c. of water, excess of hydrochloric acid is added, and the whole filtered. Fifteen c.c. of the filtrate are shaken with ether (to remove alizarin, flavopurpurin, and anthrapurpurin), the ethereal layer is separated, and sodium hydroxide solution added to the aqueous portion. The presence of hydroxyanthraquinonesulphonic acid is shown by a blue coloration. To detect hydroxyanthraquinone, and anthraflavic and *iso*anthraflavic acids, 10 grams of the melt are dissolved in 100 c.c. of water, and to the boiling solution 100 c.c. of barium chloride solution are added. The resulting precipitate is filtered off. To the boiling filtrate is added sodium carbonate solution, the precipitate filtered off, the liquid allowed to cool, and acidified with hydrochloric acid. Hydroxyanthraquinone or anthraflavic or *iso*anthraflavic acid separates in yellow flocks.

When it has been ascertained that the process is finished, the fire is drawn and the vessel emptied by opening the tap at the bottom. The pressure in the vessel is sufficient to force the mass through the pipe leading to the large, wrought-iron reservoirs set on a high level. These reservoirs (20,000–30,000 litres) are previously charged with hot water so that the melt can be at once diluted as it enters. The degree of dilution of this solution and the method of precipitation have a great influence on the appearance and other properties of the Alizarin paste. From concentrated solutions, on acidification, dark-coloured precipitates are obtained, which, when used for printing, often give rise to difficulties. It is advisable, therefore, to work with as dilute and hot solutions as possible. On a stage lower than the reservoirs are the precipitating vessels. According as to whether sulphuric acid or hydrochloric acid is employed, these consist of lead-lined wood or iron vessels of 4000–5000 litres capacity, or simply pitch-pine vessels of the same size.

For the precipitation are required three times the weight of hydrochloric acid (20° Bé.) or one and a quarter times the weight of sulphuric acid (66° Bé.) of the sodium hydroxide used in the

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* The temperature is not given by the author.

melt. When the water supply is strongly calcareous it is best to use hydrochloric acid.

Water is run into each of the precipitating vessels and so much hydrochloric acid or sulphuric acid as will maintain a definite acid reaction after the proper quantity of the diluted melt (adjusted according to the size of the precipitating vessels and the quantity of the melt) has been added.

The dilute acid solution is then heated to boiling, stirred, and the proper quantity of the hot solution of the dye is run in. The precipitating vessels are covered with a wooden lid on which is fixed a vertical wooden vent reaching to the roof, so that the steam and small quantities of sulphur dioxide may escape without harming the workmen.

The contents of the precipitating vessels are now run into wooden or lead-lined iron receivers and blown into filter-presses.

The free acid still present in the cakes must be completely removed by washing. This can be done, at any rate partly, by blowing water from the receiver through the press, but it is better, and indeed necessary in order to remove the last traces of acid, to mix the cake with water so as to obtain a thin, uniform paste. This is effected in horizontal wooden cylinders fitted with wooden stirrers and the paste must not come into contact with iron. The mixture is then blown into the filter-presses as described above, and the process repeated, if necessary, until every trace of acid is removed. When the ordinary water supply is very hard, distilled water should be used for the later washings.

Finally, the press cakes are transferred to the wooden cylinders and brought, by means of distilled water, to a 20 per cent. paste. Comparative dyeings against the standard are made and generally the dry weight is also determined as well as the ash. The anthraflavic acid is sometimes estimated.

The distilled water required in the above operations may be obtained in the preparation of the " silver salt." Dilute solutions of this are produced which have to be evaporated to a certain concentration and if a vacuum evaporating plant is used in connexion with this concentration the necessary distilled water can be provided.

The variations of this process, given by Schultz (" Die Chemie des Steinkohlentheers," 1901, II, p. 262) do not differ much from the above. The wrought-iron melt pans are tested to 15–20 atmospheres, and are of two sizes, either of 8000 litres capacity or of 2000 litres. It is possible to carry out the reaction more quickly in the latter, as the concentration of the charge can be increased somewhat and therefore the time of operation and the amount of sodium hydroxide can be lessened. The finer qualities of Alizarin are preferably made in the smaller pans.

(*a*) The pan is charged with 100 parts of "silver salt," 250–300 parts of sodium hydroxide, 12–14 parts of potassium chlorate, and just so much water as is required to dissolve the mixture. The pan is then closed, stirring being continuous, and heated in an oil-bath or better in an air-bath or with gas burners for about two days at about 180°. With an air-bath the temperature can be better regulated and the process is sooner finished. At the end of two days a sample is boiled with milk of lime and filtered. If, on adding hydrochloric acid, much hydroxyanthraquinone separates, the heating must be continued. When the reaction is at an end the contents of the cylinder are worked up as described above. The diluted solution of the product must have a specific gravity of 1·075–1·1 (10–13° Bé.).

(*b*) A mixture of 300 kilos. of "silver salt," 54 kilos. of potassium chlorate, 750 kilos. of sodium hydroxide, and 1100 litres of water is heated quickly at 160°. The mass is kept at this temperature, and under a pressure of 4·5–5 atmospheres for about twenty hours, within which time the reaction is usually complete. The operation is stopped when a sample, tested as above, shows the absence of hydroxyanthraquinone. The pressure is released through the safety valve, the mass diluted with water, and blown to the reservoir. The solution is brought to 4° Bé. and precipitated boiling hot with hydrochloric or sulphuric acid. In most cases the excess of alkali hydroxide in the fusion is used for precipitating the chromium hydroxide from the filtrate from the anthraquinone, and for this purpose the solution of the Alizarin melt is brought to 20° Bé. and the calcium lake of Alizarin is precipitated hot with calcium chloride solution. The lake is filtered off, washed, boiled with water, and decomposed with hydrochloric acid.

(*c*) A mixture of 900 kilos. of crude sodium anthraquinone-sulphonate (obtained by direct neutralisation of the sulphonic acid with sodium carbonate), 162 kilos. of potassium chlorate, 1800 kilos. of sodium hydroxide and 5400 litres of water is heated within twenty-four hours at 160° and kept at this temperature and under about 4 atmospheres pressure for thirty-six to forty hours. The product is worked up as described under (*b*). Pure Alizarin is obtained by fractional precipitation with calcium chloride solution. For this purpose, the solution of the melt is brought to 12° Bé. and to the boiling hot solution dilute calcium chloride is added carefully until a drop on filter-paper shows a pure red rim. With a little practice a sharp separation can be obtained. The calcium lake after filtration and decomposition with hydrochloric acid furnishes Alizarin "extra blue." The filtrate contains anthrapurpurin and a little flavopurpurin. The yield of Alizarin from 100 kilos. of anthraquinone is 105–110 kilos.

According to Lefévre ("Traité des Matières Colorantes," 1896, II, p. 1374), the fusion is effected in an ordinary vertical melt pan, fitted with a jacket containing oil, and furnished with a lid carrying an agitator and pierced for a thermometer, blow-out pipe, manometer, pipe for taking samples and compressed air. The amount of sodium hydroxide (70–80 per cent.) should be about two to three times the weight of the "silver salt"; it is dissolved in sufficient water to give a mass neither too viscid nor too fluid at 170–190°. The quantity of chlorate is calculated from the amount of hydrogen liberated in the reaction (1 mol. for 1 mol. of "silver salt"). The charge is heated at 170° and the duration of the reaction depends on the capacity of the pan. As a rule, it varies from seventy to ninety hours. After two days, the sampling tube is forced into the mass and a little of the latter is blown out. It is boiled with milk of lime and filtered. If the filtrate gives a precipitate on acidifying, the reaction is not finished; if only a turbidity is formed, the conversion to Alizarin may be considered to be complete. The melt is then worked up in the usual way.

As an example of the use of potassium nitrate instead of potassium chlorate, the following may be quoted (*Dyer*, 1915, p. 34). The fusion is carried out in a horizontal cylindrical vessel as described above. The cylinder holds about 800 gallons and is 6½ feet long and 3½ feet in internal diameter and is tested at a pressure of 12 atmospheres.

The water must be pure and especially must be free from every trace of iron, or the Alizarin will have an impure shade, owing to the presence of a calcium iron lake.

This mischance may also be due to defects in the lead lining of the precipitating vat. It is useless to dissolve in sodium hydroxide again. The only remedy is to heat with hydrochloric acid and potassium chlorate, with great precaution so as to destroy as little of the Alizarin as possible.

The fusion with sodium hydroxide is conducted as follows: The cylinder is charged with 12½ cwt. of "silver salt" (60 per cent.), 1 ton of sodium hydroxide dissolved to a solution of

45° Bé., and 2½ cwt. of saltpetre. The sodium hydroxide solution and saltpetre are put in first and heated at 125°, whereupon the "silver salt" is put in and the temperature raised to 180°, which means a pressure of 4–5 atmospheres. After thirty-six to forty-eight hours, the formation of the sodium alizarin is usually complete, but towards the end a sample from the cylinder must be tested occasionally. The test consists in boiling the sample with milk of lime, filtering off the lake, and adding acid to the filtrate. It should remain clear. If the process is not complete, yellow flakes of hydroxyanthraquinone will separate out. The finished melt is blown into a lead-lined vat, where it is diluted to 6° Bé. and precipitated after warming with direct steam by means of sulphuric acid (about 80 per cent.). For Alizarin extra blue, the diluted melt in the vat is mixed with slaked lime at the boiling temperature until it gives a pure red filtrate, and the calcium lake is filtered off and decomposed with hydrochloric acid. The Alizarin in either case is washed free from acid and made into a 20 per cent. paste as described above. The paste can be thickened, to avoid settling by adding ½–1 per cent. of salt, or especially for export to India, addition of glucose, starch, or glycerol.

Alizarin in lumps can be prepared as follows: One thousand kilos. of the 20 per cent. paste are mixed with 3000 litres of cold water and 466 kilos. of dry starch, previously obtained in the finest possible state of sub-division by repeated levigation. The vat must have a good stirrer. The thin paste thus obtained is freed as far as possible from water in a filter-press and the press cakes are carefully dried, first at a low, then at a higher temperature, in a vacuum oven, the temperature of which must not exceed 60°. These precautions are necessary to obtain the conchoidal fracture which is expected from the lumps, and it is impossible to obtain this if the temperature rises enough to cause the starch to swell up. In this way, 666 kilos. of Alizarin (30 per cent.) are obtained (Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 5444^{94}; G.P. 81230).

An interesting modification of this reaction is the following. Six parts of powdered potassium hydroxide (90 per cent.) and 6 parts of "silver salt" are well mixed in a closed, rotating vessel, with the exclusion of air, 1 part of ethyl alcohol is added gradually, and the whole is rotated until it forms a uniform homogeneous powder. This is now spread out in thin layers as rapidly as possible, and exposed to the air when the mass becomes warm, and the reaction begins almost immediately and a dark, violet-brown cake is formed. The alcohol distils away from the hot mass. If the layer is too thick, the reaction does not proceed at the bottom of the mass and after a few minutes the cake must be turned over as to allow all parts to come into contact with the air. The reaction is so rapid that it can be effected on an endless travelling band whereby the alcohol which distils off can be easily recovered.

The product is boiled with water and the Alizarin is isolated from the violet solution by means of acids (Badische Anilin- & Soda-Fabrik, E.P. 20664^{13}; G.P. 287270).

Alizarin can also be prepared from anthraquinone directly, without the intermediate production of the sulphonic acid, and the following is an account of the methods patented.

(1) To a solution of 20–30 kilos. of sodium chlorate (or nitrate) in 100 kilos. of water, 300 kilos. of sodium hydroxide or potassium hydroxide are added, and finally 100 kilos. of anthraquinone are stirred in. The paste is heated in an open pan fitted with a stirrer and set in an oil-bath or in a cylinder fitted with a stirrer and similarly placed in an oil-bath, at about 200° until the oxidising agent has been used up. The mass is then dissolved in water and the hydroxyanthranol which is formed is converted into anthraquinone by means of a current of air. The Alizarin is precipitated with milk of lime and filtered off. The filtrate contains a little benzoic acid.

The precipitate is decomposed with hydrochloric acid, the residue filtered from the calcium chloride solution, and finally the Alizarin is separated from anthraquinone with dilute sodium hydroxide solution (*idem*, E.P. 7398^{04}; F.P. 344680; G.P. 186526).

(2) In this example, the alkali hydroxide (a mixture of sodium and potassium hydroxides) is used in a very concentrated solution and the addition of a reducing agent, in these circumstances, increases the yield.

A mixture of 1200 kilos. of an 80 per cent. solution of the hydroxides, 100 kilos. of sodium sulphite, and 200 kilos. of anthraquinone is heated at 200° until the quantity of Alizarin does not increase. The dye is worked up as usual (Farbenfabriken vorm. F. Bayer & Co., E.P. 19641^{08}; F.P. 395137; G.P.A.F. 25018).

(3) The transformation can be effected by using dilute alkali hydroxide as follows: A mixture of 120 parts of anthraquinone, 25 parts of potassium nitrate, 82 parts of crystallised sodium sulphite, and 1375 parts of sodium hydroxide solution (29 per

cent.) is heated in a pressure vessel in an oil-bath for three to four days at about 180–200°. The product is dissolved in water, air passed through the solution to oxidise any reduction product to anthraquinone, the latter is filtered off, and the Alizarin isolated from the filtrate in the usual way.

In the two other examples given in the patent, the same conditions as to temperature and time of heating are observed, the quantities being 74·5 parts of anthraquinone, 31 parts of sodium nitrate, 102 parts of crystallised sodium sulphite, and 1460 parts of sodium hydroxide solution (17 per cent.), in the first, and 40 parts of anthraquinone, 27 parts of crystallised sodium sulphite and 1730 parts of sodium hydroxide solution (23 per cent.) in the second (*idem*, F.P. 435118; G.P. 241806).

Instead of sodium sulphite, other substances which give rise to this substance in the process may be used, such as sodium thiosulphate, sodium hyposulphite, sodium nitrilosulphonate, sodium naphthalene-1 : 3 : 5-trisulphonate, or sodium sulphide, but in these cases some unchanged anthraquinone is obtained, so that this modification does not appear to have any advantage over the original process (*idem*, E.P. 24642^{11}; F.P. 435118; G.P. 251236).

(4) A mixture of 100 parts of "silver salt," 50 parts of anthraquinone, 25 parts of potassium nitrate, and 1425 parts of sodium hydroxide solution (28 per cent.) is heated under the same conditions as in the preceding cases (*idem*, E.P. 2354^{11}; G.P. 245987; U.S.P. 1036880).

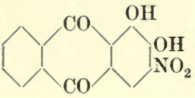
Finally, even the preparation of anthraquinone may be avoided for the 9 : 10-nitro-derivatives of anthracene, obtained by the action of nitric acid or nitrogen peroxide on the hydrocarbon, furnish Alizarin when heated with alkali hydroxides. The mixture of trinitrodihydroanthracene and nitroanthrone prepared by the action of excess of nitric acid on a suspension of anthracene in glacial acetic acid (Meisenheimer, *Annalen*, 1904, **330**, 163) is very suitable for reaction. This is carried out as follows:

(1) A mixture of 50 parts of 9 : 10-dinitroanthracene made into a paste with 100 parts of water, 167 parts of sodium hydroxide, 80 parts of sodium hydrogen sulphite solution neutralised with 35 parts of sodium hydroxide solution (35° Bé.), 60 parts of lime, 20·6 parts of sodium nitrate, and 626 parts of water is heated for two to three days in an iron pressure vessel fitted with a stirrer at 200°. The brownish-red calcium lake of Alizarin is filtered off, decomposed with hydrochloric acid, and, after

being filtered and washed, the product is dissolved in dilute sodium hydroxide solution. This is treated with a current of air and a slight residue is filtered off. The filtrate is treated with dilute hydrochloric or sulphuric acid and the Alizarin is collected.

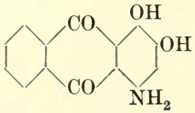
(2) A mixture of 40 parts of nitroanthrone, 134 parts of sodium hydroxide, 16·5 parts of sodium nitrate, 32 parts of lime, 64 parts of sodium hydrogen sulphite, neutralised with 28 parts of sodium hydroxide solution (35° Bé.) and 581 parts of water is heated for fifty hours at 200° and the product is worked up as in the preceding case (Chemische Fabrik Griesheim-Elektron, E.P. 16859[14]; F.P. 475141; G.P. 292247; U.S.P. 1150152).

Alizarin orange,



Alizarin orange, or β-nitroalizarin, has been prepared by treating dry Alizarin with nitrous or nitric fumes (Rosenstiehl, *Compt. rend.*, 1876, **82**, 1455; **83**, 73; *Ann. Chim. Phys.*, 1877, [v], **12**, 519; Caro, E.P. 1229[76]), by passing nitrous fumes into a solution or suspension of Alizarin in glacial acetic acid, petroleum, nitrobenzene, or ether (Caro, *loc. cit.*), by treating a sulphuric acid or glacial acetic acid solution of Alizarin with nitric acid (Caro, *loc. cit.*, Schunck and Roemer, *Ber.*, 1879, **12**, 583), or by boiling 1 : 3-dinitro-2-hydroxy-anthraquinone with dilute sodium hydroxide solution (Simon, *Ber.*, 1882, **15**, 692). The most satisfactory method of preparation appears, however, to consist in nitrating the boric ester in sulphuric acid solution, as follows:

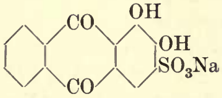
Ten kilos. of Alizarin are dissolved in 200 kilos. of sulphuric acid (66° Bé.) and 10 kilos. of crystallised boric acid are stirred in. The mixture is strongly cooled and 3 litres of nitric acid (42° Bé.) are run in gradually, the temperature not being allowed to rise appreciably above 0°. After some hours, the mixture is poured into cold water, the precipitate filtered off, dissolved in sodium hydroxide solution, and hydrochloric or sulphuric acid is added to the boiling solution. The β-nitroalizarin separates in a pure state, the boric acid having been split off in the above operation (Farbenfabriken vorm. F. Bayer & Co., G.P. 74562). The pure substance crystallises from glacial acetic acid in long, shining, orange-yellow needles, or sometimes in plates, melting at 244°.

Alizarin garnet R, 

α-Nitroalizarin, which is required for the preparation of this dye, is obtained in good yield by adding dibenzoylalizarin to a well-cooled mixture of nitric and sulphuric acids and hydrolysing the product (Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 14717^{92}; F.P. 223766; G.P. 66811), but a simpler method consists in dissolving 240 parts of Alizarin in 2000 parts of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide), and adding gradually at – 5° to – 10° a solution of 96 parts of potassium nitrate in 190 parts of sulphuric acid (100 per cent.). The nitration is complete in one and a half to two hours, and the α-nitroalizarin is isolated by pouring the mixture into water and filtering (*idem*, G.P. 74431).

An alternative process is the following:

Ten kilos. of Alizarin are dissolved in 200 kilos. of sulphuric acid (66° Bé.) and 10 kilos. of arsenic acid are stirred into the solution. This is strongly cooled and 3 litres of nitric acid (42° Bé.) are added gradually, the temperature not being allowed to rise appreciably above 0°. After remaining for some time, the mixture is poured into cold water, the precipitate filtered off, dissolved in sodium hydroxide solution, the solution heated to boiling, a large excess of sulphuric acid added, and the whole boiled until the arsenic ester of α-nitroalizarin is completely decomposed. This point is indicated when a sample dissolves in sodium hydroxide solution with the violet colour of α-nitroalizarin. The dye is then filtered off and washed (Farbenfabriken vorm. F. Bayer & Co., E.P. 2695^{93}; G.P. 74598).

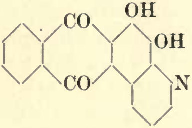
Alizarin red S, 

Alizarin is heated for several hours at 100–150° with 3 parts of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide) until the product is soluble in water. The mixture is poured into water, neutralised with slaked lime, the calcium salt of the sulphonic acid converted into the sodium salt, and the latter solution evaporated to dryness (Österreichische Alizarinfabriksgesellschaft Przibram & Co., E.P. 1117^{78}; G.P. 3565).

The temperature of sulphonation is also given as 170° (Schultz, "Farbstofftabellen," 1914, 270).

The acid can be salted out of solution.

Alizarin blue,



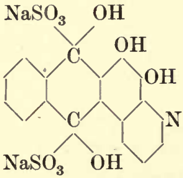
In the early methods of preparing Alizarin blue, by the interaction of β-nitroalizarin, glycerol, and sulphuric acid, the reaction became very violent (compare Koch, *Mon. Sci.*, 1878, 1163; Witz, *Bull. Soc. Ind. Rouen*, 1878, 82; Auerbach, *Trans.*, 1879, **35**, 799), but this can be avoided by the following procedure. An intimate mixture of 40 kilos. of β-nitroalizarin paste (17·5 per cent.), 3·5 kilos. of glycerol, and 3·5 kilos. of sulphuric acid (66° Bé.) is heated in an oil-bath for about thirty hours at 175°. When the mass is dry, 3·5 kilos. of glycerol and 3·5 kilos. of sulphuric acid (66° Bé.) diluted with 2 litres of water are added, and the temperature is maintained at the same point for twelve to fifteen hours. A second addition of the above quantities of glycerol and sulphuric acid is then made and finally the mass is kept for about eight to ten hours at the same temperature, until it has become blue and dry. The product must be well washed with water (Gnehm, "Die Theerfarbstoffe," 1895–1897, V, iii, 1738).

Better results are obtained by using a mixture of β-aminoalizarin and β-nitroalizarin instead of the latter.

In another process, described only on the laboratory scale, β-aminoalizarin is condensed with glycerol by the aid of arsenic acid. Seventeen grams of arsenic acid are dissolved in 150 grams of concentrated sulphuric acid contained in a 2-litre flask on a water-bath and to the clear solution, after cooling, 45 grams of glycerol are added. During this operation the flask is shaken under cold water in order to avoid overheating. To the contents of the flask are now gradually added 30 grams of β-aminoalizarin with good shaking, and finally the whole sets to a red mass. It is slowly heated on the oil-bath under reflux at 105° and maintained at this temperature for about three-quarters of an hour to an hour. The softened mass is shaken carefully and the temperature slowly raised to 110°. The reaction begins at 108° and proceeds very smoothly and uniformly. When the first vigorous reaction has subsided, during the course of which the mass becomes a dark red liquid, the flask is heated for some time in the oil-bath at 110° until the small bubbles have disappeared from the surface of the liquid. The latter is then poured into cold water and the mixture well stirred. After cooling, the precipitate is filtered off, well boiled out four times with very dilute sulphuric acid (100 c.c. of 96 per cent. and 6 litres of water) and collected by means of a hot-water filter.

The Alizarin blue sulphate soon crystallises from the hot filtrate and collects on the bottom of the vessel as a heavy brown precipitate, which is filtered off and washed until neutral. By this washing the sulphate is decomposed and the free Alizarin blue remains on the filter as a blue paste. For further purification it may be mixed with water and borax added until the liquid is brownish-violet. This is filtered and the blue residue washed until the wash water is blue. The boron compound is decomposed with dilute hydrochloric acid and the dye filtered off and washed (Knueppel, G.P. 87334; *Ber.*, 1896, **29**, 703).

Alizarin blue S,



Alizarin blue, in the form of a 10–12 per cent. paste, is stirred with 25–30 per cent. of a solution of sodium hydrogen sulphite (30° Bé.; *d* 1·25) and the mixture left for eight to fourteen days. If it is now filtered, some unchanged Alizarin blue remains behind and can be used again and the filtrate containing the bisulphite compound is either used direct or the compound is isolated from it by precipitation with salt or by evaporating the solution at a low temperature.

The solution of Alizarin blue S is decomposed on the addition of strong acids or of alkali carbonates or by warming it at about 70°. It can be treated with acetic or tartaric acid or with calcium, magnesium, or chromium acetates at the ordinary temperature without decomposition or formation of lakes, but decomposition occurs on steaming (70–100°). Aluminium or iron salts decompose the dye more easily than does chromium acetate and give the corresponding lakes (Badische Anilin- & Soda-Fabrik, E.P. 3603^{81}; G.P. 17695).

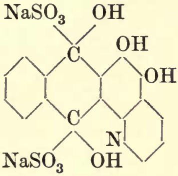
Zinc sulphite or other sulphites may be used instead of sodium hydrogen sulphite and the action of the latter on Alizarin blue accelerated by the presence of a solvent of the dye. For example, 10 kilos. of Alizarin blue (20 per cent. paste), 10 kilos. of sodium hydrogen sulphite solution (30° Bé.; d 1·25), and 2 kilos. of acetic acid (8° Bé.; d 1·06) are well mixed together and the mixture is protected from air and allowed to remain at the ordinary temperature. After eight days, the conversion into the bisulphite compound is almost complete. The mixture is filtered, the residue washed with water, and the dye precipitated from the filtrate by salting out. Instead of using acetic acid, the Alizarin blue may be mixed with a salt of this acid and the mixture saturated with sulphur dioxide. Another modification of the process consists in treating the leuco-compound of Alizarin blue as described above. Five kilos. of Alizarin blue in the form of 20 per cent. paste are gently warmed with a solution of 1 kilo. of grape-sugar in 1 litre of water and 5 kilos. of sodium hydroxide solution (20 per cent.) until a clear deep-brown reduction-vat is obtained. The solution is saturated with sulphur dioxide in the absence of air, and after eight days the mixture is filtered and the Alizarin blue S is salted out or precipitated by adding alcohol.

The reduction-vat may be faintly acidified with dilute hydrochloric acid and then mixed with zinc sulphite solution, the dye being isolated as described above (*idem*, E.P. 3603^{81}; F.P. 144386 and addition; G.P. 23008; U.S.P. 258530).

The dye can also be obtained by treating Alizarin blue with aniline sulphite and decomposing the product with alkali salts, or by treating Alizarin blue with sulphur dioxide and converting the product into Alizarin blue S by adding sodium acetate or similar sodium salts, but this patent is practically worthless and was taken out only to prevent infringement (*idem*, G.P. 54390).

The sodium compound of Alizarin blue may also be similarly treated with sodium hydrogen sulphite (Koenig, E.P. 4531^{81}; U.S.P. 263964, 263965) or neutral ammonium sulphite may be allowed to act on Alizarin blue or its sodium compound (*ibid.*, E.P. 627^{82}; U.S.P. 261600).

Alizarin green S,



Fifteen parts of α-aminoalizarin (Alizarin garnet R) are dissolved in 110 parts of sulphuric acid (66° Bé.) and 15 parts of glycerol and 1 part of picric acid are added. The solution is heated at 100–120° until a sample dissolved in alcoholic sodium hydroxide no longer shows the spectrum of α-aminoalizarin, which takes about two hours. The mass is then poured into water, heated to boiling, and the insoluble dye filtered off.

Instead of 1 part of picric acid, 5 parts of nitrobenzene or 7–8 parts of α-nitroalizarin may be used with the same effect.

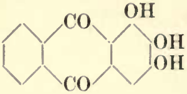
The dye may also be prepared from α-nitroalizarin by heating 1 part with 14 parts of sulphuric acid (66° Bé.) and 1½ parts of glycerol gradually at 70–80°, keeping at this point for three hours, and then raising the temperature to 110°. After heating for a short time at 110–115°, the mixture is poured into water and the dye filtered off.

By heating 1 part of α-aminoalizarin with 1⅓ parts of glycerol and 8–10 parts of sulphuric acid (66° Bé.) at 120°, the dye is also obtained, but the time of heating is longer than when oxidising agents are employed.

The crude dye is treated with hot dilute sodium hydroxide solution, and the sparingly soluble sodium salt obtained in this way is washed until the filtrate is colourless. The sodium salt is decomposed with dilute sulphuric acid and the base liberated from the resulting sulphate by treating it with much water. The paste obtained on filtration is mixed with an equal volume of a concentrated solution of sodium hydrogen sulphite and left for eight days. Water is then added to dissolve any bisulphite compound that has separated, the mixture filtered, and the carmine-red solution is salted out and the dye filtered off and dried. Any unchanged quinoline derivative can be separated from the bisulphite solution by boiling or by adding acid

(Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 14717^{92}; F.P. 223766; G.P. 67470).

Anthracene brown (Anthragallol),



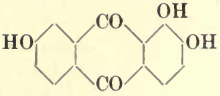
This is obtained by condensing gallic acid and benzoic acid in sulphuric acid solution, or by heating gallic acid and phthalic anhydride with zinc chloride.

One part of gallic acid and 2 parts of benzoic acid are mixed with 20 parts of concentrated sulphuric acid and gradually heated. The reaction begins below 70° and after some eight hours' heating, during which time the temperature is very gradually raised to 125°, the reaction is complete. The product is allowed to cool, and poured into much cold water when brownish-yellow flocks separate which are repeatedly extracted with water. The moist paste which should now contain almost entirely anthragallol and a small amount of rufigallic acid (1 : 2 : 3 : 5 : 6 : 7-hexahydroxyanthraquinone) is boiled with faintly acidified alcohol until crystals no longer separate from the filtrate on cooling. When these are recrystallised once or twice from alcohol faintly acidified with acetic acid, pure anthragallol is obtained in a yield of about 40 per cent. of the theoretical. A yield of 30 per cent. of the theoretical is obtained by heating a mixture of 1 part of pyrogallol and 2 parts of phthalic anhydride with 50 parts of sulphuric acid very slowly to 160°, and extracting the product, worked up as above, with ether (Seuberlich, *Ber.*, 1877, **10**, 38).

On the large scale, the moist paste is adjusted to 20 per cent. strength and used direct, or, if not sufficiently finely divided, dissolved in alkali and reprecipitated with acid.

Pure anthragallol sublimes at 290° and melts at 310°.

Anthrapurpurin,



This is prepared by melting anthraquinone-2 : 7-disulphonic acid with sodium hydroxide in the presence of an oxidising agent in the same way as is Alizarin (p. 226). In the process, *iso*-anthraflavic acid (2 : 7-dihydroxyanthraquinone) is formed and this can be treated as above to give Anthrapurpurin.

According to Schultz (" Die Chemie des Steinkohlentheers," 1901, II, p. 286), a mixture of 200 kilos. of sodium anthraquinone-2 : 7-disulphonate, 40 kilos. of potassium chlorate, 700 kilos. of sodium hydroxide, and 1260 litres of water is heated at 170° under 5 atmospheres pressure. The sodium salt must be as free as possible from sodium sulphate. The product is worked up as in the case of Alizarin.

According to a later recipe, the conversion of the disulphonic acid is carried out as in the case of " silver salt " (see p. 226) except that the temperature is higher, namely, 200–225° (*Dyer*, 1915, p. 35). If, in the sulphonation of anthraquinone, the 2 : 6- and 2 : 7-disulphonic acids are not separated, but are used direct in the fusion process, a mixture of Anthrapurpurin and Flavopurpurin (p. 242) is obtained.

According to Schultz (*loc. cit.*, p. 284), a mixture of 900 kilos. of the sodium salts of the disulphonic acids (obtained by neutralising with sodium carbonate), 144 kilos. of potassium chlorate, 2100 kilos. of sodium hydroxide, and 6500 litres of water is heated within twenty-four hours at 170° and kept at this temperature and under 4–4·5 atmospheres pressure for forty-two to forty-eight hours. The product is diluted to 4° Bé. and worked up as in the case of Alizarin.

The following proportions may also be used : (1) 2000 litres of liquid containing the mixed sodium salts partly in solution and partly in suspension (containing 27·65 per cent. of dry material, that is, 553 kilos.), 180 kilos. of potassium nitrate, 1012 litres of sodium hydroxide solution (45° Bé., equal to 618 kilos. of pure dry sodium hydroxide), and 795 kilos. of solid sodium hydroxide; (2) 1850 litres of the liquor (equal to 514 kilos. dry), 250 kilos. of potassium nitrate, 900 litres of sodium hydroxide solution (45° Bé., equal to 549·5 kilos. of pure dry sodium hydroxide), and 795 kilos. of solid sodium hydroxide. The temperature must be raised as rapidly as possible and therefore the liquid containing the disulphonates together with the sodium hydroxide solution and the potassium nitrate are heated together before the solid sodium hydroxide is added. The reaction takes at least forty-eight hours (Ullmann, " Enzyklopädie der technischen Chemie," 1914, I, p. 203).

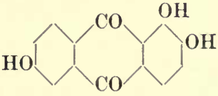
Mixtures of Anthrapurpurin and Flavopurpurin, together with

Alizarin, are obtained direct from anthraquinone as shown in the following examples :

(1) A mixture of 100 parts of anthraquinone, 42 parts of potassium nitrate, 136 parts of crystallised sodium sulphite, and 1370 parts of potassium hydroxide solution (33 per cent.) is heated in a pan set in an oil-bath and fitted with a stirrer, at 190–195°. The product is diluted with water, filtered from a little unchanged anthraquinone, and air passed through the filtrate. If necessary, this is again filtered and the filtrate acidified. The product consists of a mixture of about 25 per cent. of Anthrapurpurin, 25 per cent. of Flavopurpurin, and 50 per cent. of Alizarin.

(2) A mixture of 75 parts of anthraquinone, 62 parts of potassium nitrate, 204 parts of crystallised sodium sulphite, and 1350 parts of potassium hydroxide (19 per cent.) is heated as above for about seventy-five hours at 180–190°. The product, worked up as above, is a mixture of about 25 per cent. of anthraflavic acid (2 : 6-dihydroxyanthraquinone), 30 per cent. of Anthra- and Flavo-purpurins, and 45 per cent. of Alizarin (Farbenfabriken vorm. F. Bayer & Co., E.P. 11915^{12}; F.P. 435118; G.P. 249368; U.S.P. 1036880, 1036881).

Flavopurpurin,



This is prepared by melting anthraquinone-2 : 6-disulphonic acid with sodium hydroxide in the presence of an oxidising agent as in the case of Anthrapurpurin (p. 241). The by-product formed in this case is anthraflavic acid.

A mixture of 200 kilos. of sodium anthraquinone-2 : 6-disulphonate, 36 kilos. of potassium chlorate, 400 kilos. of sodium hydroxide, and 890 litres of water is heated at 170–180° under a pressure of 5–6 atmospheres for twenty-five to thirty hours. The product is worked up as in the case of Alizarin (Schultz, *loc. cit.*, p. 284). According to Jellinek (*Ber.*, 1888, **21**, 2524), commercial Flavopurpurin in the year 1888 contained about 70 per cent. of the pure substance, the rest being mostly anthraflavic acid. He effected the purification in the following way : The powdered material (500 grams) is suspended in about 3 litres of hot water, potassium hydroxide added until an alkaline reaction is produced, and the liquid filtered. The filtrate is diluted with water to about 15 litres, heated to boiling, and lead acetate solution added to the well-stirred liquid until a sample, treated with lead acetate gives a precipitate which, on passing carbon dioxide, is coloured only bright leather-yellow, due to traces of the lead salt of Flavopurpurin. For this purpose, 550 grams of crystallised lead acetate were required. The precipitate is collected on cloth and allowed to drain for twenty-four hours. It is difficult to wash the precipitate, so the open end of the cloth is tied together with string and the whole boiled with water in a copper pan. The bag containing the precipitate is pressed, the lead salt decomposed by sulphuric acid with the addition of alcohol, and the hot, moderately diluted alcohol separated from the lead sulphate. The solution is concentrated; the first separation is rejected and the rest of the product allowed to crystallise out. In purifying small quantities of Flavopurpurin, alcohol may be used instead of water in preparing the lead salt, in which case the subsequent filtration is much quicker. The precipitation is done in dilute solution, 50 grams of the material requiring 3–4 litres of alcohol.

The deep red aqueous liquid from the lead salt of Flavopurpurin deposits on keeping or on concentration ruby-red needles of anthraflavic acid.

Another method of separating Flavopurpurin, alone or mixed with Anthrapurpurin and Alizarin, from anthraflavic acid, *iso*-anthraflavic acid, and hydroxyanthraquinone is based on the fact that whilst the calcium lakes of the dyes are insoluble in the presence of an excess of alkali hydroxide, the lakes of the non-dyeing constituents are soluble. The process is carried out by acting on the finished dyes, the finished alkali hydroxide fusion, the lime fusion, or the mixed alkali hydroxide and lime fusion, with alkali hydroxide and lime in the proportions, respectively, of not less than 100 per cent. and 40 per cent. of the whole amount of hydroxyanthraquinones present. The non-dyeing constituents are recovered from the filtrate by acidification or their sodium salts are obtained by concentrating the filtrate to 20° Bé., if necessary, and allowing to crystallise. The process may also be based on the insolubility of the sodium salt of anthraflavic acid in sodium hydroxide solution (10–20° Bé.), the salt being separated by dissolving the finished sodium hydroxide melts of Flavopurpurin or mixtures thereof with Anthrapurpurin and Alizarin, in water to a strength of 10–20° Bé., or the finished dye in sodium hydroxide solution and evaporating to 10–20° Bé. (Iljinsky and Wedekind & Co., E.P. 20201^{01}; F.P. 314914; G.P. 137948).

The presence of anthraflavic acid in the Flavopurpurin melt, noticed by Jellinek in 1888 (*loc. cit.*), was still unavoidable in 1906, for in that year a patent was taken out with the object of converting this acid into Flavopurpurin, although R. Schmidt (*J. pr. Chem.*, 1891, [ii], **43**, 236) had stated that it could not be changed by fusion with alkali hydroxide and oxidising agents. The difficulty was overcome by the use of very concentrated alkali hydroxide acting at a high temperature. The process can be applied to sodium anthraquinone-2 : 6-disulphonate with success, as shown in the second example.

(1) Anthraflavic acid (100 parts), together with 50 parts of potassium nitrate, is added to about 1500 parts by volume of sodium hydroxide solution (boiling at 185°) and the mixture is heated in a pressure vessel fitted with a stirrer, at 215–225° for a long time. On working up the product as described above, 75 parts of very pure Flavopurpurin were obtained, 15 parts of anthraflavic acid being recovered.

(2) Dry sodium anthraquinone-2 : 6-disulphonate (100 parts) is heated with 24 parts of potassium nitrate and 500 parts of sodium hydroxide solution (boiling at 210°) under pressure at about 220°. From the product were isolated 36 parts of pure Flavopurpurin and only 2 parts of anthraflavic acid (R. Wedekind & Co., G.P. 194955).

It was shortly after claimed that the conversion of anthraflavic acid into Flavopurpurin could equally well be effected by using a large excess of sodium hydroxide solution of the ordinary concentration, as follows :

(1) A mixture of 21 parts of anthraflavic acid, 10 parts of sodium nitrate, and 1800 parts of sodium hydroxide solution (30 per cent.) is heated in a pressure vessel at about 195–200° for about four days or until a sample contains not more than a trace of anthraflavic acid. A good yield of very pure Flavopurpurin is obtained.

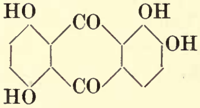
(2) A mixture of 10 parts of sodium anthraquinone-2 : 6-disulphonate, 2·5 parts of potassium chlorate, and 450 parts of sodium hydroxide solution (30 per cent.) is heated in a pressure vessel at 195–200° for eighty hours or until a sample shows that not more than a trace of anthraflavic acid is present. A good yield of very pure Flavopurpurin is obtained.

In both these cases the temperature of the melt may be

220–230° and the time consequently shortened (Farbenfabriken vorm. F. Bayer & Co., E.P. 24601^{08}; G.P. 205097).

It was soon found to be unnecessary to use such a large excess of alkali hydroxide as given above and also that a more dilute solution suffices, thus in one example 25 parts of anthraflavic acid, 12 parts of sodium nitrate, and 700 parts of sodium hydroxide (20 per cent.) are heated at 180–200° as above; in a second, 50 parts of anthraflavic acid, 25 parts of potassium nitrate, and 925 parts of sodium hydroxide solution (34 per cent.) are heated at the same temperature, and in the third, 10 parts of sodium anthraquinone-2 : 6-disulphonate, 2·5 parts of potassium chlorate, and 210 parts of sodium hydroxide solution (35 per cent.) are similarly heated (*idem*, E.P. 24601^{08}; G.P. 223103).

Quinalizarin Bordeaux (Alizarin Bordeaux).



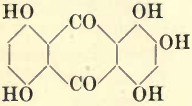
Ground and dry Alizarin (10 kilos.) is added to 100 kilos. of fuming sulphuric acid (containing 70 per cent. of sulphur trioxide), care being taken that the temperature does not rise too high. The mixture is kept for twenty-four to forty-eight hours at 35–40° until a sample, poured into ice-water and rendered alkaline with sodium hydroxide solution, gives a yellowish-red colour.

The mixture is then added to 200 kilos. of sulphuric acid (either 66° Bé. or monohydrate) and then the whole is poured on ice. A reddish-yellow precipitate separates which is filtered off, and consists of the neutral quinalizarin ester of sulphuric acid. It is dissolved in sodium hydroxide solution and the solution is acidified in the cold with hydrochloric or sulphuric acid, too large an excess being avoided, when a clear reddish-brown solution is obtained. On boiling, a precipitate is formed which is filtered off and washed. It can be obtained in a chemically pure state by distilling it from a small glass retort and crystallising from glacial acetic acid, or better, nitrobenzene. It forms garnet-red needles which do not melt at 280° (Farbenfabriken vorm. F. Bayer & Co., E.P. 8725^{90}; F.P. 206564; G.P. 60855; U.S.P. 446893; R. E. Schmidt, *J. pr. Chem.*, 1891, [ii], **43**, 237).

Instead of Alizarin quinizarin (*idem*, E.P. 17712^{90}; F.P. 3rd addition to 206564; G.P. 63693) or hydroxyanthrarufin (1 : 2 : 5-trihydroxyanthraquinone) may be used in the above example (*idem*, E.P. 4871^{91}; F.P. 6th addition to 206564; G.P. 67063).

Quinalizarin was synthesised by Liebermann and Wense (*Ber.*, 1887, **20**, 862) by condensing hemipinic acid and quinol in sulphuric acid solution to 5 : 8-dihydroxy-1 : 2-dimethoxyanthraquinone and heating this with hydrochloric acid.

Alizarin cyanin R,



Ten kilos. of dry Alizarin Bordeaux are dissolved in 200 kilos. of sulphuric acid (66° Bé.), the solution is well stirred, and 10 kilos. of finely powdered pyrolusite (88 per cent. MnO_2) are added gradually, the temperature not being allowed to rise above 25°. The product is poured into water, the temperature not being allowed to be too high, and sodium hydrogen sulphite is added to the liquid until the odour of sulphur dioxide persists after some time. The quinone which is formed in the above process is thus reduced and this is shown by the change in colour from violet to reddish-brown. The mixture is then heated to boiling, filtered, and the dye is dissolved in hot dilute sodium hydroxide solution and reprecipitated from the filtered solution with acid (Farbenfabriken vorm. F. Bayer & Co., E.P. 12715^{90}, 4871^{91}; F.P. addition to 206564; G.P. 62018, 66153; U.S.P. 446892, 506265; R. E. Schmidt, *J. pr. Chem.*, 1891, [ii], **43**, 237).

"Purpurin Bordeaux," prepared in the same way as Alizarin Bordeaux, starting from purpurin (1 : 2 : 4-trihydroxyanthraquinone), may be substituted for the latter dye in the above process (*idem*, E.P. 17712^{90}; F.P. 3rd addition to 206564; G.P. 62506).

The dye can also be prepared by dissolving 10 kilos. of hydroxyanthrarufin * (1 : 2 : 5-trihydroxyanthraquinone) in 200 kilos. of sulphuric acid, stirring well, and adding 12 kilos. of finely powdered pyrolusite (90 per cent. MnO_2), the temperature not being allowed to rise above 20–25°. The product is poured into

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* In the patent, the formula given is that of this compound although it is called hydroxychrysazin, which is the 1 : 2 : 8-derivative.

water, treated with sodium hydrogen sulphite, and worked up as above (*idem*, E.P. 4871^{91}; F.P. 6th addition to 206564; G.P. 68114).

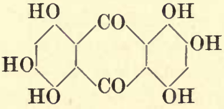
It is further obtained by electrolytically oxidising Alizarin Bordeaux in sulphuric acid solution (*idem*, E.P. 12579^{92}; F.P. addition to 206564; G.P. 74353).

Alizarin cyanin G.

Ten kilos. of Alizarin Bordeaux are dissolved in 200 kilos. of sulphuric acid (66° Bé.) and 12 kilos. of finely powdered pyrolusite (70 per cent. MnO_2) are gradually added with good stirring. Care is taken that the temperature of the mixture does not exceed 30–40°, as the intermediate compound produced decomposes above this point. The reaction may be regarded as finished when a sample, diluted with concentrated sulphuric acid, no longer appears violet in transmitted light, but pure blue. The mixture is then poured into ice-water, care being taken that no rise in temperature takes place, when the intermediate product separates in dark violet flocks.

It is dissolved in 50 kilos. of ammonia (20 per cent.), the solution filtered, diluted with water, and the dye precipitated with acid (Farbenfabriken vorm. F. Bayer & Co., E.P. 17712^{90}; F.P. 3rd addition to 206564; G.P. 62505, 62019; U.S.P. 476419).

Anthracene blue WR,



(1) Ten kilos. of 1 : 5-dinitroanthraquinone are heated with 50–100 kilos. of fuming sulphuric acid (containing 40 per cent. of sulphur trioxide) at 100–130° for three hours.* The resulting dye is isolated by pouring the mixture into water and salting

* Patents were refused for processes of treating dinitroanthraquinone or aminonitroanthraquinone at the ordinary temperature with fuming sulphuric acid (containing 70 per cent. of sulphur trioxide) or the latter compound at 130–160° with acid containing 40 per cent. of sulphur trioxide (Farbwerke vorm. Meister, Lucius, & Brüning, E.P. 21167^{92}, 21168^{92}). The products obtained with concentrated sulphuric acid at 200° have been examined by Lifschütz (*Ber.*, 1884, **17**, 891).

out. The dry substance dissolves in water with a dirty red, in sodium carbonate solution with a dirty bluish-violet, and in sodium hydroxide solution with a dirty greenish-blue colour. It is added to ten times its weight of sulphuric acid (66° Bé.) and the mixture heated at 130° for five hours or until the product has become insoluble in water. The mass is poured into water, the dye filtered off, and washed with warm water. It can be used direct in paste form or converted into an alkali salt and dried.

(2) If the above processes are combined, a very similar dye is obtained, which is, however, slightly greener. After the dinitroanthraquinone has been heated with the fuming sulphuric acid, the mixture is diluted with 100 kilos. of sulphuric acid (66° Bé.), and heated at 130° until the product is insoluble in water. It is then worked up as above. The greenish-blue colouring matter, which is evidently contained in this product, contains nitrogen and sulphur.

Instead of pure 1 : 5-dinitroanthraquinone, the crude dinitro-compound, prepared by nitrating anthraquinone in sulphuric acid solution may be employed (Badische Anilin- & Soda-Fabrik, E.P. 19589^{91}; G.P. 67102; U.S.P. 502603).

(3) An alternative process, which also furnishes a mixture of two colouring matters, consists in gradually adding 10 kilos. of 1 : 5-dinitroanthraquinone (or the crude dinitro-derivatives) to 100 kilos. of fuming sulphuric acid (containing about 12 per cent. of sulphur trioxide) previously warmed at about 130° and then heating the mixture for two and a half to three hours at about 160°. The product is poured into water and the dye salted out. The dry material is added to ten times its weight of sulphuric acid (66° Bé.) and the mixture heated at 130° for five hours or until the product is insoluble in water. It is then poured into water, and the dye filtered off and washed (*idem*, E.P. 13147^{92}; G.P. 71435).

In this process the partly reduced derivatives of 1 : 5-dinitroanthraquinone or of the mixture of 1 : 8-dinitroanthraquinone and other isomerides can be substituted for 1 : 5-dinitroanthraquinone (*idem*, G.P. 88083).

In examples (1) and (3) given above, the intermediate dye soluble in water, consisting of a sulphuric ester, can be converted into the insoluble finished product by heating 10 kilos. with 100–200 kilos. of hydrochloric acid (20° Bé.) under pressure for five to ten hours at 180–200°, allowing to cool, diluting with water, filtering, and washing, or by using dilute sulphuric acid (50° Bé.)

in this operation, in which case no pressure is employed. Further, the hydrolysis can be effected by means of phosphoric acid or even of water. In the former case, 10 kilos. of the intermediate dye are heated with 100 kilos. of phosphoric acid (87 per cent. H_3PO_4), the mixture being well stirred. The temperature keeps at 140° for a long time and froths owing to the escape of steam. It is then raised to 200–240° and maintained at this point for half an hour or until the product is insoluble in water. The mixture is poured into water, filtered, and the dye is dissolved in alkali hydroxide and reprecipitated with hydrochloric acid, being then filtered off and washed.

For the hydrolysis with water, 15 kilos. of the intermediate dye are heated with 100 litres of water in an autoclave at 150–200° for eight to ten hours until the product is insoluble in water.

These processes are applicable to the water-soluble dyes obtained as described below (*idem*, E.P. 13029^{92}; G.P. 76941).

If the crude mixture of dinitroanthraquinones is separated by extracting with alcohol or acetone, the 1 : 5-derivative remains behind and the solution, on evaporation, yields the 1 : 8-derivative mixed with several other isomerides. If this mixture is substituted for 1 : 5-dinitroanthraquinone in the first of the examples given above, a greener dye is obtained (*idem*, E.P. 19588^{91}, 19589^{91}; G.P. 72685; U.S.P. 519229; details of the various isomeric dinitroanthraquinones are given by Farbwerke vorm. Meister, Lucius, & Brüning, G.P. 167699).

Another process consists in partly reducing 1 : 5-dinitroanthraquinone, by using an amount of reducing agent equivalent to 3–6 atoms of hydrogen per molecule, so that the product is a mixture of unchanged dinitroanthraquinone diaminoanthraquinone, and probably nitroaminoanthraquinone or hydroxylamino-compounds. Instead of 1 : 5-dinitroanthraquinone, the crude mixture of dinitro-derivatives can be used, or the 1 : 8- and other isomerides obtained as above.

Ten kilos. of 1 : 5-dinitroanthraquinone are mixed with 10 kilos. of crystallised sodium sulphide and 200 litres of water, and the whole is heated to boiling for one to two hours. When sodium sulphide can no longer be detected, the mass is filtered, washed, and dried. When this product is treated as described in examples (1) or (2) above, identical dyes are obtained.

The reduction may also be effected by boiling a mixture of 10 kilos. of 1 : 5-dinitroanthraquinone, 10 kilos. of stannous chloride, 75 kilos. of sodium hydroxide solution (30° Bé.), and 500 litres of water for a half to one hour, or 10 kilos. of 1 : 5-dinitroanthraquinone, 30–50 kilos. of stannous chloride, 50 kilos. of concentrated hydrochloric acid, and 500 litres of water for one to two hours.

The reduction and formation of the water-soluble dye can also be performed in one operation by heating a mixture of 10 kilos. of 1 : 5-dinitroanthraquinone, 50–100 kilos. of fuming sulphuric acid (containing 12–40 per cent. of sulphur trioxide), and 1·5 kilos. of finely powdered sulphur for several hours at 100–130°, and working up the product as described in example (1) (*idem*, E.P. 13029^{92}; G.P. 76262, 87729; these two German patents are almost word for word identical). The nature of the intermediate products obtained in this reaction was explained later (*idem*, E.P. 19009^{98}; F.P. 281125; G.P. 105567) and the compounds produced by carrying out the reaction at 40–45° have been examined by R. E. Schmidt and L. Gattermann (*Ber.*, 1896, **29**, 2934).

In the above two examples many nitro-, nitrohydroxy-, nitroamino-, and diamino-derivatives of the anthraquinone series may be used (for example, nitroaminoanthraquinone, tetranitroanthrachrysone, and diaminoanthraquinone) can be substituted for dinitroanthraquinone and, when feasible, the nitro-derivatives need not be isolated (*idem*, E.P. 974^{94}; F.P. 235896; G.P. 83055).

The reduction of 1 : 5-dinitroanthraquinone can also be effected electrolytically as follows: Ten parts of 1 : 5-dinitroanthraquinone are dissolved in 200 parts of fuming sulphuric acid (containing 40 per cent. of sulphur trioxide). This solution contains the cathode and is separated from the anode, immersed in sulphuric acid (66° Bé.) by a suitable diaphragm. An electric current of 80 amperes per square decimetre is passed through the cell at the ordinary temperature. The mass becomes warm and, by a suitable cooling arrangement, is kept at 100° until all the dinitroanthraquinone has dissolved, and a sample of the mixture dissolves in sulphuric acid (66° Bé.) with a red, and in water with a brownish-red colour. The mass is then quickly cooled and poured into ice-water, the solution being heated to boiling and filtered. On salting the filtrate, a chocolate brown precipitate is obtained which is soluble in water. This dye is identical with that produced as described above (from dinitroanthraquinone, fuming sulphuric acid, and sulphur) and is converted into the water-insoluble dye as in example (1).

If the action of the electric current is continued until a sample of the mixture dissolves in sulphuric acid (66° Bé.) with a brown colour, and gives a dark violet precipitate with water, Anthracene blue WG (q.v. example 1) is obtained (*idem*, E.P. 1962^{97}; G.P. 92800, 92998; these two German patents are practically identical).

The water-insoluble dye can be produced in one operation by treating 1 : 5-dinitroanthraquinone (or its isomerides or the crude mixture) with a solution of sulphur in fuming sulphuric acid at a comparatively low temperature. Thus 10 kilos. of pure 1 : 5-dinitroanthraquinone are added gradually with good stirring to a solution of 2·5 kilos. of sulphur in 200 kilos. of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide), care being taken that the temperature does not exceed 35°. The formation of the dye begins at once and is complete after warming the solution for one to one and a half hours at 50–60°. The solution is poured direct, or after dilution with 100 kilos. of cold sulphuric acid (100 per cent.), into water and the water-insoluble dye which separates in quantitative yield is filtered off and washed. If sulphuric acid containing 40 per cent. of sulphur trioxide is used instead of the 20 per cent. acid, heating for one hour at 40° is sufficient. In the above process, instead of dinitroanthraquinone may be used crude dinitromethylanthraquinone, crude dinitroanthrarufin or tetranitroanthrachrysone (Farbenfabriken vorm. F. Bayer & Co., E.P. 17674^{92} [Patent refused]; F.P. 224740; G.P. 96197, 101486).

What appears to be the same dye is obtained by heating a mixture of 10 kilos. of 1 : 5-dinitroanthraquinone, 10 kilos. of crystallised boric acid, and 200–300 kilos. of sulphuric acid (92–93 per cent.) in an enamelled pan fitted with a stirrer. A fairly vigorous reaction begins at about 220–230°, and the temperature rises to 250–260°. When the reaction is complete, the solution is allowed to cool, poured into 3000 litres of cold water, heated to boiling, and the dye is filtered hot and washed. The reaction can be carried out at 190–200°, in which case careful heating is necessary and the time of heating is rather longer (*idem*, E.P. 14345^{93}; F.P. 224740; G.P. 79768).

The nitration of anthraquinone and the conversion of the dinitro-derivatives into the above dye can also be done in one operation, thus 10 kilos. of dry sodium nitrate are stirred into a solution of 10 kilos. of anthraquinone in 200 kilos. of sulphuric acid (66° Bé.), the mixture is warmed at 60–80° and kept at this temperature for about twelve hours. At the end of this time, 5 kilos. of crystallised boric acid are added and the mixture is slowly heated to 190–200°, with good stirring. The reaction proceeds smoothly and is complete in about three to four hours. The product is poured into water and the dye is filtered off and washed (*idem*, E.P. 974^{94}; F.P. 224740; G.P. 81244).

Anthracene blue WG.

Ten kilos. of 1 : 5-dinitroanthraquinine are gradually added to 100 kilos. of fuming sulphuric acid (containing about 12 per cent. of sulphur trioxide) previously heated at about 130° and the mixture is heated for two and a half to three hours at about 160°. It is then diluted with 200 kilos. of sulphuric acid (66° Bé.) and heated at 130° for two hours or until the intermediate product, soluble in water with a dirty bluish-violet colour, is changed into a dye almost insoluble in water. The product is poured into water and the precipitate filtered off and washed with cold water. It can be purified by dissolving it in sodium acetate solution or in solution of other weakly alkaline salts and reprecipitating with acid.

The dye, which contains nitrogen and sulphur, dissolves very sparingly in hot water, with a weak violet colour. It gives in concentrated sulphuric acid a reddish-brown, and in sodium hydroxide solution a blue colour (Badische Anilin- & Soda-Fabrik, E.P. 19588^{91}; G.P. 67102; U.S.P. 502603).

The same dye, or a very similar one, is prepared as follows :

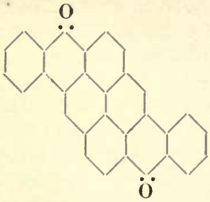
Ten kilos. of 1 : 5-dinitroanthraquinone are added to 100–150 kilos. of fuming sulphuric acid (containing 70–100 per cent. of sulphur trioxide, care being taken that no rise in temperature takes place, and the mixture is allowed to remain at a temperature not exceeding 40° for some hours. The product is now diluted carefully with two to three times its weight of well-cooled sulphuric acid (either 66° Bé., or 100 per cent.) and poured on ice, when the reddish-brown intermediate product separates. This is rapidly filtered off, washed, boiled with water, and sodium hydroxide solution is added to the boiling liquid, which is then immediately acidified with a little hydrochloric acid. The precipitate dissolves in sodium hydroxide solution with a blue, and in concentrated sulphuric acid with a red colour, with a brown fluorescence. The same dye is obtained if the intermediate product, after being isolated, is heated with concentrated sulphuric acid for some hours at about 130°. If the diluted mixture, instead of being poured on ice, is heated at about 120–130° for two to three hours, then poured into water, and the precipitate filtered off and washed a dye is obtained which dyes chrome-mordanted wool in rather greener shades than the preceding.

In the above example, the 1 : 5-dinitroanthraquinone may be replaced by the products of partial reduction described in E.P. 13029^{92} (p. 249) and the reduction can be effected in the process itself. Thus 10 kilos. of 1 : 5-dinitroanthraquinone are mixed with 1·5 kilos. of finely divided sulphur and 100–150 kilos. of fuming sulphuric acid (containing 70–100 per cent. of sulphur trioxide), care being taken to avoid any rise of temperature. The mixture is allowed to remain for some hours at a temperature not exceeding 40°, and worked up by one of the methods described above (Badische Anilin- & Soda-Fabrik, E.P. 15325^{92}; G.P. 89144). For the preparation of Anthracene blue WG by the electrolytic reduction of 1 : 5-dinitroanthraquinone in the presence of fuming sulphuric acid, see under Anthracene blue WR, p. 247.

Anthracene blue WGG.

A mixture of 10 kilos. of 1 : 5-dinitroanthraquinone, 10 kilos. of crystallised boric acid, 2 kilos. of sulphur, and 100–200 kilos. of fuming sulphuric acid (containing 30–40 per cent. of sulphur trioxide) is heated for two to two and a half hours at 120–130°. The mass is diluted with 2000–3000 kilos. of water, and the precipitate filtered off and washed. The dye is sparingly soluble in cold, but readily so in hot water. It dissolves in concentrated sulphuric acid with a yellow, and in sodium hydroxide solution with a pure blue colour. In the above reaction, the isomeric dinitroanthraquinones may be used, but the blue dyes produced do not give such pure blue shades as when 1 : 5-dinitroanthraquinone is employed. The partial reduction products mentioned on p. 249 may also be used (Badische Anilin- & Soda-Fabrik, E.P. 16495^{97}; F.P. 269849; G.P. 109613; U.S.P. 617686).

Indanthrene gold orange G,



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(1) In the first patent concerning this dye (pyranthrone), the following methods of preparation from 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl are given. (1) One part is heated with 15 parts of powdered potassium hydroxide and 5 parts of methyl alcohol for one to two hours under reflux at 165–170° (temperature of oil-bath). The product is dissolved in water and a current of air is passed into the boiling carmoisine-red solution until no increase in the brown colour of the precipitate is observed. The mixture is faintly acidified and the precipitate filtered and washed. (2) One part is added to a mixture of 3 parts of potassium hydroxide and 2·6 parts of ethyl alcohol; the whole is stirred and heated slowly at 140–145°, at which temperature it is kept for two to three hours. The product is worked up as above. The same result is obtained by boiling 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl with about thirty times its weight of 50 per cent. aqueous potassium hydroxide or by melting with ten to fifteen times its weight of potassium hydroxide with the addition of 1 part of anhydrous sodium acetate, at 220–250°. (3) The substance is heated with constant stirring and avoidance of local superheating at about 350–380°. The greenish-brown melt gradually becomes reddish-brown. After heating for about half an hour the mass is allowed to cool and then dissolved in ten to fifteen times the weight of the original material of sulphuric acid (66° Bé.). The dye is precipitated with ice and water and washed with water. (4) One part is added to 30 parts of molten zinc chloride at about 280°. Hydrogen chloride is evolved and the blood-red, viscid mass is kept at this temperature for about fifteen minutes. When cold, it is dissolved in warm water containing hydrochloric acid and the precipitate is filtered, and washed with hot water (Badische Anilin- & Soda-Fabrik, E.P. 14578^{05}; F.P. 357239; G.P. 175067, 174494 [application in dyeing]; U.S.P.

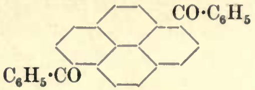
845129, 856811; a similar account of the preparation is given by Scholl, *Ber.*, 1910, **43**, 346; 1911, **44**, 1448).

In a later patent (*idem.*, G.P. 212019), it is stated that a better process and one which proceeds extremely smoothly is to heat a 5–10 per cent. aqueous paste of 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl in a closed vessel for ten to twelve hours at 230–250° and that, instead of water, aqueous ammonia or salt solutions can be used.

The reaction may also be carried out by placing 8 parts of powdered potassium hydroxide (90 per cent.) and 2 parts of 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl in a closed rotating vessel, with the exclusion of air, adding one part of absolute alcohol, and revolving the vessel until a uniform, homogeneous powder has been obtained. This is spread as rapidly as possible in thin layers on an endless travelling band; on exposure to the air the mass becomes warm and the reaction proceeds almost immediately. The use of the travelling bands permits of the recovery of alcohol. If the layer is too thick, the cake must be turned over so as to allow air to penetrate to all parts. The reddish-brown mass is dissolved in hot water and worked up as described above (*idem*, E.P. 20664^{13}; G.P. 287270).

(2) The dye can also be produced from 1 : 1′-dianthraquinonyl-2 : 2′-dialdehyde (obtained by condensing 2 mols. of 1-halogen-anthraquinone-2-aldehyde by means of copper) as follows: (1) A mixture of 100 parts of 1 : 1′-dianthraquinonyl-2 : 2′-dialdehyde in the form of a 10 per cent. paste, 2000–4000 parts of water, 50 parts of solid sodium hyposulphite (hydrosulphite), and 100 parts of sodium hydroxide solution is warmed for a half to one hour at 50–80° and the dye is precipitated from the carmoisine-red solution by means of a current of air. (2) Ten parts of powdered 1 : 1′-dianthraquinonyl-2 : 2′-dialdehyde are dissolved in 100 parts of sulphuric acid (66° Bé.) and to the solution are added gradually 15 parts of water until a light precipitate begins to form. At this point 5 parts of zinc dust are stirred in and the mixture is stirred for one to two hours at the temperature of the water-bath and the dye is isolated by diluting with water, boiling, filtering, and washing. The dye may also be produced on the fibre by mixing the dialdehyde with an alkaline reducing agent and dyeing cotton from this bath, the colour being developed on oxidising with air, or by printing it, along with the usual thickening materials, and developing in the usual way (Badische Anilin- & Soda-Fabrik, E.P. 24486^{10}; F.P. 357239, addition of April 10, 1911; G.P. 238980, 241472; U.S.P. 1004433).

(3) One part of dibenzoylpyrene,



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is intimately mixed with 8 parts of aluminium chloride, the mixture placed in a hot bath heated at 155–160° and kept for one hour at this temperature. The violet product is decomposed by water and washed on the filter with hot dilute hydrochloric acid, alcohol, and ether. The residue can be purified through its leuco-compound. It crystallises from nitrobenzene in orange-yellow needles. The dibenzoylpyrene can be obtained by the action of benzoyl chloride or pyrene in the presence of carbon disulphide and aluminium chloride. The mixture can be separated, by extraction with methyl alcohol and crystallisation of the residue with glacial acetic acid, into tribenzoylpyrene (m. p. 235–237°) and dibenzoylpyrene (m. p. 155–157°), of which the former is the more sparingly soluble in glacial acetic acid (Scholl, E.P. 16271^{10}; F.P. 418435; G.P. 239671; *Annalen*, 1912, **394**, 111).

Indanthrene gold orange R.

This appears to be a trichloro-derivative of pyranthrone (Indanthrene gold orange G), which is prepared as follows:

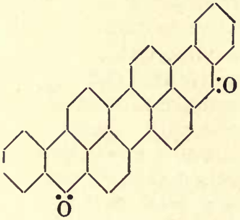
A mixture of 10 parts of pyranthrone, 100–200 parts of nitrobenzene, 20 parts of sulphuryl chloride, and 0·1 part of iodine is heated for two to four hours at 130° under reflux or at 100° in a closed vessel. The dye obtained in this way, on analysis, gives figures corresponding with those required for a trichloro-derivative. Alternatively, it is prepared by introducing chlorine into a mixture of 10 parts of pyranthrone, 100 parts of sulphuric acid (66° Bé.), and 0·3 part of iodine at 100–130° until a sample, worked up and dyed on cotton, shows no increase in the redness of the shade (Badische Anilin- & Soda-Fabrik, E.P. 12568^{09}; F.P. 3rd addition of Nov. 18, 1909, to 357239; G.P. 218162; U.S.P. 955105, 1003268).

Indanthrene scarlet G (Dibromopyranthrone).

A mixture of 10 parts of pyranthrone, 100–200 parts of nitrobenzene, and 24 parts of bromine is boiled under reflux for one to two hours. The reaction proceeds at a lower temperature, but in that case a longer time is required. After cooling, the dye is filtered off and freed from adhering nitrobenzene. It may be obtained as a paste by dissolving it in concentrated sulphuric acid and precipitating it in a finely divided condition with water (Badische Anilin- & Soda-Fabrik, E.P. 12568^{09}; F.P. 3rd addition of Nov. 18, 1909, to 357239; G.P. 218162; U.S.P. 955105, 1003268).

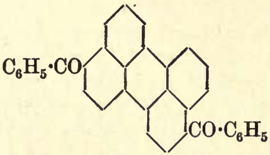
Scholl (*Monatsh.*, 1918, **39**, 231) states that the dye when produced at 100° is the dibromo-derivative, $C_{30}H_{12}O_2Br_2$.

Indanthrene dark blue BO (Violanthrone).



Ten parts of benzanthrone are added to 50–60 parts of molten potassium hydroxide at about 180° and the temperature is raised to 230–240° and maintained at this point until no further increase in the formation of the dye is observed. The product is then dissolved in much water, boiled, filtered boiling, and the violet paste washed with hot water. The dye is best used in paste form (Badische Anilin- & Soda-Fabrik, E.P. 16538^{04}; F.P. 349531; G.P. 185221; U.S.P. 818992).

The dye can also be obtained by heating a mixture of 1 part of dibenzoyl-1 : 1′-dinaphthyl,



(prepared from 1 : 1′-dinaphthyl and benzoyl chloride), and 8 parts of aluminium chloride for eight to nine hours at 95–100°. The black mass is decomposed with water and the residue washed with dilute hydrochloric acid, alcohol, and ether (Scholl, E.P. 16271^{10}; F.P. 418435; G.P. 239671; *Annalen*, 1912, **394**, 111).

Indanthrene violet RT.

This is a chloro-derivative of Indanthrene dark blue BO (Formánek, *Chem. Zeit.*, 1917, **41**, 713), and is prepared according to one or other of the two following examples.

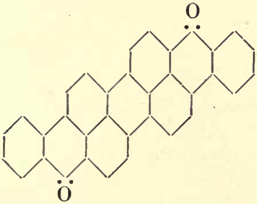
(1) A suspension of 1 part of the above dye in 10 parts of nitrobenzene is treated at the ordinary temperature with one part of sulphuryl chloride. The mixture is heated at 60–70° until the evolution of hydrogen chloride has ceased. On diluting with alcohol, the chloro-derivative is precipitated and is filtered off, washed with alcohol, and dried. It gives a bluish-violet vat from which cotton is dyed in bright, reddish-violet shades.

(2) The same suspension as above is treated at 60–70° with a stream of dry chlorine until a sample precipitated with alcohol and treated with alkaline hyposulphite gives a greenish-blue vat. The dye is isolated as in the first example. The greenish-blue vat produces a very bluish-violet blue on cotton (Badische Anilin- & Soda-Fabrik, E.P. 22519^{05}; F.P. 7th addition of Nov. 9, 1905, to 349531; G.P. 177574).

Indanthrene green B (Viridanthrene B).

The constitution of this dye is not known, but it appears to be an amino-derivative of Indanthrene dark blue BO. The second example given in the patent describes the production of a nitro-derivative, and the third of the product of reduction of this, which gives the same shade. From the fact that the dyeing on cotton can, when treated with sodium nitrite and dilute sulphuric acid, be developed with amines and phenols, the presence of an amino-group is indicated (Badische Anilin- & Soda-Fabrik, G.P. 226215). A suspension of 10 parts of Indanthrene dark blue BO in 100 parts of glacial acetic acid is treated at the ordinary temperature with a mixture of 30 parts of nitric acid (47° Bé.) and 60 parts of glacial acetic acid, with constant stirring. The mixture is then slowly warmed and stirred for about twelve hours at about 60°. After cooling, the nitro-derivative is filtered off, washed with glacial acetic acid and then with water, and dried. It can be crystallised from nitrobenzene. Ten parts of this dye are suspended in 600 parts of a 10 per cent. solution of sodium sulphide and warmed for about three hours on the water-bath. The hot mass is then filtered and the dye is freed from sodium sulphide by washing with hot water (*idem*, E.P. 1818^{05}; F.P. 4th addition of June 14, 1905, to 349531; G.P. 185222; U.S.P. 796393, 876679).

Indanthrene violet R extra (*iso*Violanthrone; Caledon brilliant purple R),



This dye is obtained by alkaline fusion of chlorobenzanthrone which is prepared as follows: (1) Twenty parts of benzanthrone are finely suspended in 1000 parts of water and a slow stream of chlorine is passed in for about four hours at the temperature of the water-bath until the green colour of the paste has changed to yellow and does not change further. After diluting with water, the precipitate is filtered, washed, and dried. (2) Ten parts of finely sieved benzanthrone are suspended in 2000 parts of acetic acid (50 per cent.), treated with 6 parts of potassium chlorate, and warmed on the water-bath at 90–95°. Twelve parts of pure, concentrated hydrochloric acid are now added slowly within one hour, and when the acid has been added the mixture is warmed for an hour, when the green paste changes to yellowish-green. When the reaction is finished, the mixture is diluted with water and the precipitate is filtered off and washed. The chlorobenzanthrone is a yellowish-brown powder which dissolves in most organic solvents with a yellowish-brown colour. Its solution in concentrated sulphuric acid is bluish-red with yellowish-brown fluorescence. By extraction with alcohol and subsequent crystallisation from glacial acetic acid, golden-yellow needles melting at 176° are obtained. For the preparation of the dye, 20 parts of potassium hydroxide are heated with 20–25 parts of absolute alcohol until a homogeneous product is obtained and the temperature has reached 140°. To this, 5 parts of chlorobenzanthrone are added and the mixture is heated for about half an hour at 150°. The chlorobenzanthrone dissolves with a blue colour which gradually becomes reddish-violet. When the reaction is at an end the mixture is dissolved in hot water, in which the dye, or its leuco-compound, is soluble. By boiling the solution for a long time or by passing in a current of air, the dye is precipitated; it is then filtered off and washed with hot water. It gives a blue vat from which cotton is dyed in blue shades which, on exposure to the air, become reddish-violet.

An alternative process consists in mixing 5 parts of absolute alcohol with 100 parts of anhydrous xylene, adding gradually 2 parts of metallic sodium, and heating the mixture in an oil-bath under a reflux condenser, the top of which is closed by a soda-lime tube, at 110–120°. The sodium dissolves slowly and the sodium ethoxide is suspended in the xylene as an extremely finely divided gelatinous mass. Ten parts of chlorobenzanthrone are now added and the mixture is heated to boiling in the oil-bath at about 140–150° until the substance has been converted into the dye. After cooling, this is filtered off, and washed successively with xylene, alcohol, and hot water (Badische Anilin- & Soda-Fabrik, E.P. 20837^{06}; F.P. 9th addition of Oct. 1, 1906, to 349531; G.P. 193959, 194252; U.S.P. 906367).

Indanthrene violet 2 R extra (Caledon brilliant purple RR).

This is a dichloro-derivative of *iso*violanthrone (Indanthrene violet R extra, p. 259).

(1) A suspension of 10 parts of *iso*violanthrone in 100 parts of nitrobenzene is treated at the ordinary temperature with 15–20 parts of sulphuryl chloride. The mixture is warmed slowly at 50–60° and kept at this temperature until the evolution of hydrogen chloride has ceased. The product is then filtered off, washed first with nitrobenzene, then with alcohol, and dried. It gives a blue vat from which cotton is dyed in blue shades changing to bright reddish-violet on washing and drying.

(2) A current of chlorine is passed through a suspension of 10 parts of *iso*violanthrone in 250 parts of nitrobenzene at 50–60° until the chlorination is complete. After cooling, the product is filtered off and worked up as described above (Badische Anilin- & Soda-Fabrik, E.P. 7931^{09}; F.P. 12th addition of April 30, 1909, to 349531; G.P. 217570; U.S.P. 1003268).

Indanthrene violet B extra.

This is a dibromo-derivative of *iso*violanthrone.

(1) A mixture of 6 parts of finely divided *iso*violanthrone, 500 parts of nitrobenzene, and 20 parts of bromine is gently boiled for several hours. After cooling, the dye is filtered off, washed with nitrobenzene and alcohol, and dried. It gives a blue vat from which cotton is dyed in blue shades changing to bluish-violet on washing and drying.

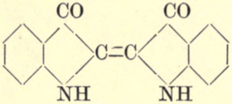
(2) A mixture of 5 parts of *iso*violanthrene and 5 parts of bromine is heated under pressure for ten hours at 150°. The product is mixed with water, filtered, washed, and dried (Badische Anilin- & Soda-Fabrik, E.P. 7931^{09}; F.P. 12th addition of April 30, 1909, to 349531; G.P. 217570; U.S.P. 1003268).

CHAPTER XVII

INDIGOID COLOURS

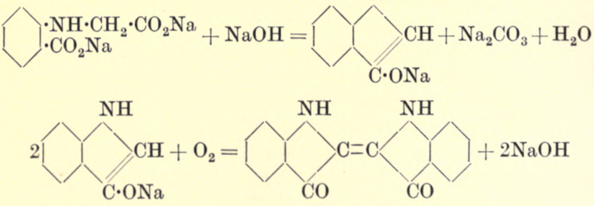
INDIGO—THIOINDIGO

Indigo,

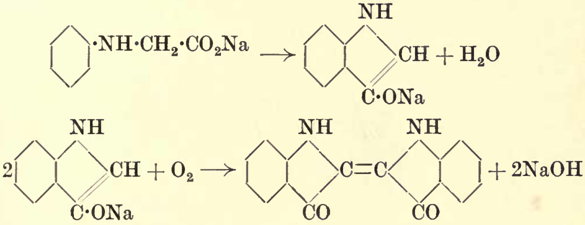


The manufacture of indigo by fusing phenylglycin-*o*-carboxylic acid with sodium hydroxide which has been perfected during the present century by the Badische Anilin- & Soda-Fabrik has been described by Levinstein (*J. Soc. Dyers*, 1901, **17**, No. 6), by Möhlau and Bucherer (*Farbenchemisches Praktikum*, 1908, p. 288) and Michel (*Chem. Zeit.*, 1911, **35**, 755). The phenylglycine-*o*-carboxylic acid is mixed with its own weight of sodium hydroxide and an equal amount of paraffin and the whole is heated at 260–270° in a pan fitted with a scraper which is kept in motion throughout the process. The fused mass, which acquires a strong yellow colour, is cooled, boiled out with water in the absence of air, filtered, and the indigo precipitated from the filtrate by treatment with a stream of air.

Equations :

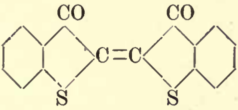


The method developed by the firm Meister, Lucius, & Brüning (D.P. 190394) consists in an application of the original Heumann synthesis, the important feature being the use of sodamide which enables the fusion of phenylglycine to be conducted at a lower temperature. A mixture of sodium hydroxide (40 parts), potassium hydroxide (60 parts), and metallic sodium (11 parts) is melted at the lowest possible temperature and exposed to a current of dry ammonia gas until no further absorption takes place. The stream is then considerably reduced and the potassium salt of phenylglycine (42 parts) added. The temperature is then raised to 200° and maintained at this point until no further evolution of ammonia occurs, the stirrer being kept in motion throughout the process. The lixiviation and precipitation of indigo by oxidation are carried out as in the previous case. Equations :



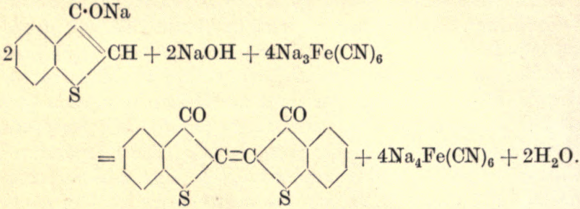
A process which appears likely to prove a competitor to the older method consists in fusing ω-hydroxyethylaniline (137 parts) with potassium hydroxide (500 parts) for one hour at 280–290°. The indigo is isolated by lixiviation and atmospheric oxidation as before (E.P. 6225^{01}; D.P. 171172; A.P. 772775).

Thioindigo,



The preparation of thioindigo by oxidation of 3-hydroxy-(1)-thionaphthen has been described by Friedländer (*Ber.*, 1906, **39**, 1062) and by Möhlau and Bucherer (*Farbenchemisches Praktikum*, 1908, 295). The hydroxythionaphthen (15 parts) is dissolved in 5 per cent. aqueous solution (160 parts) of sodium hydroxide, and a saturated solution of sodium ferricyanide run in until the precipitation of dye is complete. It is then filtered off, washed, and dried.

Equations :



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