The Chemical Technology of Dyeing and Printing

The Second German Edition bears the title:

Neueste Fortschritte und Verfahren
in der chemischen Technologie
der Textilfasern

Erster Teil:

Die neuesten Fortschritte in der Anwendung
der Farbstoffe

Erster Band

The CHEMICAL TECHNOLOGY *of* DYEING and PRINTING

Vat, Sulfur, Indigosol, Azo and Chrome Dyestuffs and Their Auxiliaries

by

DR. LOUIS DISERENS
Technical Director of Alsatian Print Works
Scheurer-Lauth & Co., Thann

Translated and Revised from Second German Edition

by

PAUL WENGRAF
and
HERMAN P. BAUMANN

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Abbreviations

PATENTS

Aus.P.	Austrian Patent
B.P.	British Patent
Can.P.	Canadian Patent
F.P.	French Patent
G.P.	German Patent
Holl.P.	Dutch Patent
Russ.P.	Russian Patent
S.P.	Swiss Patent
U.S.P.	United States Patent

TECHNICAL JOURNALS

Am. Dyes. Rep.	*American Dyestuff Reporter*, New York
Ann.	*Annales de Chimie*, Paris
Annalen	*Annalen der Chemie*
Ber.	*Berichte der Deutschen Chemischen Gesellschaft*
Biochem. Z.	*Biochemische Zeitschrift*
Bull. Fed.	*Bulletin de la Fédération Internationale des Associations des Chimistes du Textile et de la Couleur*
Bull. Mulh.	*Bulletin de la Société Industrielle de Mulhouse*
Bull. Rouen	*Bulletin de la Société Industrielle de Rouen*
Can. Text. J.	*Canadian Textile Journal*
Chem. Abstr.	*Chemical Abstracts*, New York
Chem. Umschau	*Chemische Umschau auf dem Gebiete der Fette, Öle, Wachse und Harze*
Chem. Ztg.	*Chemiker-Zeitung*, Cöthen
Chem. Ztg. Rep.	*Chemiker-Zeitung Repertorium*
Chem. Zent.	*Chemisches Zentralblatt*
Chim. Ind.	*Chimie et Industrie*, Paris
Comptes rendus	*Comptes rendus de l'Académie des Sciences*, Paris
D.F.Z.	*Deutsche Färber-Zeitung*, Ligwitz
Dyer	*The Dyer, Textile Printer, Bleacher and Finisher*, London
Fischer's Ber.	*Jahresberichte über Leistungen der Chem. Tech.*, Leipzig
Frb. Ztg.	*Färber-Zeitung*, of Dr. Lehne
Frdl.	*P. Friedländer, Fortschritte der Teerfarbenfabrikation*, Berlin
Helv. Chim. Acta	*Helvetica Chimica Acta*, Basle
Ind. & Eng. Chem.	*Industrial and Engineering Chemistry*, New York
J. Chem. Soc.	*Journal of the Chemical Society*, London
J. Am. Chem. Soc.	*Journal of the American Chemical Society*
J. Soc. Dy. & Col.	*Journal of the Soc. of Dyers and Colourists*, Bradford

Koll.	*Kolloidzeitschrift*, Leipzig
J. Tex. Inst.	*Journal of the Textile Institute*, Manchester
Mell.	*Melliand's Textilberichte*, Heidelberg
Mon. f.S.K.Z.	*Monatshefte für Seide, Kunstseide und Zellwolle*, Krefeld
Öst. W.u.L. Ind.	*Österreichische Wollen-und Leinen-Industrie*, Reichenberg
Ray.Tex.Mon.	*Rayon Textile Monthly*, New York
Rev. Chim. Ind.	*Revue de Chimie Industrielle*, Paris
Rev. Gen. Mat. Col.	*Revue Générale des Matières Colorantes*, Paris (former periodical of the A.C.I.T., now *Teintex*)
Seifensieder Ztg.	*Seifensieder-Zeitung*, Augsburg
Teintex.	*Revue universelle de Teinture, Impression, Blanchiment, Apprêt*, Paris
Text. Col.	*Textile Colorist*, New York
Text. Mfr.	*Textile Manufacturer*, Manchester
Text. Rec.	*Textile Recorder*, Manchester
Tiba.	*Teinture, Impression, Blanchiment, Apprêt Revue*, Paris
Wengraf's Ber.	*Wengraf's Berichte* (Microfilm at N.Y.C. Public Library)
Z.f.angew.Chem.	*Zeitschrift für angewandte Chemie*
Z. f. ges. Tex. Ind.	*Zeitschrift für die gesamte Textilindustrie*, L.A. Klepzig, Leipzig
Z. f. Frb. Ind.	*Zeitschrift für Farbenindustrie*
Z. f. Phys. Chem.	*Zeitschrift für Physikalische Chemie*
Z. f. Elek. & Phys. Chem.	*Zeitschrift für Elektrische und Physikalische Chemie*

Associations

A.C.I.T.	Association des Chimistes de l'industrielle Textile
I.V.C.C. or Intern. V. Chem. Col.	Internationaler Verein der Chemiker-Coloristen (International Association of Chemists and Colorists)

Manufacturing Firms

A.A.P.	American Aniline Products, N.Y.C.
A.C.N.A.	Aziende Colori Nazionali Affini, Milan
A.G.F.A.	Aktiengesellschaft für Anilin-Fabrikation, Berlin (now I.G.)
L'Air Liquide	Société Anonyme l'Air Liquide, Paris
Arkansas	Arkansas Co, Newark, N. J.
Aussig	Vereinigte Chemikalien und metallurgische Fabriken, Aussig and Karlsbad
Badische A.S.F.	Badische Anilin-und Soda-Fabrik, Ludwigshafen a/Rhein (now I.G.)
Baumheier	Chemische Fabrik R. Baumheier A. G., Oschatz-Zschöllau
Bayer	Farbenfabriken vormals Friedrich Bayer u. Cie., Leverkusen (now I.G.)
Blandola	The Blandola Co., Ltd., Whalley Bridge, Stockport
Böhme F.C.	Böhme Fettchemie, G.m.b.H., Chemnitz

Böhme, (A.Th.)	A. Th. Böhme, Chemische Fabrik, Dresden
Brit. Dyes	British Dyestuffs Corp. Ltd., Huddersfield and Manchester (now I.C.I.)
Brotherton	Brotherton and Co., Ltd., Birkenhead
Calco	Calco Chemical Division, American Cyanamid Co., New York
Carbic	Carbic Color and Chemical Co., New York
Cassella	Leopold Cassella u. Cie., Frankfurt a/Main (now I.G.)
C.C.C.C.	Carbide and Carbon Chemical Corp., New York
Ciba	Gesellschaft für chemische Industrie, Basle
Clayton	Clayton Aniline Co. Ltd., Manchester
Diamalt	Diamalt A.G., Munich
D. & H.	Durand and Huguenin A.G., Basle
Du Pont	E. I. du Pont de Nemours & Co., Wilmington, Del.
F.P.C.T.M.	Fabriques de Produits Chimique de Thann et de Mulhouse, Alsace
Francolor	Francolor, Société Anonyme de Matières Colorantes et de Produits Chimiques, Paris
G.D.C.	General Dyestuff Corp., New York
Geigy	Joh. Rud. Geigy A.G., Chemische Fabrik, Basle
Griesheim-Elektron	Chemische Fabrik Griesheim-Elektron, Frankfurt a/Main (now I.G.)
Heyden	Chemische Fabrik von Heyden A.G., Radebeul, near Dresden
Holliday	Read, Holliday & Sons, Huddersfield (now I.C.I.)
I.C.I.	Imperial Chemical Industries Ltd., London
I.G.	I.G. Farbenindustrie A.G., Frankfurt a/Main
J. Wolf	Jacques Wolf and Co., Passaic, N. J.
Kalle	Kalle u Cie. A.G., Wiesbaden-Biebrich a/Rhein
Kulhmann	Compagnie Nationale de Matières Colorantes et Manufactures de Produits Chimiques du Nord réunies, Paris
Lab. Zündel, Joliet, or L.Z.J.	Laboratoires Zündel, Joliet et Cie., Genevilliers, Paris
L.B.H.	L. B. Holliday & Co. Ltd., Huddersfield
M.L.B.	Farbwerke vorm. Meister, Lucius und Brüning, Höchst a/Main (now I.G.)
N.A.C., or National	National Aniline Division, Allied Chemical and Dye Corp., New York
Onyx	Onyx Oil and Chemical Co., Jersey City, N. J.
Oranienburg	Oranienburger Chemische Fabrik A.G., Charlottenburg
P.C.M.R.	Produits Chimiques de la Mer Rouge, Mulhouse
Pfersee	Chemische Fabrik Pfersee, G.m.b.H., Augsburg
Pharma	Pharma Chemical Co., New York
Pyrgos	Chemische Fabrik Pyrgos, Radebeul, near Dresden
Röhm & Haas	Röhm und Haas A.G., Darmstadt. In U.S.A., Rohm and Haas Co., Philadelphia 5, Pa.
Rohner	Chemische Fabrik Rohner A.G., Pratteln, Switzerland
Royce	Royce Chemical Co., East Rutherford, N. J.

Saint-Clair-du-Rhône	Compagnie Française de Produits Chimiques et Matières Colorantes de Saint-Clair-du-Rhône, Paris
St. Denis	Société Anonyme des Matières Colorantes et Produits Chimiques de Saint-Denis, Paris
Sandoz	Chemische Fabrik Sandoz A.G., Basle
Soc. Dériv. Soufre	Société Industrielle des Dérivés du Soufre, Lomme-les-Lille, Nord, France
S.P.C.M.C.	Société de Produits Chimiques et Matières Colorantes de Mulhouse, Mulhouse, Alsace
Stockhausen	Chemische Fabrik Stockhausen u. Cie., Krefeld
ter Meer	Chemische Fabrik vorm. Weiler-ter-Meer, Urdingen a/Rhein

Translators' Preface

This book, presented here in English translation, was first published in French under the title, "*Progrès réalisés dans l'application des Matières Colorantes*", in Paris in 1937. The French edition was immediately acclaimed not only because a modern textbook in this field was sorely needed, but because of the author's theoretical knowledge and his background of practical experience.

Dr. L. Diserens is known as a skilled chemist-colorist having worked in the well-equipped printing and dyeing plants of pre-war Russia, famous for their high coloristic standards, as well as in one of the leading Alsatian print works which produces tasteful textile fabrics for the world-wide trade. The success of the French edition encouraged the author to produce a German translation, in which one of us took an active part. Despite the unfavorable conditions in war-torn Europe, the German translation which was published by Birkhäuser in Basle, Switzerland, was soon sold out and had to be followed by a second edition in 1946. This second edition contained new and abundant material so that a complete and voluminous textbook resulted. The first part of this book, consisting of the chapters on the application of Vat colors, Sulfur colors, Indigosols, the insoluble Azo dyestuffs and Mordant colors is here offered to the English-speaking public.

We are happy to have had the opportunity of translating this book and we have undertaken this difficult task with pride. Many references which have not been accessible to our European colleagues have been added. Some of the facts, less important partly because of their limited industrial value, have been abridged. The detailed introduction has been changed for technical reasons and some data regarding the new nylon fiber developments have been inserted. We sincerely hope that we have presented a true and comprehensive translation of the author's valuable work and that it will find the appreciative judgment it so well deserves.

New York, New York P. W.
June, 1948 H. P. B.

Introduction

The rapid and unprecedented development of the dyestuff industry which has been manifest since the beginning of this century has had a parallel growth in the dyeing and printing of textiles. Up to the turn of the century the manufacture of dyestuffs was restricted to substantive, acid, basic and mordant colors, and insoluble azo dyestuffs derived from β-naphthol. A sudden advance can be noted in the years since 1901 when René Bohn made the invention of that most remarkable compound, Indanthrone.

Indanthrone, which is commercially Indanthrene Blue, was quickly followed by its fusion product, Flavanthrone. These first fast dyestuffs, developed by Bohn, led further research into the anthraquinone vat colors, and stimulated study of the derivatives of indigo and thioindigo. The success met by these vat dyestuff types promoted activity in all lines of dyes manufactured in England, Germany, France, Switzerland and the United States and resulted in an abundant flow of new coloring matters.*

No doubt this decisive progress could be accomplished only with the assistance of the very important discovery of the water-soluble hydrosulfites and the formaldehyde-sulfoxylates connected with the names of Decamps, Baumann, Thesmar and Frossard. These compounds were as important to the vat dyestuffs as gasoline to the automobile motor, and their invention was in every way as remarkable as it was timely. A further consequence of the research on hydrosulfites was the invention of the Leucotropes by Reinking in 1910, making it possible to discharge indigo and other vat dyestuffs by reducing agents and without risk of tendering the fiber.

In another direction, important research led to the development of the naphthols. Credit belongs to the chemists of the Griesheim-Elektron plant for their valuable series of arylides of oxynaphthoic acid, known as Naphthols AS. This basic invention leading to the production of fast bright yellows, oranges, reds, browns, bordeaux, and black, navy and violet will be discussed in all pertinent details in Chapter IV of this book.

Efforts to combine the Naphthol AS in a print paste with a compound capable of producing the diazo derivative by a subsequent treatment after printing, were sought, so that development might be accomplished in one

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* References: Dr. Karl Holzbach, "75 Jahre Farbstoffsynthese in Ludwigshafen (Rhein)" (Synthesis of Dyestuffs of 75 Years), *Mell.*, **21**, 225 (1940); Dr. Karl Holzbach, "Entwicklung der deutschen chemischen Industrie auf dem Gebiete der Farbstoffsynthese" (Development of the German Chemical Industry in the Field of Dyestuff Synthesis), paper read at the conference of the I.V.C.C. in Stuttgart, Germany on May 28, 1936.

operation. The successful solution of this problem was found in several ways, and resulted in the Rapid Fast colors, the Rapidogens and the Rapidazols of the I.G. and G.D.C., while the Neocotones of Ciba, the Neogenoles of Sandoz and Tinogenales of Geigy represent another and quite original method.

In 1922 new progress was brought to the field of vat dyestuffs by Dr. Marcel Bader, who perfected the stabilization of the reduced soluble vat colors. These soluble leuco-vat dyestuffs, stabilized in the form of their sulfuric acid esters, are known as Indigosols. Success did not follow quite as rapidly as for the previously discussed dyestuff groups, but their worth eventually was established. With the Indigosols it became possible to combine vat dyestuffs with Rapidogens, to employ vat dyestuffs widely for colored resists and discharges and to produce generally textile prints of the highest fastness properties.

The chrome acid dyestuffs were effectually supplemented by the Eriochrome dyes of Geigy in 1904. These dyes are sulfonated or carboxylated azo compounds with no chromium in the molecule. Many of them can be dyed in one bath with bichromates. Later, the metachrome mordant, consisting of sodium chromate and ammonium sulfate, simplified the application of chrome dyestuffs. Another important step was the introduction of chromium into the dyestuff molecule itself. These dyes, developed by Ciba and called Neolans, were followed by similar products, the Palatine Fast colors of the I.G. and G.D.C. and Inochrome colors of Kuhlmann-Francolor. They dye wool from a bath containing sulfuric acid and Glauber's salt, and can be discharged with formaldehyde-sulfoxylate. These complex products have the chromium linked by secondary valence forces. In general, they have excellent fastness properties and many dye in bright shades. Their only drawback is the relatively high amount of acid necessary in dyeing, although new methods have been found which require less mineral acid, and in some cases, as with Palatine Fast Black WAN, organic acids suffice.

While other dyestuff groups remained more or less eclipsed by the development of the vats and Naphthols AS, they were not entirely neglected. Substantive colors of exceptional light-fastness were brought out, as the Chlorantine Fast colors of Ciba, Solar colors of Sandoz, Benzo Fast dyes of I.G. (Fastusol dyes of G.D.C.) Solantine dyes of National, etc. It was also found that introduction of the copper atom in certain substantive colors greatly increased their light-fastness.

The basic dyestuffs were more or less abandoned in the last twenty years, although some attempts were made to improve the mordanting process by employing Katanol (sulfurized phenol) instead of tannic acid.

The art of printing pigments has undergone remarkable changes, especially in the last few years. In its original form, pigment printing involved pasting mineral colors or insoluble organic dyestuffs with hardening oils, or printing from a water medium with thermosetting agents such as albumen, casein, etc. Later, lacquers of nitrocellulose or cellulose acetate were used with attendant disadvantages of poor fastness and hazardous plant conditions. Next came resin binders in solvent media.* A new turn was given this style by application of recent experiences in emulsion technique.

There are three systems, the water-in-oil emulsion, the oil-in-water emulsion and the emulsion binder with gum thickening. The methods of Aridye (Interchemical Corp.) and Sherdye (Sherwin-Williams) are water-in-oil emulsion systems containing pigments. The emulsion breaks in drying, and the pigmented layer covers the surface of the single threads without bridging the fabric's interstices, as in the older printing processes. The results are soft, supple prints of extremely high fastness to light and soaping.

The general trend toward improvement in the fastness of dyed and printed fabrics is reflected in a desire of consumer and retailing interests for informative labeling** of materials and garments. In the United States, government action has resulted in acts which require labeling of garments for fiber content, but fastness standards have not been set. In Germany, the unified dyestuff trust advertised under the "I" label any material of fastness corresponding to the best Indanthrene dyestuffs.

The tremendous progress in the manufacture of dyestuffs also gave rise to a meteoric upsurge in the production of textile auxiliary chemicals. Before World War I (1914 to 1918) very few auxiliaries were known. The ratio of these products to dyestuffs produced after the war was actually reversed. The auxiliary agents far surpassed the number of dyestuffs invented during the same time.

A textile auxiliary*** is any substance which has the property of improving, in boil-off, bleaching, dyeing, printing or finishing, the hand, quality or appearance of the goods, or of increasing the efficiency of the process.

The first textile auxiliaries were fatty derivatives, as soap and sulfonated

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* Mattiello, "Protective and Decorative Coatings", John Wiley & Sons, Inc., 1941.

** Henry F. Herrmann, "The Informative Labeling of Textiles", *Am. Dyes. Rep.*, **1946**, 616.

*** References: Chwala, "Textilhilfsmittel, ihre Chemie, Kolloidchemie und Anwendung" (Textile Auxiliaries, Their Chemistry, Colloid Chemistry and Application), Vienna, 1939; Schoenfeld, "Chemie und Technologie der Fette" (Chemistry and Technology of Fatty Compounds), Vol. **2**, Chap. 4, p. 315 ff.: "Die sulfonierten Oele" (The Sulfonated Oils), Vienna, 1937; *Ibid.*, Vol. **4**, Part I: Theory, Chap. 1: "Anion Activity and Cation Activity of Soaps and Soap-like Products", Vienna, 1939; "Report on 'Inverted' Soaps", *Koll.*, **101**, 213 (Nov. 1942); "Alkylierte organische Sulfosäuren" (Alkylated Organic Sulfonic Acids), *Chem. Ztg.*, **64**, issue 67/68, 325 (1940); "100 Years in the Field of Wetting Agents Chemistry", **59**, issue 7, 73 (Jan., 1935); Young and Coons, "Surface-Active Agents", Chem. Publishing Co., 1945.

castor oil. But the restricted use of fats during World War I stimulated research for a fat-free wetting agent. Incidentally, the term "wetting agent" is often incorrectly used for any substance of the general category of auxiliary agents, because the first known auxiliaries were actually wetting agents. The expression, however, applies only to a substance capable of lowering interfacial tensions existing in aqueous solutions.

The first auxiliary found was an alkylated naphthalene sulfonate (Nekal), a wetting agent (*G.P. 336,558*—1916). Since this time the number of auxiliaries for wetting, dispersing, emulsifying, scouring and other purposes has grown immensely, so that confusion often arises regarding the specific technical use of many of these products. The Igepons, Peregals, Emulphors and Igepals of the I.G. and G.D.C., the Ultravons and Albatexes of Ciba, Lissapols of the I.C.I., the Duponols of Du Pont, and so forth, might be enumerated at random. The details regarding these products will be presented by the author in a separate work.

The textile auxiliaries which form salt-like water-soluble compounds can be divided into two groups—the anion-active and the cation-active compounds—according to the nature of the component which confers the wetting or emulsifying effect to the product. So, for example, the fatty alcohol sulfates of the Gardinol type, the fatty acid condensates of the Igepon type, are anion-active, having the fatty chain in the anion. On the other hand, cation-active compounds, for example, the Sapamines are condensates of long-chain fatty acids with asymmetrical diamines. While these auxiliaries are of comparatively recent origin, the first high-molecular amine salts were described by Krafft in *Ber.*, **1886,** 1330 (cetylamine hydrochloride).

The Gardinol and Sapamine patents initiated a period of intensive research in the field of synthetic auxiliaries in general. The anion-active compounds were developed on a large scale. The sulfuric acid esters of fatty alcohols, known as Duponols, the amides or fatty acid esters containing sulfo groups in the amino or alkyl radicals, such as the Igepons, and the sulfonates of substituted benzimidazoles, known as the Ultravons are a few of the principal types. It is interesting to note that the compounds themselves have been known for more than 100 years but their application was not discovered for some time. The acid sulfuric acid ester of cetyl alcohol was described in "Annales de la Pharmacie" in 1836 (**19,** 293) by Dumas and Peligot, while the cetyl sulfuric acid ester is mentioned by von Cochenhausen in 1837 (*Dingler's Polytech. Journal*, **303,** 284). The technical application of these fatty alcohol derivatives has been made possible by the latest progress in high-pressure hydrogenation which solved the necessary problem of converting high-molecular fatty acids into the corresponding alcohols.

The development of fine pastes and powders of vat dyestuffs revealed compounds which had not previously been considered as useful for textile auxiliary purposes. Urea was recommended for fixation of chrome mordant prints in short ageing, and for fixation of direct and acid dyestuffs in printing on viscose rayon. The use of anthraquinone in discharge printing of naphthol dyeings might be mentioned, as well as the aftertreatment of substantive dyeings with quaternary bases of the Sapamine type to improve wash-fastness. Finally the newly synthesized solvents derived from glycol, as Cellosolve, Carbitol, Glyecine, etc., must also be classified as textile auxiliaries.

The field of thickening agents has been enlarged by new synthetic products which have found use for specific purposes, such as sodium carboxymethyl cellulose (Carboxy Methocel) hydroxyethyl cellulose (Cellosize WS) or polymerizates of vinyl or acryl derivatives (Plextoles). Modified, cold-water-soluble starch derivatives have been prepared as thickening agents.

The discovery of the regenerated celluloses and the newer synthetic fibers greatly influenced the manufacture of dyestuffs and the technique of their application. It is well known that the first rayons were nitrocellulose (Chardonnet), cuprammonium rayon or Bemberg (Schweizer, Fremery, Urban, Bronnert, Despaissis), and then viscose, (Cross and Bevan, 1892) still leading in the field of regenerated cellulose. The next milestone was the invention of cellulose acetate fibers (Cross and Bevan, 1894).

In historical order came the casein fibers, followed by immunized cotton, ether cellulose filaments, animalized cellulose fibers like Vistra PX (I.G.), viscose rayon filaments containing resins (Artilana) and finally the completely synthetic fibers like nylon, Perlon and Vinyon.

The manufacture of rayon or artificial silk does not date back more than 50 years, and it is the more astonishing that such a short time has been sufficient to give this material the importance that it has. While viscose and Bemberg, being regenerated cellulose, dye very much like cotton, acetate cellulose (Celanese, Acele, Seraceta) is conspicuous by its indifference to water and swelling agents, causing a problem in dyestuff affinity. After thorough research connected with the names of Clavel, De Green, Baddiley and others, special dyestuff groups known as Ionamines or Duranoles, and the dispersible types, such as Cibacet dyestuffs (Ciba), Cellitone dyestuffs (I.G.) (G.D.C.), etc. appeared on the market. In addition to these typical water-dispersible but -insoluble dyestuffs a new class of soluble colors was introduced, called Astrazone dyes by I.G. and Solacet dyes by I.C.I.

Spun rayon (German, "*Zellwolle*"; French, "*Fibranne*") is produced by cutting the filaments into short lengths and spinning these short fibers together, in a method analogous to the spinning of chappe silk. Spun rayon may be made from viscose, cuprammonium rayon or acetate cellulose, and is found blended with natural fibers and casein fibers in all proportions.

Imitation of the wool fiber has long been attempted. Todtenhaupt was first (1904) to develop a fiber derived from natural proteins and particularly from milk casein (*G.P. 170,051, 178,985, 182,574, 183,317, 203,820; U.S.P. 836,788; F.P. 356,404; Aus.P. 28,290*). The Italian government, needing wool fibers during the Ethiopian campaign, promoted research in this field. Ferretti succeeded in manufacturing a fiber which he called Lanital* (*B.P. 483,730, 483,807–483,810*). Lanital differs from wool in that its sulfur content is lower. It is sensitive to temperatures over 85°C. In recent times other protein materials have been proposed for fiber manufacture, for instance, soy bean protein, zein, and peanut globulin (Speakman).

The problem of producing a fiber containing nitrogen was eventually solved in a completely satisfactory way on a purely synthetic basis. The development of this fiber, known the world over as nylon, was consummated in the United States by the research chemist Wallace H. Carothers** of the E.I. du Pont de Nemours laboratories. Nylon won an outstanding place in a short time, not only in the textile field, but in the related industries of rope, cord, bristles, etc. The first patents, *U.S.P. 2,071,250, -1, -2, -3*, granted to Carothers in February, 1937, describe the history of former attempts to introduce amino groups into long chains of linear superpolymers. It was accomplished by reacting bifunctional acids with bifunctional amides of the same number of carbon atoms in the chain, and polymerizing these reaction products.

Although other combinations are possible, the typical nylon fiber is composed of hexamethylamine diamine (a diamine of 6 C atoms) and adipic acid (a dicarboxylic acid of 6 C atoms), as follows:

$$NH_2 - (CH_2)_6 - NH_2 + COOH - (CH_2)_4 - COOH \rightarrow \\ [\ldots NH{-}(CH_2)_6{-}NH{-}CO{-}(CH_2)_4{-}CO{-}NH{-}(CH_2)_6{-}NH \ldots]_x$$

It was observed that these condensates can be polymerized to molecular weights of 10,000 and over. The polymerization is carried out in two steps: The mixture is first heated to 170° to 220°C, followed by recrystallization of the product. The reaction mixture is then placed in a vessel capable of high vacuum, called a molecular still. The mass is placed so close to the condensing surface that molecules emanating from the heated surface reach the condenser without colliding with other molecules. Molecular distillation is not new in itself, but it permits separation from residual bodies of substances previously considered impossible of distilla-

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* Other names are Aralac (U.S.A.), Casein Fiber (England), Cargan (Belgium), Tiolan (Germany), Lactefil (Holland).

** *U.S.P. 2,071,250, -1, -2, -3, 2,130,947-8; B.P. 461,236, -7, 474,999, 487,734; F.P. 828, 848, 833,755, -6, 845,691.*

tion. The escaping molecules are removed by high vacuum, and cannot return to the mixture. The use of the molecular still in esterification and polymerization is a fundamental characteristic of the nylon process. The high orientation of the fibers is achieved by cold drawing the final polymer, this operation being essential for imparting the desired properties of tensile strength and elasticity to the filaments.

Within the scope of the original patent, *U.S.P. 2,071,250*, polyesters, polyamides, polyethers and polyanhydrides are included as capable of forming linear condensation superpolymers.*

Parallel research work has been done by I.G. in Germany, yielding three types of linear polymer fibers, called Perlon L, T, and U. These are apparently fibers of the polyamide and polyurethane type.

A new fiber, similar to nylon in that it is claimed to be a linear superpolymer, though not of the polyamide type, has recently been developed by I.C.I. and the Calico Printers Assoc. It has been given the name Terylene, and is prepared by copolymerizing terephthalic acid and ethylene glycol (*B.P. 578,079*, *579,462*, Whinfield and Dickson).

The dyeing of nylon presents the same essential difficulties encountered with acetate cellulose.** Carothers and Godlove had already suggested the use of the acetate dyestuffs (*U.S.P. 2,220,129*). Certain auxiliary agents such as Lissolamines are claimed to have an exhausting effect on direct dyes, if used in very small amounts (*U.S.P. 2,371,536*). Leucogallocyanines have been recommended recently by Durand and Huguenin (*U.S.P. 2,411,249*).

Another completely synthetic fiber, known as Vinyon, and patented by Carbide and Carbon Chem. Co. is produced by American Viscose Corp. It is a copolymer of vinyl chloride (90%) and vinyl acetate (10%). The equivalent German product is called "P.C. Faser", an abbreviation of "Polyvinyl Chlorid Faser". The properties of these are almost identical. They are exceedingly stable to chemical reagents, being impervious to aqua regia and to 50% caustic potash, and to bacterial destruction. The fibers lend themselves to the manufacture of filter cloth, fishing seines and leader tape. The melting point of these thermoplastic filaments is very

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* Specifically, aminocaprolactame, intramolecularly condensed, *U.S.P. 2,241,322, -3*, Du Pont; substituted diurethanes, as ethyl hexamethylene diurethane, C_2H_5-OOC-NH$(CH_2)_6$NH·COOH, *U.S.P. 2,181,663*, Du Pont; isocyanates such as hexamethylene diisocyanate, OCN-$(CH_2)_6$-NCO, *U.S.P. 2,268,586*, Du Pont.

For a résumé of the nylon patents, see the Nylon Patent Review in *Rayon Textile Monthly*, Jan. to Oct. **1947** by P. Wengraf.

** A. K. Saville, "Some Aspects of Nylon Dyeing", *Am. Dyes. Rep.*, **1946**, 51; P. L. Meunier, "Printing of All-Nylon Fabrics", *Am. Dyes. Rep.*, **1942**, 232; J. Boulton, "Some Experiments on the Dyeing of Nylon Yarn," *J. Soc. Dy. & Col.*, **62**, 65 (1946); R. H. Peters, "Nylon Fiber: A Study of the Mechanism of the Dyeing Process with Acid Dyes," *J. Soc. Dy. & Col.*, **61**, 95 (1945).

low and shrinkage begins at 70°C. Dyeing and printing has been unsuccessful,* except with pigments bound with suitable plastic film.

This short survey of the fibers, while by no means complete nor supplied with the many references which the interesting details of their manufacture and application deserve, has been given to remind the readers of the different kinds of fibers which must be processed wherever dyestuffs are applied.

In the difficult science of textile finishing a gradual change has become evident, from superficial and impermanent finishes to more durable types. Here the different resins play an important part. Originally used for crush resistance and shrinkage control, they now play manifold roles in textile processing. Besides the urea-formaldehyde resins, first to be applied as a unique finishing product, the melamine-formaldehyde resins, the glyptal (glycerine-phthalic acid) resins of the thermosetting type, the polyvinyl and polyacryl resins of the thermoplastic type, and the alkyl and acyl celluloses, have become very popular. They are used for definite and durable effects, as flameproofing agents by themselves or for fixing other active ingredients, and in printing in the form of solutions or emulsions.

Some of the most important innovations of recent years are the delustering, crepe and Gauffrage effects on greige cloth particularly produced in Lyons, France and in Alsace (Scheurer, Lauth and Co.), the dulling and parchmentizing effects according to the methods of Heberlein in Wattwil, crease-proof finishes, first described by Tootal, Broadhurst, Lee and Co., the permanent finishes on the basis of cellulose derivatives, the water-repellent finishes, such as Impregnole, Aquarol, which are semipermanent, and Velan (I.C.I.) and Zelan (Du Pont) which are durable, the Arlin process of Arnold Print Works by treatment with cuprammonium solutions to solubilize the surface of the fibers, the Kopan process using cellulose-zincate solutions for permanent sizing (Edelstein), the Trubenizing process (Liebowitz) for imparting durable stiffness for collars and cuffs, the shrinkproofing methods developed in the laboratories of Cluett, Peabody and Company (Sanforizing for mechanical preshrinking of cottons and Sanforset for chemical control of rayon shrinkage), the Alrose. Definized process for shrinkage control by special caustic treatment, and many others.

It is impossible to give here more than a superficial account of the achievements in manufacturing fibers or in the application of resins. The chemist who supervises the application of dyestuffs in dyeing and printing should acquire as much information in these related arts as possible. Very often special fiber materials or pretreatments of fabrics influence the appli-

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* *F.P. 865,918* (Rhodiaceta) suggests acetate dyestuffs in organic solutions; *F.P. 913,917* of the same company acetate dyestuffs dissolved in tetrahydrofurane.

cation of color, and finishing operations must be understood to determine compatibility of colorings with the finish.

The progress made in the manufacture of dyestuffs, industrial and textile chemicals, fibers and resins has indeed been gigantic, and an outline of the scope of these industries has been attempted in this introduction. But what is the special task of the chemist-colorist, for whom this book is principally intended? A modern opinion is that the expert in a dyeing or printing plant performs his duties by organizing the daily work and adapting the requirements of his customers as well as possible to the productive capacity of the mill. This is, however, merely a preliminary requisite. It degrades the chemist's task to a daily routine, and demands but a mechanical training. The essential function of the chemist in a dyeing and printing plant should rather rest in an energetic and intensive pursuit of progress, as much in the interest of the company for which he works as for the development of knowledge in his special art. He should remember that the outstanding achievements in dyestuff application have been discovered by practical mill chemists. To mention a few, the hydrosulfites, the sulfoxylates, the manganese resists under vat dyeing, the crease-proof and shrink-proof finishes, have been revealed by mill men. While the dyestuff manufacturers may be helpful in solving some pertinent problems, the chemist in the textile plant should be able to develop new and valuable methods by modification and elaboration of his daily formulas.

Even though the chemist-colorist can be imaginative and inventive, his ideas must fail when the simplest laboratory equipment is denied him, so that one of the principal requirements for really productive work is an adequate laboratory stocked with modern apparatuses and chemicals. This is a prime prerequisite for investigation of routine production and for study of new processes and inventions.

It is also to be noted that the chemist in the average dyeing and print plant does not have time to digest all the current literature and references regarding dyestuff application and related subjects. It is the principal aim of this book to facilitate the chemist's task by arranging references in their proper dyestuff groups and by explaining the chemistry of the dyestuffs in relation to their application to textiles.

Contents

Chapter I

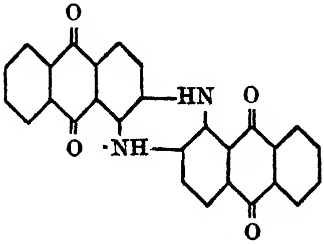
Vat Dyestuffs

The first vat dyestuffs were offered for sale about forty years ago. The keen interest they aroused, and the consistent interest which has been attached to them ever since, has proved them to be a milestone in the history of dyeing and printing.

The early derivatives of indigo, and the first members of the Indanthrene series were prepared in the first years of the twentieth century. The most important representatives of this group, such as thioindigo and its derivatives, the tetrahalogenated indigo products, the condensates of acenaphthenequinones with thioindoxyl, the derivatives of benzanthrone, of the anthraquinonimides and of the acylamino compounds of anthraquinone were developed between the years 1905 to 1912; but this short span of years was sufficient to conquer a considerable portion of the dyestuff market. Even before the first World War (1914 to 1918), nearly every printing or dyeing plant had adopted dyes of this group.

Incessant and methodical research, extraordinary in its outlines as well as in ingenious imagination, has expanded the range of vat dyes by the invention of new indigoid and anthraquinoid dyestuffs. The principal work has been done in the laboratories of the I. G. Farbenindustrie, Ciba in Basle, Imperial Chemical Industries, Kuhlmann in Paris, and E. I. Du Pont de Nemours Co.

The Indanthrenes proper, derived from N-dihydro-1,2-1′,2′-anthraquinonazine

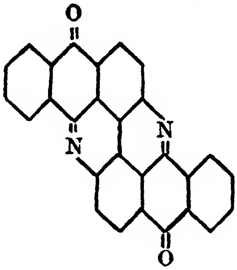


Indanthrene Blue RS
(R. Bohn, 1901)

were followed by the halogen derivatives of this group: Indanthrene Blue GCD or monochloro derivative; Indanthrene Blue BC or 3,3′-dichloro derivative; Indanthrene Blue GC or 3,3′-dibromo derivative.

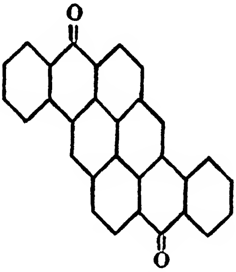
Subsequently the following groups were developed:

Dyestuffs of the Flavanthrene and Pyranthrone type:



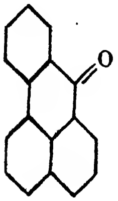
(R. Bohn, 1901)

The Indanthrene Yellows G and R (blue-violet vat) were used for many years in textile printing:

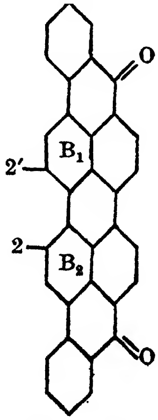


Pyranthrone

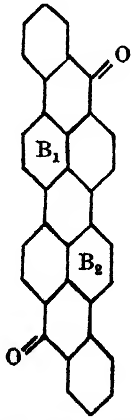
Dibenzanthrones, derived from benzanthrone, a reaction product of glycerin and anthraquinone in the presence of sulfuric acid:



Benzanthrone
(Colorless
substance)



Violanthrene
(*Dibenzanthrone*)

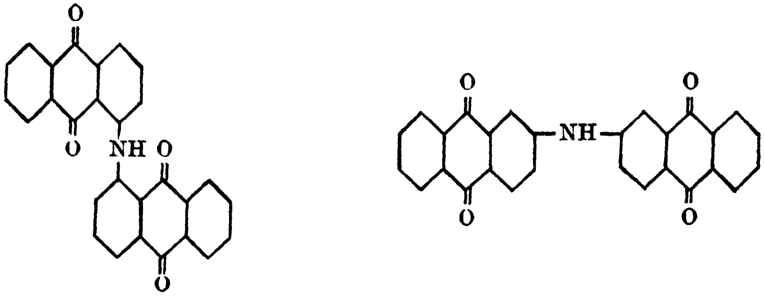


Isodibenzanthrone
(Bally, 1905)

Indanthrene Violet R extra (formerly Violanthrene R extra) is identical with isodibenzanthrone.

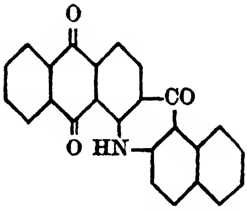
Indanthrene Dark Blue BO (dibenzanthrone) and Indanthrene Brilliant Violet 4R (dichloro-iso-Violanthrene) (Just and Wolff, 1909) belong to the same group.

The anthraquinonimides or -anthrimides, i.e., condensates of aminated and halogenated anthraquinones (Isler, 1905):

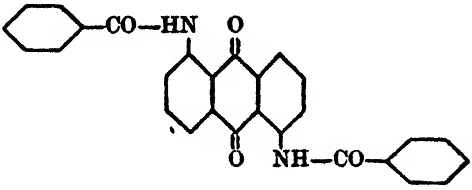


Algol Orange R, or Indanthrene Orange 6RTK belongs to this group, as well as Indanthrene Olive R, Golden Orange 3G, Brown R, Brown BR, and Red Brown 5RF.

Dyestuffs of the acridone group: The first bright red dyestuff of the Indanthrene class, Indanthrene Red RK, belongs here:



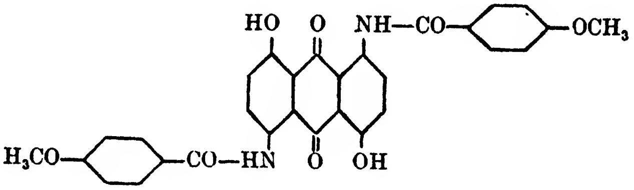
The acylamino compounds of anthraquinone, to which the dyes known as "Algols" (Fr. Bayer & Co.) belong:



(Tomaschewski and Deinet, 1908)

The unsubstituted α-aminoanthraquinones are not dyestuffs by themselves, but linking an acidyl radical to them transforms them into dyestuffs of special importance. While the acetyl radical has almost no effect, the benzoyl radical is very efficient.

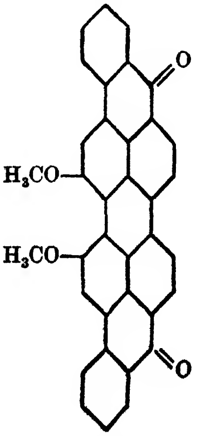
Belonging to this group are Indanthrene Red 5GK (formerly Algol Red 5G), or dibenzoyl-1,4-diaminoanthraquinone; Indanthrene Yellow GK (formerly Algol Yellow R), or dibenzoyl-1,5-diaminoanthraquinone; and Indanthrene Brilliant Violet RK, or di-*p*-methoxybenzoyl-4,8-diamino-1,5-dioxyanthraquinone.



The reaction products of cyanuric chloride with α-aminoanthraquinones, produced by Ciba, and the *thioxanthones*, described by Ullmann [*Ber.*, **43,** 436 (1910)], must be mentioned. They are dyestuffs of various shades and great fastness to light.

Another group are the anthraquinonimidazoles, -oxazoles, and -thiazoles; they are yellow to red dyestuffs of good washing fastness.

The anthrone dyestuffs, particularly those derived from benzanthrone, are interesting from the standpoint of their wide application in textile dyeing and printing. The most important dyestuff of this series is Caledon Jade Green (Scottish Dyes, Ltd.), also known as Indanthrene Brilliant Green B, Solanthrene Brilliant Green NB, etc. It fills a popular need, because up until the time of its discovery the green shades could be produced only by mixtures of divergent components, giving irregular results.



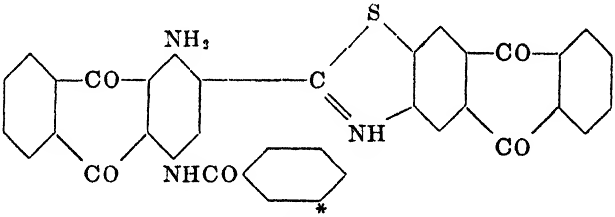
[Davies, Thompson and Thomas of Scottish Dyes Corp. Ltd. (now I.C.I.), 1920]

It is 2,2-dimethoxydibenzanthrone, which can be prepared by alkylating 2,2-dioxydibenzanthrone. Other derivatives of benzanthrone give green, blue, grey and violet dyes, especially the products obtained by reacting hydroxylamine with dibenzanthrone, or with isodibenzanthrone or its derivatives such as anthraquinonyl aminobenzanthrone.

The most recent report of work in this field has been given by Max A. Kunz, in a paper read April 7, 1933 in Mulhouse (Alsace). The paper was repeated at meetings of the International Assn. of Chemists and Colorists in Marienbad (Czechoslovakia) and Zurich (Switzerland), and describes an isomer of pyranthrone (the 5,6,8,7-dibenzoylene pyrene or allo-meso-naphthodianthrone) and the meso-anthradianthrone. Halogen derivatives of these compounds are very brilliant yellow to orange dyes.*

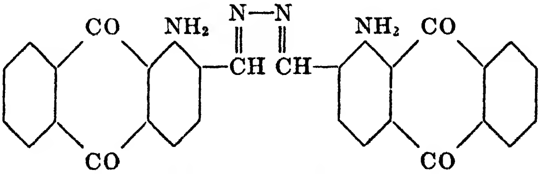
In recent times research work done in the laboratories of the I. G. proved the beneficial effect of introducing the trifluoromethyl (CF_3) group into Indanthrene Blues. The formula below gives the constitution of Indanthrene Blue CLG. By substituting the CF_3 group at the place marked by an asterisk, a considerable increase of the fastness to chlorine could be observed. The new dyestuff was given the brand name Indanthrene Blue CLB.

CLG:



*introduced CF_3 = *CLB*

The same company also offered other dyestuffs containing the CF_3 group: for instance, Indanthrene Brilliant Violet F 3RK and Blue FG for Printing. Other important types have been developed in recent years. From amino-anthraquinone:



Indanthrene Bordeaux B

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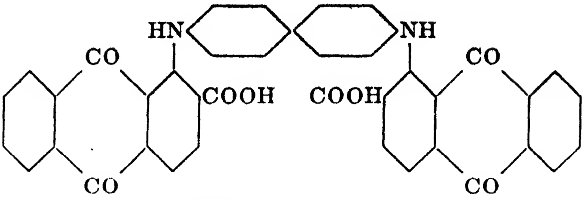
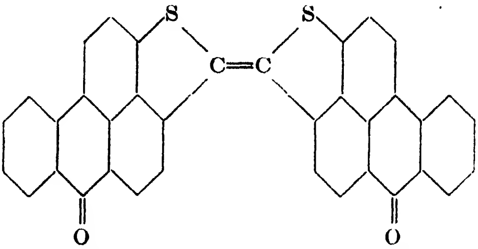
* Indanthrene Golden Orange G is isopyranthrone, obtained by condensation of chloromethylanthraquinone with *o*-dichlorobenzene. Indanthrene Orange RRT is the dibromo derivate obtained by the action of bromine on isopyranthrone in the presence of chlorosulfonic acid and sulfur, while Indanthrene Orange 4R is the tribromo derivative which results by substitution of iodine for sulfur in the bromination.



Indanthrene Red Brown R

From benzanthrone:



Indanthrene Brilliant Green FFB

Indanthrene Brilliant Green 2G is obtained by bromination of the Green FFB.

The general fastness properties, the resistance to chlorine and light, and the completeness of the color range obtainable by the vat dyestuffs brought about a radical change in the usual methods of dyestuff application. They became the basis of modern dyestuff production. The policy of the I. G. Farbenindustrie A.G. of promoting the use of their Indanthrene dyestuffs by insisting that these products be used on material sold with the advertised "I" label, had a great success in Germany. Customers were assured of maximum fastness of dyed or printed goods which carried the "I" tag.

It is difficult at the present time, considering the complicated structures of the vat dyestuffs, to define them unequivocally as "indigoids" or "anthraquinoids". It might be better to confine any subdivision to the fastness properties, and thus to classify them as (1) vat dyestuffs of optimum fastness and (2) of fair general fastness.*

* Robert E. Schmidt: "Sur l'état actuel de la chimie de l'anthraquinone" (The Present Situation in the Chemistry of Anthraquinone), Paper read in the conference of the Soc. Ind. Mulhouse of April 25, 1914; *Bull. Mulh.*, **84,** 423–435.

René Bohn: "Ueber die Fortschritte auf dem Gebiete der Küpenfarbstoffe" (Progress in the Field of Vat Dyestuffs), Paper read in the conference of the Deutsche Chemische Gesellschaft on March 5, 1910; *Ber.*, **43,** 987 (1910); *Rev. Gen. Mat. Col.*, **1910,** 235 and 319; *Chem. Ztg.*, **1908,** 69 and 809; **1910,** 247.

Dr. Engi (Ciba): "Les colorants à cuve Ciba" (The Ciba Vat Dyestuffs), *Rev. Gen. Mat. Col.*, **1909,** 105; *Chem. Ztg.*, **1908,** 1179.

Friedländer: "Die indigoiden Farbstoffe," *Z. f. angew. Chem.*, **1911,** 1107; *Chem. Ztg.*, **1911,** 640; *Rev. Gen. Mat. Col.*, **1911,** 233.

Masera: "Die Küpenfarbstoffe" (The Vat Dyestuffs), Paper read on the 3rd meeting of the Intern. V. Chem. Col. in Torino (Italy) 1911; *Frb. Ztg.*, 1911, 336.

Impressive figures concerning the unparalleled growth of the use of vat dyes had been given by Max A. Kunz.* The value of the dyes, indigo included, exceeded $50,000,000 in 1933. The following chart gives the trade names of the vat dyes produced by different companies.

Company	*First Group*	*Second Group*
B.D.C.	Chloranthrene	
Brotherton	Anthrone	
Calco Chemical Div.	Calcosol, Calcoloid	
Ciba	Cibanone	Ciba
Du Pont	Ponsol	Sulfanthrene
Geigy	Tinonchlorine	Tinon
General Dyestuff Corp.	Indanthrene	Algol, Hydron, Helindone
I.C.I.	Caledon, Alizanthrene	Durindone
I. G. Farbenindustrie	Indanthrene	Algol, Hydron, Helindone
Kalle	Thioindone	Thioindigo
Kuhlmann-Francolor	Solanthrene	Solane
L.B.H.	Paradone	
M.L.B.		Helindone
National Aniline Div.	Carbanthrene	Vat
St. Clair	Luxiane	Heliane
Saint-Denis	Colorants pour cuve	
Sandoz	Sandothrene	Tetra
Scottish Dyes	Caledon	
Y.D.C.	Benzadone	

This chapter is intended to demonstrate the progress made in the application of vat dyestuffs, and to provide references in the technical literature. The subject will be divided into three divisions: (1) Preparation of pastes and fine powders for printing; (2) printing methods, including application, discharge and resist printing; (3) dyeing, and stripping.

PREPARATION OF DYESTUFF PASTES AND FINE POWDERS

Vat printing and vat dyeing must be carried out with care. The color yield in printing depends to a great extent on the degree of dispersion of the vat color. The more homogeneous and the finer the dispersion, the easier the dyestuff can be distributed throughout the printing paste, the better the reducing action in ageing the prints, and the less the yield will depend on variable steam conditions.

Vat dyestuffs are now manufactured in the form of fine pastes for printing, in the form of fine, readily dispersible powders, and in improved paste form, corresponding quite generally to the conditions set forth above. The regular vat colors in powder form are rarely used for printing but can

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* Max A. Kunz: "État actuel de la connaissance des colorants du type Indanthrene" (The Present Knowledge of the Indanthrene-type Vat Colors), Paper read on April 7, 1933 in the Chemistry College in Mulhouse, Alsace and repeated at meetings of the Intern. V. Chem. Col. in Marienbad (Czechoslovakia) on May 27 and on Oct. 1, 1933 in the Swiss section of this association.

be printed in the chemically reduced state. Notable success has been achieved with the improved paste-form colors, the fine dispersion of the dyestuff in these types aiding in transforming the dyes into their leuco compound, and increasing color yield. These paste-form dyes are known as "Suprafix" of I. G. Farbenindustrie, "Optima" of St. Clair-du-Rhone, "Leucosol" of Du Pont, "Superfine" of St. Denis, "Ultrafix" of Sandoz, and "Micropaste" of Ciba. The "Leucosols" of Du Pont are vat dyestuff ground with the triethanolamine salt of disulforicinoleic acid, according to *U.S.P. 2,038,591* (1933).

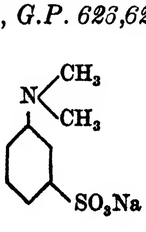
In order to make the pastes resistant to freezing, the dyestuff manufacturers have incorporated various organic solvents with the dye, as glycerin and glycols. Literature concerning the preparation of vat pastes for market is abundant. It embraces the most diversified classes of chemical compounds, making any systematic classification nearly impossible.

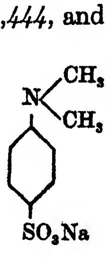
Use of Hydrotropic Substances

The phenomenon of hydrotropy, or the ability of water-soluble substances to solubilize otherwise water-insoluble substances, has been studied by a number of investigators. Carl Neuberg (*Biochem. Z.*, **1916**, 107–176) was the first to observe these properties. Others were Tumba (*Biochem. Z.*, **1924**, 415 ff.), Chelmi (*Chem. Umschau*, **1929**, 198) and Noll (*Seifensieder Ztg.*, **1927**, 769).

Some hydrotropic substances are benzoic acid, salicylic acid, benzene sulfonic acid, naphthenic acid, sylvinic and abietic acids, potassium salts of sulfovinylic, isobutyric, valerianic, caprylic, caproic acids, salts of acids of thiophene and furan series, mandelic acid, cinnamic acid, urea, thiourea, hexamethylenetetramine, etc.

Many other compounds with hydrotropic properties have been used in pasting vat dyestuffs. The salts of dimethylmetanilic and dimethyl sulfanilic acids are used as hydrotropic substances according to *B.P. 343,102* and *343,527*, *G.P. 623,626*, *F.P. 715,444*, and *S.P. 149,067* (I.G.).





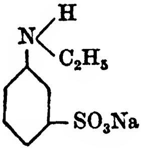
Use of these products gives uniformly dispersed vat dye pastes, of good stability. Shades are full, and fixation quick.

As an example, a paste containing 30% vat dyestuff, 15% sodium salt of dimethylsulfanilic acid, 40% glycerin and 25% water is well mixed.

This patent, and others following, cover the manufacture of the "Suprafix" colors. *G.P. 626,627* uses the sodium salt of *p*-toluene sulfonic acid; *G.P. 626,811* (1929) and *626,812* recommend use of alkali salts of benzene sulfonic acid, benzylsulfanilic acid, benzoic, naphthalene-1-monosulfonic acids, etc. Other compounds in this group are sodium salts of salicylic, *o*-cresotinic, or *p*-chlorosalicylic acids.

Dyestuffs in finely powdered state, useful for printing purposes, can be prepared according to *G.P. 626,813* by mixing 100 parts of a 20% dyestuff with 15 parts of the sodium salt of benzylsulfanilic acid and 20 parts of ferrous sulfate, and spray-drying the mixture in a stream of hot air.

B.P. 446,281, G.P. 622,255 (1934), *F.P. 793,986, S.P. 177,231* (Ciba) state that the addition of monoalkylmetanilic acid salt has a favorable influence in printing vat dyestuffs. The patent names as example the sodium salt of 1-monoethylamino-3-benzene sulfonic acid.



Ciba used urea as dispersing agent for the manufacture of homogeneous fine powders. The method has been patented in *U.S.P. 1,835,926, F.P. 681,566*, and *G.P. 570,583* (1929). 50 Parts of dyestuff, and 160 parts of urea are ground with 30 parts of sulfite cellulose waste liquor and 9 parts of a wetting agent. After thorough mixing, the paste is dried under reduced pressure. The mass thus obtained is ground to fine powder.

Alkali salts of hydroaromatic acids are mentioned as efficient hydrotropic substances in *G.P. 583,315* and *U.S.P. 1,987,583* (I.G.). In pasting up the dyestuff Indocarbon CL, the sodium salt of tetrahydronaphthalene-2-sulfonic acid was used.

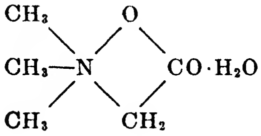
Besides the above, salts formed from organic acids and alkylated aliphatic amines have important hydrotropic properties, and they are used as auxiliary products in preparing vat pastes. They aid in obtaining better fixation in printing, better yield and more uniform results. They form the basis of a series of printing assistants available in the trade.

The hydrotropic effect of organic salt solutions finds many industrial uses (McKee, *Ind. & Eng. Chem.*, Apr., **1946**). Expensive organic solvents can be replaced by these hydrotropic aqueous solutions. As examples, 60 grams of nitrobenzene can be dissolved in 100 grams of aqueous solution of sodium xylene sulfonate at 80°C; ethyl acetoacetate can be mixed in all proportions with a saturated solution of ammonium thiocyanate at 25°C.

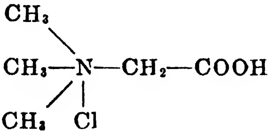
The I. G. Farbenindustrie took out general patents covering the manufacture of vat pastes using "hydrotropic compounds". Because of the great number of derivatives having more or less hydrotropic properties, nearly any chemical substance might allegedly be able to facilitate the distribution of a dyestuff in a paste. A selection of some of the references, classified according to chemical constitution, follows:

Betaine and Its Derivatives. *B.P. 420,095* (I.G.), *B.P. 446,448, U.S.P. 1,989,784, F.P. 795,683, Aus.P. 145,504* and *145,505.* It has been observed that betaine and its derivatives, added to the printing paste, have the effect of improving fixation of the color and of increasing the stability of the paste. Thus the printed fabrics could possibly be stored for some time before ageing without danger of lack of uniformity. This agent can be added to the dyestuff, or to the print paste.

Betaine is trimethyl glycocoll, made by warming trimethylamine with monochloroacetic acid. It forms deliquescent crystals of the formula



The aqueous solution has a neutral reaction and it is stable to acids. Betaine chlorohydrate crystallizes in monoclinic plates; it can be obtained according to Ehrlich's *G.P. 157,173*

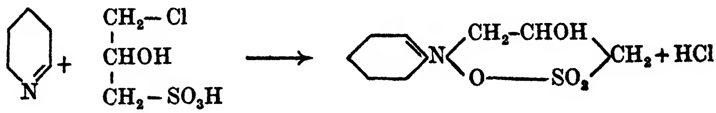


and is sold under the name "Acidol" (I.G.) as a substitute for hydrochloric acid; it is also called "solid hydrochloric acid". The derivatives particularly important for printing purposes are the sulfobetaines (*U.S.P. 2,146,646; B.P. 446,265, 446,269, 446,337;* and *G.P. 651,733);* that is, compounds with group

$$—SO_2—O—N\equiv \text{ instead of } —CO—O—N\equiv$$

the latter being characteristic of the betaines. They are obtained by condensing an aliphatic sulfonic acid which contains a reactive halogen atom with a tertiary amine. The N atom of this amine can belong either to a pyridine or a quinoline nucleus, or to another tertiary amine

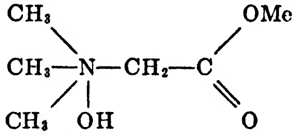
substituted by alkyl, aryl, or aralkyl groups. Examples are trimethylamine, dimethyl laurylamine, dimethyloleylamine. Aliphatic sulfonic acids used in this process are α-chloro-β-oxypropane-γ-sulfonic acid, 2-chlorobutane-4-sulfonic acid, or chloroethane-β-sulfonic acid. The reaction is as follows:



Pyridine *Pyridinium-β-oxypropane sulfobetaine*

F.P. 795,683 (I.G.) covers all aliphatic or aliphatic aromatic sulfonic acids with not more than eight carbon atoms in a side chain, having the general structure, $R—CH=CH—SO_2H$, as well as more complicated compounds formed by reacting sulfonic acids with tertiary bases such as pyridine. A paste is prepared by mixing 20 parts of dry dyestuff with 4 to 5 parts of glycerin and 4 parts of pyridine betaine.

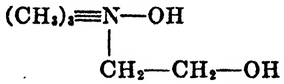
According to *U.S.P. 2,081,017* (I.G.-Nuesslein-Daimler-Platz) alkali salts of betaine according to the formula



Me = Alkali metal

are used instead of pyridine sulfobetaines. This compound is especially recommended for giving deeper prints with Indanthrene Blue RS.

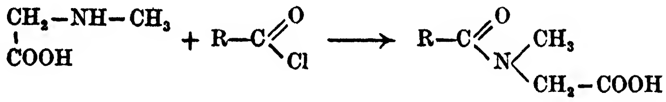
Choline and Its Derivatives. *U.S.P. 2,003,960, G.P. 651,733, B.P. 385,606* (I.C.I.). These patents cover auxiliaries for preparing vat printing pastes which are quaternary ammonium bases substituted by alkyl or aralkyl groups, especially choline and its derivatives. Choline has been detected in the human bile by Strecker (*Annalen*, **1862**, 353). It has the formula

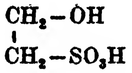


$$\begin{array}{l}(CH_3)_3{\equiv}N—OH\\ \qquad\quad\;\; |\\ \qquad\quad\; CH_2—CH_2—OH\end{array}$$

and can be defined as trimethyl ethoxy ammonium hydroxide. (Older names are Amanitine, Bilineurine, Sinkaline and Fagine.) It forms deliquescent crystals of a strongly basic reaction, readily soluble in water and alcohol, and absorbing considerable quantities of CO_2 from the air. It can be obtained from ox brains, or in a synthetic way by reacting ethylene oxide and trimethylamine in aqueous solution (Wurtz, 1868). It is transformed into betaine by gentle oxidizing. Choline chlorohydrate, obtained by the reaction of trimethylamine on ethylene chlorohydrin, forms deliquescent needles. Choline is a constituent of lecithin, being linked in its structure to phosphoric acid and the glycerides of higher fatty acids (palmitic, stearic, oleic acids).

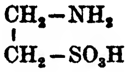
Sarcosine. *B.P. 462,384* (I.G.) recommends the condensation product of oleyl chloride and sarcosine (Medialan of the I.G.) for pasting up vat dyestuffs. Sulfite cellulose waste liquor and sodium pyrophosphate must be added to the mixture. Good stability and fine dispersion are claimed as special advantages of such pastes, and they will not scratch doctor blade or printing roller. Sarcosine is methylated glycocoll (discovered by Liebig in 1874, in treating meat creatin with barium hydroxide). It is made synthetically by heating chloroacetic acid ester with monomethylamine in aqueous solution. Fatty acid amides are produced by reacting these amines with fatty acid chlorides. The fatty acid amines so formed are analogous to amides prepared by reacting fatty acid chlorides with taurine or methyltaurine. They have a structure somewhat similar to that of isethionic acid. The reaction follows. Compare the formulas of isethionic acid, taurine, and methyltaurine.





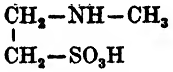
$$\begin{array}{l}\mathrm{CH_2{-}OH}\\ |\\ \mathrm{CH_2{-}SO_3H}\end{array}$$

Isethionic acid



$$\begin{array}{l}\mathrm{CH_2{-}NH_2}\\ |\\ \mathrm{CH_2{-}SO_3H}\end{array}$$

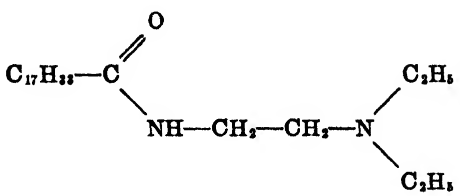
Taurine



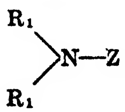
$$\begin{array}{l}\mathrm{CH_2{-}NH{-}CH_3}\\ |\\ \mathrm{CH_2{-}SO_3H}\end{array}$$

Methyltaurine

The Sapamines of Ciba are substituted fatty acid amides, for example, diethylaminoethylene oleylamide.



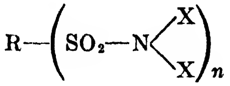
Glucamines. Compounds having the structural formula,



where R_1 is H or an alkyl radical and Z is a monosaccharide radical, belong to the glucamine group, such as methylglucamine, butylglucamine. According to *U.S.P. 2,073,116* (I.G.-Nuesslein-Balle) they are likewise useful as pasting agents for vat dyestuffs.

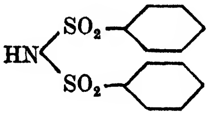
Hydrotropic substances are important for the manufacture of the "Suprafix" colors.

Sulfamides.* This group of agents for pasting vat dyestuffs has been developed by Ciba (*U.S.P. 2,029,999, B.P. 437,977, F.P. 775,617, S.P. 172,340, G.P. 623,751*). The general formula is

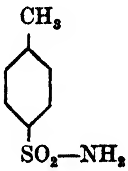


$$R{-}\left(SO_2{-}N\begin{matrix}X\\X\end{matrix}\right)_n$$

in which R represents H or alkyl radical, and X represents H or an organic radical. Examples are aminobenzene sulfamide, oxynaphthalene sulfamide, diphenylsulfimide and *p*-toluene sulfamide.



Diphenylsulfimide



p-Toluene sulfamide

Dispersing Agents

Cellulose Sulfite Waste Liquor (Dekol). A valuable dispersing agent which might also be used for preparing printing pastes. *U.S.P. 1,828,592, S.P. 148,451*, and *G.P. 548,870* (Ciba) suggest its use for preparing vat pastes, and for dispersing the water-insoluble acetate dyestuffs. The dyestuff is dissolved in concentrated sulfuric acid, precipitated with ice water, mixed with cellulose sulfite waste liquor, dried and ground. A fine dyestuff powder is obtained which is readily reducible. The process is especially adaptable for vat dyes of the benzoquinone group, which are difficult to reduce without strong alkalis, but when treated as above, may be printed on animal fibers.

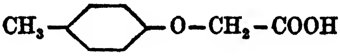
Lignin sulfonic acids and polyacrylic acids are capable of forming resinous condensates which are useful for the same purpose (*G.P. 578,939* of the I.G.).

B.P. 396,050 describes another application of high molecular protective colloids combined with salts, hydroxides or oxides of magnesium, zinc or cadmium. As examples of the high molecular colloids, sugar, starch, or cellulose sulfite liquor, are noted. These preparations are recommended for preparing pastes for printing animal fibers.

G.P. 564,778, B.P. 371,836 and *F.P. 772,885* suggest pasting vat dye-

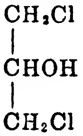
*The sulfamides are perhaps better known as sulfonamides.

stuffs with the reaction products of halogen fatty acids and aromatic compound with OH group. Such a compound is cresoxyacetic acid:



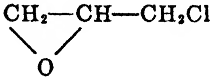
Supplementing this patent is *G.P. 604,468* (I.G.), which extends the method to reaction products of halogenated aliphatic acids with isocyclic bases (aniline) or heterocyclic bases (pyridine). *S.P. 169,662* treats of parallel methods. For example, starting with aminoanthraquinone, anthraquinone glycine is formed. Another variation is the reaction of halogenated fatty acids with sulfur compounds, as thioglycollic acid. The reaction products are used for pasting vat and sulfur dyestuffs, and also as auxiliary products to be added to the printing paste.

The reaction product of α-dichlorohydrin with ammonia was suggested as dispersion agent by Gubelmann. Improvements on this process are protected in *U.S.P. 1,977,250–1* and *–3*, *G.P. 659,670* (Du Pont), wherein the compound formed by epichlorohydrin and ammonia is described. Normal dichlorohydrin has the formula



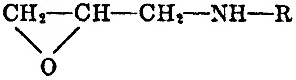
$$\begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2Cl \end{array}$$

and a boiling point of 174 to 175°C. Epichlorohydrin (discovered by Berthelot) has the formula



$$\underbrace{CH_2—CH}_{O}—CH_2Cl$$

with boiling point of 117°C. Its condensate with ammonia therefore corresponds to the formula



$$\underbrace{CH_2—CH}_{O}—CH_2—NH—R$$

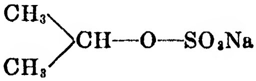
wherein R is H, or an alkyl or aryl group. A later patent of Gubelmann (*U.S.P. 1,977,272*) declares that with either epichlorohydrin or dichlorohydrin equally useful products are formed.

Urea-Formaldehyde Condensates. These compounds are used for pasting vat dyes of the anthraquinoid group. The most important patents are *U.S.P. 1,909,221*, *B.P. 366,524*, *S.P. 159,024–026* (I.G.-Pasquin). The condensates of ammoniacal formaldehyde and urea are preferred. Another patent, *U.S.P. 1,856,424* (*G.P. 543,462*) suggests the use of condensates of urea and alcohols (for example, butylene glycol, or urea and organic acid esters) to aid dye dispersion. *B.P. 299,533* (Bedford) recommends condensates of cresol and formaldehyde for the same purpose. In *U.S.P. 1,979,248* (Du Pont) recommendations for pasting indigoid and anthraquinoid vat dyestuffs which are dyed by the cold method, such as Indanthrene Blue GCD, and Indanthrene Violet 2R, are given. Instead of dispersing agents, a large excess of glycerin (up to 30% figured on weight of the dyestuff), diglycerin or sodium ricinoleate is added. The same company obtained a patent (*U.S.P. 1,979,409*) covering the method of pasting dyestuffs with sodium cellulose glycollate (Cellocel, Colloresin V) a product used as a substitute for starch thickening (*G.P. 662,926*). An analogous process was published in *B.P. 424,085* (I.C.I.). It may be noted that the reaction between alkali cellulose and monochloroacetic acid giving sodium cellulose glycollate was first patented by the Deutsche Celluloid Co. in Eilenburg (*B.P. 138,116*).

According to *U.S.P. 2,155,326* (Collway Colors) vat dyestuff pastes may be prepared by mixing lactose with a dispersing agent, for example, Tamol. Tamol is the sodium salt of disulfodinaphthyl methane (*U.S.P. 2,154,405*), produced by the action of formaldehyde on naphthalene disulfonic acid. Instead of Tamol, Medialan can be used, which is the product formed by reacting oleyl or stearyl alcohol with sarcosine.

In order to obtain vat dyes in a definite particle size, it has been found advantageous to dissolve the dyestuff first and then to precipitate it under carefully controlled conditions of temperature with selected precipitating agents. *U.S.P. 1,991,647* (Du Pont) recommends the following method of dispersing the vat dyes: the dyestuff is dissolved in sulfuric acid, the solution poured quickly through a fine jet into a soda ash solution. The carbonic acid liberated creates an energetic action of the liquid, whereby a finely dispersed precipitate is obtained, which is then rinsed and dried. In a later patent of the same company (*U.S.P. 2,065,928*), more details concerning the temperature of the precipitating medium are disclosed. In pouring the dyestuff dissolved in excess acid into boiling water, the precipitate consists of microscopically small but filterable crystals. A similar method was developed by National Aniline Div. (*U.S.P. 2,026,623*). In this patent the method consists of producing a homogeneous paste by dissolving the dyestuff in sulfuric acid and gradually adding water to the solution, whereby the dyestuff settles out in flakes with the gradually decreasing action of the diluted acid. Compare also *U.S.P. 2,032,458* of Du Pont.

According to patents of National Aniline Div. (*B.P. 439,114* and *S.P. 187,672*), compounds prepared from a polybasic acid and an aliphatic or aromatic substance of less than five C atoms are used as pasting agents. Examples given are isobutyl sulfate or *n*-butyl sulfate, $C_4H_9—O—SO_3Na$. A series of patents (*U.S.P. 2,067,926–30*) suggest applying these products especially for vat dyeing and printing purposes (National Aniline-Kern). The vat dyestuff is pasted with sodium salts of esters of short chain alcohols or glycols and mineral acids. The longer chain esters, comprising the well-known fatty alcohol sulfate dispersing agents are specifically excluded, but emphasis is placed on such compounds as sodium glycol bisulfate or sodium isopropylsulfate:



$$(CH_3)_2CH{-}O{-}SO_3Na$$

B.P. 355,363 (Celanese Corp.) describes vat dyestuffs pasted with sodium sulforicinoleate. By adding acetic or formic acid until the mixture shows an acid reaction, pastes are obtained which are stable to the atmosphere and can be concentrated and used for printing or dyeing animal fibers.

A process for preparing fine powders of vat dyestuffs is found in *U.S.P. 2,070,739* and *S.P. 170,424* (I.G.). The vat dye is pasted with sodium benzylsulfanilate (Dissolving Salt B), and then dried by spraying in a hot-air drier.

B.P. 361,350 and *364,052*, *F.P. 702,019* and *G.P. 623,713* (I.G.) propose use of salts or oxides of heavy metals such as ferric chloride, cupric sulfate, zinc sulfate, as intensifying agents for vat color prints. This general idea of an accelerated action was applied (*B.P. 416,878*, *G.P. 628,756* and *630, 207*) to mixtures of heavy metal compounds with wetting agents or hydrotropic substances, like sodium dimethylsulfanilate. It was observed that the pastes were of higher dispersion under these conditions.

Derivatives of Anthraquinone. These compounds are also used in the manufacture of vat pastes for commerce. The patents *U.S.P. 1,970,644*, *B.P. 349,995*, *S.P. 154,478*, *F.P. 727,605*, *G.P. 626,862* (I.G.) mention oxyanthraquinones and reduced derivatives thereof, having the O atom in the meso-position. One example is given. 40 Parts of oxyanthraquinone, 80 parts of glycerin and 300 parts of water are ground together, then 80 parts of concentrated ammonia and 16 parts of hydrosulfite are added at 70°C. A mixture of oxyanthraquinone and its reduction product is obtained and the whole evaporated on the steam bath to a 25% solid content. For preparation of the printing paste, 60 parts of the 25% oxy- and hydroxyanthraquinone paste, 200 parts of a 20 or 30% dyestuff paste and 40 parts of glycerin, were mixed. *B.P. 350,963* and *G.P. 627,425* recommend as a variation of the above, the use of aminoanthraquinone and *B.P. 380,860* (*G.P. 627,468*) the use of anthraquinone sulfonic or carboxylic acids.

Arylsulfonyl-β-aminoanthraquinones, formed by the action of β-aminoanthraquinone on substituted or unsubstituted aromatic sulfochlorides, are mentioned as pasting agents in *U.S.P. 1,990,854*, *B.P. 371,848*, *G.P.*

627,467 (I.G.). Also noted are sulfur compounds of the anthraquinones, as anthraquinone mercaptan, or anthraquinone sulfocyanates such as, 1-chloro-2-sulfocyanoanthraquinone (*B.P. 379,360, G.P. 628,303*).

Various Other Products. Other compounds obtained by sulfonating the residues of the distillation of benzaldehyde, turpentine or other rosins (by the process of *G.P. 506,838*) can be used as dispersing agents according to *G.P. 525,303* of Ciba.

Fine dispersions of insoluble pigments, as well as of vat dyes, can also be produced by adding about 10% on the weight of the dyestuff of methylcellulose (*G.P. 523,910*, I.G.). This acts colloidally and must be added before the pigments have a chance to settle in crystalline state.

Vat color pasting agents from polychlorinated naphathalenes are described in *G.P. 521,123* (I.C.I.). The example given is sodium trichloronaphthalene sulfonate.

Special lubricating or wetting agents, for example, oil or fat emulsions, emulsions of fatty acids and water-soluble and cellulose derivatives of fatty acids used in pasting unreduced vat dyestuffs have the effect of permitting greater penetration of the pigments into the fibers, according to *G.P. 518,197* (I.G.), than when strongly alkaline vat dyes are employed in reduced state. The alkali causes swelling of the fibers, substantially reducing penetration. An example of a fatty ester, Prestabit Oil V (*G.P. 614,702*) can be mentioned.

A process for producing vat dyestuffs in fine powdered form by using acid aryl phosphates, which aid in dispersing them readily in water, is proposed in *B.P. 508,554*, *G.P. 534,549*, and *F.P. 863,256*. As example, 0.1% of sodium dicresylphosphate is added to Indanthrene Blue RS paste. Upon drying, a dispersible powder is obtained.

B.P. 368,294 (Newport Corp.) recommends as pasting agents the sulfonation products of abietines and the salts therefrom; *B.P. 368,746* (I.G.), hydroxyalkyl ethers of aliphatic amines; *B.P. 371,286* (I.G.), salts of hydroxynaphthalene carboxylic acids, as 2-naphthol-3-carboxylic acid.

Leveling agents prepared from condensates of higher fatty acids and albuminoid substances (glue or albumen) are suggested as addition products to printing pastes according to *F.P. 772,585* (I.G.). The glue produced from the skins of rabbits or hares is treated with caustic soda at 150°C in an autoclave; then oleylchloride is added while agitating vigorously. When the condensation is complete, the excess oleic acid is removed. Destruction products of albuminoid compounds are known as dispersing agents, but the condensates with fatty acids introduced a new series of auxiliaries.

In pasting up reduced vat dyestuffs, water-insoluble hydrotropic substances are recommended (*B.P. 389,915, S.P. 157,312, F.P. 727,605, G. P. 628,756–8*, and *G.P. 630,207*) such as the tin salt of benzylsulfanilic acid. It can be assumed that such reduced pastes are more stable than when analogous water-soluble auxiliaries are used, because of the lower speed of reaction. In the same way, more stable and better fixing pastes are produced by addition of heavy metal salts such as ferrous sulfate, whereby the speed of reoxidation is retarded. This phenomenon can be observed more specifically in the case of the thioindigoid vats (*B.P. 361,350*, *S.P. 156,413*).

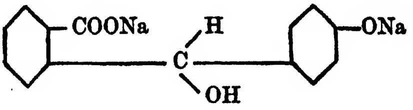
In order to obtain indigo in dispersible powder form, *U.S.P. 1,827,757* (National Aniline Div.) proposes the following. The paste obtained in regular dyestuff manufacture is neutralized, dried, pasted again with products like dextrin, phenols, alcohols and then dried again. The powders so prepared are suitable for printing as well as dyeing.

Aromatic sulfonic acids, substituted by long chain aliphatic groups (as stearyl, palmityl) are recommended in *G.P. 533,811* (Oranienburg) for preparing vat paste, while vat pastes for printing wool are made from alkali starch in *U.S.P. 1,858,632* (I.G.).

A Swiss patent (*156,743*) suggests the formation of small globular particles of metal salts, together with vat dyestuff, by rotation in a drum with simultaneous drying in a stream of hot air, the object being production of uniformly dispersible dyestuff which can be easily measured out.

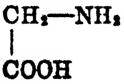
B.P. 384,304 (Du Pont) discloses a new method for manufacturing an indigo vat preparation. Zinc powder is allowed to react on a suspension of indigo in bisulfite. Zinc hydrosulfite is formed, which reduces the indigo, and is in turn changed to zinc bisulfite. Acid is added, developing sulfur dioxide, and converting the zinc salt to the sulfate. The leuco indigo settles out of the acid solution. It is dissolved in caustic soda and used as a ready-made vat.

U.S.P. 2,087,866 (Du Pont) may be quoted here. Compounds characterized by two benzene nuclei linked by a carbon atom are recommended as dispersing agents. An example is the sodium salt of oxyphenylphthalide



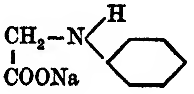
melting point 180°C (*Ber.*, **27**, 2632, and **31**, 2790).

U.S.P. 2,086,831 (National Aniline Div.) proposes pasting vat dyes with certain glycine derivatives. Glycine, also known as glycocoll or aminoacetic acid



$$\begin{array}{l} CH_2\text{—}NH_2 \\ | \\ COOH \end{array}$$

is prepared by the action of ammonia on monochloroacetic acid. It occurs as water-soluble rhombic crystals. Phenylglycine

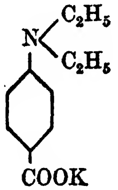


made from aniline and monochloracetic acid is an effective vat dye pasting assistant.

(Several patents relating to the application of glycine compounds to the textile field are not directly concerned with their use as dispersing agents. For example, there are references to the use of glycine as a protective agent for wool fibers against the action of alkalis. The glycine derivatives may also be used as assistants in the stripping of vat dyed wool and as auxiliaries in discharge printing of dyed woolens. The betaine and sarcosine compounds mentioned previously are derivatives of glycine.)

Dow Chemical Co. (*U.S.P. 2,086,574*) describes the preparation of fine powder dyes by drying vat dyestuffs together with sodium acetate under reduced pressure.

According to *F.P. 813,680, S.P. 188,298* and *G.P. 670,961* (Ciba) vat dyestuffs, particularly Cibanone Blue GCD and Ciba Brown G are pasted with water-soluble salts of aminocarboxylic acids in which the H atom of the amino group has been substituted with an alkyl group. Examples given are the potassium salts of alkyl aminobenzoic acid, particularly potassium diethylaminobenzoate.

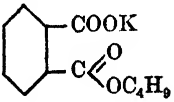


Following is a formula for a commercial vat dye powder preparation:

120 gm	Cibanone Blue GCD 30 % paste
50 gm	sulfite waste liquor 50%
33 gm	potassium diethylaminobenzoate
4 gm	glucose

The mixture is dried in a current of hot air and then ground. The powder which contains 28.7% dry dyestuff can be stirred directly into the printing gum (see also *Rev. Gen. Mat. Col.*, **1938,** 186–7). It is further disclosed in *F.P. 813,856* (Ciba) that the salts of esters or of acid amides, having alkali sulfate or alkali carboxylic groups, might also be used as dispersing agents.

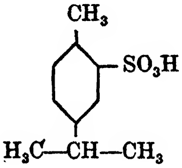
The potassium salt of isobutyl phthalic acid is mentioned as an example. It is also recommended as a printing assistant,



as follows:

100 parts Ciba Brown G paste
600 parts starch thickening
65 parts water
25 parts British gum
10 parts glycerin
150 parts sulfoxylate formaldehyde
50 parts potassium isobutyl phthalate

Analogous usage is suggested also for Na, K, NH_4 or organo-basic salts of cymene sulfonic acid:



in *B.P. 486,445* and *F.P. 813,856*. Other examples given include chlorocymene sulfonates, which can be prepared by chlorinating cymene at 50°C in the presence of iron as a catalyst, followed by sulfonation. These products are said to possess excellent dispersing properties. Finally condensates of urea with the reaction products of alkylene oxides on organic bases have proved suitable for pasting dyestuffs (*F.P. 821,750*, I.G.), particularly

$$HO—CH_2—CH_2—NH—CH_2—CH_2—NH_2$$

Monoethanol ethylenediamine

Fuller and brighter shades can be obtained with its use and the fixation takes less time.

F.P. 839,086 (Ciba) suggests using mixtures of two different groups of organic compounds as auxiliaries in dyeing and printing and especially for pasting vat dyestuffs. These two groups are (1) aliphatic or hydroaromatic organic acids, of at least 8 C atoms (oleic, stearic, cetyl sulfonic acids or octyl alcohol sulfonates) and (2) basic compounds like glycocoll, sarcosine or salts of aminobenzoic acid.

Mechanical methods are also the subject of patents. *U.S.P. 2,070,739* (I.G.) describes dispersion of vat dye paste with benzylsulfanilate of soda (Dissolving Salt B) and spray drying in current of hot air. In similar fashion, *U.S.P. 2,071,492* (Boehmer) describes pasting of the press cakes with water and spray-drying in chambers.

Reduced vat dyes are the subject of *B.P. 378,828* and *373,312* and *S.P. 150,588.* Aqueous dye dispersions are treated with a polyalcohol and reduced with sulfoxylate formaldehyde and titanous chloride. The pre-reduced dyestuffs form a special group of products which are sold ready for use.

F.P. 761,342 mentions a problem which concerns only the dyer. The ratio of caustic soda and hydrosulfite to dyestuff must be constant, but this ratio changes during the dyeing operation. This problem is solved by using two kinds of preparations, the first containing dyestuff, hydro and caustic in correct proportions for vatting, the second, in proportions suitable for adding to the dye bath according to the volume of the dye liquor.

A special leuco composition prepared from tetrachloroindigo is described in *S.P. 163,549* (I.G.). The dyestuff is dissolved in alcohol, then sulfur dioxide is passed through the solution until a white precipitate settles out which is insoluble in cold caustic soda, but is soluble in hot caustic solutions. This leuco compound is resistant to atmospheric oxidation.

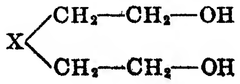
In *B.P. 414,426* and *S.P. 166,184* a ready-made vat dyestuff preparation is explained, containing dyestuff, hydrosulfite, Nekal (an alkyl aromatic sulfonate) and trisodium phosphate as alkaline constituent. A similar idea is described in *B.P. 431,278* (I.G.), wherein a leuco vat dyestuff is made by working up dry vat dyestuff with sodium metasilicate and anhydrous sodium hydrosulfite.

G.P. 622,761 discloses that certain vat dyestuffs of the thioindigo series can be transformed into sparingly soluble, but stable, reduced compounds by treating them with a reducing agent and an alkali in quantities which are molecularly sufficient to bring about complete solution of the vat dyestuff.

Solvents.

In most cases, vat dyes in paste form are prepared with the aid of solvents, such as glycols, polyglycols and ethers and esters of the glycols, like ethylene glycol, diethylene glycol, thiodiethylene glycol. The use of the glycols is important especially where non-freezing types are desired.

B.P. 392,139 (Du Pont) and *S.P. 159,928* (I.G.) both mention the simultaneous use of hydrotropic substances and polyalcohols as glycerin, diethylene glycol, thiodiethylene glycol, and in general, compounds of the structure:

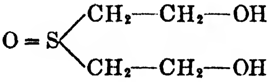


$$X\left\langle\begin{matrix}CH_2-CH_2-OH\\CH_2-CH_2-OH\end{matrix}\right.$$

where X is O or S.

S.P. 157,912–3 (Newport Corp.) recommends generally the admixture of glycols to vat pastes; *U.S.P. 2,038,591, 2,047,650, 2,069,209–10* (N.A.C.) compositions of diethylene glycol, dibutylene glycol, or hydroxyalkyl ethers in general, and triethanolamine.

U.S.P. 1,968,926, B.P. 424,588, S.P. 170,425, and *G.P. 591,547* (I.G.) suggest the preparation of vat color pastes using the oxidation product of thiodiethylene glycol, *i.e.*, thionyldiethylene glycol:



$$O{=}S\begin{cases}CH_2{-}CH_2{-}OH\\CH_2{-}CH_2{-}OH\end{cases}$$

Particularly good results are reported. The pastes are not only homogeneous and stable, but the prints obtained are of fullest possible yield.

G.P. 609,908 (I.G.) discloses an interesting process for pasting colors using phosphates, as disodium phosphate. Such pastes are stable to hard water.

The water-soluble products obtained in wood saccharification, *i.e.*, in treating wood cellulose with concentrated acids such as hydrofluoric or oxalic acids, are also dispersing agents according to *B.P. 428,590* (I.G.).

PRINTING

Application Printing with Indigo

It is not intended to review here all the numerous formulas for the printing of indigo. More complete details can be found in the Haller-Glafey textbook, "Chemische Technologie der Baumwolle" (J. Springer, Berlin), and in Georgievics-Haller's "Handbuch des Zeugdrucks" (Leipzig, 1927).

Although this style of printing has all but been eclipsed by the later vat dyestuffs, a short history of the process will still be found interesting from the standpoint of the technical equipment available at the time, and the means employed to utilize that equipment. At the same time it can be shown how scientific progress was reflected in practical mill work.

Apparently the printing of indigo dates back a thousand years, originating in India where the reduced dyestuff was applied to the fabric by means of a brush. This process was brought to Europe at the beginning of the 18th century, and was generally known under the name "bleu au pinceau", that is, brush blue, or in German, "Pinselblau" or "Schilderblau".

The preparation of the indigo was carried out by dissolving it in a mixture of arsenic sulfide and lime, and then thickening this solution with gum senegal. This method was also used in preparing pastes for printing from plates.

Another process, of English origin, was discovered in 1826 (J. J. Dingler). This was called the "bleu reduit", and was an improvement over the older formula, as it substituted for the dangerous arsenic sulfide, a paste composed of stannous oxide and cane sugar.

Another process, also discovered in England, was based on the use of the so-called copperas vat ($FeSO_4 + Ca(OH)_2$). It was called English blue or Fayence blue, and was prepared as follows (H. v. Kurrer, "Die Druck und Färbekunst", 1849): Indigo was pasted with water, ferrous sulfate and ferrous acetate. The solution was thickened with gum arabic. After printing, the dye was oxidized in the air, then treated successively with lime water, ferrous sulfate, weak caustic, and acidified and washed. The method was too complicated for success.

It is interesting to review other methods which were the forerunners of the hydrosulfite process, as for instance, the method of Schützenberger and Lalande (Sansone, "Der Zeugdruck", Berlin, 1890), which used sulfurous acid as a reducing agent. Similarly, it was found that red phosphorus and caustic soda could cause reduction on steaming. Vatting with sodium hydrosulfite was patented by Blanchon and Allegret (*U.S.P. 522,042*).

Other methods are based on the property of certain thickening agents, when mixed with alkalis, to act as reducing agents during steaming. Dextrin was proposed by Ward, while the Badische A.S.F. recommended roasted potato starch (*F.P. 278,376*, 1898, and *G.P. 123,007, 126,596.*)

Wilhelm describes in *F.P. 284,224* (*Rev. Gen. Mat. Col.*, **1902,** 137) a process which he introduced in the plant of Konschin at Serpoukhoff (Russia). A strongly alkaline solution of indigo was pasted with glycerin and then put into mixed thickening, as follows:

20 gm	indigo
124 gm	water
16 gm	glycerin
440 gm	caustic soda 48° Bé
250 gm	roasted starch thickening 33%
150 gm	British gum thickening 40%
1000 gm	

After printing, the goods were steamed 2½ hours in air-free steam, rinsed, soaped in rope form, rinsed and dried.

The indigo printing process developed by A. Schlieper of the firm of Schlieper and Baum in Elberfeld was one of the most important in this field (*Bull. Mulh.*, **1883,** 585, **1884,** 49; Gallois, "On the Fixation of Indigoid Vat Dyestuffs by Steam", paper read at conference of I.V.C.C., Turin, 1911; *Frb. Ztg.*, **1911,** 305–314; Badische A.S.F. "Indigo Rein"). It is based on the reduction of indigo with glucose in the presence of alkalis. Bancroft had discovered the reducing action of sugar and molasses as early as 1816 (Voelker, address to Academy of Sciences in Erfurt, 1816). In

1863, Leese printed a paste containing indigo, glucose, caustic soda and thickening agent, and developed the prints by steam.

The reducing action of glucose in a concentrated alkaline medium is so great that indigo may easily be over-reduced to desoxyindigo, which cannot be oxidized on the fiber again to indigo. Thereby poorer shades and uneven prints might be expected. Glucose is transformed to lactic acid by the action of strong alkalis. Since the indigo printing paste had to be in strongly alkaline condition to obtain best possible yield, the concentration of the alkali was stepped higher, thus increasing the danger of over-reduction. This reaction was somewhat minimized by substituting lime for part of the sodium hydroxide. Ward attempted this substitution (1857) with but little success.

Schlieper developed a method fit for practical use on a large scale by separating dyestuff from reducing agent (glucose). The process enjoyed a great vogue, particularly in the blue-red style consisting of indigo printed on Turkey red. The various steps in the process are as follows:

(1) Preparation of the white goods on a padding mangle with a solution of glucose of 7 to 8° Bé (formulas varied from 100 to 250 gm per liter).

(2) Printing with paste as follows:

750 gm alkaline thickener→
100 gm caustic soda 22° Bé
150 gm indigo paste 20%
1000 gm

25 gm wheat starch
55 gm British gum
120 gm water
800 gm caustic soda 45° Bé
1000 gm

(3) Drying, and ageing in air-free steam.

(4) Washing.

Instead of glucose, maltose can also be used (*G.P. 168,288*).

The first attempts to use sodium hydrosulfite as reducing agent for indigo were unsuccessful. The yield of the prints was poor because reduction of the indigo started in the print paste and the unstable hydrosulfite decomposed.

In order to avoid these drawbacks, the firm of E. Zündel in Moscow proposed using insoluble zinc hydrosulfite (*Bull. Mulh.*, **1904**). The Badische A.S.F. patented (*G.P. 125,023, 139,217*, and *141,450*) the method of preparing the goods with a solution of borax or silicate and of printing with a paste containing indigo and soluble zinc hydrosulfite.

Bulard (*Bull. Mulh.*, **51**, 36) used a mixture of soda ash and zinc powder as reducing agent, while Zuber and Pelizza (*Bull. Mulh.*, **1900**) proposed zinc powder and bisulfite-aldehyde or bisulfite-ketone. Had these last two inventors cared to pursue their reaction of zinc and bisulfite-aldehyde further, they would certainly have discovered the product sulfoxylate formaldehyde.

Farbwerke Höchst were first to suggest the use of sodium sulfoxylate formaldehyde in connection with strong alkalis. (*G.P. 173,878* and *180,069.*) This process has the advantage of combining dyestuff, alkali and reducing agent without premature reduction, thus precluding the necessity for preparing the goods.

High concentrations of alkali, which are necessary when printing dark shades of indigo, can bring about a partial destruction of the color during the steaming operation. Moreover, the back greys and the woolen blankets, as well as the printing rollers themselves, are attacked by the strong alkalis. Badische A.S.F. experimented with substitutes for the strong bases, using such weak bases as zinc oxide, potassium sulfite, magnesium oxide, zinc carbonate and sodium silicate. The results of these tests were explained in *Fischer's Ber.*, **1908,** 392 (also *G.P. 196,693*).

Strongly Alkaline Indigo Print Pastes

I	II	III	
120	60	75	sulfoxylate formaldehyde
50	40	208	water
680	650	617	alkaline British gum thickening*
150	150	50	indigo paste 20%
—	100	25	caustic soda 40° Bé
—	—	25	alcohol

1000 gm

* Alkaline British Gum Thickening

100 gm British gum dry
900 gm caustic soda 40° Bé

1000 gm

Weakly Alkaline Indigo Print Pastes

I	II	III	
50	100	100	indigo 20% paste
300	300	100	gum thickening
35	60	60	sulfoxylate formaldehyde
100			soda ash
150	150	200	water
	160	100	zinc oxide
	130	100	glycerin
365	100	200	British gum thickening
		140	sodium sulfite

1000 gm

The weakly alkaline pastes are suitable for printing only light and medium shades.

After printing, the goods are aged for 3 to 7 minutes in air-free steam, washed, acidified and rinsed.

Good results can also be obtained using borax as alkali. The following formula was used with success:

40 gm borax
500 gm tragacanth thickening
160 gm indigo ground with trag. paste
75 gm Hydrosulfite NF
225 gm textile gum
——
1000 gm

(*Note: The dyestuff must be well milled with the gum to prevent sticking in the engraving. Heating the paste is dangerous as reduction may take place.*)

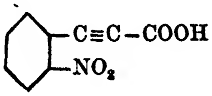
The printed cloth, after drying, is aged twice four minutes through the ager, oxidized with bichromate, rinsed, soaped and rinsed again. In the case of large objects, the prints are preferably hung 24 hours after ageing.

From a theoretical and historical viewpoint, the printing methods used before the Schlieper and Baum process and before the invention of sulfoxylate formaldehyde are of interest. These relate to the production of artificial indigo on the fiber, and because of the high cost of the ingredients and the poor yield, could not compete with the glucose method.

Method Using *o*-Nitrophenyl Propiolic Acid

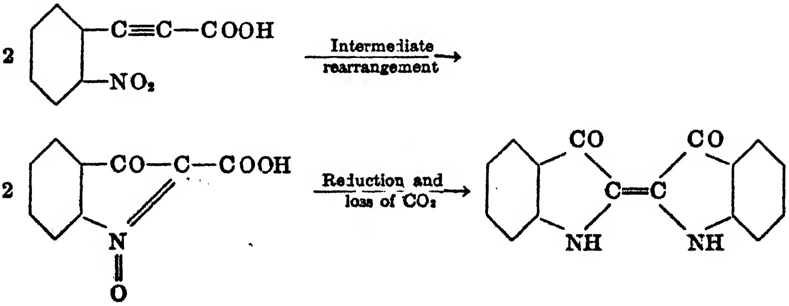
The basic material for this process was *o*-nitrophenyl propiolic acid, Indophor, Indigo Salt T of Kalle or dehydroindigo bisulfite.

Bayer found (1881) that *o*-nitrophenyl propiolic acid was reduced by alkaline reducing agents, particularly by sodium xanthogenate to Indigotine:



o-Nitrophenyl propiolic acid

The formation of indigo can be explained by an intermediate rearrangement of the *o*-nitrophenyl propiolic acid into isatogenic acid under the influence of the alkaline reducing agents. The latter product is reduced to indigo by splitting off CO_2



Indigo

The steps employed in using this equation in printing were: (1) Printing with the chemicals. (2) Hanging the printed goods for 48 hours at 30°C. (3) Washing in soda bath of 10 gm per l concentration and soaping.

Print Paste

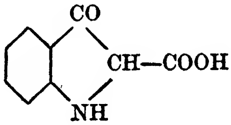
296 gm	*o*-nitrophenyl propiolic acid 25%
74 gm	sodium acetate
518 gm	starch-trag. thickening
112 gm	sodium xanthogenate, *added before printing*
1000 gm	

The paste must always be freshly prepared.

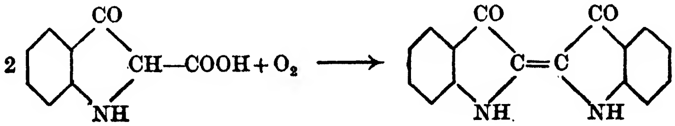
The disadvantages of this process were the persistent odor of mercaptan, and the high cost of the chemicals.

Indophor Method

Indophor is indoxyl carboxylic acid:



which can be transformed into indigo by oxidation under acid or alkaline conditions.



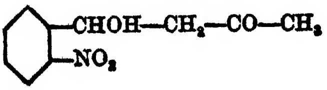
A thickened solution of Indophor is printed and the color developed in a ferric chloride bath. Oxidation can also be brought about by steaming, or hanging the printed cloth in the air.

Printing Formula

10 gm	Indophor (Badische A.S.F.)
100 gm	alcohol
90 gm	boiling water
800 gm	gum tragacanth
1000 gm	

Method Using Indigo Salt T (Kalle)

According to Bayer and Drewsen, *o*-nitrobenzaldehyde and acetone are condensed to *o*-nitrophenyl lactic acid methylketone



which was sold by Kalle under the name of Indigo Salt T. This product is transformed into indigo by treatment with an alkali.*

The printing process can be carried out either by printing a thickened paste of sodium hydroxide on a fabric treated with Indigo Salt T, or by printing the Indigo Salt T on the white cloth and developing in an alkaline bath. Because of the high cost of the material, only the latter method seems to have found practical application.

Indigo Salt T is sparingly soluble in water, so it must be dissolved with the aid of bisulfite at 50°C.

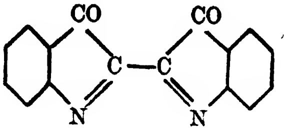
Printing Recipes

I	II	
40	50	Indigo Salt T
60	80	sodium bisulfite 38° Bé
	2	soda ash
300	120	water
600	748	gum thickening
1000 gm		

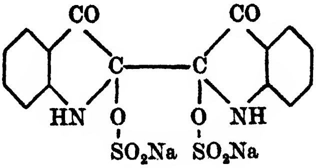
The printed fabric is aged 3 to 10 minutes in an air-free ager, then passed through hot caustic bath (16 to 20°Bé), rinsed, acidulated, and rinsed again. Disadvantages of this method were poor solubility of the bisulfite compound of Indigo Salt T, the poor stability of the substance, the poor yield of dyestuff, and the extreme alteration of the fabric from mercerizing in concentrated alkali.

Kalb's Method (1908)**

Kalb obtained dehydroindigo



by oxidizing indigo with lead peroxide or potassium permanganate in acetic acid solution. Dehydroindigo is readily transformed into its bisulfite addition product:



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* *Bull. Mulh.*, **1893**, 210; *G. P. 108,722, 109,800, 123,607, 123,608, 126,595, 126,596.*

** *G.P. 222,460.*

which is soluble in water, and can be easily changed again into indigo by action of acids or alkalis. It was possible to print a thickened solution of dehydroindigo bisulfite and treat the prints with an acid bath at 80°C, whereupon indigo was produced on the fiber. However, the poor yield of indigo and the generally uneven prints contributed to the method's failure.

"Indigo Grey"

Dr. Elbers of Hagen* developed a process of fixation of indigo by adsorption. It was characterized by finely grinding indigo with vegetable or animal oils, and printing the thickened suspension on the fabric. The indigo dyestuff adheres strongly after steaming the goods for one to two hours, preferably under pressure. Grey shades were obtained which proved to be very fast to washing and soaping. It was first assumed that the dyestuff might be fixed merely by sublimation, but R. Haller demonstrated** that indigo adopted another degree of dispersion in contact with oil and thickening agent, whereby better conditions resulted for the adsorption of the indigo pigment.

Vat Color Printing Methods—General

Vat dyestuffs are compounds of the ketone type, being insoluble in water, acid and alkalis. They are transformed by reduction into leuco compounds, characterized by the group

$$\equiv C-OH$$

which are soluble in alkalis. These alkaline-reduced vat dyestuff solutions are absorbed by vegetable fibers in much the same way as the direct substantive dyestuffs. Actually these alkali-enolates of vat dyestuffs are colloid-electrolytes exactly like direct dyestuffs (see Haller, *Chem. Ztg.*, **1912,** 169, 255; Knecht and Batey, *J. Soc. Dy. & Col.*, **1910,** 4). That is, they are salt-like compounds which in weak solution do not conduct the electric current to a degree corresponding to complete ionic dissociation. A part remains in undissociated, colloidal state. These colloid-electrolytes penetrate the fiber as positive or negative ions (Na, or organic radical).

As the cotton fiber has a negative charge, the positively charged ion (Na) adheres to it. The fixation of the negative ions (organic groups) can be explained either by accumulation of Na-ions forming a second layer of positive ions, or by the phenomenon of concentration and flocculation within the cellulose molecule (Kaufler, *Z.f. Phys. Chem.*, **1903,** 692; also Dr. Bader, Thesis, Univ. Lausanne, Switzerland, 1917).

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* *G.P. 101,190, 106,708.*

** *Koll.*, **1919,** 49.

Fixation of the dyestuff is carried out by oxidation. The vat colors are very fast because the reoxidized compounds cannot form ions.

Printing of vats can be carried out by the following methods:

(1) Steam Methods. The vat color is printed together with a reducing agent and an alkali, and fixed by ageing in air-free steam without superheat. The dyestuff is only partially reduced in the print paste, the complete transformation into the leuco compound, the solution of the leuco compound and its adsorption by the fiber taking place only during the passage through the ager. The dyestuff is developed by oxidation in a bath containing perborate, bichromate or other oxidixing agents.

This method can be varied by first impregnating the fabric with a reducing agent, and printing thereon a paste containing dyestuff and alkali. This is the principle of the glucose process of Schlieper and Baum, which although used in printing indigo, is not employed for printing vat colors. Another variation was proposed by the firm of Koechlin Frères in Mulhouse (Alsace). Briefly, this method consisted of printing the thickened vat dyestuff without other addition, drying, then padding the fabric with solution containing alkali and reducing agent, ageing and subsequently oxidizing and washing (*Bull. Mulh.*, **1929**, 221).

The application of the "vat-acid" process to printing is carried out as follows: The vat dyestuff is first transformed to its leuco compound, then the vat acid formed by neutralizing the alkali of the solution. Finally potash or soda ash is added, re-forming the leuco compound. The printing and development is carried out in the usual way: ageing, oxidizing and washing. The printing formula is as follows:

200 gm	vat dyestuff paste or 50 gm powder
80 gm	glycerin
340 gm	thickening
60 gm	caustic soda 38°Bé
20 gm	Setamol WS
30 gm	sodium hydrosulfite, *heat to 60°C until reduced, cool and add:*
70 gm	acetic acid 8°Bé
	Before use add:
120 gm	potash
80 gm	sulfoxylate formaldehyde
1000 gm	

The addition of the dispersing agent is said to improve the yield. It has also been observed that deeper prints are obtained by preparing the goods before printing with alkaline solutions.

The vat acid print colors are relatively stable but otherwise this process has no apparent advantage over the regular potash-sulfoxylate formaldehyde method. It is hardly possible therefore that this complicated method will become important in the printing practice.

Another steam method has been described by Dr. Haller. It employs alkali and stannous oxide, according to the following print formula:

100 gm dyestuff in paste
40 gm stannous oxide 50% paste
50 gm glycerin

$$700\text{ gm alkaline thickening}\begin{cases}320\text{ gm dextrin paste }600{:}400\\340\text{ gm textile gum}\\1000\text{ gm NaOH }40^\circ\text{ Bé}\end{cases}$$

110 gm textile gum
———
1000 gm

The printed and dried goods are aged, then soured off for 15 minutes in weak sulfuric acid bath, and well rinsed.

(2) Methods without Use of Steam. The method of Jeanmaire (*G.P. 132,402*), later assigned to Badische A.S.F., was employed to fix vat dyestuffs by printing with a reducing agent and subsequently developing in alkali. This process is based on the reduction of the dyestuff on the fiber by stannous chloride and ferrous hydroxide. The latter is produced by printing ferrous sulfate and treating the prints with caustic soda. The best conditions exist in this method for penetration and fixation of the dyestuff, because the reduction takes place on the fiber and in sufficient solvent for complete wetting-out. However, this process was not widely employed, and its failure can be attributed to the necessity for special equipment for strong caustic development, and also to the fact that colors of other groups could not be printed alongside. Furthermore, the Jeanmaire formula cannot be used with equal success for all vat colors. Its value is limited today to special forms of novelty printing.

A typical example of formula for this style is as follows:

335 gm starch-trag. thickening
360 gm ferrous sulfate 1:2 solution
20 gm glucose 1:1 solution
15 gm stannous chloride 1:2 solution
50 gm lactic acid 50%
20 gm tartaric acid 1:1 solution
200 gm vat dyestuff paste
———
1000 gm

After printing and drying, the fabric is treated open-width in continuous box containing a 20°Bé caustic soda solution at 75°C. The dyestuff is fixed in this operation. The cloth is treated in a second box, without a squeeze, with cold caustic of the same strength, then squeezed, washed down with cold water spray and acidulated with 3°Bé H_2SO_4 to which

0.2% oxalic acid is added. The acidulation should take 15 to 30 minutes. After thorough rinsing, the cloth is soaped at the boil.

To prevent staining of the whites, it has been found advisable to add some precipitated manganese dioxide to the first, hot caustic bath.

In order to avoid bleeding of the colors in the alkaline bath, *B.P. 417,322* and *G.P. 622,885* suggested treating the printed goods with very hot caustic solution of 32°Bé for 15 seconds, then over cold dry-cans, mercerizing under tension and finally acidifying for 1 to $1\frac{1}{2}$ hours.

A method derived from the Jeanmaire process has been suggested in *U.S.P. 2,069,919* and *B.P. 427,900* (I.C.I.-Hardacre), whereby vat dyestuffs may be printed alongside Rapidogen colors. The inventor states that in the usual potash-Hydrosulfite NF vat formula, adjacent Rapidogen colors are dulled in the ageing. He recommends, instead, a formula for vat colors containing ferrous sulfate, stannous chloride and tartaric acid. The prints are first acid-aged to develop the Rapidogens, then given the Jeanmaire caustic treatment, washed and soaped. The vat color fixation is excellent and the shades of the Rapidogens are brilliant, but the process is too involved to be popular. A simpler solution has been found, by adding neutral chromate to the Rapidogen color pastes to protect them against vat ageing conditions.

(3) Colloresin Method. This method was brought out by the I. G. Farbenindustrie in 1927. It proposes the use of a special thickening agent for the vat colors, called Colloresin DK, which is a cellulose methylether, soluble in cold water, but insoluble in hot water or in alkalis. The vat dyestuff, thickened with Colloresin DK, is printed, and the fabric is then padded in an alkaline hydrosulfite solution, aged and washed.

Print Paste

125 gm Indanthrene dyestuff paste
250 gm Colloresin DK—4% paste
350 gm starch-trag. gum
275 gm water

1000 gm

The development can be carried out in either of two ways:

(a) Potash-Rongalite method
(b) Caustic soda-hydrosulfite method

For method (a) the developing bath is prepared as follows:

100 gm Rongalite C
100 gm potash
100 gm glycerin
3 gm Nekal BX
50 gm sodium sulfate, anhydrous

to 1 liter

The printed and dried goods are padded or quetsched to 100% take-up with above solution at 25°C and dried. The goods are aged, washed in cold water to remove the Colloresin and soaped.

For method (b) the developing bath is made up of:

200 gm sodium sulfate or sodium chloride
15 gm glycerin
3 gm Prestabit Oil V
20 gm acetone
65 gm NaOH 38°Bé
40 gm sodium hydrosulfite
to 1 liter

The printed and dried fabric is padded on a three-roll mangle, and passed immediately into the ager without intermediate drying, after which it is rinsed, soured, oxidized with perborate, rinsed and soaped.

A variation in the Colloresin method, worked out in the Alsatian plant of Scheurer-Lauth by Drs. Diserens and Hess, consists of applying the developing solution on a stipple roller. The printed and dried goods are blotched with the solution:

200 gm Rongalite
100 gm sodium carbonate
50 gm sodium sulfate
to 1 liter

then aged six minutes, soured, rinsed, oxidized and soaped. The principal advantage of this method lies in the fact that it requires no special equipment.

The Colloresin process is used principally for block, spray, and screen printing; it is less important in machine printing.

Vat Color Printing—Steam Method

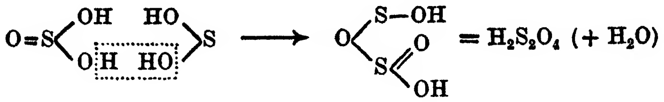
Since the steam method is the only one used at present, it will be discussed in detail.

The print paste components are dyestuff, thickening agent, alkali and reducing agent. Besides these, certain auxiliaries can be added to improve the yield, the stability and the conditions of fixation.

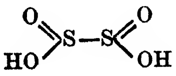
The Reducing Agents

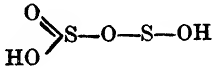
Practically without exception, sulfoxylate formaldehyde is used as the reducing agent at the present time.

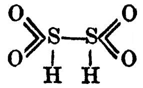
The hydrosulfites are the salts of hydrosulfurous acid, which can be regarded as a mixed anhydride of sulfurous and sulfoxylic (hyposulfurous) acids:



Three structural formulas of the hydrosulfurous acid are possible:


Symmetrical form


Unsymmetrical form


Disulfinic acid

Hydrosulfite is decomposed by water in two different ways, according to the absence or presence of atmospheric oxygen.

In absence of air: $2Na_2S_2O_4 = Na_2S_2O_3 + Na_2S_2O_5$

Thiosulfate *Metabisulfite*

$Na_2S_2O_5 + H_2O = 2NaHSO_3$

Bisulfite

In presence of air: $Na_2S_2O_4 + H_2O + O_2 = NaHSO_4 + NaHSO_3$

Further, in water the bisulfite splits off hydrogen, yielding bisulfate

$$NaHSO_3 + H_2O = NaHSO_4 + 2H$$

This reaction goes to completion only in the presence of a reducible substance.

The first attempts to fix indigo with hydrosulfite can be traced to Schützenberger and Lalande in 1871 (*Bull. Mulh.*, **1874,** 25). The method was not successful practically because the print paste was not stable. However, as early as 1898, the relatively high stability of the sparingly soluble or quite insoluble Ca, Zn, Ba and Pb salts of hydrosulfite was pointed out by Grossman.

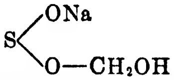
Zinc hydrosulfite was first used by the firm of Zündel in Moscow (*Bull. Mulh.*, **1904,** 36–44). Compare also *G.P. 218,192, 130,408, 137,474, F.P. 374,673, 336,943* (1902), *311,928* (1901). The zinc salt is definitely soluble and remarkably stable. Badische A.S.F. recommended the zinc-sodium double salt (see *G.P. 134,478, 135,735* (1900); *F.P. 297,370; Rev. Gen. Mat. Col.*, **1905,** 60; also *G.P. 125,023, 139,217, 141,450,* and *Fischer's Ber.*, **1903,** 453. The fabric is prepared with a solution of borax or sodium silicate and printed with a paste containing indigo, zinc-sodium-hydrosulfite and thickening agent.

Experiments were also made using calcium hydrosulfite. See *F.P. 320,227* (1902), *G.P. 112,774, 113,940, 113,949* (1898); *Rev. Gen. Mat. Col.*, **1903,** 35–7, 85; *G.P. 117,991, 217,038.* The product was known under the trade name "Redo".

A further improvement in this field was due to the work of Zuber and Pellizza (*Rev. Gen. Mat. Col.*, **1900,** 117; **1904,** 130; *Bull. Mulh.*, **1900,** 48), wherein a mixture of zinc powder and bisulfite-aldehyde was used. As remarked in the section on indigo printing, these inventors came very close to discovery of the property of formaldehyde and hydrosulfite to form a stable compound.

With the discovery of the compounds of hydrosulfite and formaldehyde the industry was presented with very valuable products, characterized by their stability and reducing powers. The earlier hydrosulfite methods were discarded, and the new products became the prime reducing agents for vat printing purposes.

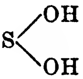
There are two different theories today concerning the constitution of the sulfoxylate formaldehyde. One of them proposes the formation of the ester of sulfoxylic acid.



$$\mathrm{S}\left\langle\begin{array}{l}\mathrm{ONa}\\ \mathrm{O{-}CH_2OH}\end{array}\right.$$

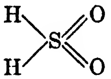
Oxymethane sulfoxylic acid

Derived from



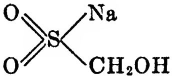
$$\mathrm{S}\left\langle\begin{array}{l}\mathrm{OH}\\ \mathrm{OH}\end{array}\right.$$

The other postulates the constitution as a derivative of hyposulfurous acid



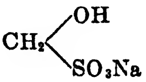
$$\left.\begin{array}{r}\mathrm{H}\\ \mathrm{H}\end{array}\right\rangle\mathrm{S}\left\langle\!\!\left\langle\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right.\right.$$

and having the structural formula:



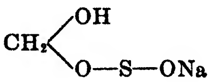
$$\left.\begin{array}{r}\mathrm{O}\\ \mathrm{O}\end{array}\right\rangle\!\!\rangle\mathrm{S}\left\langle\begin{array}{l}\mathrm{Na}\\ \mathrm{CH_2OH}\end{array}\right.$$

The first products to be placed on the market were mixtures of the sodium salt of oxymethane sulfonic acid



$$\mathrm{CH_2}\left\langle\begin{array}{l}\mathrm{OH}\\ \mathrm{SO_3Na}\end{array}\right.$$

and oxymethane sulfoxylic acid



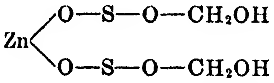
$$\mathrm{CH_2}\left\langle\begin{array}{l}\mathrm{OH}\\ \mathrm{O{-}S{-}ONa}\end{array}\right.$$

The trade names were Hydrosulfite NF (M.L.B.), Hyraldite (Cassella), Rongalite C (Badische A.S.F.). These products were called sodium-hydrosulfite-formaldehyde. The first to manufacture an almost chemically pure sodium sulfoxylate formaldehyde was Badische A.S.F., sold under the name of Eradit C (1905).

Some of the present trade names are:

Royce	*Discolite*
Brotherton	*Formosul*
Rohm & Haas, Phila., Pa.	*Formopon*
Onyx	*Hydronyx*
Arkansas	*Hydrosulfite AW*
Geigy	*Hydrosulfite FD conc.*
Ciba	*Hydrosulfite R conc.*
Rohner	*Hydrosulfite RF conc.*
J. Wolf & Co.	*Hydrosulfite AWC*
Sandoz	*Hydrosulfite RFN and RN*
Soc. Deriv. Soufre	*Hydrosulfite SC*
I.G., G.D.C.	*Rongalite C*
Lambiotte	*Sulfoxal C*
Du Pont	*Sulfoxite C*
Kuhlmann-Francolor	*Rongeol NC extra*

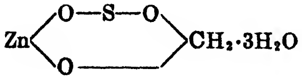
Two zinc salts of formaldehyde sulfoxylic acid are known. The primary salt:



$$Zn\left\langle\begin{matrix}O-S-O-CH_2OH\\ O-S-O-CH_2OH\end{matrix}\right.$$

Sandoz	*Arostit ZET*
Kuhlmann-Francolor	*Decolorant NZ*
G.D.C., I.G.	*Decroline sol. conc.*
Rohner	*Hydrosulfite AZL conc.*
Ciba	*Hydrosulfite BZ water sol.*
Soc. Deriv. Soufre	*Hydrosulfite SZS sol.*
Geigy	*Hydrosulfite Z water sol.*
Royce	*Parolite*
Rohm & Haas	*Protolin*
Brotherton	*Redusol Z*
Du Pont	*Sulfoxite S conc.*

The secondary salt:



$$Zn\left\langle\begin{matrix}O-S-O\\ O\text{———}\end{matrix}\right\rangle CH_2\cdot 3H_2O$$

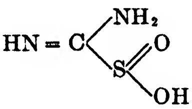
Kuhlmann-Francolor	*Decolorant N*
G.D.C., I.G.	*Decroline* #4
Ciba	*Hydrosulfite BZ acid sol.*
Soc. Deriv. Soufre	*Hydrosulfite SZ*
Geigy, Sandoz, Rohner	*Hydrosulfite Z*
Sandoz	*Hydrosulfite Z spec.*
Brotherton	*Zinc Formosul*

For detailed explanation of the invention of sulfoxylate formaldehyde, see pages 283–286.

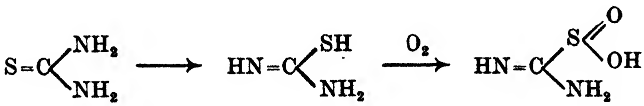
In *Bull. Mulh.*, **1929,** 75, a report of Dondain and Stiegler, dated 1911, was published. The authors had proposed to substitute formaldehyde with acetaldehyde for vat color and indigo printing. It might be noted that in 1921 Farbwerke Höchst offered a product, Hydrosulfite NFA, which was the sodium salt of acetaldehyde sulfoxylic acid. The product however, is less stable than the formaldehyde compound, starting to decompose at 80°C.

A new group of reducing agents is made public in *U.S.P. 2,112,567* (Du Pont). Complex salts of zinc hydrosulfite and ethylene diamine (or its homologs) are prepared by adding ethylene diamine to a technical solution of zinc hydrosulfite, made as usual from zinc powder, water and sulfur dioxide. The compound, which has the formula $ZnS_2O_4 \cdot 3(C_2H_8N_2)$, is concentrated under reduced pressure, and crystallized by adding alcohol. The products are resistant to dilute acids and have been found useful for dyeing acetate cellulose with indigo. Other amines, such as triethanolamine, are not capable of forming complex salts.

U.S.P. 2,164,930 (Du Pont-Lubs) describes a new reducing agent which can be used in dyeing or printing vat dyestuffs, or for stripping. It is a chemical compound detected by Barnett in 1910 (*J. Chem. Soc.*, **1910,** 63–65) and known as iminoaminomethane sulfinic acid or formamidine sulfinic acid



The product is formed by the oxidation of thiourea with peroxide in aqueous solution according to the following equation:



Thiourea *Pseudo-thiourea*

The compound is stable in the cold as well as at higher temperatures, and its reducing power is said to be 75 to 100% better than that of hydrosulfite or Rongalite C. Its stability to acid and alkaline solutions is very good. The following printing formula is given:

200 gm	**Vat Brown paste**
50 gm	**formamidine sulfinic acid**
50 gm	**caustic soda 35%**
50 gm	**potash**
20 gm	**Solution Salt B**
630 gm	**starch-trag. thickening**
1000 gm	

The stability of the paste should make the product interesting for block and screen printers.

As a reducing agent, glucose has value only when used in strongly alkaline medium. It is a strong reducing agent; some indigoid dyes are over-reduced even in short ageing. Lichtenstein recommended glucose for printing Hydron Blue (*Frb. Ztg.*, **1912,** 444; *Aus.P. 33,611; Öst. W.u.L.Ind.*, **1912,** 313). In a later reference, Lichtenstein and Klein state (*U.S.P. 1,919,792*) that glucose is itself not sufficient as reducing agent for printing vat-dyestuffs, but that an increased reducing effect which is said to be superior even to that of sulfoxylate formaldehyde, can be obtained by adding certain anthraquinone derivatives to the glucose. Compounds which can be changed to oxanthranol compounds, especially the so-called "silver salt", β-anthraquinone sodium sulfonate, are recommended. The process is intended mainly for hand-printing of indigoid colors.

Glucose was used as reducing agent in the printing of indigo (see page 23). Adolf Schlieper is credited with the invention of the process which made indigo application so successful. By separating the glucose from the alkali he fulfilled two objectives: reduction of the dye in the print paste was prevented, and the mercerization which took place at the printed areas was obviated.

A reducing agent, called Candit V, has been offered by the Chem. Fabrik Pyrgos in Radebeul, near Dresden. It is made by combining glucose and sodium hydrosulfite (*Mell.*, **1928,** 41; **1929,** 630 and 717). It is based on the work of Haller and Solbach (Hackl, "Neuerungen in der Reduktionstechnik", *Mell.*, **1930,** 383, 530). It is said to possess stronger reducing action than sulfoxylate formaldehyde, and to be more stable, and therefore to be especially important for jig dyeing at temperatures of 70 to 80°C. However, when tried in printing it had little success. The work of Perndanner, Hackl and Bartl regarding this matter might be mentioned here. These investigators were able to ascertain the formation of aldehyde-type compounds in the action of alkali on glucose. These substances can react with hydrosulfite in a manner similar to formaldehyde. Glucose which has been treated with alkali has therefore a stronger reducing action than glucose which has not been so treated. The phenomenon is explained by the formation of aldehyde bodies:

$$C_6H_{12}O_6 \xrightarrow{NaOH} CH_2OH{-}CHOH{-}CHO + CH_3{-}CO{-}CHO + H_2O$$

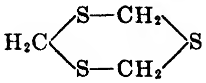
$$C_6H_{12}O_6 \xrightarrow{\qquad} CH_2OH{-}CO{-}CH_2OH + CH_3{-}CO{-}CHO + H_2O$$

Such aldehyde substances, as glycerin aldehyde (glycerose) have been used instead of glucose itself to build compounds with hydrosulfite. The sulfoxylate of sodium glycerose is a very powerful reducing agent (*Mell.*, **1930,** 42, 533; *Tiba*, **1930,** 963; Pomeranz, *Mell.*, **1930,** 286).

Ward proposed dextrin as printing assistant for indigo. Wilhelm described a similar method for printing indigo. (These processes are explained in a previous section.)

Another reducing agent has been tried out by Cheshire at the firm of Voronin, Luetschy and Cheshire in St. Petersburg, 1910 (reported in *Bull. Mulh.*, **1932,** 555, and *Rev. Gen. Mat. Col.*, **1933,** 101). The product is formed by reacting sodium sulfide with formaldehyde in the presence of bisulfite-formaldehyde. It can be used with the raw sulfur dyestuffs which still contain polysulfides or alkali sulfides. It minimizes the blackening of rollers and doctor blades when printing with sulfur colors. Print pastes containing this compound keep well and the colors show no tendency to pre-reduce. [Compare *G.P. 164,506* (Cassella); *G.P. 217,587* (1907, ter Meer); Baumann, "Trithioformaldehyde", *Ber.*, **23,** 60, 1869; Wohl, *Ber.*, **19,** 2344.] The researches of Chartscheff of the firm of Voronin (*Frb. Ztg.*, **1913,** 255) disclosed also the condensate of formaldehyde and sodium sulfide which is formed by dissolving sodium sulfide in a mixture of formaldehyde and bisulfite. This compound crystallizes in colorless needles. It is very stable, and not only reduces vat dyestuffs but also dissolves the resulting leuco compound. Chartscheff claimed this compound did not have the disadvantages of pre-reduction or over-reduction of the vat dyestuff which he met with sulfoxylate formaldehyde. The compound reduced the vat color so slowly that two phases could be observed: firstly, formation of an intermediate leuco compound in the print paste, and secondly, complete reduction in the ager to the leuco compound.

Cassella produced a similar compound in another way (*G.P. 164,506*) in 1910. A concentrated solution of sodium sulfide is heated with formaldehyde at 100°C. The principal compound formed is trithioformaldehyde



In ageing, sodium sulfide is reproduced in alkaline medium, thereby causing reduction of the vat color.

Inorganic reducing agents are the bases of *F.P. 363,533* and *G.P. 209,427** wherein stannous oxide is recommended, and *F.P. 687,734* of the I.G., 1930, proposed compounds of trivalent titanium compounds, as $TiCl_3$ or $Ti_2(SO_4)_3$.

These products are of academic interest only.

The Alkaline Agents

In general, the various printing formulas for vat colors differ principally in the alkali used. The selection of the alkali is determined by the ease of

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* Badische A. S. F.; *Frb. Ztg.*, **1909,** 301.

reduction of the dyestuff and the solubility of its leuco compound in that medium.

Sodium hydroxide alone can be used in the printing of indigo* and certain other vat dyestuffs, particularly Indanthrene Blue RS paste. In such cases the print color contains up to 500 gm NaOH 38°Bé per 1000 gm,** the thickening being British gum or roasted starch.

Weak alkalis, particularly the carbonates, are suitable for those vats which are easily reducible, and whose leuco compounds have a strong affinity for the fiber. Of these, the thioindigoid vats may be mentioned, and the halogenated indigos. Most of the vat dyestuffs give good yields when printed with potassium carbonate, and for this reason the method using potash is most widely employed. The potassium salt is preferred to the sodium, because of its better solubility and greater hygroscopicity.

The steaming methods may be classified according to the alkali used, as follows:

(1) Potash—Rongalite C (Hydrosulfite NF) method.
(2) Potash—Hydrosulfite NF with pre-reduction.
(3) Potash and caustic method.
(4) Bicarbonate method.
(5) Soda methods.
(6) Strongly alkaline (NaOH) paste.
(7) Other alkalis.

Potash—Hydrosulfite NF Methods. Of these different methods, the potash-Hydrosulfite NF is by far the most widely used, because of the simplicity of the formula and the comparatively reliable results (see Dr. Sieber, "Über Indanthren-Dampfdruckverfahren", *Mell.*, **1926,** 141–3).

The vat dyes may be printed either with or without pre-reduction, according to following formulas:

(1) *Without pre-reduction:*
100–200 gm vat dyestuff paste
50– 75 gm glycerin, or 50 gm Glyecine A
0– 30 gm Solution Salt B
500–350 gm starch-trag. gum, or starch-British gum
80–120 gm potash
60–100 gm Hydrosulfite NF
210–125 gm water
1000 gm

(2) *With pre-reduction:*
100–200 gm vat dyestuff in paste
50– 75 gm glycerin or 50 gm Glyecine A

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* *G. P. 180,069.*

** "Scratching of Copper Rollers in Printing with Alkaline Pastes", *Mell.*, **1930,** 46; **1931,** 328; **1940,** 536.

30– 30 gm Solution Salt B
500–375 gm starch-trag. or starch-British gum
120 gm potash
40 gm sodium hydrosulfite powder
Warm at 60°C for ½ hour, then cool and add:
160 gm Hydrosulfite NF 1:1 solution
1000 gm

The method involving pre-reduction is seldom used, but in special cases a better color yield is obtained.

Potash and Caustic Method. The combined potash-caustic soda method, developed by Dr. Diserens at Scheurer Lauth & Co., in Thann, Alsace, works well, giving reliable results with most vat dyestuffs. As examples the following formulas are given:

(1) *Without pre-reduction:*
500 gm alkaline thickening A or B (*below*)
80 gm vat dyestuff
140 gm neutral thickening
120 gm water
160 gm Rongalite C 1:1 solution
1000 gm

(2) *With pre-reduction:*
300 gm Ciba Brown G micropaste
100 gm British gum dry
230 gm British gum 1:1 paste
20 gm Glyecine A
20 gm urea
100 gm potash liquid 45°Bé
30 gm caustic soda 38°Bé
40 gm sodium hydrosulfite
Warm to 60°C; then cool and add:
160 gm Rongalite C 1:1 solution
1000 gm

Alkaline Thickenings

A

100 gm Tylose MGA
700 gm water
Cook 2 hr; add
30 gm potato starch
115 gm water
Cook 20 min; add
90 gm Débécuvol C*
375 gm potash liquid 45° Bé
90 gm caustic soda 38° Bé
1000 gm

B

537 gm cold water
114 gm wheat starch,
Cook ¾ hr; add
294 gm British gum dry
90 gm Débécuvol C*
375 gm potash 45°Bé
90 gm caustic soda 38°Bé
1000 gm

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* See page 148.

Bicarbonate Method. The bicarbonate method has little practical value. The method finds limited use in such cases where vat dyestuffs must be printed which are difficult to fix uniformly, but which can be dissolved by pre-reduction in caustic soda and hydrosulfite.

Typical Print Formula
30 gm dyestuff powder
30 gm alcohol
80 gm glycerin or Glyecine A
145 gm water
400 gm thickening
65 gm caustic soda 38° Bé
40 gm hydrosulfite conc.
Warm at 60°; cool and add:
60 gm sodium bicarbonate
150 gm Rongalite C 1:1 solution

1000 gm

Sodium or potassium bicarbonate were recommended at one time for printing vat colors of the Algol type (*G.P. 263,419*, 1911; *Frb. Ztg.*, **1913,** 463; *Chem. Ztg.*, **1913,** 453). Since some dyestuffs of the Algol series are acylamino derivatives, they are easily hydrolyzed by strong alkalis. The dyes, after vatting in caustic and hydrosulfite are mixed with bicarbonate.

Soda Methods. The soda ash methods are similar to the corresponding potash methods, substituting soda ash for the potash of the given formulas.

Strongly Alkaline Paste Method. The strongly alkaline vat printing recipes are restricted to a few colors only. Among others, Cibanone Blue RS or O can be printed with good yields with pastes containing high percentages of alkali (*F.P. 800,980*, *B.P. 473,353* of Ciba-Haller).

Formulas using as high as 500 to 600 gm NaOH 50% per kilo are used, with relatively small amounts of Rongalite C.

Print Color
150–250 gm dyestuff in paste
0–100 gm NaOH 38° Bé
100–150 gm Rongalite C 1:1 solution
750–500 gm. alkaline thickening WB*

1000 gm

* Alkaline thickening WB
90 gm dry British gum
60 gm starch
120 gm water
10 gm NaOH 38° Bé
Paste up and allow to stand overnight
720 gm NaOH 38° Bé

1000 gm

Method with Other Alkalis. In place of caustic soda, L. Lantz in 1911 proposed using water-glass of 35°Bé (*Bull. Mulh.*, **1925**, 159).

Certain indigoid vat dyestuffs such as Ciba Red 3B or Algol Orange R are well fixed by using potassium sulfite, either alone or preferably in connection with some caustic soda.

Typical Formula

150 gm	Ciba Red 3 B paste
300 gm	British gum paste 1:1
200 gm	water
250 gm	potassium sulfite 45° Bé
100 gm	Rongalite C 1:1 solution
1000 gm	

A part of the potash or caustic soda alkali content can be replaced by organic bases such as triethylamine, piperazine, etc., according to *G.P. 555,305*, *B.P. 373,558* or *F.P. 729,412* (Ciba). It is claimed by this process that formation of halos when printing vat color resist under aniline black can be minimized.

Some adaptations have been made to the print formulas for printing on animal fibers, in order to protect the material. For example, Bayer & Co. proposed (*Frb. Ztg.*, **1912**, 449; *Öst W.u.L. Ind.*, **1912**, 401) the use of sodium stannate as an alkaline constituent in wool printing, because this chemical does not attack the wool fiber. Grossheintz (*Bull. Mulh.*, **1912**, *Frb. Ztg.*, **1913**, 420) recommends ammonia instead of fixed alkali in wool printing. In similar fashion, Kalle recommends replacing the fixed alkali necessary in pre-reduction with ammonia, ammonium carbonate or bicarbonate (*G.P. 391,995*, 1917).

G.P. 486,488 (I.G., 1925) describes the method of replacing the caustic or carbonate alkalis with sodium phosphate or sodium aluminate, or other bases of weak acids. The substitution of the strong alkalis by sodium salts of organic compounds, as sodium phenolate, sodium glycollate or sodium-β-naphtholate, is found in Ciba's *S.P. 166,186* and *F.P. 763,509*. These pastes do not contain any additions of potash, and only small amounts of Hydrosulfite NF are used with 10% glucose, but to accelerate reduction, agents such as anthraquinone or salts of trivalent titanium may be added.

In *B.P. 386,433* (I.G.), a formula for wool printing with vat dyestuffs is given. The sulfoxylate formaldehyde is replaced by glucose, and the fixed alkali by ammonia, sodium phosphate or triethanolamine.

It is known that cellulose acetate may be damaged by alkaline printing colors. Therefore the *B.P. 417,978* and *F.P. 765,960* (Rhodiaceta) selects appropriate basic agents for this fiber. It is important that the alkali does not penetrate the cloth too rapidly. The usual alkalis are replaced here by magnesium hydroxide. Fifty grams of $Mg(OH)_2$ are added per 1000 gm of print paste containing sulfoxylate formaldehyde.

Thickening Agents

British Gum. This is the best thickening agent for vat dyes, considering all phases. It is suitable for every printing formula, for those containing caustic alkalis as well as for pastes which do not. The high percentage of solids in this thickener facilitates steam condensation on the printed areas and for this reason the fixation of the leuco derivative proceeds regularly and under the best possible conditions. British gum thickenings are superior to starch-tragacanth gums for keeping the dyestuff in suspension, thus aiding in penetration.

However, prints with British gum turn out weaker than prints with starch-tragacanth. This phenomenon can be explained by the deeper penetration of the British gum pastes into the fiber as compared with the more superficial prints of starch-tragacanth pastes.

Finally, British gum pastes do not mark off readily in the ageing treatment (see Gerber, *Mell.*, **1937**, 316).

Mixtures of soluble gum Senegal, gum Karaya or insoluble India gums with British gum give good results, particularly on fabrics where level prints are difficult. A method of preparing textile gums which withstand alkalis is described by Pfister in *U.S.P. 2,011,728.* It is assumed that Shiraz and Karaya gums coagulate with alkali because of the calcium content of these gums. On heating the gums with soda ash solution, and separating the insolubilized calcium salts by filtration, it is possible to produce gums which will not "liver" on alkali addition.

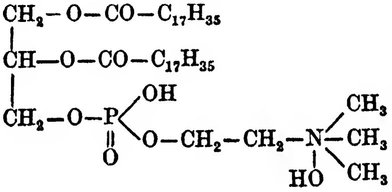
The yield of prints from slightly alkaline pastes is improved by using starch or starch mixed with tragacanth or British gum. Addition of Solution Salt B (sodium benzylsulfanilate) is recommended especially in starch-thickened vat gums. This salt has the function of preventing an adsorption of the leuco vat by the starch. It has been experimentally shown that the addition of Solution Salt has very little effect where thickeners other than starch are used (Peters, *Frb. Ztg.*, **1912**, 134, 436; Lichtenstein, *Frb. Ztg.*, **1912**, 205; *Öst. W.u.L. Ind.*, **1912**, 313).

Starch Pastes. Peters recommends starch as the best thickener for vat printing. Assuming that textile gum is not liquefied in the ageing by the alkalis present in the printing formula, then a homogeneous mixture is present; the penetration is satisfactory but the color fixation is poor because of the rapid oxidation of the leuco compound. On the other hand, starch is transformed by the action of the steam into a homogeneous substance, changing on cooling to the highly viscous state of the starch solution. The starch paste envelops the leuco compound and retards the oxidation, whereby a good fixation of the color results (Peters, "Über Solutionssalz", *Rev. Gen. Mat. Col.*, **1912**, 214; **1913**, 27).

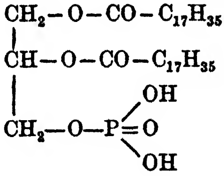
Starch thickeners offer some problems in their practical use. They are difficult to remove, and the print pastes have a tendency to mark off in the ager as well as in the washing operation. The use of sodium benzylsulfanilate may help retard this mark-off. The principal advantage of starch as vat color thickener is in its comparatively higher color yield.

According to patent *U.S.P. 1,986,360* (Hansawerke), a substantial improvement in the properties of starch thickeners (flexibility, shortness) has been attained by adding certain phosphatides of vegetable origin, for example, lecithin, prepared from soy bean oil. The 60 to 80 gm of lecithin are stirred into 300 gm of mineral oil and this mixture is added to a starch paste; the whole is boiled and cooled to 60°C (*G.P. 566,149*, 1931; *Rev. Gen. Mat. Col.*, **1932,** 262; *B.P. 353,873*).

It will be remembered that lecithin is also a constituent of egg-yolk. It belongs to the class of lipoids. Chemically it is the distearyl glycerophosphoric acid ester of choline:



By hydrolysis with hydrochloric acid, lecithin forms choline and the distearyl glycerin ester of phosphoric acid:*



The aqueous emulsions of lecithin are not sufficiently stable. This property is improved by adding small quantities of alkali peroxides as suggested in *U.S.P. 1,972,764* (Engelmann). Sieber published a report in *Mell.*, Feb., **1926,** showing the advantage of a starch thickener prepared by heating starch with glycerin. When heated to the boil, a clear and homogeneous liquid is formed, which is cooled, and later sodium hydroxide added.

According to the research of Schindler (*Mell.*, **1927,** 1030), starch-tragacanth pastes yield very full prints, but two disadvantages are encountered. The gum is not very compatible with alkalis, and soon becomes watery. Although it behaves well in the ager, it does not level well in large blotch print patterns (compare *Wengraf's Ber.*, May, **1937,** 16).

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* *Mell.*, **1931,** 123.

Starch-British gum thickening has better vat color fixing properties than British gum alone. W. Hess recommends as special gum for printing vats a starch paste treated at 80°C with caustic soda, and an addition of aluminum rosinate.

Wheat starch mixed with textile gum makes a good thickening, especially where level blotch prints are desired.

Soluble starches (cold swelling starches) are different from the modifications of starch which require heat for dissolving. They are also different from dextrins, being further degraded products. (Blinc and Samec, *Koll.*, **77**–1, 134). These cold swelling starches are well-known in the food industry and in the manufacture of adhesives. They have also been introduced into the textile field, particularly for finishing operations. "Quellin" is the trade name of one such product, made by Scholten Chemical Product Co. This company suggested (*F.P. 723,306*) using the product for preparing printing pastes. Another similar starch is Solvitex of Doitteau in Corbeil, France. These starches give thick pastes, but further study is required before predicted results in printing can be established.

The manufacture of soluble starches is based on a partial decomposition of the starch granules under carefully regulated conditions of temperature. This transformation is not a hydrolysis. According to *Aus.P. 130,649* of Henkel & Co., starch is treated at 140 to 160°C under pressure of 2½ atmospheres. *B.P. 383,786* of the Metallges. A.G. proposes spraying a starch slurry into an overheated chamber. The water is evaporated at a temperature higher than that required for degradation of the starch. Soluble starch in powder form is obtained.

Other methods mentioned in the literature are as follows: *S.P. 160,428, Aus.P. 136,009:* A starch slurry is sprayed in a mixture of air and steam at 70°C.

Aus.P. 135,000 (Chem. Ind. Rannersdorf): Cold swelling starch results when bivalent metals (Cd, Zn) are added to alkaline starches.

G.P. 582,679 (Henkel-Schulz): Starch is treated with caustic at room temperatures in the presence of an emulsion of organic solvents such as trichloroethylene or of aldehydes or amines, which prevent too rapid a conversion.

G.P. 602,832 (Grüninger): Starch-milk and triethanolamine are mixed, treated with 25% caustic alkali and neutralized with oxalic acid.

The variety of these products makes any recommendation of a soluble starch for printing incident on thorough investigation.

Locust Bean Gum. This gum is on the market under many names, as Tragasol, Lisogum, Lupogum, Siliqua, Leicogum, Cefen, Okatol, etc. It is also called Carob bean and Johannis bread meal. Thickenings made from locust bean become watery when alkalis are added, and are therefore not suitable for vat color printing. According to *G.P. 578,776* (Kaestner, 1933), it is possible to obtain this gum compatible with carbonates by treating the slurry with acids or diastatic ferments while warming, until the desired consistency is obtained. By this process, the gum changes its characteristics considerably, and acquires reductive properties (*B.P. 444,838; Mell.*, Feb., **1931,** 163). The *Aus.P. 150,992* (Ver. Färb. A.G.) suggests heating the meal in double-jacketed kettle under continuous additions of acid.

The Diamalt A.G., Munich, states in *G.P. 719,786* (1934) that Carob bean gums, stable to the action of alkalis can be obtained by mixing the dry meal with polyoxyaromatic compounds, such as resorcinol, pyrocatechol, hydroquinone, pyrogallol, and heating the mixture for some time at 100°C.

G.P. 749,708 (Kaestner, 1944) concerns treatment of locust bean gum wherein the boiled gum solution is heated with acids or diastatic substances; the heating is interrupted when the desired consistency is reached. This thickener, although compatible with alkalis, is recommended to be used as in the Colloresin DK process, mentioned below.

Another method of solving the problem of the sensitivity of Carob bean gum to alkalis is given in *F.P. 838,904* (D. & H.). The beneficial effect of a proteinaceous substance is cited, acting as a protective colloid. A thickening is prepared of 20 parts of Carob bean gum, 10 parts of glue and one part of salicylic acid as preservative, with 1000 parts of water. This preparation, sold under the name of Universal gum, has been recommended for all kinds of dyestuff prints, one example naming Vat Jade Green B printed by the usual potash-Rongalite method.

Bentonite. It has been shown that in printing vat colors on cotton piece goods, the use of bentonite as thickening agent, or as part of the thickening, gave increased value of dyestuff. Whereas print pastes of starch-British gum or starch-tragacanth showed loss in strength after milling, no loss in strength of print was noted in the case of bentonite thickenings. Photomicrographs of the resulting prints with different thickening agents proved that the presence of bentonite prevents reagglomeration of the vat dyestuff particles, and has the effect of reducing penetration, thus insuring maximum color yield (Jacoby, *Am. Dyes. Rep.*, **1944,** 502–509. Compare also *F.P. 812,944* Beraud).

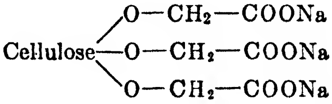
Bentonites correspond to the general formula, $Al_2O_3 \cdot SiO_2 \cdot H_2O \cdot nH_2O$.

G.P. 440,321 (Holzhydrolyse A.G.) and *B.P. 360,015* (International Sugar & Alc. Co.) describe the formation of sugars from wood. (The structural chemistry has not been given.) Three steps are necessary in the process: (1) Treatment of wood with mineral acids; (2) precipitation of the carbohydrates by alkaline earths in the cold (this step requires rigid control); and (3) decomposition of the alkaline earths with carbon dioxide. The products obtained are capable of forming thickening agents which have been proposed for printing vat colors.

Cellulose Derivatives. Cellulose derivatives can be used for printing and some of them are useful for vat color printing. Colloresin DK, already mentioned, is a cold-water-soluble cellulose alkyl ether which is rendered insoluble in alkalis or in hot water. (*G.P. 495,712* of I.G.—Gmelin; and Kerth, *Mell.*, **XVI,** Nov., 791.) Kerth asserts in *Mell.*, May, **1937,** 378, that Colloresin DK is compatible with starch and tragacanth thickener but that mixtures with textile gum or British gum do not keep in a homogeneous state. Colloresin DK is further precipitated by different electrolytes as sulfates, soda ash; also by Hydrosulfite NF, Nekal and by tannic acid. It can be used for printing vat colors which will be later treated with caustic soda and hydrosulfite for reduction; the Colloresin is insoluble in the alkali, thus preventing bleeding of the vat color.*

Colloresin DK can be used in acid color printing on wool, and has found use in printing resists under aniline black. In printing vat color resists under aniline black, the formation of halos is avoided by adding a certain amount of Colloresin to the aniline black padding liquor, because the Colloresin is insolubilized on the printed portions, making sharp outlines. (See also *U.S.P. 1,922,978*—Pfeffer; "Colloresin Ager": *G.P. 574,939*—I.G.; also *U.S.P. 1,870,516*, and *G.P. 582,114*—Ciba, concerning the use of other substances which are coagulated by alkalis in place of Colloresin DK.)

On the other hand, the oxyalkyl ethers of cellulose (*G.P. 562,985* of I.G.—Sponsel) are soluble in hot water and are stable to alkalis. This patent proposes as thickener a derivative of wood cellulose which, after treating with alkali, is reacted with monochloroacetic acid. The final product has the character of a cellulose ether (like Colloresin DK) but corresponds to the sodium salt of a glycollic acid-cellulose ether, and probably represents the commercial Colloresin V extra



Sodium cellulose glycollate

One of the first publications dealing with the manufacture of cellulose glycollic acid was *G.P. 332,203* (Deutsche Celluloid A.G.-Eilenburg, 1918). Mercerized cellulose is reacted in the presence of caustic alkali with chloroacetic acid.

U.S.P. 2,268,612 (Dow Chem. Co., 1942) discloses the following formula: A 75% concentrated chloroacetic acid solution is brought in contact with the same quantity of cellulose for a few seconds. Thereafter the cellulose is treated with a 41.3% NaOH solution. Another formula is given in Du

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* *G.P. 525,182*

Pont's *U.S.P. 2,236,545*, 1941: 1000 parts of cellulose reacted with 10,000 parts of caustic soda 25%, pressed out to 3000 parts and reacted with 725 parts of dry sodium chloracetate.

Different uses are suggested: As thickeners, *B.P. 508,547* and *526,845* (I.G.); as plasticizers, *B.P. 538,909* and *537,980* (Du Pont); as waterproofing agents, the Al salts mixed with waxes, *U.S.P. 2,308,664* (Dow Chem. Co.). As stabilizers for emulsions, *U.S.P. 2,357,469* (I.C.I. 1944); as additions to alkylcellulose thickeners, *U.S.P. 2,377,834* (Dow Chem. Co.). As cleaning agents, *U.S.P. 2,335,194* (Pauser and Nuesslein). Trade names for this product are Collocel, Cellappret, Carboxymethocel and Cellofas WFZ (see also *J. Soc. Dy. & Col.*, **1941,** 254–258).

The properties of Colloresin V extra have been discussed by Nestelberger (*Mell.*, **1940,** XXI, 74–76). The product can be used as a substitute for tragacanth, textile gum and British gum, because it is soluble in acid as well as in alkaline medium. Colloresin V extra gums are not "short," and yield clean, sharp prints. During the war, Germany and the Axis countries had little starch and starchy products, and the use of substitutes such as Colloresin V extra was extensive. But the special kind of wood needed for this product was available with difficulty after 1942, so that another brand, Colloresin KB, or Tylose MGA, was substituted for Colloresin V. This product is water-soluble and may be mixed with starch, giving good results in printing vat colors. The following formula for a thickening agent on the basis of Tylose MGA may be given:

100 gm Tylose MGA
770 gm water
Cook 2 hr; add
30 gm potato starch meal
100 gm water
Boil 20 min longer

1000 gm

Other Thickeners. Various products, consisting of chemically converted starches, are being used with great success for printing vat colors. They are used either alone, or with British gum, or with gums of other desired properties. These modified starches are sold under the names of Kovat gum (National Starch Prods.), Gum KAC4 (Stein-Hall Co.), Hevtex, etc.

Thickeners consisting of polyvinyl alcohols have also been proposed. According to *F.P. 691,070* (I.G., 1930), Indanthrene colors are dispersed in a solution of 100 gm polyvinyl alcohol in 900 gm water. By this process, the goods are first printed with the vat color, then padded in solution of 110 gm Rongalite C and 75 gm potash per liter, dried and aged.

Intermediate products occurring in the copolymerization of vinyl and polyvinyl compounds, can be used as thickeners according to *B.P. 464,283*

(I.G.). An example is a mixture of methyl vinyl ether and octadecyl vinyl ether. Similarly, in *U.S.P. 2,108,994* it has been found that a water-soluble interpolymerization product is derived from two or more vinyl ethers. At least one water-soluble vinyl ether and at least one water-insoluble vinyl ether, capable of polymerization under the same conditions, are necessary. Fabrics printed with vat dyes thickened with such products are dried, padded with Rongalite C and potash, dried, aged and washed.

It has also been found that copolymerizates of acrylic acid derivatives are suitable as printing pastes (see Dr. H. Gerber, *Mell.*, **1939**, XX, 286). An aqueous solution of mixed polymers of polyacrylic acid having a dry content of 15% was used, consisting of 65% polyacrylonitrile

$$(CH_2{=}CH{-}C{\equiv}N)_x$$

and 35% sodium polyacrylate

$$(CH_2{=}CH{-}COONa)_x$$

This organic mixture is neutralized with ammonia. In this connection, *G.P. 662,936* (I.G.) suggests the use of water-soluble copolymers of vinyl ethers as thickening agents.

These thickeners can be improved by the addition of water-soluble silicates. A better yield is said to be realized (*G.P. 713,903*, Röhm & Haas, 1938).

Another thickening agent for vat colors is the sodium salt of alginic acid, preferably used with other gums or starches. The alginates are sold under various trade names, as Keltex, Algin, Sodium alginate, etc. One formula for their use is as follows:

60 gm sodium alginate
30 gm calgon
18 gm potato starch

1000 gm with water

Vat colors can be printed with this gum, with results comparable to starch-British gum thickening.

Finally, the inorganic thickeners might be briefly mentioned. One product known as Sisol (Gignoux, Lyons) is a colloidal silica gel, and can be used either alone or with starches as vat color thickener. The gel has a remarkable ability to retain the color in suspension. The gel is neutral and chemically inert, and has the advantage of being readily removable from the fiber. It does not absorb dyestuffs and thereby the color yield is considerably increased.

In *G.P. 696,722* (1937) a process for printing vat colors is described using as thickeners suitable metaloxide sols or amphoteric gels. They are prepared from metal halides by reaction with ethylene oxide. After extraction with ether, the metal hydroxides remain in colloidal suspension.

Auxiliaries Added to the Print Paste

The fixation of vat dyestuffs can be improved by a great number of auxiliary products. It has been proved that in the case of irregular ageing conditions, which is a frequent occurrence, certain agents which aid hygroscopicity, in solution or dispersion, aid in improving absorption of the dyestuff. By means of these auxiliary agents more uniform results are obtained, fuller shades are possible and the time of ageing may be reduced.

By the use of hydrotropic substances or certain dispersing agents, the stability of the print paste is increased, as well as the stability of the prints themselves before ageing, permitting longer storage of printed goods before steaming without risk of deterioration.

These auxiliary agents will be discussed and the effect they produce pointed out. These agents may be divided into three groups: (1) Solvents and hygroscopic agents; (2) substances which increase fixation, or shorten time of ageing; and (3) dispersing agents, and other substances which improve levelness and stability of the prints.

Naturally, the distinction between the groups cannot be rigorous, as many compounds act in more ways than one. For example, hydrotropic substances not only assist in fixation, but also act as dispersing agents in the print paste.

Solvents and Hygroscopic Agents. Glycerin, being highly hygroscopic, has proved efficient under poor steaming conditions (dry and superheated steam). Its addition to the print paste however, can be considered as a preventive measure only, for by controlling steam conditions far greater quantities of water can be condensed on a fabric than glycerin might accumulate by its hygroscopic property. It can be assumed, however, that glycerin improves the solubility of the leuco compound and thereby facilitates the penetration and fixation of the dye. The use of polyglycerol for this purpose was proposed in *G.P. 578,821* (I.G.). Glucose and acetine are also suitable (*Rev. Gen. Mat. Col.*, **1924,** 316).

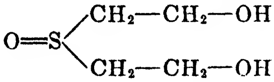
Thiodiethylene glycol was recommended in 1919 as printing assistant (*G.P. 339,690, B.P. 147,102, S.P. 159,928, F.P. 711,869*—Newport Chem. and *G.P. 713,460* I.G.). The compound was used in the first World War as an intermediate in the preparation of Yperite, dichloroethylene sulfide. It is readily prepared by the action of sodium sulfide on ethylene chlorohydrin at 90 to 100°C, according to the equation:

$$2\ \begin{matrix}CH_2-Cl\\ |\\ CH_2-OH\end{matrix} + S\Big<\begin{matrix}Na\\ Na\end{matrix} \longrightarrow S\Big<\begin{matrix}CH_2-CH_2-OH\\ CH_2-CH_2-OH\end{matrix}$$

(B.p. 282°C)

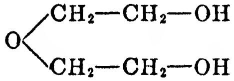
Thiodiethylene glycol was found to have a particularly good solvent action for dyestuffs, especially basic colors. At the present time it is frequently used in the printing of vat dyestuffs in order to obtain fuller shades, to obtain more uniform and level prints and to facilitate reoxidation. The chemical is sold under many trade names, as Glyecine A (G.D.C.), Kromfax Solvent (C.C.C.C.), Neocotone Solvent II (Ciba), Dehapan GB (D. & H.), Brecolane NCI (Kuhlmann), etc. It is a viscous liquid, miscible with water, and with a sweet, penetrating odor. Contact with hydrochloric acid must be avoided.

Its oxidation product is thionyldiethylene glycol



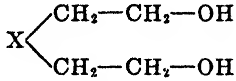
which is recommended for increasing the yield of vat prints (*S.P. 170,425*, *G.P. 591,547*, *U.S.P. 1,968,926*).

Diethylene glycol,



(B. p. 245° C, Sp. Gr. 1.12)

a product of the Carbide and Carbon Chemical Corp., is made by the action of ethylene oxide on glycol. It is miscible in all proportions with water. This vat printing auxiliary has found extensive application because of its good solvent and hygroscopic properties.* A patent covering its use as a printing assistant was granted Du Pont (*U.S.P. 2,047,650*). Other patents cover its use in the manufacture of dyestuff pastes, as *S.P. 157,912–3* and *B.P. 368,910*. The latter, issued to Newport Chem. Corp., describes the application of ethers and thioethers of the general composition:



where X = S or O, thus covering all glycols and thiodiethylene glycol.

Other names for diethylene glycol are Polyglycol (I.G.) and Brecolane NDG (Kuhlmann-Francolor).

The polymerization of glycols using ethylene glycol and suitable catalysts may be carried further, producing triethylene glycol, nonaethylene glycol, and such high polymers as the wax-like compounds known as Carbowaxes (*U.S.P. 2,293,863*-C.C.C.C.; also *G.P. 597,496*, *613,261*, *616,428*). Triethylene glycol may be advantageously used as a printing assistant. The Carbowaxes can be used as sizing agents, slipproofing compounds, etc.

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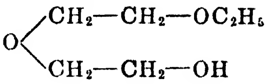
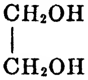
* *G.P. 340,552, 391,007; B.P. 392,139.*

Carbide and Carbon Chem. Corp. also produces the ethers of diethylene glycol. Carbitol is the ethyl ether



while Butyl Carbitol is the butyl ether. Carbitol (boiling point 200°C, specific gravity 1.02) is an excellent vat printing auxiliary. Other names are Fibrit D (Carbic Color) Débésol C (Lab. Zündel, Joliet).

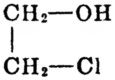
Glycol itself, or ethylene glycol is obtained on an industrial scale from natural gas. Ethane is isolated from the gas by liquefaction and fractional distillation. Catalytic dehydration of ethane at 750°C produces ethylene from which glycol is readily obtained.



$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

Glycol (B.p. 197°C, specific gravity 1.118) is a thick liquid with sweetish taste, and is miscible with water and alcohol in all proportions. It is a very good vat printing assistant. A mixture of glycol and ethylene chlorohydrin has been recommended as auxiliary to aid fixation and leveling (*F.P. 587,269*—Geigy, 1924).

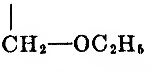
Ethylene chlorohydrin,



$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH_2\text{—}Cl \end{array}$$

is a water-miscible liquid, boiling at 132°C. It forms a constant boiling mixture with water. 42.5 Parts of ethylene chlorohydrin and 57.5 parts of water boils at 97.85°C.

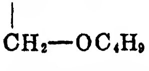
The ethers of glycol, also produced by C.C.C.C. are important solvents. Cellosolve is the monoethyl ether



$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH_2\text{—}OC_2H_5 \end{array}$$

(B.p. 135°C, Sp.Gr. 0.937)

while the butyl ether is called Butyl Cellosolve,

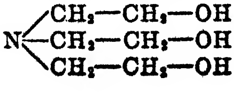


$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH_2\text{—}OC_4H_9 \end{array}$$

(B.p. 165–173°C, Sp.Gr. 0.899)

Other names for Cellosolve are Indigosol Developer GA (I.G.) Developsol GA (D. & H.).

The oxyalkyl amines, particularly triethanolamine,



have been proposed as pasting compounds for vat dyestuffs. As an addition to the printing paste, it improves the color yield of some colors, as Indanthrene Blue GCD and Indanthrene Grey 3B, but does not improve the yield in other cases, as Ciba Brown G (*B.P. 302,252, 324,315, F.P. 648,954*).

A method of printing vat colors, wherein the dyestuff is pasted up with triethanolamine and ferrous or stannous oxide is suggested in *U.S.P. 2,147,635* (Du Pont, 1938). The mixture is thickened with gum and potash, printed, aged and reoxidized as usual.

Use of triethanolamine to replace part of the alkali of the print paste is the basis of Ciba's *G.P. 555,305.* Other organic bases are also mentioned, as piperazine. When using such print pastes as resists under aniline black, halos are avoided (*B.P. 373,558, F.P. 729,412, U.S.P. 1,952,247*). The solvent action of ethanolamines in dyeing with vat colors is shown in *B.P. 295,025* (Du Pont—Kern). The addition of triethanolamine to the reduced vat gives more uniform dyeings, particularly with Indanthrene Blue GCD. In *B.P. 386,433,* triethanolamine is recommended in vat printing of wool to reduce the alkalinity.

Auxiliaries which Aid Fixation.

Anthraquinone Derivatives. A great deal of research has been done on this class of chemical auxiliaries. They offer advantages not only for preparing vat colors for the market, but also as additions to the print pastes. Anthraquinone itself is a hydrogen transferring agent and improves thereby the dyestuff's fixation.

Oxyanthraquinones have been found to increase color yield and to speed fixation in vat prints, especially 2,6- and 2,7-dioxyanthraquinones (anthra- and isoanthraflavinic acid). (*F.P. 727,605,* 1931; *G.P. 626,862; U.S.P. 1,970,644; B.P. 378,553, 349,955* and *S.P. 154,478* of I.G.—Berthold.) They are used in the following way: 4 gm Oxyanthraquinone are ground with 8 gm glycerin, and 50 gm water and 2 gm sodium hydrosulfite are added. The mixture, containing anthraquinone and reduced anthraquinone, is evaporated to 25% dry content. Sixty to 100 gm of this paste are added to 1000 gm of printing paste.

Further investigation has shown that the aminoanthraquinones work as well (*U.S.P. 1,970,649; F.P. 727,605, 727,727; G.P. 627,425; B.P. 350,963* —1931). Aryl sulfamide anthraquinones are proposed in *U.S.P. 1,990,854* and anthraquinone sulfonic or carboxylic acid in *B.P. 380,260; G.P. 627,468;* and patent addition *40,889* to *F.P. 727,727.*

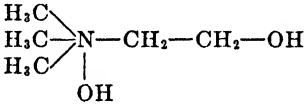
Other anthraquinone derivatives are mentioned in *G.P. 628,303* (I.G.—Berthold); *B.P. 456,357* (I.C.I.); *U.S.P. 2,024,973-5* (Du Pont).

The sulfo compounds of anthraquinone are here discussed; for instance, anthraquinone-2-mercaptan, or thiocyanoanthraquinoyl chloride.

A series of patents (*G.P. 626,262, 624,267–8,* and *627,425*) recommend reaction products of oxy- or aminoanthraquinones with aromatic sulfonyl chlorides.

Silver salt (β-anthraquinone sodium sulfonate) was proposed by Lichtenstein and Klein in *U.S.P. 1,919,792.* Recently the American Cyanamid Co. patented the use of arylamine (as aniline) salts of anthraquinone sulfonic (mono- or di-) acids (*U.S.P. 2,405,151*). Pastes to which these products are added yield fuller prints.

Choline and Its Derivatives. The use of quaternary ammonium bases in the preparation of vat dyestuff pastes has already been mentioned. According to *B.P. 385,606* and *U.S.P. 2,003,960* (I.C.I.), the addition of these compounds to the print paste has certain advantages. Especially recommended are the alkyl or aralkyl derivatives of choline.

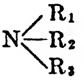


$(H_3C)_3N(OH)—CH_2—CH_2—OH$ (Oxyethyl trimethyl ammonium hydroxide)

Choline

Derivatives of Betaine. The following patents relate to the use of betaine derivatives in vat color printing: *B.P. 420,095, 446,265, 446,269, 446,337, 446,488; G.P. 671,996* (1934); *U.S.P. 1,929,784, 2,146,646; F.P. 795,417, 795,683, 729,304; Aus. P. 145,504–5.*

The use of betaine, and particularly the sulfobetaines, for fixing vat colors has been the subject of much research. One such investigation (I.G.—Berthold—Albrecht) shows interesting functions of these compounds. Sulfobetaines can be obtained by reacting an aliphatic sulfonic acid containing an exchangeable halogen atom, with a tertiary amine, of the general formula



$$N(R_1)(R_2)(R_3)$$

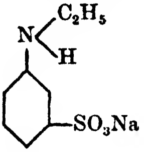
where R_1, R_2, and R_3 represent alkyl, aryl or aralalkyl groups. Examples of tertiary amines are trimethylamine, dimethyl laurylamine or dimethyloleylamine. The research work relates to all the aliphatic or aromatic-aliphatic sulfonic acids bearing a side chain of not more than eight C atoms. Examples given are 1-chloro-2-oxypropane-3-sulfonic acid and 2-chloro-3-butane-4-sulfonic acid.

Other betaines, which have been mentioned as suitable for preparation of vat dyestuff pastes, are also recommended as additions to the print paste (see page 10). Among these are the compound pyridinium β-oxypropane sulfobetaine and the alkali betaines. These compounds increase the dispersion of the vat color in the print paste, and improve the stability of the prints before ageing.

Hydrotropic Compounds. Hydrotropy has already been defined as the property of certain water-soluble compounds to dissolve otherwise water-insoluble substances in water. Since there are countless substances for which hydrotropic action has been indiscriminately and rather arbitrarily claimed, it is difficult to single out those which are important for vat printing purposes. Some of the more pertinent ones are here listed.

G.P. 626,626; B.P. 343,102, 343,527; and *F.P. 715,444* recommend the alkali salts of aminobenzene sulfonic acids, as sodium salts of dimethyl metanilic or dimethyl sulfanilic acid and homologous compounds (compare page 8). The sodium salt of dimethyl metanilic acid has been marketed under the name of Dinaton as a substitute for Solution Salt.

G.P. 626,627 mentions *p*-toluene sodium sulfonate as a hydrotropic agent. Alkali salts of sulfo- or carboxylic acid in general (benzene sulfonates, benzylsulfanilates) as the lithium salt of benzoic or α-naphthalene monosulfonic acids are recommended as hydrotropic products to be added to print pastes (*G.P. 626,811; S.P. 149,067*—I.G., 1929). The use of sodium salicylate, sodium *p*-chlorosalicylate or sodium-*p*-cresolate is disclosed in *G.P. 626,812* (1929). Ciba has investigated the effect of hydrotropic substances in *G.P. 622,355* (1934); *F.P. 793,926; S.P. 177,321;* and *B.P. 446,381.* Herein addition of 5% of salts of monoalkyl metanilic acid to the print paste is mentioned. The method is especially suited for improving the fixation of vat dyes of the halogenated indigo type, also Cibanone Orange and Cibanone Blue RS. The example given was the sodium salt of 1-monoethyl amino-benzol-3-sulfonic acid.

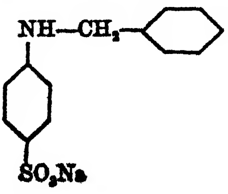


Alkali salts of hydroaromatic acids, for example, sodium salt of tetrahydronaphthalene-2-sulfonic acid, are disclosed in *G.P. 583,315,* and in *U.S.P. 1,987,583.*

Interesting results are obtained with aliphatic amine salts of certain organic acids. These give results comparable with Solution Salt.

Dispersing Agents. Dispersing agents, since they increase the stability of the dyestuff dispersion, also aid in penetration, leveling and fixation of the dyestuff.

Benzyl Sodium Sulfanilate. This product, with formula,



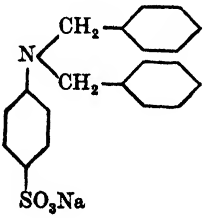
is marketed under various names, of which Solution Salt is the best known. The more specific trade names* are Solutions Salt B, and B, new, Sel dissolvant SB, S, NB, NBS, and B; Dissolving Salt B and B new.

It is a fine white powder, soluble in water (17 parts in 100 parts water) and widely used as a dispersing agent for vat dyes.

According to a study made by Lichtenstein and Peters, the migration of the dyestuff through the thickening agent is speeded up by the dispersing action of Solution Salt, and the absorption of the leuco compound by the starch paste is prevented. The yield and uniformity of the color are improved, and even in print pastes which do not contain starch, a better yield of color is noticed.**

It is claimed that more stable print pastes are obtained by substituting the soluble sodium salt of benzylsulfanilic acid by the insoluble salts of the acid. So, for example, in *B.P. 389,915*, *F.P. 727,605*, and *S.P. 157,312*, the use of the tin or benzidine salts, which are soluble only in hot water, is advocated. These compounds pose an interesting point. By their use with vat colors, the leuco compounds of the vat colors would not be considered as having formed in the print paste, but would have formed intermediate compounds which would be transformed into the leuco compounds in the presence of steam. When the soluble sodium benzylsulfanilate is used, it is possible that the leuco compounds are formed in the print paste, or on the printed goods before ageing, with unavoidable loss in depth.

Compared to the monobenzylsulfanilate (Solution Salt) the dibenzylsulfanilate has superior dispersing properties (*B.P. 421,606*).



Commercial benzylsulfanilate contains small amounts of the dibenzyl derivative.

The triethanolamine salt of benzylsulfanilic acid is especially useful for obtaining uniform prints. It is manufactured by Lab. Zündel, Joliet, under the names Débécuvol A and C.

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* See page 148.

** Peters: *Frb. Ztg.*, **1912**, 134 and 436; *Rev. Gen. Mat. Col.*, **1913**, 27; **1912**, 214.

Lichtenstein: "Ueber die Wirkung von benzylsulfanilsaurem Natron in Druckfarben" (The Effect of Benzylsulfanilate of Sodium in Printing Colors), *Frb. Ztg.*, **1912**, 205; *Öst. W. u. L. Ind.*, **1912**, 313.

Haller: *Frb. Ztg.*, **1913**, 22; **1914**, 8 and 76; *Frb. Ztg.*, **1910**, 333; **1912**, 444; **1913**, 22 and 442; *Aus. P. 33,611*; *B. P. 27,742*, A.D. 1908 (Bayer).

Protein Degradation Products. Certain degradation products of albuminoid substances, called lysalbinic or protalbinic acids, are produced by acid or alkaline hydrolysis of proteins.* According to Lichtenstein (*Frb. Ztg.*, **1913,** 21) the sodium salts of these acids have a dispersing effect similar to Solution Salt. They are also able to prevent adsorption of the leuco compounds by starchy thickeners.

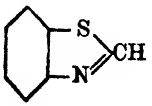
The same nomenclature for these proteinaceous products is used in the patent literature on the manufacture of Lamepon and Egalisal, which are condensation products of the proteins (*U.S.P. 2,119,872, 2,015,912,* Landshoff & Meyer).

The action of ethylene oxide or butylene oxide on casein, glue or other protein results in formation of oxyalkylated albumenoids. These compounds are water-soluble, and because of their good dispersing property are able to facilitate penetration of vat colors in printing and dyeing (*G.P. 562,889*—1931).

β-Naphthol. It was observed as early as 1907 that vat and sulfur dyestuffs gave better yield when printed on cloth prepared with β-naphthol (*F.P. 383,583; G.P. 209,429,* Badische A.S.F.). In order to avoid preparing the goods, Aubert recommended addition of the naphtholate to the print paste (*Bull. Mulh.*, **1909,** 476). Preparation of the goods before printing with β-naphthol is at once an advantage, since the cheap Azo red and Azo orange can be printed alongside the vat colors (see M. Richard, *Bull. Mulh.*, **1923,** 386). It was brought out, however, that it was difficult to obtain a pure white on goods which had been prepared with β-naphthol and aged or steamed. M. Richard later changed to another process, wherein he applied the naphtholate in a stipple-pad process before ageing (*Bull. Mulh.*, **1925,** 94).

The use of sodium naphtholate as substitute for stronger alkalis in the printing of wool was proposed by Ciba in *F.P. 753,141.*

Benzothiazoles. In *U.S.P. 2,024,502,* I.G.—Berthold recommend the addition of mercaptobenzothiazoles or mercaptobenzimidothiazoles



Benzothiazole

to the print paste in order to obtain stability and increased depth of shade. About 40 gm of the product is added to 1000 gm of print paste. The advantage is said to lie in greater stability of the prints, allowing longer storage of printed goods before ageing (*F.P. 785,822; G.P. 633,103*).

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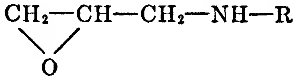
* *G.P. 120,031, 132,322* (Kalle-Paal).

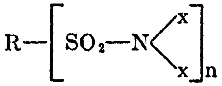
Derivatives of Epichlorohydrin. A process for increasing the color yield of vat colors in printing is described in *U.S.P. 1,977,250-1-2-3* and *B.P. 438,523* of Du Pont. Addition is made of reaction products of epichlorohydrin with ammonia, an amine or an alkylene diamine. The formula for products so obtained is



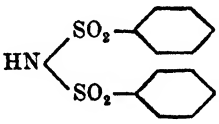
wherein R is H, or alkyl or aryl group. Compare *U.S.P. 1,977,272* (Gubelmann).

Heavy Metal Salts. Small quantities of the salts of heavy metals have the property of increasing the depth of shade of the indigoid vat dyes (*F.P. 702,019; G.P. 623,713; B.P. 364,052* and *361,350; G.P. 630,391; S.P. 150,891*—I.G.).

*Sulfamides.** *G.P. 623,751, U.S.P. 2,029,999, F.P. 775,617, S.P. 172,340* of Ciba-Grieshaber, 1934, relate to sulfamides of the general formula



where R is H or an alkyl group and X is H or a radical which does not contain COOH. Examples given are alkylsulfamides, methyl-4-phenyl sulfamide (*p*-toluene-sulfamide), amidophenyl sulfamide, 1-oxynaphthalene-8-sulfamide, diphenylsulfamide:



The quantity necessary in print paste is 60 to 80 gm per 1000 gm.

Glucamines. Sugar derivatives containing nitrogen, such as the glucamines, have a noticeable effect on the color yield of the vat colors in printing. *F.P. 783,093, U.S.P. 2,073,116,* and *B.P. 449,171* mention glucamines such as methyl glucamine, benzyl glucamine, and recommend the addition of 40 gm to 1000 gm of print paste.

Fatty Acid Condensates. In *F.P. 727,885* 1931, *G.P. 564,778* (I.G., 1930), it is suggested to add condensates of chlorinated fatty acids with hydroxyaromatic compounds (as sodium salts of hydroxyphenyl acetic acid or cresoxyacetic acid) to printing pastes. The yield of vat and sulfur colors is said to be increased, especially in the presence of a polyalcohol.

Sulfite-Cellulose Waste Liquor. References: *G.P. 229,191* (Badische A.S.F.); *S.P. 148,451; F.P. 681,566* (Ciba); *G.P. 313,840; Frb. Ztg.*, **1911,**

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* See footnote page 13.

358; *Z. f. Frb. Ind.*, **1911,** 45, *Z. f. ges. Tex. Ind.*, **1911,** # 23; *Bull. Fed.*, **1,** 132; *Mell.*, **1921,** 353; **1930,** 610; **1932,** 546.

Sulfite-cellulose liquor makes an interesting dispersing agent which has been found useful in dyeing and printing processes and in the dispersion of vat dyestuffs. It is a by-product of paper manufacture. The sulfite lye used in paper making is prepared by saturating a lime solution with sulfur dioxide. In the treatment of the woodpulp, about 12% organic substances are dissolved, of which 1.5% are polyoses, *i.e.* bioses of the sugar type, but the major portion consists of monoses of the lignin type which are present as lignin sulfonates. The raw lye is separated (calcium bisulfite). The remaining waste liquor has as active ingredients sodium lignin sulfonate mixed with glucose, gums and tannins.

Sulfite-cellulose waste is readily soluble in water and generally applied in the form of a 50% solution. It has remarkable dispersing properties and prevents the coagulation of calcium salts of fatty acids in dyeing and scouring operations. It has a retarding effect on the absorption of vat dyestuffs by the fiber, thus improving penetration and leveling of the colors, especially in light shades. Moreover, since sulfite-cellulose waste is a protective colloid, it lessens the action of alkalis on animal fibers.

Formaldehyde Condensation Products. Condensation products of formaldehyde with phenol or with urea have been recommended as printing auxiliaries, in *G.P. 237,368* and *239,336* (*Fischer's Ber.*, **1911,** 452; *Chem. Ztg.*, **1911,** 500, 656). In later patents other resins were recommended, and the field extended to cover condensation products of urea with aldehyde-ammonia, aldolammonia or with aliphatic aldehydes in general (*S.P. 156,726; G.P. 562,382; U.S.P. 1,909,221; B.P. 366,524; F.P. 724,771*). The same problem was handled in *S.P. 159,034–5–6*. It was proposed to use these resins as auxiliaries in the print paste, but results have not proved them practicable.

B.P. 399,533 (Bedford) recommends condensates of formaldehyde and cresol as printing assistants. It was found that vat dyestuff penetration was aided by the addition of condensates of aldehyde and triethanolamine (*G.P. 562,382*).

U.S.P. 1,856,434 and *G.P. 543,462* (I.G.—Schmidt) state that condensates of urea with alcohols, such as butanol, or with acid esters improve the stability of vat pastes. In another patent it is proposed to increase the color yield of anthraquinoid vat dyestuff prints by adding condensates of urea with certain amines. Alkyl urea is mentioned as an example of one component, and reaction products of ethylene oxide on ethylene diamine or *p*-phenylene diamine as the other. The printing paste is prepared by first pasting the vat dyestuff with the resin condensates, then mixing with the printing gum. It is claimed that the color yield of prints is substantially improved, especially on viscose rayon (*F.P. 821,750*).

Urea. Urea possesses both hydrotropic and solvent properties. Urea also has hygroscopic properties, and aids and speeds reoxidation. Ciba studied these qualities[*] and found that addition of urea to the print paste increased the color yield of many vat colors. They particularly recommended adding the urea to the thickening containing potash, pasting with the dyestuff and then adding the Hydrosulfite NF. Urea seems to be most efficient in those cases where the leuco compounds are sparingly soluble, as with Ciba Brown G (Brown RRD) Ciba Brown 2B, Indanthrene Grey 3B, and with blacks generally. It is found that uniformity of prints is maintained and mark-off in washing minimized. Ciba offered urea under the trade name Intensifier Ciba, which they recommended to be added to the print paste in the ratio of 80 to 100 gm per 1000 gm of print paste.

Organic Boric Acid Esters. The addition of compounds of this class has the effect of improving color yield under poor steam conditions (*B.P. 367,240*, Sandoz). The boric acid ester of glycerin is marketed under the name Liovatin FL by Sandoz. It has proved to be a good dispersing agent for Sandothrene Golden Orange NG, to facilitate reduction and therefore improve fixation of the dyestuff. Liovatin FL is a viscous liquid, colorless and odorless, and easily miscible with water. It is suggested that 20 to 25 gm per 1000 gm of printing paste be used. No noteworthy effect has been observed with many indigoid vats, however.

Organic Phosphates. Water-soluble salts of a phosphoric acid ester are recommended as vat print paste additions in *B.P. 508,554* (1939). The ester should contain an aliphatic or cycloaliphatic radical of at least six C atoms. One such phosphoric acid ester is mentioned, obtained by the reaction of phosphoric anhydride with heptanol. The product is added to the print paste with some butanol and glycerin.

Difficultly soluble or insoluble esters of phosphoric acid are also recommended, such as tributyl phosphate, triphenyl phosphate, tricresyl phosphate and triisobutyl phosphate (*G.P. 713,902*, *F.P. 863,256*—I.G, 1938); These compounds are also used as defoaming agents, and mention can be made of a product of the I.G., called Etingal, which was a mixture of 87% triisobutyl phosphate and 13% isopropanol.

Other Auxiliaries. A new vat printing assistant was proposed in *S.P. 184,008* (I.G.). It is a condensate of urea and the compound formed by the reaction of propylene oxide with ethylene diamine, having the formula:

$$H_2N—CH_2—CH_2—NH—CH_2—CH_2—CH_2—OH$$

The constitution of the condensate was not determined.

Compounds of the general structure,

$$R_1—CO—R_2$$

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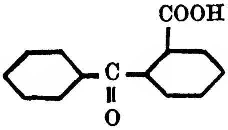
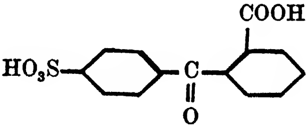
[*] *F.P. 681,566* (1924), *731,270; U.S.P. 1,835,926; G.P. 570,583.*

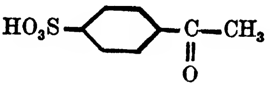
are disclosed as vat color assistants in *U.S.P. 2,074,150* (N.A.C.), R_1 representing an aryl group and R_2 a carboxylic acid or sulfonic acid of low molecular weight. As examples, ketonic compounds like the following are mentioned:



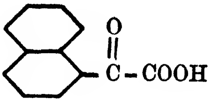
o-Benzoyl benzoic acid



p-Sulfo-o-benzoyl benzoic acid



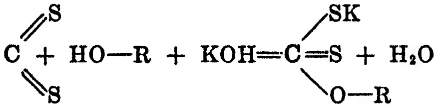
Acetophenone-p-sulfonic acid



α-Naphthoyl formic acid

According to *U.S.P. 2,069,215* (Du Pont), it has been observed that salts made from alkali or organic bases and fatty acids of six to twelve C atoms exert a noticeable effect; for example, the 1,3 dimethyl valerianic acid salts, also methyl or 1,3-dimethyl caprylic acid salts. These acids are obtained by treating synthetic alcohols having branched chains by the caustic dehydrogenation process (*U.S.P. 1,886,263*). Further work has elicited the information that branched fatty acids, having side chains linked to main aliphatic chains of four to six C atoms, are suitable as vat print assistants (*U.S.P. 2,079,788*, Du Pont).

In *S.P. 192,013* Ciba claims that better yield of vat colors is obtained by adding to the print pastes soluble xanthogenates, obtained by the reaction of carbon bisulfide with alcohols or oxyaromatic compounds in alkaline solution. As an example, isobutyl alcohol is dissolved in alkali and treated with an ethereal solution of carbon bisulfide (1:1). The result is potassium salt of isobutyl xanthogenic acid,



$$C{\overset{\textstyle\nearrow S}{\underset{\textstyle\searrow S}{}}} + HO{-}R + KOH = C{\overset{\textstyle\nearrow SK}{\underset{\textstyle\searrow O{-}R}{=}}}S + H_2O$$

where R is the isobutyl radical.

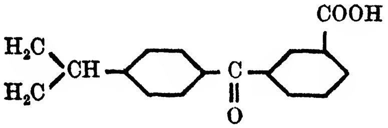
As vat printing auxiliary, Dow Chem. Co. recommends (*U.S.P. 2,101,828*) hydrogenated phenols, such as cyclohexanol. These compounds seem especially suitable for use with indigoid vat dyestuffs.

Condensates of urea with bases such as polyamines, polyethylene diamine or ethoxyethyl ethylenediamine are described in *B.P. 443,426* and *U.S.P. 2,117,623* as applicable in this field.

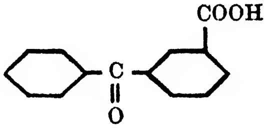
U.S.P. 2,110,081 of I.C.I. recommends soluble salts of anthraquinone sulfonic acids or sulfaminic acids, for printing indigoid and thioindigoid vat dyestuffs. As examples, the following are given: anthraquinone sulfonic acid, anthraquinone sulfaminic acid, hydroxyanthraquinone sulfonic acid ester. Sulfonation is carried out with sulfuric acid anhydride in pyridine solution.

According to *B.P. 479,847* (Du Pont), sulfates of primary or secondary aliphatic alcohols, having six to twelve C atoms are leveling agents for vat colors, and also for Indigosols. The alcohols are obtained from fractions of synthetic methanol production and especially those containing primary alcohols of six to ten C atoms and those with secondary alcohols of seven to ten C atoms.

Salts of organic ketocarboxylic acids are described in *S.P. 195,626* (Ciba) as agents suitable for pasting vat dyestuffs as well as additions to the print paste. Examples are levulinic acid, or the following (compare *F.P. 833,100*):

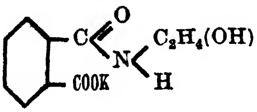


Cymene benzoic acid



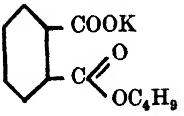
Benzophenone carboxylic acid

Further, Ciba recommends (*B.P. 429,929*) the use of water-soluble salts of carboxylic acid esters or sulfocarboxylic acid esters; for example, potassium salt of isobutyl phthalic acid or ethyl phthalic acid; also salts of carboxylic acid amides, substituted on the N atom, as N-hydroxyethylene phthalic acid amide.



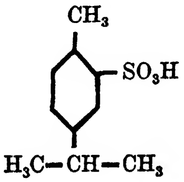
This potassium salt proved effective with Ciba Brown G, Cibanone Blue 3G and Cibanone Golden Orange G.

Phthalic acid derivatives aid in producing superior color yield when used as vat dyestuff pasting assistants or when added to the print paste. Ciba's *F.P. 813,856*, *S.P. 187,407* and *G.P. 694,312* (*Mell.*, **1941**, 296) describe the application of water-soluble salts of carboxylic acid monoesters or monoamides, having water-solubilizing groups such as COOK or KSO_3. For example, potassium salt of monoisobutyl phthalic acid;



obtained by reaction of phthalic anhydride and isobutanol at 80 to 85° for 20 hours, and potassium salt of isopropyl phthalic acid ester or potassium salt of phthalic acid monophenylamide.

In connection with this work an analogous application of alkali salt of cymene sulfonic acid is recommended



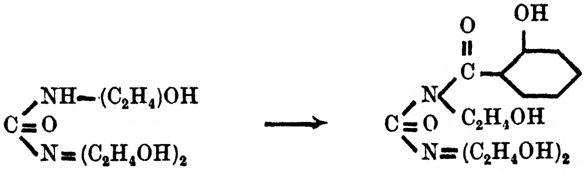
as well as its organic base salts (*B.P. 486,445*). The sodium salt of chlorocymene sulfonic acid can be used as printing assistant, by adding 5% to the print paste. It is obtained by chlorinating cymene in the presence of iron, followed by sulfonation.

Leveling agents which also intensify vat print colors, are disclosed in *U.S.P. 2,128,599; S.P. 190,599, 190,600.* These are the water-soluble salts of aromatic monosulfonic acids of aliphatic compounds having at least three C atoms. The potassium salt of sulfuric acid esters of hydrogenated cresol is named as example. These patents also cover the use of cymene sulfonic acid salts, mentioned above.

Carrying this research further, Ciba describes the preparation of a quaternary salt, by forming the methylester of cymene sulfochloride by treatment with methanol in alkaline solution, and finally combining it with pyridine. Adding 5% of this product to the print paste improves the yield of such vat colors as Ciba Brown G and Cibanone Blue 3G. (*S.P. 200,662*).

F.P. 833,100 of Ciba recommends the water-soluble salts of ketocarboxylic acids (of the aliphatic, aliphato-aromatic and aromatic series) as textile auxiliaries for vat prints. Examples are benzoyl acetic acid, cymene benzoic acid, etc. These agents are used in the ratio of 5% per kg printing paste.

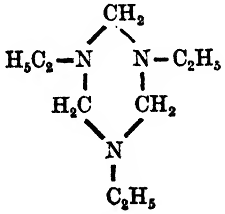
F.P. 883,197 (Rosenthal A.G.) proposes as an assistant for vat printing, as well as for acetate color prints and for white discharges, the compound formed by the reaction of salicylic acid and triethanol urea, according to the formula:



Triethanol urea

The condensate is a thick brownish liquid, resistant to organic acids but readily decomposed by mineral acids. Its effect is due to dispersing action of urea and urea derivatives, while for acetate it has a swelling action.

F.P. 835,148 and *B.P. 491,896* (I.C.I.) propose adding 3 to 4% of an alkylated trimethylene triamine to the printing paste of anthraquinoid vat dyestuffs. Such dyes as Caledon Blue R, 3G and RCS, being difficult to fix without the use of strong alkalis, can be printed with such organic bases; for example, triethyltrimethylene triamine:



One of the main advantages is the possibility of printing rayons with reduced alkalinity. The specifications consider also other substituted compounds as tribenzyltrimethylene triamine, and the use of these compounds in manufacturing dyestuff pastes and fine powders.

According to *U.S.P. 2,173,824* (Du Pont, 1939) an addition of benzyl alcohol and a sulfonated auxiliary product, as, sodium salt of sulforicinoleic acid or medium-high alkyl sulfate containing six to twelve C atoms, has proved to be an efficient printing assistant.

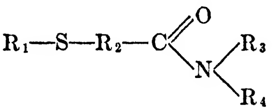
Sandoz suggests (*F.P. 822,739*) for this purpose the use of aliphatic amines containing OH groups. The examples name a condensation product of one molecule of α-γ-dichlorohydrine of glycerin and two of ammonia or of primary, secondary, or tertiary amine. It is emphasized that even very difficultly leveling vat dyestuffs, such as Sandothrene Violet N2R or Sandothrene Blue NRSC, dye uniformly on mercerized cotton in light shades, which can be explained only by excellent penetration of the leuco compound. Description of further improvement of this process can be found in *U.S.P. 2,155,135* (Sandoz-Kartaschoff) in the section on Dyeing, p. 131.

Better color yield, increased penetration, and uniformity are claimed for prints with such difficult vat dyestuffs as Indanthrene Blue GCD and RS when water-soluble polyalcohols are added (*B.P. 562,479*—I.G.). Vat colors and basic colors show improved fixation with the use of tetrahydroxy-octane, obtained by reduction of the corresponding aldol, according to the equation

$$\underset{\textit{Aldol}}{CH_3—[(CHOH)—(CH_2)]_3—CHO} \rightarrow \underset{\textit{1,3,5,7-Tetrahydroxyoctane}}{CH_3—[(CHOH)—(CH_2)]_3—CH_2OH}$$

Sodium salts of products having the general formula R-X-A, where R is alkyl or benzothiazol group, X is O or S and A is an organic or inorganic residue, are recommended; for example, sodium salt of dibenzylthioglycollic acid (*U.S.P. 2,174,486*-DuPont).

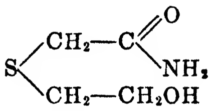
Ciba (*B.P. 514,078*) observes that amides of the formula



R_1 = alkyl or hydroxyalkyl
R_2 = alkylene
R_3, R_4 = H, alkyl or hydroxyalkyl

increase the affinity of vat colors when added to the print paste. An example is glycollic acid amide.

U.S.P. 2,184,495 (Ciba) in similar manner recommends the addition of auxiliary agents of the type of ethanol thioglycollic amide:



U.S.P. 2,327,405 (I.C.I.) recommends as auxiliary agents for printing halogen-containing indigoid and anthraquinoid dyestuffs, iron phthalocyanine, *i.e.* iron-organic pigment dyestuffs obtained by *o*-cyanobenzamide with metallic iron at 250°C.

B.P. 571,274 (Amer. Cyanamid Co.) states that better results in printing vat dyestuffs can be obtained by adding small quantities of aliphatic polycarboxylic sulfonated acid esters of the Aerosol type, for instance di-isobutyl sulfosuccinate of sodium.

Vat Color Prints on Wool or Silk

The desire for fast color prints on wool and silk has led naturally to a study of the possibility of using vat colors, but the danger of tendering with the strong alkalis necessary has been an obstacle. Despite a considerable number of patents issued in this special field, the problem has not been entirely solved.

The I.G. developed a process to avoid tendering of the animal fibers by the addition of 2½ to 5% of sodium aminoacetate to the regular potash-Hydrosulfite NF print paste. The patents covering this protective addition were issued in 1932: *B.P. 394,632; U.S.P. 1,990,852; G.P. 583,533, 591,476; F.P. 753,141; S.P. 167,489.* The quantity of potash can be considerably lessened when printing the animal fibers in the presence of the aminoacetates, and the recommended quantity is 75 gm per 1000 gm, instead of the 120 to 150 gm usually employed.

In place of the expensive aminoacetic acid salts, Dr. Diserens found that they could be substituted with aminosalicylic acid. This product is an intermediate in the manufacture of Diamond Black F. Aminosalicylic acid is obtained by the reduction of nitrosalicylic acid, the reduction yielding both the *p*- and *o*-acids, the mixed acids being added directly to the print paste.

Further, the partial or complete substitution of the alkali carbonate by other bases has been attempted, as in *F.P. 763,509* (1933) and *S.P. 166,186* (Ciba). The suggested bases are alkali salts of hydroxy compounds, as glycollic acid, lactic acid, phenol or β-naphthol. The reduction of the dyestuff can be aided by catalysts, for example, anthraquinone or its sulfoderivatives, or salts of Fe, Ti, Cu, Ce. In an example given, all of the potash has been replaced, and part of the Hydrosulfite NF.

450 gm	British gum thickening
125 gm	Ciba Blue 2B paste
125 gm	sodium glycollate
100 gm	glucose
90 gm	dioxyanthraquinone 20% paste
85 gm	water
25 gm	Hydrosulfite NF
1000 gm	

The best results are obtained with phenolates or naphtholates. The process of Lichtenstein and Klein, mentioned previously, wherein glucose and "silver salt" are used, should work well on animal fibers, although the patent does not specifically refer to the fiber.

B.P. 386,433 (I.G.) proposes replacing the Hydrosulfite NF with glucose and the carbonate alkali with ammonia, sodium phosphate or triethanolamine. Bayer Co. suggested sodium stannate as a replacement for the alkali (*Frb. Ztg.*, **1912,** 480; *Öst W. u L. Ind.*, **1912,** 401), while according to *G.P. 486,488* (I.G., 1925) the caustic or carbonate alkali should be replaced with sodium phosphate or sodium aluminate.

U.S.P. 1,967,569 (Du Pont) suggests a method which treats the problem from an entirely different angle. Compounds are added to the print paste which release acids during the ageing, in order to partially counteract the effect of alkalis on the fiber. The example cites the addition of 10% formamide. The effect of the acid on the fixation of the leuco compound is not explained.

Ethylene diamine or its homologs as substitute for at least part of the alkali of the print paste, is the subject of *F.P. 817,585* (I.G.). Typical formula of the print paste is:

200 gm	vat dyestuff in paste
80 gm	glycerin
50 gm	water
440 gm	starch-trag. thickening
150 gm	ethylenediamine
80 gm	Hydrosulfite NF
1000 gm	

A process for printing wool with vat dyestuffs has been described in *U.S. P. 2,085,145* (Du Pont) which involves preparation of a dry leuco salt. The dyestuff is first reduced with alkali and hydrosulfite, then neutralized with hydrochloric acid and salts of alkaline earth metals or heavy metal salts ($CaCl_2$ or $FeCl_3$). A sparingly-soluble salt of the leuco compound results, which is dried and pulverized. This is added to the print paste containing carbonate alkali, or sodium phosphate, thus forming ferric phosphate and the alkali salt of the leuco compound. In this way a print paste free of alkali and without reducing agent is employed, minimizing danger of fiber attack. The formula is 200 parts of salt of the leuco compound, 400 parts of thickening, 100 parts of potash and 100 parts of diethylene glycol.

The alkali of the regular vat printing formula may be substituted by amines of the aliphatic series containing at least two basic N atoms, for example by polyethylene diamines. These polyethylene diamines have the constitution:

$$H_2N—(CH_2—CH_2—NH)_n—CH_2—CH_2—NH_2$$

Printing pastes prepared with these amines give brilliant results and good color yield, while the fiber is protected from the harmful effect of free alkali. *B.P. 471,808, U.S.P. 2,126,964, G.P. 692,895* (1936, IG-Kerth).

Similarly, the condensates of urea with the products formed by the reaction of alkylene oxides on ethanolamines, can be used for the same purpose (*B.P. 443,436*).

A process based on an entirely different principle has been recommended in *F.P. 793,141* (I.G.) for printing animal fibers, or mixtures of animal fibers with vegetable fibers. By this method, Rapidogens can be printed alongside vat colors. It is assumed that the animal fibers can adsorb the free acid enolate of the dyestuff, as vegetable fibers adsorb the alkali salt of the leuco compound. The printing paste contains for instance, 100 gm dyestuff paste, 100 gm Hydrosulfite NF, 50 gm tartaric acid and 25 gm betaine or a derivative thereof per kg. The dyestuff is said to be fixed by ageing, the "acid vat" being the intermediate transformation compound which is adsorbed.

The use of the acid-vat is also mentioned in *U.S.P. 2,045,476-7* (I.G.). A stable reduced compound in paste form is prepared by gradual neutralization of the vatted dyestuff with acids. The printing paste, however, contains potash and Hydrosulfite NF as usual. The method is recommended particularly for dyestuffs of the halogenated thioindigoid groups.

Replacement of the alkali carbonates by ammonia and alkali sulfite is recommended by Grossheintz (*Bull. Mulh.*, **1913**; *Frb. Ztg.*, **1913**, 420). His formula was 200 gm vat dyestuff paste, 100 gm ammonia 10%, 100 gm potassium sulfite 45°Bé and 200 gm Hydrosulfite NF per 1000 gm.

The substitution of the alkali carbonate by ammonia, ammonium carbonate or bicarbonate is mentioned in *G.P. 291,995* (1917, Kalle).

F.P. 765,960 (Rhodiaceta) replaces the alkali of the printing paste with magnesium hydroxide. This formula is also useful when printing acetate cellulose to avoid saponification of the fiber.

The addition of ammonium monochloroacetate to the printing paste is recommended by Ciba in applying vat colors on wool or wool-mixed fabrics. The product is offered for sale by Ciba under the name Albatex L. It may be prepared by neutralizing monochloroacetic acid with ammonium hydroxide. The printing paste should contain 4% of this protective agent. It has also been noticed that addition of this product to the printing paste prevents pre-reduction of the vat color (R. C. Geering).

Ageing

The ageing of vat dyestuffs is the most important and critical operation in the process of vat printing. Every colorist has had the problem in his own shop, and has had to study this matter, which at first glance might appear to be a routine treatment. It is no exaggeration to state that the ageing problem has been only partly solved in all its practical and scientific aspects.

The ageing process is an important function of vat color printing and the most delicate operation in their fixation. Thus it is surprising to note that this question has received little attention until recently and that systematic research has not been applied to its study. Of course it must be admitted that the problem is complicated by many unknown factors. Intimate cooperation of experts in the fields of chemistry and thermodynamics is an indicated prerequisite, a condition hardly to be achieved in the customary printing shops. Certainly the knowledge of thermodynamics possessed by the average chemist-colorist would not be sufficient for a thorough research in this field. The ageing problem therefore remains unsolved, the chemist generally contenting himself with making adjustments which his local conditions seem to require.

The ageing process is of critical importance because various reactions of entirely different kinds must proceed under optimum conditions. These reactions are reduction of the vat dyestuff into its enolate form—that is, the soluble leuco compound, the solution of the leuco compound in water condensed on the fiber, and the absorption of the leuco solution by the fiber. Thus ageing may be considered a local dyeing operation, carried out in a highly concentrated solution, at a temperature in the neighborhood of 100°C, in water which is obtained by condensation of the steam.

In order that these steps of reduction, solution and fixation should proceed under the best possible conditions, in the necessary medium of condensed steam, the steam must be superheated as little as possible, so that it will condense upon contact with the fabric surface. But some superheat must be maintained to prevent water spots.

A fabric which has been aired and well cooled offers the ideal preliminary conditions for a uniform and regular condensation, while a well-controlled steam supply, and proper steam conditions in the ager complete the essential requirements for fixing vat color prints. Unfortunately, all these important conditions are almost impossible to achieve in practical work. It is thus necessary to insure an adequate condensation by the use of hygroscopic agents and solvents. The addition of these agents acts as protection against dry steam conditions and over-dried prints.

The reduction of the dyestuff is the first step in the train of operations which takes place in the ageing process. Since there is a substantial excess of reducing agent no difficulty should be expected here. Hydrosulfite NF begins to react in its reducing capacity at 80°C in the presence of water. However, the optimum temperatures for reduction of the vat dyestuffs lie in a range considerably below 80°C. Reduction is further facilitated by fine dispersion of the dyestuff, which condition can be assured by use of fine dyestuff pastes or micropowders, and by addition of dispersing agents added to the print paste.

An essential condition of reduction is the complete absence of air (oxygen in the air). This problem has been solved by the construction of the rapid ager, in that the steam enters the ager from the upper, rear portions, while the cloth enters and leaves the apparatus through a slit situated in the front end, and near the bottom. In front of the slit, a small chamber, connected with a steam pipe and filled with steam, is situated, which prevents the entrance of air into the ager. Provided that the ager is free from air when it is started, and that the steam intake is great enough to give good steam circulation and to maintain a slight excess of pressure over the external atmosphere, it will remain so.

In other systems, the steam is introduced from below, and along the entire apparatus, leading it off at the top, while the fabric enters from above and leaves again at the top. In another variation the steam is introduced through a distributing pipe extending over the upper part of the apparatus, and leading it off at the bottom, while the cloth enters and leaves through a slit near the bottom.

The solubility of the leuco compounds of the different vat colors varies considerably from type to type. In general, the solubility of the indigoid colors is better than that of the anthraquinoids. This difference can be noted in combination prints of colors from different groups, as of yellow and blue mixtures, which yield uneven green prints. The solubility depends on an adequate amount of dissolving liquid, in this case the water condensed on the fiber's surface. The printed fabric should therefore remain sufficiently long in the ager in contact with the condensed steam. When superheated steam is present the cloth can condense less water than in an atmosphere of saturated steam. Furthermore, the condensed water film takes considerably more time to revaporize in a saturated steam atmosphere, than in an atmosphere of superheated steam (see Dr. Gerber and P. Grünn, "Condensation of Print Gums in Ageing," *Mell.*, **1939,** 439).

The best conditions for ageing, it has been found, exist in steam which has had a maximum pressure of two atmospheres (30 lb) and has been allowed to expand in a tank before introduction into the ager. In this way steam is obtained in a nearly saturated state, becomes slightly superheated in contact with the hot plates of the ager as well as by the exothermic reactions taking place within the printing pastes. The ideal temperature is between 100 and 101°C, though this is almost impossible to attain in practice.

The influence of the hot plates in the top of the ager is very marked. Thermometers, placed at different parts of the ager, indicated that there is a region, amounting to about $\frac{1}{5}$ or $\frac{1}{4}$ of the total volume, where a temperature increase of 3 to 6°C can be measured. This abnormal condition can be helped by careful regulation of the temperature of the hot plates, but since there must be some degree of superheat in the plates to prevent water spots, another method is suggested in the design of an ager where the plates are placed sufficiently high above the rollers to permit the rollers to be below the overheated space.

The reactions taking place on the fiber are accompanied by considerable evolution of heat. An increase of 3 to 4°C in the temperature of an ager can be noted after passage of only 500 yards of printed cotton. For this reason the quantity of steam circulating through the ager must be increased to maintain the temperature at 101°C, or as near this as practicable.

An article by Dr. W. Hess discusses the phenomena occurring in ageing vat dyestuffs. The most important points of this publication (*Mell.*, **1942**, #7) are given here, because they are the results of experiences and observations made in many years of working together with Dr. Diserens and Zündel in the Scheurer-Lauth print plant in Alsace.

"The ageing of vat colors is based on two kinds of processes, namely, processes of a physical nature and those of a chemical nature. These processes, taking place at the same time, may work in the same direction or in opposite directions.

"(*A*) *Processes of Physical Character.* An adequate ageing operation of vat dyestuffs depends principally on the normal development of the physical conditions, which are as essential as the chemical reactions on the fiber. In order to obtain the best ageing effect, the optimum preliminary conditions of steam, fiber and printing paste must be present.

"*Fiber conditions:* After printing, the goods are led through the dry tower, or over cans. The goods are then piled in folds on trucks while still hot in such a way that circulation of air through the goods is impossible. The inner folds of the goods remain hot, while the outer parts along the selvages cool off relatively quickly. It thus happens that printed areas in the center of the goods may lie a comparatively long time in a hot condition, whereby part of the sulfoxylate formaldehyde necessary for reduction is destroyed. On the other hand, the printed portions along the selvages cool rapidly, and draw some moisture from the air. The reducing agent is not destroyed, and the moisture condensed on the goods aids in producing fullest yield from the prints in this part of the design.

"Furthermore, as the cloth is opened out preparatory to ageing, the hot dry portions can reabsorb the necessary moisture only slowly and incompletely, while the cooled areas have already absorbed a full amount of moisture. Every colorist has had the experience of seeing prints which showed fullest depth along the selvages, gradually becoming weaker toward the center of the cloth. The explanation for this is brought home more forcibly by a study of the total amounts of water which can be condensed on the goods. If the cloth is viscose rayon, it can absorb about 10% moisture in simple air circulation, but it may be able to condense an amount of moisture during the ageing process equal to half the weight of the rayon. The portions of the fabric which were dry before ageing can condense much less steam than those portions which were already cool. Thus the fixation of the prints is uneven across the goods from side to side.

"The best conditions are obtained by drying at the lowest possible temperatures, using a hot-air dry tower in preference to cans and piling the goods in as cool a condition as possible. Thereafter the goods should be aired over skying rollers, or through a cold, moist chamber, so that the prints can absorb a maximum amount of moisture. Fabrics which have been cooled by air passage can be stored for many hours before ageing.

"(*B*) *Chemical Processes.* The chemical reactions should proceed to normal completion, provided that the physical conditions mentioned above are adequately fulfilled.

"The print paste is gradually heated to 100°C in the ager. At 80° the decomposition of the sulfoxylate formaldehyde begins. Below 80°C the compound is stable, but upon reaching this temperature, decomposition begins, the products formed being sodium sulfoxylate, formaldehyde, and water. At this point the reduction of the vat color begins. The decomposition of sulfoxylate formaldehyde requires supplying of heat, because the heat of formation of the compound is positive, and its decomposition therefore is endothermic.

> "The reduction of the vat dyestuff is rapid, and is complete in ½ to 1 minute. This reaction takes place with evolution of considerable amount of heat. It can be interpreted as reduction of the dyestuff and oxidation of the sulfoxylate. Together with the reduction of the dyestuff, the absorption of the leuco compound by the fiber begins. This part of the process requires the longest time of any of the chemical processes involved, and uses most of the time of the ageing operation. It is doubtful whether the absorption and fixation of the enolate in the short time of ageing (5 to 8 minutes) is comparable to a dyeing operation such as the dyeing of cellulosic fibers with substantive dyestuffs. It is a question whether there may be other forces at work, such as osmotic pressure, or electric forces working to attract the leuco-compound molecule and the fiber.
>
> "The amount of water condensed upon the fiber must be sufficient for the process. In the first place there must be enough moisture to ionize the chemicals. Should there be an osmotic phenomenon, water is important for the absorption process, for the osmotic pressure is determined, in this case, by the ratio of the concentration of the leuco compound in the condensed water, which is zero at the start, to that in the printing paste, which is high. In other words, water condensed on the fiber's surface will attract the soluble salts in the printing paste, as well as the enolate, the printing paste acting as a semipermeable diaphragm.
>
> "Simple affinity of the leuco compound to the fiber cannot be the only reason for the absorption of the reduced dyestuff by the fiber. This is proved by the fact that vat dyestuffs printed according to the Colloresin DK method are absorbed as fast as colors printed with regular thickeners, although Colloresin is practically insoluble in alkaline medium, allowing very little mobility of the leuco dyestuff particles."

It is pointed out in *Am. Dyes. Rep.*, **16**, 33, that a lowering of the temperature takes place when Hydrosulfite NF is decomposed.

Schlatter states in *Am. Dyes. Rep.*, **26**, 154, that the following chemical reactions take place in the rapid ager. At the moment of entrance into the ager, two groups of reactions must be taken into account: (1) the reduction of the dyestuff by the Hydrosulfite NF and alkali, and at the same time the local dyeing of the fiber; (2) secondary processes such as condensation of steam and formation of an aqueous layer on the fiber, solution of the soluble salts, oxidation of the Hydrosulfite to bisulfite and decomposition of the leuco compound by over-reduction. The author asserts that the main reactions (1) take place without evolution of heat, while only the secondary reactions can cause local overheating.

It is necessary to subject the printed fabrics to an aerating and humidifying treatment before ageing to avoid topical overheating, and to keep the fabrics as moist as possible, *i.e.*, to condense as much water as possible on the fiber surface. The use of glycerin or other hygroscopic agents for this purpose in the print paste is recommended.

Most print shops find it necessary to pad the printed goods before ageing to eliminate doctor streaks, especially when printing vat colors as discharge on dyed grounds. The padding solution contains either hydrogen peroxide, or Ludigol, or both, in a thin gum medium. The padding may be carried out on the print machine with a stipple blotch, or on the three-bowl mangle, using only the upper two rollers. The goods are nipped face down against the middle bowl, which may have a fine stipple engraving for added effect. The same precautions of drying and laying-up in a hot condition must be observed here, as noted for drying of the prints.

M. Richard suggested (*Bull. Mulh.*, **1921,** 93) placing a two-roll padding mangle in front of the ager, the lower roller to be stipple-engraved copper. This roller dips into a thin tragacanth solution containing glycerin and 5 gm of sodium naphtholate per l. The excess gum is removed by a doctor blade. The fabric is thereby blotch-printed as it enters the ager, the object being to moisten it uniformly. The method was found suitable for shirting patterns, but some difficulties were encountered on thin fabrics.

Selection of the thickening agent plays a large part in the condensation effect, thickeners having a high dry content generally showing the best results. The more solids deposited on the fabric, the more heat is required to raise the temperature of the printed surface, and therefore the more moisture is condensed. Dr. Diserens recommends the addition of substances having a high specific heat to minimize variations of prints from variable steam conditions.

Using a direct steam line from the boiler to the ager, Dr. Reinking made a study of the optimum pressures at which the vat colors gave fullest prints (*Mell.*, Mar., **1927**). Assuming that the fixation of the vat color depends on the pressure and temperature of the steam used in the ager, he recommends a pressure of 4.5 lb as most suitable for the indigoid colors. Indanthrene Yellow G was most readily fixed, requiring only 1.5 lb pressure. The indigoid colors begin to fix at low pressures, have an optimum value at 4.5 lb, diminishing in strength above this pressure. Other colors behaving like the indigoids are Indanthrene Brown G, Golden Yellow GK, Pink IB, Violet RF, BF, and BBF. On the other hand, fixation of the anthraquinones does not proceed in the same way. At pressures of 3 lb no essential fixation takes place, but at 4.5 lb fixation proceeds quickly and completely. Beyond this pressure no further improvement is noted. It is Dr. Reinking's opinion that the anthraquinones are not fixed under certain steam pressures but that the indigoids are gradually fixed even in insufficient steam quantities. It was therefore his conclusion that a special steam supply should be available for the agers to avoid fluctuation of steam conditions.

An ideal solution of this problem is the Ruth steam accumulator, which compensates for variable steam supply.

The theory that vat color yield depends on steam pressure lacks persuasive power from a physical standpoint. Actually the only important point is the amount of moisture condensed on the fiber. The flow of steam has no other function than to maintain the ageing condition, which is an air-free steam as near 100°C as possible. The quantity of steam must be enough to compensate for overheating brought about by hot plates and exothermic reactions. So long as the quantity of water essential for the solution of the leuco compound is condensed on the fiber, the pressure of the steam supply is of small moment.

In a study of the physical conditions existing in an ager, Driessen finds the use of wet steam advisable (*Mell.*, Aug., **1928**, 670).

In order to clarify the terms used to describe the condition of the steam, the following is quoted from the "Engineering Encyclopedia" (F. D. Jones, Editor).

> "Steam is water changed to a gaseous form by the application of heat. It may be either *saturated*, *superheated*, *dry* or *wet*. *Saturated steam* is that which is in the presence of, and at the same temperature as, the water from which it was evaporated. There is always a definite relation between the pressure and temperature in the case of saturated steam. For example, saturated steam evaporated under atmospheric pressure always has a temperature of 100°C. Steam evaporated under a pressure of 5 pounds (gage) has a temperature of 109°C; under 10 pounds pressure, 116°C, etc. *Superheated steam* is that which has been heated to a temperature above that due to its pressure. Steam is superheated by passing it through pipes or coils exposed to the hot gases from the furnace, after it leaves the steam space of the boiler. . . *Dry steam* is that which contains no moisture. It may be either saturated or superheated. *Wet steam* contains more or less moisture in the form of spray; in other ways it does not differ from saturated steam, having the same temperature at different pressures.
>
> "*Steam Quality:* The percentage of dry steam in steam containing moisture is called the quality of the steam. For example, if a pound of a given sample of steam contains 0.04 pound of water in the form of spray, and 0.96 pound of dry saturated steam, the quality is said to be 96%. . . .The proportion of moisture in steam is found by means of a device called a calorimeter."

The following are descriptions of some special ager constructions.

A new construction, permitting a controlled quantity of steam intake into different parts of the ager, is explained in *B.P. 457,952* (Horridge). There are other interesting devices intended to avoid local overheating by special regulation of the intake of steam and water (cf. *G.P. 609,922*—Chapuis). In a special construction, larger spaces are left between the rollers in the ager (*G.P. 578,400*—Deltex). The use of separate ager compartments to avoid local overheating is suggested in *B.P. 422,117* (Spooner). Separate steam inlet and exhaust pipes are provided for each compartment; the steam is circulated at a high rate, and each section may be controlled for quantity of steam flow.

An original and novel method of vat color fixation is described in *F.P. 756,817*, *B.P. 421,237* and *Aus. P. 138,746*. Although the practical results obtained by this method have not been extensively published, the known facts are quite promising. The use of air-free steam is abandoned, the reduction and fixation taking place at the temperatures generally used for dyeing and within the limits in which hydrosulfite acts, *i.e.* between 70 and

80°C. Decomposition of hydrosulfite is complete at 100°C, the higher temperatures of steam being required for dyestuff pastes containing sulfoxylate formaldehyde. It is to be noted that the optimum conditions of temperature for reduction of vat dyestuffs is 50 to 60°C for warm-dyeing colors and 20 to 25°C for cold-dyeing colors. These conditions, ideal for dyeing, are here applied to printing by the use of a simple device. The printed cloth is brought to the required temperature in an electrically heated chamber. Most of the examples refer to the "Colloresin" process and very probably the invention was first developed for this type of printing. As example, fabrics printed with dyestuff thickened with Colloresin are padded with an alkaline hydrosulfite solution and finally brought to the proper temperature for reduction of the dyestuff by regulation of the electric heating device. An example is also given using the potash-sulfoxylate formaldehyde print formula. It has also been reported that fixation of vat colors can be carried out with the aid of resin condensates, by using this heating chamber, which can hardly be called an ager.

This type of fixation chamber, using electrical heating coils, and suitable for rapid development of printed vat colors, has been described in trade journals, and is called the Electro-fixer by its inventor, Aubauer (*G.P. 651,607; Mell.*, **1937,** *308*).

The principle of the Electro-fixer consists of bringing the printed cloth to the desired temperature at once, the heating being produced electrically. The reactions are not gradual, but very rapid. This effect is attained by a special construction, permitting the incoming goods to be heated to 180 to 200°C in a preheating chamber. Thereupon the goods are conveyed into a lower chamber, where the desired temperature of reaction is carried out. Finally the cloth is led through an open-width washing machine. The apparatus was first intended only for vat printing, but other applications have been found for it. Besides the fixation of vat dyestuffs in printing, it has been found that plain-dye shades can be fixed in this apparatus, and there are many other fields where it may be used, as in discharge printing, Rapid Fast Color and Rapidogen color applications, and direct color printing. The apparatus could even serve as a curing device for textile treatments with resin pre-condensates, or for reacting fibers with formaldehyde. An additional patent on this subject (*G.P. 652,085*) consequently claims that discharge prints may be carried out on the same apparatus, with the temperature within the 120 to 170°C range. The device has a small mass, so that saving of heat is undoubtedly one of its advantages. Moreover, it may be conveniently connected in series with washing and finishing machines, which is interesting for the printer and dyer.

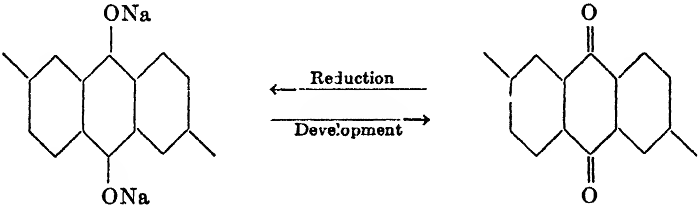
Another new ager construction has been described in the trade literature. This is the Gerber ager, (*B.P. 486,029* and *486,070*) which utilizes a construction wherein the cloth touches all rollers on the back (unprinted side). This ager is of conical form, hollow in the center. The printed goods are fed in from a truck or roll inside the hollow. The goods are conveyed into the ager, and around, above and below the hollow in concentric lines, finally leaving the ager at the top. The advantage is complete freedom from mark-off, especially adaptable therefore to large blotch prints as encountered in screen printing.

As employed in the United States, the rapid ager is generally constructed with a water layer at the bottom. Steam enters through a perforated pipe which extends the length of the ager, often with branched perforated extensions. The pipes are set below the water level. A baffle plate above the water layer prevents splashing of the goods. This arrangement makes it possible to supply every part of the ager with fresh, completely saturated steam.

A development of the screen printers, who require an ager which would eliminate danger of mark-offs, and which can be used for knitted fabrics, such as jerseys which curl easily, is the so-called tower ager. This ager may be 20 to 30 feet high, with one roller at the apex, the goods entering and leaving at the bottom. Refinements of this simple tower allow preheating chambers, and the possibility of running two lines at once, using two apex rollers (Geering, *Ray. Tex. Mon.*, Mar., **1946**; *Textil Rundschau*, Nov., **1946**).

Development

After the alkali-enolate of the vat dyestuff has been absorbed by the fiber, the original insoluble vat dyestuff must be developed again. Chemically, this is an oxidation:



Although this process is in no way difficult, it plays an important role in obtaining best possible color yield. An incomplete reduction may result in uneven, weak or poorly fixed prints. On the other hand, over-reduction may produce compounds which cannot be quantitatively regenerated.

The same is true for the development by oxidation. An incomplete oxidation of the enolate will produce prints of inferior fastness, and of uneven appearance. Over-oxidation may partially destroy and alter shades of many vat colors.

The oxidants employed are chlorine compounds as chlorinated sulfonamides, perborates, percarbonates, peroxides—especially hydrogen peroxide—, persulfates, bichromates, and the oxygen of the air. Any of these, except the last, can cause over-oxidation.

According to their construction and to the degree of dissociation of their leuco compounds, the vat dyestuffs require more or less oxygen for their regeneration. We can divide the vat dyes into groups: those which are easily reoxidized and those which are difficult to reoxidize. Full and level prints depend to a large extent therefore on the conditions of the oxidation process, that is, on the choice of oxidant, and the time and temperature of the developing bath. Failure to give a good oxidation may result in mark-offs, uneven printed areas and inferior fastness to washing, crocking or light.

The color development takes place in two phases: firstly, the destruction of the alkali and the surplus reducing agent in the print, and secondly, the proper oxidation of the leuco compound. Removal of the thickening agent proceeds throughout the oxidation and subsequent washing.

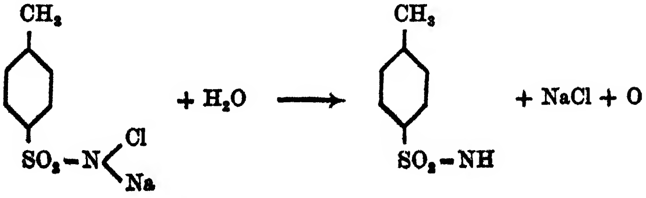
Oxidation by Oxygen of the Air. This would be the cheapest oxidant, and simplest to handle, but unfortunately its action is too slow, and it is impossible to attain a complete oxidation in the limited time afforded in a continuous operation. In treating the fabrics in rope form, complete reoxidation of the prints is possible. In order to neutralize the alkali and accelerate the destruction of the reducing agent, a pretreatment with dilute mineral acid may be given (1 to 2 gm H_2SO_4 66° Bé per liter).

Oxidation with Chlorinated Sulfonamides. There are many interesting compounds of this class.

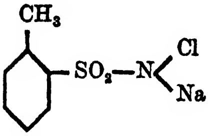
References: *Z. f. ges. Tex. Ind.*, **1932,** #35, 168; Bonnet, *Teintex*, **1937,** #2, 95, 158; *Mell.*, **1927,** #8, 172; **1929,** 240; Feibelmann, *Mell.*, **1931,** 263; Hausner, *Mell.*, **1932,** 268; Herbst, *D.F.Z.*, **1934,** 395.

Aktivin or Chloramine T is the sodium salt of *p*-toluol chlorosulfonamide [*G.P. 390,658, 422,076, 461,637, 504,997, 530,894, 559,250* (Heyden); *B.P. 241,579, 241,580* (Bayer, 1925)].

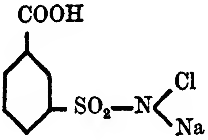
Aktivin is a white powder, with a faint odor of chlorine, crystallizing with three molecules of water, and readily soluble. The aqueous solution is stable in the cold, and decomposes only at the boil.



Chloramine TO is the corresponding *ortho* derivative

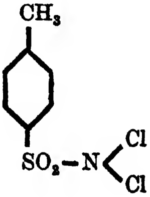


Chloramine BX or Holazone is a similar compound, in which the methyl group is replaced, in the *meta* position, by a carboxylic group. It gives acid reaction in water solution:



Peraktivin (Kosche, *Z. f. ges. Tex. Ind.*, **1933,** 578; Thiebaud, *Teintex*, **1937,** #2, 366) differs from the foregoing in that both of the amino hydrogens are replaced by chlorine. It has a strong odor of chlorine, is insoluble in water, but soluble in alkalis.

Peraktivin is prepared according to *G.P. 563,387* (Pyrgos-Feibelmann). It has both oxidizing and bleaching properties, but has not found wide distribution because of its insolubility in water. It may be mixed with sodium carbonate, in which case it forms a ready-made bleaching composition (*Mell.*, **1931,** 263). It has the formula



Aromatic compounds of dichlorosulfonamide can be formed having COOH groups linked to the nucleus (*G.P. 647,566*). In this way water-soluble compounds can be obtained which have more active chlorine than the monochlorinated products such as Aktivin T or Chloramine T.

The above mentioned products can be used as bleaching agents, in chlorinating wool, in solubilizing starches, for water disinfecting, etc. They are also recommended for oxidizing vat prints. The developing bath is prepared with 2 to 3 gm Aktivin per liter at a temperature of 50 to 60°C. Either 1 or 2 gm of acetic acid, or 1 to 2 gm of soda ash can be added, to accelerate hydrolysis. Decomposition proceeds slowly in the absence of oxidizable material.

Oxidation with Sodium Perborate. The perborates are boric acid salts containing active oxygen. Their constitution has long been uncertain. It was not clear whether they should be regarded as true per-salts, like the persulfates or percarbonates, or simply as additive products of hydrogen peroxide, like the percarbonates of Tanatar (1910) or the ammonium persulfate of Willstaetter (1903).

The work of Le Blanc on perborates and of Riesenfeld and Mau, on percarbonates and persulfates (*Ber.*, **1911**, 3595) made it possible to arrange these compounds in three classes.

(1) Additive products of hydrogen peroxide.

(2) Per-salts prepared from peroxide and acid anhydride. (Perborates and percarbonates of this type are known; persulfates are unknown.)

(3) Per-salts, prepared electrolytically. (Persulfates formed this way are the intermediate products in the manufacture of electrolytic hydrogen peroxide).

Perborates of the first group are known:

$NaBO_2 \cdot H_2O_2 \cdot 3H_2O$—the perborate of commerce
$Na_2B_4O_8 \cdot 10H_2O$—Perborax (*F.P. 336,062*, 4.17% active O)
$Na_2B_4O_{11} \cdot 6H_2O$

Of the perborates of the second group, the following have been isolated

$$2KBO_3 \cdot H_2O$$
$$2NH_4BO_3 \cdot H_2O$$
$$NaBO_3$$

Sodium perborate can be obtained by:

(1) Reaction of hydrogen peroxide on a borax solution:

$$Na_2B_4O_7 + 2NaOH = 4\ NaBO_2 + H_2O$$
$$NaBO_2 + H_2O_2 + 3H_2O = NaBO_2 \cdot H_2O_2 \cdot 3H_2O$$

(2) Action of boric acid and sodium peroxide.

(3) Electrolytic process (Landshoff and Meyer, *G.P. 297,223*)

The developing bath contains 2 to 4 gm of sodium perborate per liter at 60 to 70°C. The oxidation proceeds very slowly, and the product is not suitable for continuous set-up. Goods may be treated with perborate, then laid up before the soaping operation.

Oxidation with Percarbonate. This product can be used as a substitute for sodium perborate. Sodium percarbonate has been manufactured by L'Air Liquide (Paris) under the name Carbal.*

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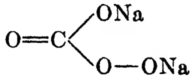
* *Teintex*, **1942**, 566–568.

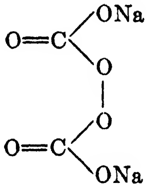
We distinguish two types of percarbonates. The one, the true per-salt, is characterized by the linkage —O—O—; the other type comprises the so-called peroxide additive compounds. The hydrogen peroxide is attached to the molecule in much the same way as water of crystallization (Riesenfeld *Ber.*, **1909,** #42, 4377; Wilstaetter, *Ber.*, **1903,** #36, 1828).

Two sodium salts of percarbonic acid are known: sodium permonocarbonate



or Na_2CO_4

and sodium perbicarbonate



or $Na_2C_2O_6$

The permonocarbonates are obtained by the reaction of carbon dioxide and sodium peroxide at temperatures below 0°C, as follows:

$$2CO_2 + 2\,Na_2O_2 + 3H_2O = 2Na_2CO_4 \cdot 3H_2O$$

The percarbonates can be formed by anodic oxidation of alkali carbonate solutions at —30°C, by the action of CO_2 gas on sodium peroxide hydrate, or by the reaction of sodium peroxide and phosgene.

The sodium percarbonate of commerce is a pure white product, corresponding in structure to sodium perbicarbonate $Na_2C_2O_6$. The powder cakes up in moist atmosphere; its solutions develop carbon dioxide and oxygen. In acid solution it can be used as an oxidant of vat colors, using 2 to 3 gm of percarbonate per liter at 50 to 60°C. Alkaline earths have a stabilizing effect on percarbonates, so that it is advantageous to work in hard water.

Oxidation with Peroxides. Sodium peroxide and hydrogen peroxide are used as reoxidizing agents. Albone is hydrogen peroxide of 27.5% concentration. Perone is the name of the 35% concentration. These strong oxidizing agents should be used at temperatures of 60 to 70°C, with sodium silicate as stabilizer, in concentration not exceeding 4 gm per liter.

Oxidation with Persulfates. Potassium persulfate, $K_2S_2O_8$, and ammonium persulfate, $(NH_4)_2S_2O_8$, are produced electrolytically. They can be used as sources of oxygen for vat color development. The goods are treated at 70°C with 2 to 3 gm of ammonium persulfate per liter.

Oxidation with Bichromates. Sodium and potassium bichromates have been widely used for the oxidizing process, but they can very easily cause over-oxidation. Ciba Scarlet G and Brilliant Indigo 4B, and in general, thioindigoid vats, are dulled in shade. The Indanthrene Blues BCD, GCD, RS and 3G and Indanthrene Brilliant Blue R must be developed at low temperatures, or the shades will be substantially altered. The bichromates are used with acid, preferably acetic acid. However, other oxidizing agents, as perborates or peroxides, are preferred, as they do not influence the true vat shade.

Ondal. An interesting product is described in *G.P. 594,806*, which consists of a fatty alcohol sulfate containing an available oxygen atom. The product, called *Ondal double conc.*, was brought out by Boehme. It is a pyrophosphoric acid ester of a higher alkyl sulfate, and is said to combine detergent action with oxidizing action of the persulfates. Heide (*Z. f. ges. Tex. Ind.*, **1936,** #39, 133) describes the advantage of Ondal. The operation of oxidation and soaping takes place in the same bath, and there is no risk of over-oxidation. In the case of continuous operation, the first bath contains 13 gm of Ondal per liter at 30°C, the second at 40°C, and following baths to 80°C (see also *G.P. 589,778*, *B.P. 425,804*, *S.P. 183,447*).

The size of developed dyestuff particles has a special bearing on the brightness of the prints, on the light fastness and on the fastness to crocking. Coarse particles near the surface of the fibers impair the fastness to crocking. They also cause duller prints by breaking up the light reflection. These particles can be removed by thorough soaping. It has also been found that light fastness is improved by soaping, as small particles in the fiber are agglomerated into larger aggregates (Haller and Ruperti, *Cellulose Chem.*, **1925,** #6, 169; *Mell.*, **1925,** #6, 664; **1927,** #8, 942).

When soap is used, it is recommended as a general precaution to use water softeners, like Calgon or Quadrafos to prevent precipitation of alkaline earth soaps.

Soap has largely been replaced with other detergents, such as Orvus, Lamepon, Gardinol, etc., which have the properties of aiding crock-fastness and removing gum thickeners, without breaking in hard water. (see table at the end of the chapter.)

Thus the field of vat printing has been covered. Certain methods for fixing vat colors, which have not proved practical have been omitted, as for example, the fixation of vats on metallic mordants. It will suffice to mention the following references: *G.P. 253,293* (Bayer); *F.P. 453,799*, *Frb. Ztg.*, **1912,** 517; *G.P. 259,293* (1912); J. Mueller, *Bull. Mulh.*, **1914,** 220; M. Richard, *Bull. Mulh.*, **1923,** 282.

Vat Colors–Discharge Printing

Vat dyeings can be discharged by oxidizing agents as well as by reducing agents. For a long time the oxidation process was used exclusively for discharging indigo-dyed material, and was not used for other vat dyes, with the possible exception of a few indigoid colors, as the halogenated indigo brands. At the present time the oxidation discharge has been almost completely discontinued, and the reduction discharge methods, using sulfoxylate formaldehyde, are the only important ones.

A short survey of these discharge methods follows.

(I) Oxidation processes:
  (1) Chromate discharge (Thompson, 1826; Koechlin, 1874)
  (2) Ferricyanide discharge (Mercer, 1845)
  (3) Chlorine and chlorate discharge (Persoz, Jeanmaire, 1889)
  (4) Bromine and bromate discharge (Brandt & Binder)
  (5) Nitrate discharge (Freiberger, 1908)
(II) Reduction processes:
  (1) Zinc dust, copperas and zinc salts discharge
  (2) Glucose discharge
  (3) Sodium or zinc hydrosulfite discharge (Schützenberger, produced by Zündel in Moscow)
  (4) Sulfoxylate formaldehyde (Badische A.S.F., Zündel, M.L.B. Höchst)
  (5) Sulfoxylate formaldehyde and Leucotrope (Reinking, Badische A.S.F.)

Oxidation Discharge on Indigo

Chromate Discharge. The oldest discharge methods were based on chromates. As early as 1826 Thompson in Manchester proposed padding indigo-dyed fabrics with a bichromate solution, then printing with oxalic or tartaric acid. Indigo is oxidized on the printed portions to isatin by the chromic acid formed, and in this form is easily removed. Later a mixture of citric acid and potassium bisulfate was recommended (Depierre, Vol. III, p. 381) as print on medium blue indigos prepared with bichromate.

The Thompson process had several disadvantages: large amounts of bichromate were necessary, and padded goods were sensitive to light exposure. Besides the expense, only white discharges were obtainable on light and medium blues. The first improvement which made it possible to produce the style on a practical scale was developed in 1874 by Camille Koechlin of Mulhouse in Alsace (*Monit. Scient.*, **1892,** 80; *Bull. Mulh.*, Dec., **1892**).

The method, as invented by Koechlin, is actually used in Russia at the present time. The cloth, dyed with indigo, is printed with a paste containing sodium or potassium bichromate, neutralized with soda or ammonia, then the cloth is treated with a bath containing a mineral acid. Working this way, there is a saving of bichromate, besides avoiding the extreme light-sensitivity of the Thompson method.

The following formulas give the approximate proportions for white discharge prints on indigo (Morosoff Co., Kalinin, Russia, 1918).

Dark Blue	*Medium Blue*	*Light Blue*	
150	120	80	potassium bichromate
580	—	560	water
100		120	wheat starch
—	790	—	British gum paste 1:1
—	60	—	caustic soda 38° Bé
20	—	20	ammonia 26%
150	30	220	Leio gum 1:1 (roasted starch)
	1000 gm		

Thus the pastes contain sodium or ammonium chromate. The printed goods can be laid up for a few days without risk of tendering.

The fabrics are developed in a sulfuric-oxalic acid bath prepared as follows: 50 kg Leio gum is boiled with 50 l of water and brought up to 1000 l in a lead-lined vat. Next 182 kg of H_2SO_4, 52° Bé, and 30 kg of oxalic acid are added and dissolved. The goods are passed through open width at 50°C, the time required being 25 seconds, after which they are thoroughly rinsed and dried.

It has been found that the print-back greiges become tender upon exposure to light. Special material has to be set aside for the purpose, therefore, and washed after use. The use of oxalic acid reduces danger of formation of oxycellulose, but the discharge process is somewhat retarded.

This process received much attention from investigators, the main aim being reduction of the tendering of the fiber from the very dangerous chromates. J. Müller added dextrin and glucose to the acid bath (*Frb. Ztg.*, **1891–2,** 29). H. Koechlin added glycerin (*Chem. Ztg.*, **1892,** 463). Brandt added alcohol (*Frb. Ztg.*, **1891–2,** 8, 61). Tagliani prepared the goods with glue and glycerin (*Bull. Mulh.*, **1911,** 156). Prudhomme replaced the oxalic acid of the bath with sodium oxalate (*Rev. Gen. Mat. Col*, **1903,** 67, 100, 163; *Frb. Ztg.*, **1906,** 12).

Bulard recommended the use of calcium oxalate in the print paste, and sulfuric acid alone in the developing bath (*Rev. Gen. Mat. Col.*, **1904,** 257). The greatest portion of the style has been produced by the Koechlin method, however.

Colored Discharges by the Chromate Method. By adding pigments and albumen to the above printing pastes, colored discharges can be obtained.

Yellow discharges are of particular interest, the style having been carried out to a great extent in the past, and is still in use in some plants.

The following formula is from the firm of Morosoff in Kalinin, Russia:

450 gm	Chrome Yellow paste
240 gm	blood albumen 1:1
20 gm	rape seed oil
15 gm	turpentine
10 gm	glycerin
128 gm	tragacanth gum
95 gm	sodium bichromate
42 gm	ammonia
1000 gm	

The possibility of using the insoluble azo dyes as discharge on indigo stimulated a great deal of research, and eventually the problem of producing blue-red or blue-white-red style was solved.

Blue-red style: Elbers printed a paste of diazoamino benzene with sodium bichromate on naphtholated goods, and developed in an acid bath (*G.P. 55,779*-1890). Farbwerke Höchst suggested using Azophor Red PN together with bichromate. The indigo-dyed fabric is first padded with β-naphthol, and printed with the following discharge paste:

124 gm	Azophor Red PN
370 gm	water
56 gm	NaOH 22° Bé
270 gm	gum tragacanth 6 %
180 gm	sodium bichromate
1000 gm	

None of these methods can be used for the blue-white-red style because a pure white cannot be produced on naphtholated goods (oxidation of β-naphthol with chromic acid).

Blue-white-red style: Use is made of insoluble chromates, as of Pb, Zn, Ba, Ca, in order to avoid the browning of the naphtholated goods by oxidation. The material is washed free of naphthol before the hot acid bath which produces chromic acid. (Kurtz and Kunert, *Frb. Ztg.*, **1897**, 49; *Bull Mulh.*, **1897**, 354). The indigo-dyed goods are padded with sodium naphtholate and neutral sodium chromate and printed with a paste containing lead acetate and *p*-nitrodiazobenzene. Insoluble lead chromate is formed and the red azo dye produced. After drying, the goods are passed in the open-width through a bath containing 40 gm of ammonia per liter, rinsed and soured hot with hydrochloric acid which discharges the ground.

The process of Watson and Bentz (*B.P. 2,620*—1897; *F.P. 262,097*, *Frb. Ztg.*, **1898**, 383; *B.P. 8,033*—1897), consists in printing a paste containing lead acetate and *p*-nitrodiazobenzene on naphtholated goods. The goods are then padded through sodium carbonate to transform the lead salt to the oxide. The next bath contains sodium chromate, which forms lead chromate. After rinsing, the discharge is brought about in a mineral acid bath. (Compare Longhlin, *Frb. Ztg.*, **1895**, 232; *B.P. 21,287*—1895.)

The process of Meister, Lucius and Brüning consists of printing Azophor Red PN mixed with freshly precipitated barium chromate, (or pure barium chromate) on naphtholated goods. After drying, the goods are rinsed to remove the naphthol, then soured hot to discharge the ground.

The discovery of the nitrosamines offered the possibility of printing the naphthol together with the diazo salt.* (*G.P. 81,791*, *83,010*-Badische A.S.F., 1893.) The first trials were not at all encouraging, however, and it was not until 1908 that Dziewonsky and Bourcart developed a practical process, using the nitrosamine of *p*-nitro-*o*-anisidine. The material is first prepared with boric acid and aluminum acetate, then printed with the nitrosamine paste containing naphthol, sodium chromate and Turkey red oil. The goods are aged 2 to 3 minutes, then acidified with sulfuric and oxalic acids.

Typical formulas are (*Frb. Ztg.*, **1909**, 64 and 363; *Bull Mulh.*, **1909**, 175):

Light Blue	*Dark Blue*	
632	592	gum and water
125	250	neutral sodium chromate (1:2)
30	30	nitrosamine paste
210	125	β-naphthol solution*
3	3	caustic soda 38° Bé
1000 gm		

*β-Naphthol Solution

14 gm β-naphthol	
24 gm NaOH 38° Bé	
104 gm water	135 gm aluminum hydroxide 17%
68 gm sodium aluminate solution	265 gm caustic soda 10° Bé
—	—
210 gm	400 gm

Ferricyanide Discharge. Mercer (1845) printed caustic soda on a fabric dyed with indigo and prepared with potassium ferricyanide. By changing

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* *Z.f. Frb. Ind.*, **1906**, 81, 138, 331; **1909**, 130, 282; *Frb. Ztg.*, **1909**, 64, 163, 240; **1910**, 117; *Bull. Mulh.*, **1908**, 65; **1909**, 173; *Fischer's Ber.*, **1908**, 394; *G.P. 204,702*, *204,799*, *199,143* (Felmayer), *199,843* (M.L.B.); *Rev. Gen. Mat. Col.*, **1906**, 241; *B.P. 764* and *765* (1907).

the order of operation, de Gallois made the method practicable on light and medium shades of indigo. Potassium ferricyanide is printed on dyed indigo fabrics and discharged in a subsequent passage through hot soda lye of 12° Bé. It is also possible to produce red discharges by this method. In a variation of this process, the goods are padded with 100 gm of NaOH and 10 gm of Na_2CO_3 per liter, dried and printed with the following white discharge:

650 gm British gum thickening
120 gm potassium ferricyanide
150 gm sodium silicate 30° Bé
30 gm glycerin
50 gm Turkey red oil
——
1000 gm

Red discharge can also be produced with v. Gallois' method (*Frb. Ztg.*, **1890–91,** 298; *G.P. 59,921*—1891). The indigo-dyed fabric is prepared with naphthol and printed with diazotized *p*-nitraniline and potassium ferricyanide. The dried goods are passed through a soda lye bath of 10° Bé at 50°C, rinsed and soaped.

Chlorate Discharge. The chlorate discharges played an important role in the indigo discharge style. Persoz treated the dyed fabrics with chlorates and printed pastes containing tartaric acid. Schlumberger suggested the use of aluminum chlorate $Al(ClO_3)_3$ (*Bull. Mulh.*, **1872,** 307). Cerium chlorate was recommended by Farbwerke Höchst.

The credit for making the chlorate process successful in a practical way must be given Jeanmaire. Excellent white discharges are obtained by his method, not only on indigo, but on many other dyestuffs, as for instance, the chrome colors. For many years this process was popular, and was second only to the Koechlin method.

Jeanmaire's formula consists of applying a print paste of potassium chlorate with potassium ferri- or ferrocyanide: $K_3Fe(CN)_6$ or $K_4Fe(CN)_6$ (*Bull Mulh.*, **1895,** 134; **1899,** 317).

Formula for Chlorate Discharge

Dark Blue Indigo	*Medium Blue Indigo*
300 gm milled kaolin	30 gm glycerin
200 gm sodium chlorate	150 gm sodium chlorate
270 gm thickening	685 gm thickening
50 gm sodium ferricyanide	30 gm sodium ferricyanide
180 gm lactic acid 50%	50 gm citric acid
	55 gm NaOH 38° Bé
1000 gm	1000 gm

Aluminum chlorate is a more active discharging agent (Dr. Haller, "Tech. d. Baumwolle," p. 284):

780 gm water
1500 gm British gum thickening
1000 gm sodium chlorate
2000 gm aluminum chlorate 18° Bé
500 gm potassium ferricyanide
80 gm turpentine
70 gm tartaric acid
70 gm citric acid

1000 gm

The printed pieces are aged 2 to 4 minutes in the rapid ager, whereby the printed portions become yellow from the formation of isatin. They are then rinsed, treated with hot alkaline solution of 10 cc NaOH 38° Bé per l, or 10 cc sodium silicate 36° Bé per l, rinsed, washed and dried.

Bloch and Zeidler (*Bull Mulh.*, **1898,** 50; *Frb. Ztg.*, **1899,** 140), obtained red discharges using diazotized *p*-nitraniline together with chlorate and aluminum sulfate. The prints are aged, treated with soda ash, washed and dried. (Compare Bourcart and Brandt, *Bull Mulh.*, **1908,** 242; *Frb. Ztg.*, **1910,** 7, 119; *Frb. Ztg.*, **1909,** 82, 113).

The blue-white-red style is carried out at present in Russia using the Hydrosulfite NF—Leucotrope discharge for the white and the chlorate discharge for the red, according to the following formula:

390 gm starch-trag. thickening
220 gm sodium chlorate
30 gm potassium ferricyanide
80 gm water
30 gm tartaric or acetic acid
200 gm 10% solution of diazotized *p*-nitro-*o*-anisidine
50 gm sodium acetate or sodium phosphate

1000 gm

Glycollic acid may be used instead of the citric or tartaric acid (*Frb. Ztg.*, **1910,** 199; *G.P. 198,043*).

Part of the citric acid may be replaced by boric acid, according to H. Sunder, reducing the risk of tendering (*Bull Mulh.*, **1921,** 345).

Bromate Discharge. In 1884 A. Scheurer found that bromates were more effective than chlorates in discharging indigo. Storck and Pfeiffer recommended the use of aluminum bromate (*Frb. Ztg.*, **1891–2;** *Bull. Mulh.*, **1892,** 387). Binder suggested that nascent bromine, produced by the action of strong acids on a mixture of sodium bromide and sodium bromate, be used. The print paste contained aluminum sulfate, and the acid was obtained upon ageing (*Frb. Ztg.*, **1891–2,** 226). Erban also recommended bromine salts (*Rev. Gen. Mat. Col.*, **1906,** 236 *Frb. Ztg.*, **1905,** 337). Brandt prepared red discharge on indigo using aluminum chlorate and sodium bromide. The indigo is discharged on ageing, and alumina deposited, giving the mordant for Alizarine red dyeing.

Nitrate Discharge. The destruction of indigo by nitric acid was a well-known analytical method. The use of nitrates* for discharge of indigo was attempted by Freiberger (1908). He printed a mixture of nitrates and nitrites, and formed the nitric acid by passing the prints through a bath of sulfuric acid (40 to 42° Bé) for 5 to 6 seconds at 60°C. Despite the obvious difficulties of using such a concentrated acid, the method eventually proved practical. A lead-lined vat was used for the acid, using a lead roller for the submersion (Sunder, *Bull. Mulh.*, 1921).

Discharge Paste

33 gm	cornstarch
18 gm	wheat flour
364 gm	water
5 gm	castor oil
	Boil; add:
250 gm	sodium nitrate
330 gm	barium sulfate paste
1000 gm	

The nitrate formula has the advantage of producing excellent colored discharges using azo colors, or pigments, as well as vat colors with albumen.

Other methods which have tentatively been used for indigo discharge are:

Permanganate, $KMnO_4$*:* Reber and Potier, *Bull. Rouen*, **1876,** 62; Kayser, *Frb. Ztg.*, **1901,** 278.

Manganese dioxide: Depierre, Vol. **III,** p. 388; Scoupil method, *Rev. Gen. Mat. Col.*, **1926,** 100; Badische A.S.F. "Indigo Rein," **1908,** p. 179; Schützenberger; Pokorny, *Rev. Gen. Mat. Col.*, **1917,** 66.

Red lead: Frb. Ztg., **1901,** 270; Depierre, Vol. **III,** p. 393.

In recent times Mathieson Alkali proposes the use of chlorites, *B.P. 578,528* (1946).

The chromate process of Koechlin was undoubtedly the most important of the above discharge methods, and the most widely distributed. Its success was world-wide in the cotton printing field, and the method held its foremost position over a span of many years. The process owed its success to the cleanness of the white and the sharp outlines of the print, and to its

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* *G.P. 226,694*; *F.P. 391,829*; *B.P. 13,896*—1908; *Bull. Mulh.*, **1913,** 225; *Rev. Gen. Mat. Col.*, **1910,** 169; **1913,** 207; *Frb. Ztg.*, **1910,** 334; **1912,** 381; Haller, *Z. f. ges. Tex. Ind.*, **1926.**

easy application to red and yellow colored discharges. The style finally waned in popularity when the less complicated Leucotrope method was invented.

Reduction Discharges

Indigo is transformed into the leuco compound by reduction, in which form it is water-soluble and therefore removable from the fiber. However, the leuco indigo is not a stable compound, oxidizing rapidly in contact with the air.

Zinc Powder and Tin Salts Discharges. The first process for discharging indigo by reduction was published in 1896 (*G.P. 97,593*—Badische A.S.F.). It consisted of printing a paste containing zinc powder, sodium bisulfite and acetine (*Fischer's Ber.*, **1898,** 1020). The reduction proceeds farther than the leuco indigo, and a white discharge is not obtained. Another process developed also by Badische A.S.F. was based on the application of stannous acetate as reducing agent. ("Indigo Rein," 1st. ed., p. 108). Unfortunately, over-reduction occurs here also, and a pure white effect is not attained. *B.P. 8,726* (1908) and *G.P. 217,474* recommended sodium stannite as a discharge agent (*Frb. Ztg.*, **1910,** 287).

Pomerantz (*G.P. 253,155, Frb. Ztg.*, **1912,** 120) worked with a paste containing ferrous sulfate and stannous chloride, passing the goods after printing through caustic soda at 80°C. M. Ribbert in Westphalia obtained *G.P. 264,243* (1912) for a method of printing ferrous sulfate, stannous chloride and Leucotrope W, developing the prints in an alkali bath (*Frb. Ztg.*, **1913,** 463).

Glucose Discharge. Badische A.S.F. proposed the use of glucose as discharging agent for indigo (*G.P. 214,715*—1908). Sunder, chemist at the Ribbert plant, developed a printing formula employing glucose and stannous oxide (*G.P. 267,408*—1913). Badische A.S.F. later proposed a paste of glucose, caustic soda and Leucotrope W (*G.P. 240,513, B.P. 21,052*—1916).

A method of producing red discharge on indigo was worked out by Prochoroff (Moscow), whereby Azo Red was printed with glucose. The advantage of this method is that the Azo Red is already formed in the ageing process, and the proper discharging action occurs in the alkaline bath (*Bull. Mulh.*, **1920,** 266).

White Discharge

50 gm	Leucotrope W
50 gm	anthraquinone paste
200 gm	zinc oxide-glycerin 1:1
300 gm	glucose, dry
400 gm	British gum thickening 1:1
1000 gm	

Red Discharge

200 gm	glucose
150 gm	solution of diazotized Azo Pink BB
50 gm	Leucotrope W
600 gm	thickening
1000 gm	

The printed goods are dried and aged, and passed through soda lye of 30° Bé at 80°C for 20 or 30 seconds, washed and dried. Vat colors can be printed alongside (*Frb. Ztg.*, **1912,** 233).

Haller and Hackl* found the stable compound of glucose and sodium hydrosulfite a valuable discharging agent. To this compound the chloride and oxide of zinc are added, forming a syrupy liquid. The zinc salt of glucose-hydrosulfite can be crystallized from the mixture by treatment with alcohol.

The formula of the discharge paste is:

150 gm	hydrosulfite conc.-powder
300 gm	grape sugar
60 gm	zinc oxide
60 gm	zinc chloride
430 gm	gum thickening
1000 gm	

Indigo dyed fabrics are printed with this paste and dried, then passed, without an ageing operation, through a bath of 20 gm of NaOH 40° Bé and 10 gm of sodium silicate 38° Bé per liter at 85°C for 18 to 20 seconds. The same method can be used for obtaining colored discharges with vats on indigo. The print paste in this case contains besides the vat dyestuff, ferrous sulfate, stannous chloride and Candit V. The prints are developed as for the white discharge.

Candit V is glucose-sulfoxylate, manufactured by Pyrgos (Radebeul) according to Dr. Haller's formula. A white discharge formula using this product is found in *Mell.*, **1929,** #8 (Perndanner and Hackl). The after-treatment is as above.

300 gm	Candit V
100 gm	kaolin 1:1
500 gm	gum thickening
100 gm	water
1000 gm	

Hydrosulfite Discharge. The first use of hydrosulfite as a discharging agent is recorded in *B.P. 19,518* (Ashworth, 1908). See also *G.P. 133,478, 135,725* and *194,878* (Haller).

Juteau described (*Rev. Gen. Mat. Col.*, **1914,** 191) a method for discharging indigo without ageing. It is based on the application of zinc hydrosulfite, which is produced by precipitation of sodium hydrosulfite with an excess of zinc chloride.

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* *Mell.*, **1928,** 41; **1929,** 630, 717.

150 gm hydrosulfite powder
30 gm zinc oxide
100 gm ice cold water
100 gm zinc chloride
—
to one liter

The printed goods are dried, then treated at 80°C in a bath of 10% caustic soda, 40°Bé. In order to remove the reduced indigo the goods are treated in a boiling bath containing 5% of sodium silicate (*Tiba*, Jan., **1929,** 47).

The white discharge can be extended to include colored discharges with vat colors and Azo dyestuffs. Juteau used chromic acid discharges alongside print pastes containing zinc hydrosulfite and Leucotrope W, to produce red and white discharge on indigo.

Sulfoxylate Formaldehyde Discharge. The advent of sulfoxylate formaldehyde or Hydrosulfite NF, marked the end of all previously used methods, and the beginning of a new epoch in the indigo discharge style. Two methods can be distinguished: (1) Hydrosulfite NF method; and (2) Leucotrope W method.

(1) Hydrosulfite NF Method. In 1905, Haller (*G.P. 194,878*) and, independently, Aubert (*Bull. Mulh.*, **1907,** 419) were first to discharge indigo with Hydrosulfite NF. Their process is based on the fact that leuco-indigo has but slight affinity to cotton at 100°C, and that by soaping the prints at the boil the leuco compound can be removed from the fiber. Haller found it was possible to add the soap directly to the print paste.

The goods are printed with a paste containing, besides the thickening agent, Hydrosulfite NF and soap. After ageing, they are then soaped with soda ash at 100° C to remove the reduced indigo. However, because of the rapid reoxidation of the leuco-indigo, the process must be carried out with rigid control to prevent bluing of the white discharge. In order to overcome this disadvantage, it was proposed to add substances which might retard the oxidation, such as anthraquinone (*G.P. 209,122, 213,583,* Planowsky, *Z. f. Frb. Ind.*, **1907,** 109).

Addition of alkalis to the print paste increases stability of the paste, aids in reduction of the indigo and retards the reoxidation of the leuco compound.

Zinc oxide is claimed to improve the discharge effect, according to *G.P. 166,783* (Cassella). It is probable that an additive compound of leuco-indigo is formed with the zinc oxide, which, being insoluble in water is less reactive to the air than the free leuco compound. Badische A.S.F. proposed the addition of sulfite for the same purpose (see also *Frb. Ztg.*, **1912,** 211 and 236). Schwarz recommended the addition of aniline or other amines (*G.P. 204,565*).

The addition of formaldehyde to the alkaline bath has been found advantageous. Kalle proposed replacing the alkaline bath with a mildly acid bath at 40°C, containing besides 10 cc of hydrochloric acid, 50 cc of alcohol per liter (*B.P. 20,208*, 1908; *G.P. 212,791-2*; *Frb. Ztg.*, **1910,** 287.) In another patent of Kalle, (*G.P. 200,927*) it is suggested to destroy excess hydrosulfite by dilute acids, then washing in mildly alkaline bath. According to Fussgänger (*Frb. Ztg.*, **1910,** 33) good results are obtained in using sodium silicate with formaldehyde.

A general formula in use before the Leucotrope method is as follows:

680 gm	starch-trag. thickening
100 gm	Hydrosulfite NF
80 gm	zinc oxide
40 gm	anthraquinone 30% paste
100 gm	water
1000 gm	

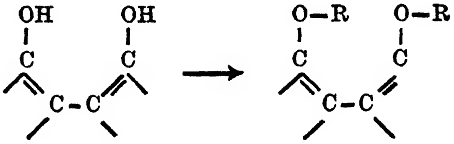
The printed fabrics are aged five minutes and then immediately passed through hot dilute caustic soda bath. (This process is discussed at length in *Bull. Mulh.*, Report of the Committee on Chemistry, Dec. 1938).

An alternate discharge formula is:

200 gm	Hydrosulfite NF
70 gm	zinc oxide
70 gm	water
100 gm	potassium sulfite 45° Bé
30 gm	glycerin
30 gm	anthraquinone 30% paste
500 gm	gum thickening
1000 gm	

The goods are printed and dried, avoiding overheating, and aged for 7 minutes at 101 to 102°C in saturated steam. The prints are rolled up as they leave the ager to minimize reoxidation, then developed in 1% sodium silicate or lime solution.

(*2*) *Leucotrope W Method.* The Leucotrope method was developed by Badische A.S.F. in 1908. The main feature of this process consists of transforming the leuco compound of indigo or other vat color into a complex additive substance which is insensitive to air oxidation. This additive transformation is brought about by etherizing the enol group of the leuco compound with dimethylphenylbenzyl ammonium chloride. In this way ethers are formed which are resistant to oxidation, and which, since they are alkali-soluble, can easily be removed from the fiber. Discharges are obtained which are not discolored by reoxidation of the dyestuff. The enol-additive compound is formed as follows

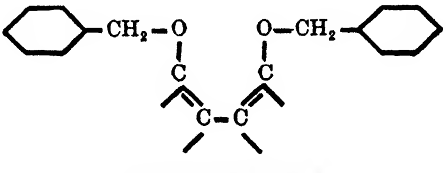


where R is an aryl or alkyl radical, such as benzyl group.

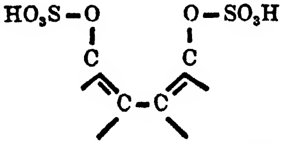
Some time before the invention of the Leucotrope method, Dr. Haller had already succeeded in transforming leuco-indigo into a non-oxidized compound by adding zinc chloride and resorcine to the reducing agent, but the additive product so formed was unfortunately not soluble. Credit must be given Reinking of Badische A.S.F. for the benzylating agent which has found such wide use under the name of Leucotrope.

References: Reinking, "The Leucotrope Method," *Frb. Ztg.*, **1910,** 243; *Frb. Ztg.*, **1912,** 250, 309; *Frb. Ztg.*, **1913,** #3, 45; *Frb. Ztg.*, **1911,** 135; Tchilikine, "Benzyl Derivatives of Indigo and Anthraquinone," *Frb. Ztg.*, **1913,** 517; H. Sunder, *Frb. Ztg.*, **1912,** 334; Bude, *Frb. Ztg.*, **1912,** 470; Diserens, "Les Rongeants et les Réserves," Vol. I.

The Leucotrope method can be considered a predecessor of the invention of the Indigosols. The aim of both is stabilization of the leuco-vat. But unlike the Indigosols, the Leucotrope-complex is soluble only in alkaline medium, and can hardly be reconverted to the vat dyestuff in consequence of its special constitution. M. Bader, the inventor of the Indigosols, was first to prepare stable leuco compounds of vats which were water-soluble and which could be completely retransformed into the original dyestuff. The comparison between the two type reactions is shown here:

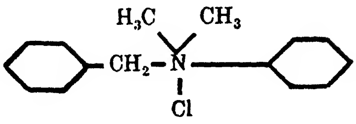


Alkali-soluble ethers

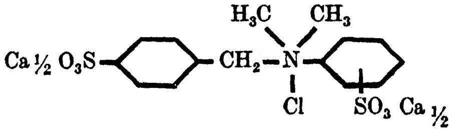


Indigosols (water-soluble ethers)

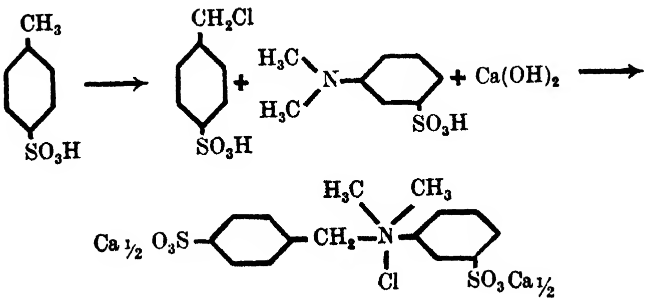
There are two products known as Leucotrope: Leucotrope O, dimethylphenylbenzyl ammonium chloride



which produces a leuco-indigo compound which is insoluble in water and in alkalis (*G.P. 231,543*—1909, *F.P. 414,937*—1910) and Leucotrope W, the calcium salt of dimethylphenylbenzyl ammonium disulfonic acid (*G.P. 235,879, 235,880, 240,513*—1910; *U.S.P. 1,106,970*).

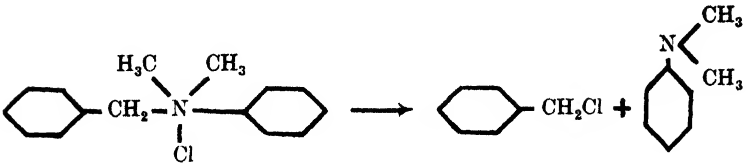


These products are obtained by the reaction of benzylchloride with dimethylaniline, or other tertiary amines, or with their sulfonic acids, as dimethyl metanilic acid. *p*-Toluene sulfonic acid is converted to chloro-*p*-toluene sulfonic acid, which is allowed to react with dimethyl metanilic acid according to the following equations

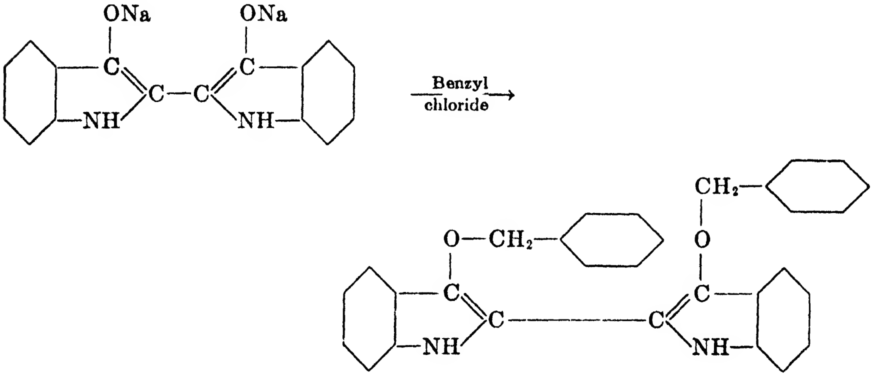


References: *Frb. Ztg.*, **1912**, 309, 374; **1911**, 102, 227, 465; *G.P. 233,328, 246,252, 247,099, 247,100-1, 249,542-3, 246,519.*

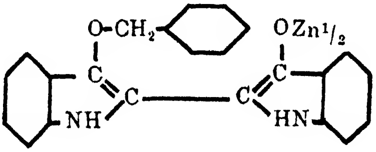
By the action of Leucotrope O on leuco-indigo, a yellow compound stable to air and water is obtained. Indigo cannot be formed again from this substance. Leucotrope O is split in the steam into benzyl chloride and dimethylaniline



The benzyl chloride combines with the OH groups of the leucoindigo, forming a benzyl ether, which according to Reinking corresponds to the following:



In the presence of zinc oxide Leucotrope O forms a yellow pigment

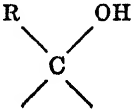


which can be used as yellow discharge on indigo.

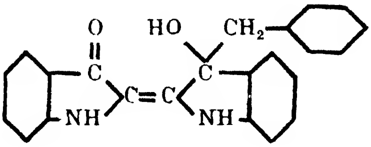
Leucotrope W produces an orange yellow compound with indigo which is soluble in alkalis and can be readily removed from the fiber.

According to Reinking (*Frb. Ztg.*, **1912,** 250) a monobenzyl derivative of leuco-indigo must be postulated, the hydrogen of the second hydroxyl group being replaced by zinc. It has been observed that in the absence of zinc or other divalent metal, derivatives of leuco-indigo are produced which are sparingly soluble in water or alkalis and therefore not suitable for white discharge on indigo.

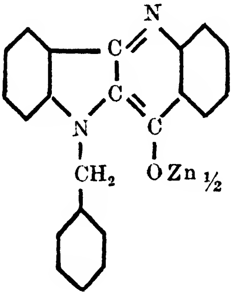
The Reinking theory was studied by Tchilikine (*Frb. Ztg.*, **1913,** 517) who advanced the idea that the group



is characteristic of the reaction. He assumes therefore that the benzyl derivative of leuco-indigo has the constitution



Grandmougin* believed that a zinc salt, derived from benzyl chinindolin carboxylic acid, was formed (*Rev. Chim. Ind.*, **1932,** 134) having the formula



A reduction of indigo on the fiber is supposed to take place, and a cleavage into isatin and indoxyl, which, by rearrangement, form chinindolin carboxylic acid.

Special brands of sulfoxylate formaldehyde combined with Leucotrope W are available on the market. The following products are intended for use as discharge agents for indigo and other vat colors;

Arostit RFL	Sandoz
Hydrosulfite CL	Rohner
Hydrosulfite SCL	Soc. Deriv. Soufre
Rongalite CL	I.G., G.D.C.
Rongeol NCL	Kuhlmann-Francolor

A typical formula for white discharge with Leucotrope is the following:

435 gm	gum thickening
150 gm	zinc white paste 1:1
15 gm	anthraquinone 15% paste
50 gm	glycerin
250 gm	Hydrosulfite CL
100 gm	water
1000 gm	

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* *Comptes rendus*, **1922,** 758.

The printed goods are dried, aged in saturated steam for 7 to 8 minutes, then treated at 80° with a 1% sodium silicate bath. The prints should be deep orange-red coming out of the ager.

The discharge effect of Leucotrope on the different vat dystuffs was investigated by Bude (*Frb. Ztg.*, **1912,** 470; *Rev. Gen. Mat. Col.*, **1913,** 54). The author establishes that Lustig and Paulus were the first to propose reduction discharges on indigo in *Frb. Ztg.*, **1907,** 57. The reduction discharge of indigo and vat dyestuffs divide the dyestuffs into four groups:

(1) *Dischargeable dyestuffs:* indigo, methylated and halogenated indigoids.
(2) *Dyestuffs not readily dischargeable:* symmetrical and asymmetrical indigoids containing S— and N—.
(3) *Dyestuffs dischargeable with difficulty:* acenaphthene derivatives.
(4) *Non-dischargeable dyestuffs:* anthraquinoids.

(1) The substitution products of indirubine give colored, insoluble compounds with Leucotrope O and soluble compounds with Leucotrope W. The halogenated indigo derivatives can be readily reduced but do not so easily undergo benzylation. Thus the quantity of Leucotrope must be substantially increased. The following print formula yields white discharge on Tetrabromindigo (Ciba Blue 2B):

325 gm	gum thickening 1:1
225 gm	Leucotrope W
80 gm	soda ash
40 gm	glue 1:2½
55 gm	water
80 gm	zinc oxide
50 gm	calcium carbonate
125 gm	Hydrosulfite NF
20 gm	oil or turpentine
1000 gm	

(2) The symmetrical and asymmetrical thioindigos form colorless benzyl derivatives with Leucotrope. Bude also found that the asymmetrical thioindigoids are more readly reducible than the symmetrical ones. The reoxidation of the leuco compounds can be greatly retarded by the addition of caustic soda to the discharge paste, making it possible to remove the reduction product with water alone (Frossard and Fleischer, *Bull. Mulh.*, **1907,** 422).

In connection with the discharge of Thioindigo Red, an older patent of Kalle & Co. may be mentioned (*G.P. 200,927, 212,791–2*) consisting of printing sodium hydrosulfite, ageing, and passage through cold acetic or hydrochloric acid bath. Thioindigo Red can be discharged with Hydrosulfite NF and stannous hydroxide (*G.P. 213,471*). The addition of glucose or any other carbohydrate to the discharge paste is recommended in *G. P. 214,715*, and anthraquinone in *G.P. 213,583*. The following formula is from *Frb. Ztg.*, **1910**, 287–297

80 gm	zinc white
100 gm	potassium sulfite
100 gm	water
90 gm	Hydrosulfite NF
600 gm	gum thickening 1:1
30 gm	anthraquinone 30% paste
1000 gm	

(3) Condensates of acenapthenequinone (Ciba Scarlet G) cannot be discharged with Rongalite CL.

(4) *Indanthrenes:* Derivatives of Flavanthrene and Benzanthrone cannot be discharged.

Certain vat colors, belonging to other groups, can be discharged with Rongalite CL,[*] such as the acylamino derivatives of the anthraquinone series (Algols).

Various Indanthrenes (or the corresponding Cibanone, etc., dyes) can be white-discharged with alkaline Hydrosulfite NF pastes containing an excess of Leucotrope W (R. Haller, "Chemical Technology of Cotton").

White Discharge with ZnO		White Discharge with Alkali	
410 gm	British gum 1:1	125 gm	British gum
100 gm	ZnO 1:1	200 gm	$BaSO_4$ 1:1
200 gm	$BaSO_4$ 1:1	50 gm	anthraquinone 30% paste
40 gm	anthraquinone 30% paste	100 gm	Leucotrope W
200 gm	Rongalite CL	175 gm	NaOH 40° Bé
50 gm	glycerin	50 gm	water
1000 gm		300 gm	Rongalite CL
		1000 gm	

The printed goods are aged 5 to 6 minutes in the rapid ager at 101°C, then passed open-width through boiling bath containing 1% sodium silicate, and well washed.

Researches of the I. G. disclose that preparation of the fabric before printing with Leucotrope W improves the discharge effect on medium and full vat color dyeings. The goods are padded with a solution of 200 gm of Leucotrope W per liter, then printed with a paste containing 300 gm Rongalite CL, 75 gm Leucotrope W and 250 gm caustic soda 40° Bé per kg. After ageing, the goods are rinsed and soaped as usual (Badische sample card 1921).

Dr. Gossler (*Mell.*, **1928**) found that a better white effect could be ob-

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[*] *G.P. 231,534, 235,879, 235,880, 240,513, 246,252, 246,519, 247,099, 247,101, 250,084.*

tained by adding pyridine to the first wash bath. He was able to discharge Indanthrene Blue RS by these means.

Other steps have been proposed for increasing the discharge effect of difficultly dischargeable vat colors, as Indanthrene Blue RS. Haller and Hackl recommended an oxidation agent in the after-treatment. Oxidation agents were also tried in the print paste, such as hypochlorite solution. The reduction products can be removed from the fiber with 2% sulfuric acid bath at 80°C. Instead of the hypochlorite, one suggestion called for alkaline pyrogallol solution, (Georgievics and Haller, "Handbuch des Zeugdrucks", p. 629). The chemical incompatibility of oxidation and reduction compounds in the same print paste, raises doubts as to the logic of this suggestion.

Heyden A.G. proposes a new discharge agent for indigo, the sodium salt of nitroso methylene sulfoxylic acid (*G.P. 231,487*).

In a more recent patent (*G.P. 568,426*) the I.G. proposes other compounds of the Leucotrope series, for example, sodium sulfonate of 1-phenyl-1-naphthomethyl ammonium hydroxide, as more effective on dyes which do not yield to regular formulas. The product is to be applied in the padder in a concentration of 250 gm per liter before printing.

Colored Discharge on Vat Dyeing. It is difficult to obtain color discharges by the Leucotrope method, as few colors withstand the strong reduction and subsequent boiling silicate bath, including chrome colors, basic colors and pigments fixed with albumen.

Yellow discharge with Leucotrope O has been mentioned. It is also possible to produce yellow using lead chromate and albumen, on goods previously prepared with ammonium sulfate (*G.P. 245,308; Frb. Ztg.*, **1912,** 519).

It was found possible to combine naphthols with Hydrosulfite NF discharges, to produce red discharge. Stiegler (*Bull. Mulh.*, **1909,** 478) developed a discharge process on substantive dyeings, wherein β-naphthol and Hydrosulfite NF are combined in a print paste, the goods are aged and coupled with diazotized *p*-nitraniline. It is possible to apply this method to discharges on indigo-dyed material. In this case the discharge paste contains Rongalite CL and β-naphthol sodium salt. The material is printed, dried and aged four minutes in saturated steam, passed open-width through diazotized *p* nitraniline solution, rinsed, soured and soaped.

This method gives unsatisfactory results because the disintegrative products of the sulfoxylate formaldehyde (sulfite and bisulfite) impair the naphthol. Schürch describes a new process (*Mell.*, Aug., **1938,** 665; *G.P. 692,743*, May, 1937; *F.P. 837,556*, Ciba) for producing red discharges, using naphthols and developing in diazo solution. By this process the indigoids are destroyed with Discharge Salt Ciba W (Leucophenine W), a quaternary ammonium compound of the Leucotrope type. No hydrosulfite is used, but large quantities of potassium hydroxide, plus anthraquinone and zinc oxide. A fabric dyed with Ciba Blue 2B (1 to 2%) is printed with pastes as given, adding any of the Naphthols, as AS, AS-G, AS-BG, etc., or according to the following:

White Discharge

550 gm British gum 1:1
100 gm Discharge Salt Ciba W
50 gm glycerin
100 gm potash
160 gm water
40 gm anthraquinone 30% paste
———
1000 gm

Color Discharge

30 gm Ciba Naphtol RTO
30 gm NaOH 38° Bé
30 gm Turkey red oil
120 gm water (*Dissolve*)
550 gm starch-trag. thickening
100 gm Discharge Salt Ciba W
100 gm potash
40 gm anthraquinone 30% paste
———
1000 gm

After printing and drying, the fabric is aged for 4 to 6 minutes then treated open-width in a diazo solution of 60 gm of Fast Scarlet Base GG, (etc), per liter; finally it is passed through a bath of 10 cc of sodium silicate 40° Bé per liter, rinsed, soaped and rinsed again. It is possible to obtain bright yellow, orange, red and brown discharges on fast blue dyeings, alongside excellent white discharges.

The Neocotone colors of Ciba (Neogenoles of Sandoz or Tinogenales of Geigy) can be used as discharges on vat color dyeings (*B.P.492,166*). These dyestuffs are insoluble azo compounds solubilized by acylating agents, for example, by benzoic acid sulfochloride (see Chapter IV). The process is based on the use of printing pastes containing, besides the dyestuff, potassium ferricyanide and zinc oxide. The discharge is printed on material dyed with Ciba Blue 2B and then developed in caustic soda of 13° Bé at 50°C.

The problem of printing vat colors as color discharge on vat color dyeings has not had a satisfactory solution. In printing vat dyestuff together with reducing agent, Leucotrope W and an alkali, it is found that the benzylating action of the Leucotrope in an alkaline medium is not complete. The unbenzylated portion of the indigo (or indigoid vat) is subject to reoxidation and the discharge effect is not clean (R. Haller, *Mell.*, **1923,** 121, 149).

The first colored discharges on indigoid vat dyeings were made without Leucotrope W. The method, as used at the Zündel plant in 1908–10, was:

2000 gm British gum 1:1
1400 gm Rongalite C 1:1
1400 gm caustic soda 40° Bé
700 gm glycerin
500 gm Indanthrene Blue RS paste
———
6000 gm

The suggested method of Dr. Haller (*G.P. 263,647*) is interesting. In this method, the Jeanmaire formula is followed, using ferrous sulfate and stannous chloride. An Indanthrene dyestuff paste is printed together with Rongalite CL stannous chloride and ferrous sulfate on dyed indigo cloth. Upon ageing, the indigo is transformed to the benzyl ether of leuco-indigo, on the printed portions. When the goods are taken through caustic soda of 18° Bé at 60 to 80°C, the Indanthrene color is vatted by the simultaneous action of alkali, ferrous hydroxide and hydrosulfite and fixed on the fiber, while the indigo-complex is at the same time removed.

Variations of this method are found in *G.P. 270,124* (1913) of Enderlin Co., Vienna (*Frb. Ztg.*, **1914,** 160). Compare also Sunder-Solbach, "Use of Stannous Hydroxide," *Bull. Mulh.*, **1925,** 755; Haller, *Mell.*, **1924, 317.**

Vat Colors—Resist Printing

Resists under Indigo

Resist prints under indigo dyeings are carried out with products which work either on a mechanical or chemical principle. Mechanical resisting agents are wax, pine rosin, starches, china clay, and barium sulfate.

Chemical resisting agents are those which have the property, because of their acidic or oxidizing nature, of precipitating the leuco-indigo in the form of an insoluble pigment and thus prevent its fixation on the fiber. Chemical agents of this nature are calcium phosphate, lead sulfate, aluminum sulfate, alum, copper sulfate, copper nitrate, copper acetate, barium formate, manganous chloride, zinc sulfate, Leucotropes , and Ludigol.

The use of the insoluble lead and copper salts of *m*-nitrobenzene sulfonic acid was recommended by Crone & Co. (*G.P. 212,171*). These salts are strongly oxidizing and have the advantage over the soluble Ludigol of not forming halos, or flushing. The resist prints are generally more stable with these salts.

Some products act both as mechanical and chemical resists. The salts of zinc, aluminum and manganese are in general acidic ,thus precipitating leuco-indigo, and forming at the same time the metal hydroxides in the alkaline medium, which are more or less water-impermeable. The thickening agent itself acts mechanically in this case. According to Persoz, a print paste of this type can be composed of copper sulfate -acetate and -nitrate, china clay and gum thickening. Persoz also developed an interesting printing style, wherein color effects were made with madder dyes on indigo blue. This style, very popular in France between 1840 and 1860 and still produced in Russia up to 1914, is based on the following principle (the so-called "Pappreserve").

The bleached cotton fabric is printed with the white resist, as described above. After storing 24 hours, the goods are dyed in an indigo vat, rinsed, acidulated to accelerate the oxidation of the indigotine and to clean the whites.

The white, resisted areas are reprinted, except for that portion which should appear light blue. The light blue color is acquired by resist under second dyeing with indigo. Aluminum mordant print will give red and pink. Yellow can be obtained by an extract of Persian berries on aluminum and zinc mordants. Green can be obtained by printing the light blue with yellow. This style is characterized by excellent fastness, but has been replaced by modern printing methods.

The so-called "Lapis" style, introduced at the beginning of the century by Hartmann, Koechlin and J. Thompson is based on similar methods. Red, yellow, green and black were printed on indigo blue, alongside white.

Davenport in *B.P. 8738*, 1912 (Calico Printers), improved the mechanical resist effect by adding rosin and stearic acid mixed with turpentine, melted and added to a dextrin paste containing copper and lead salts. The paste is printed warm, the goods passing directly to the dye vat, connected in tandem with the print machine. A resist which penetrated the cloth and gave a good white on both sides was obtained (*Frb. Ztg.*, **1913,** 236; *Öst. W.u L. Ind.*, **1913,** 402).

Schaab recommended in *G.P. 144,286, Aus.P. 15,707* (Badische A.S.F.) the precipitation of the metal salts of the resist paste with a solution of potassium carbonate and sodium hydroxide. He observed that the pastes became sufficiently hard and water-resistant to allow continuous dyeing of the indigo (*Fischer's Ber.*, **1903**).

Up to 1907, the resist style on indigo was an important, if complicated, art. It was carried out in multi-colored patterns as follows:

Yellow effects were obtained by printing a paste containing a lead salt (nitrate, sulfate or acetate) thickened with roasted starch on white ground, and after dyeing with indigo and acidulating, passing through an acidic bichromate solution. By using an alkaline chromate solution, however, an orange shade was obtained by the formation of a basic lead chromate. Yellows were also possible on zinc or aluminum mordant.

Light blue could be produced only by printing a resist on light blue dyed goods, and redyeing. Similarly, green was produced by printing a resist containing lead salts on light blue, and aftertreating with chromates. Gadda proposed adding zinc acetate to a white resist under indigo, then subsequently dyeing with basic colors (*Bull. Mulh.*, **1912,** 553).

After 1907 methods were developed which were primarily intended for resist printing under vat and sulfur color dyeings, but had importance for indigo also. These methods were based on the following: (1) manganese salts (Felmayer), (2) zinc chloride (Badische A.S.F.), (3) Ludigol (Badische A.S.F., Kalle), (4) Leucotrope (as resist under vat-color blotch prints.)

Discharge-resist prints were also employed; that is, resist prints which had discharging agents in the resist paste. They were capable, by their chemical nature, of preventing the indigo dyeing on the printed areas and of destroying any small amounts of dye which nevertheless penetrated the resist and stained the fiber.

The problem of producing colored resists with ice colors was studied by numerous investigators. The research in this field created the rich blue-red, and blue-white-red styles (Erban, *Frb. Ztg.*, **1910,** 141). As far as this process is concerned, the American plants undoubtedly had priority over the European printers.

According to Donald (*Dyer*, **1897,** 23–24), the procedure is as follows:

(1) The bleached cotton is impregnated with a β-naphthol solution, free of Turkey red oil in order to prevent lime soap formation in the alkaline vat.

(2) The goods are dried and printed with a red resist composed of lead sulfate, zinc acetate, zinc oxide, Turkey red oil and diazotised *p*-nitraniline, neutralized with lead or zinc acetate instead of the sodium acetate generally used. Turkey red oil forms insoluble soaps with the zinc and lead salts which add to the resist effect. Lead sulfate, transformed to lead chromate by after-treatment with bichromates, develops chromic acid in the sulfuric-oxalic acid bath, whereby the last traces of indigo are destroyed. It is still possible to improve the resist effect by the use of copper salts, in which case the *p*-nitraniline must be replaced by *p*-nitroanisidine which is not sensitive to copper.

(3) The goods are dyed and finished as usual.

Lurati obtained bright red resists by a similar methods (*Aus.P. 8411*—1900; *Chem. Ztg.*, **1902,** 534; *Öst. W. u. L. Ind.*, **1909,** 1523). In this case the naphtholate solution contains Turkey red oil and bichromate is added directly to the red resist, in order to produce a discharge effect in subsequent acid bath. After dyeing, the fabrics are treated with dilute sulfuric acid. Lurati also proposed using Azophor Red, nitrosamine, α-naphthylamine or nitrotoluidine in place of the *p*-nitraniline. In the case of α-naphthylamine, the bichromate must be replaced by another acid oxidant, as manganese dioxide or lead peroxide. In a later patent (*U.S.P. 700,521*—1902), he used potassium ferrocyanide in the naphthol prepare, so that the metal salts contained in the resist paste were precipitated to form an impermeable membrane for the indigo vat.

The following formulas for producing the blue-white-red resist style are from the Höchst cards.

(1) The fabric is padded in a solution of

25 gm β-Naphthol R
50 gm caustic soda 22° Bé
50 gm Para soap PN
50 gm tragacanth thickening
to 1 liter

(2) After drying, the goods are printed with the resists:

White	Red
200 gm gum thickening	80 gm Azophor Red PN
70 gm water	40 gm water
220 gm lead nitrate	840 gm white resist
330 gm lead sulfate	40 gm sodium acetate
180 gm zinc sulfate	
1000 gm	1000 gm

(3) After printing and drying, the goods are dyed in the indigo vat, rinsed, soured and washed.

Instead of Azophor Red PN, nitrosamine red can be used.

Felmayer (Austria) proposed three different methods of producing this style. All use nitrosamine red. Two of these methods require a padding operation with acetic acid to develop the red, but these were not practicable.

The third process (*G.P. 213,128; Aus.P. 45,189; Frb. Ztg.*, **1910,** 286) was very successful. It was based on the fact that Mn_3O_4 or manganese chromate can act as resist for indigo. The bleached and mercerized fabrics are padded with naphthol as follows:

25 gm β-naphthol
25 gm caustic soda 36° Bé
40 gm soda
20 gm Turkey red oil
40 gm glue
to 1 liter

then printed with

Red Resist	Diazo Solution
180 gm gum arabic 1:1	49 gm *p*-nitraniline
400 gm manganous chloride 1:1	190 gm hot water
340 gm diazo solution	131 gm HCl 21° Bé
25 gm sodium bichromate	330 gm water
55 gm sodium acetate	100 gm sodium nitrite 40%
1000 gm	1000 gm

The goods are dried, dyed on the continuous vat, rinsed, acidulated with a warm solution containing sulfuric acid and potassium thiocyanate, well washed and dried.

Resists under Indigo Blotch Prints. Resists under indigo blotch-prints or all-over pattern can be made in various ways with (1) sulfur, (2) Ludigol, (3) Leucotrope, or (4) zinc chloride and manganous chloride.

Sulfur resists have been known for a very long time. They were also used in the Schlieper and Baum process. The formula for white effect is

500 gm	milk of sulfur
500 gm	gum thickening
1000 gm	

The resist is printed on a glucose preparation, then overprinted with indigo containing caustic soda. The goods are then aged and well washed.

Colored resists are obtained by adding various mineral salts to the white. A yellow, for example, results when cadmium chloride is added, yellow cadmium sulfide being precipitated on ageing. For red, aluminum acetate is added to the print paste and after printing and ageing, the goods are dyed in Alizarine Red. Similarly sulfur dyestuffs may be printed, or any vat colors which withstand sulfur (*B.P. 17,713*—1908; *F.P. 405,151*—Bayer; *Frb. Ztg.*, **1910,** 334; *G.P. 223,104*).

Azo dyestuffs were printed under indigo prints (*Bull. Mulh.*, **1894,** 260). The process is not practical because the sulfur substantially dulls the red azo colors.

The methods using Ludigol, Leucotrope and the metal salts will be discussed next.

Resists under Vat Dyestuffs

The methods may be divided in two groups: (1) resists under dyeing produced on continuous range, and (2) resists under pad dyeing, and in short baths.

Resists Under Continuous Vat Dyeing. Oxidizing agents are used to bring about a local destruction of the hydrosulfite in dye vat. The resisting agents are:

(1) Neutral chromate: Jeanmaire, *Bull. Mulh.*, **1913,** 84; Tigerstedt, *Bull Mulh.*, **1902,** 422; Caberti, *Rev. Gen. Mat. Col.*, **1906,** 153.

(2) Ferricyanide: Raczkowski, *Bull Mulh.*, **1909,** 91; *Frb. Ztg.*, **1910,** **282.**

(3) Manganous chloride with bichromate: Felmayer, *Frb. Ztg.*, **1911,** **48,** **460;** **1910,** 286; *G.P. 215,128, 243,683; Aus. P. 45,189, 40,412; B.P. 25,312*—1908.

Manganese Resist of Felmayer

I. {400–500 gm manganous chloride
450–350 gm gum thickening 1:1

II. {75 gm kaolin
25 gm sodium bichromate
50 gm water

The resists I and II are mixed just before printing. The goods are dyed on the continuous range with Indanthrene Blue RS (compare Haller, *Mell.*, **1921,** 173).

(4) The use of copper sulfate and lead nitrate under thioindigoid vats: Kalle, *G.P. 196,658; Frb. Ztg.*, **1908,** 150; *Rev. Gen. Mat. Col.*, **1910,** 216; *Z. f. Frb. Ind.*, **1910,** 356.

(5) Manganous chloride without bichromates: Pokorny, *Bull. Mulh.*, **1920,** 257; *Mell.*, **1923,** 583.

(6) Zinc chloride: Badische A.S.F., *G.P. 237,018; Frb. Ztg.*, **1911,** 365 and 405; *J. Soc. Dy. & Col.*, **1913,** 150.

(7) Magnesium carbonate or oxide: Lauterbach (Enderlin Bros.)

(8) Manganese and zinc salts: Haller ("Handbuch des Zeugdrucks," by Georgiewicz and Haller, p. 619 ff.); Nowack, *Mell*, **1927,** 861. Haller (*Bull. Mulh.*, **1927,** 497) was the first to introduce the resist print under the continuously vat-dyed blue (Indanthrene Blue RS). The resist was a mixture of salts of zinc, lead and especially manganese. The formula consisted of:

500 gm Senegal gum 1:1
120 gm manganous chloride
240 gm zinc chloride
120 gm kaolin
20 gm picric acid

1000 gm

The goods are first prepared with Turkey red oil, printed, dried and stored 24 hours, then dyed in a continuous vat containing:

21 kg Indanthrene Blue RS double paste
6 kg regenerated color from old bath
28 kg caustic soda 40° Bé
19 kg glucose 1:1
3 kg sodium hydrosulfite

to 500 liters

Red resists are prepared by adding diazo solution and bichromate to the white resist. In this case the goods must be prepared with β-naphthol.

(9) White resist under vat color dyed from zinc chloride and ferrous sulfate vat:

330 gm	gum thickening 1:1
215 gm	lead sulfate
275 gm	water
110 gm	lead nitrate
55 gm	lead acetate
15 gm	oil
1000 gm	

The resists under Indanthrene Blue RS yield prints of almost indestructible fastness.

If the goods are to be dyed from a hydrosulfite-glucose vat, the resist paste cannot contain lead or copper salts. These metals form black sulfides with the hydrosulfite. In such cases the resist contains manganese and zinc paste.

(10) Another group of resisting agents were brought out by Kalle and Badische in 1909. These are the sodium salts of benzene, naphthalene and anthracene derivatives, which have NO_2 and HSO_3 groups. The principal representatives of this group are the sodium salt of *m*-nitrobenzene sulfonic acid (Ludigol, Revatol, Albatex BD) and the sodium salt of *o*- or *p*-toluene sulfonic acid (Reserve Salt, Kalle). These compounds have the effect of decomposing the hydrosulfite, thus preventing a fixation of the vat dyestuff on the printed portions. But the sodium salts are much too soluble to have found practical use in this respect. For this reason the less soluble manganese, zinc, and calcium salts were proposed. In *G.P. 292,171* (*Frb. Ztg.*, **1916**, 209) Crone & Co. recommended the copper, lead, zinc or manganese salts of *m*-nitrobenzene sulfonic acid. The copper salt found use as resist under indigo, while the lead salts were more satisfactory in the hot Indanthrene vat. In recent times the I.G. again took up the problem and recommended in *G.P. 548,202* the calcium, barium and magnesium salts. This patent refers to Reservol B, a sparingly-soluble white powder. The salts of dinitrobenzene sulfonic acid are mentioned in *U.S.P. 1,962,085*.

In order to avoid the halo formation caused by the good solubility of the sodium nitrobenzene sulfonates, and to improve the resist effect, it has been suggested to add polyvinyl alcohol to the print paste. This product coagulates in warm alkaline solution (*Aus. P. 126,574*, *B.P. 355,059*, *G.P. 531,475*).

A study dealing with resists under vat dyeings (Turski and Checinsky, *Mell.*, **1937**, #18, 87) brings out some interesting details regarding the use of dinitro compounds. Haller had already used picric acid (see above) and dinitrophenol (*G.P. 205,813*). Unsulfonated compounds such as dinitrobenzene and dinitronaphthalene were used instead of the soluble sulfonates. Because of their insolubility, they must be used in dispersed form: dinitrobenzene, for example, can be melted and mixed with the warm gum, while dinitronaphthalene is ground fine, pasted with sulforicinoleate and mixed with the thickening.

Thickening agents which coagulate in alkaline medium form the basis of *G.P. 642,581.* Colored resists under vat dyeings can be obtained in this way. Naphthol AS, and locust bean gum are printed on the white goods, then the vat color is printed or padded on in pigment form. The goods are then passed through an alkaline reducing bath, wherein the vat color is fixed. The azo color is developed in a subsequent diazo solution. In an earlier patent (*Aus.P. 126,753*) Zeidler and A. Haller had recommended alkalicongealing thickeners (raw starches) for resist purposes.

G.P. 638,755 (Bleachers' Assn.) describes a method for producing colored resists, using vat dyestuffs under vat dyeings. The feature of the method consists of printing with thickenings, such as Colloresin or locust bean gum, which are rendered insoluble in alkalis. The resists contain manganese salts.

Colored resists were obtained with vat colors in *Aus.P. 59,164, 59,165*—1913; *Frb. Ztg.*, **1917,** 193, 214, 247, 271. The material is printed with a resist paste containing vat color, manganous chloride, zinc chloride, stannous chloride and ferrous sulfate. Dyeing is carried out at 40°C with Hydron Blue, dissolved with sodium sulfide, sodium hydroxide and sodium hydrosulfite, followed by passage through caustic soda of 20° Bé at 80°C (15 to 20 seconds), souring and rinsing. This process was used by de Angeli Co. of Milan on an industrial scale, particularly for Indanthrene Yellow G resists under dyeings of Hydron Blue. The procedure has been described by Tagliani in *Frb. Ztg.*, **1917,** 193. The resists are prepared as follows:

White Resist	Yellow Resist
150 gm kaolin	120 gm kaolin
100 gm water	40 gm water
180 gm manganous chloride	50 gm Indanthrene Yellow G powder
180 gm zinc chloride	320 gm starch thickening
390 gm gum thickening	250 gm $MnCl_2$
	170 gm ferrous sulfate
1000 gm	50 gm zinc chloride
	1000 gm

The printed goods are dried, then dyed 30 to 40 seconds at 80°C with the following vat:

100 gm Hydron Blue R paste
50 gm caustic soda 36° Bé
30 gm sodium sulfide
6 gm Turkey red oil
15 gm sodium hydrosulfite

per liter

The goods are then passed through caustic soda 20° Bé at 80°C for 15 to 20 seconds, acidulated, washed and dried. The operations are carried out on a continuous range.

R. Haller developed an Indanthrene Yellow resist under Indanthrene Blue, using zinc oxide, ferrous sulfate and anthraquinone. The dyeing is carried out in the continuous vat (*Frb. Ztg.*, **1917,** 247, 309, 330; **1918,** 1, 51, 121; *Rev. Gen. Mat. Col.*, **1919,** 127). Haller also found an addition of Leucotrope W advantageous.

Print Paste	
2700 gm	stock gum
250 gm	Indanthrene Yellow G paste
100 gm	ferrous sulfate
50 gm	glycerin
3100 gm	

Stock Gum	
940 gm	British gum
600 gm	Rongalite C
480 gm	zinc oxide
240 gm	anthraquinone 30% paste
2490 gm	water
4750 gm	

After printing, the goods are aged at 105°C, dyed as usual in an Indanthrene Blue vat, acidulated, washed and dried. The alkali contained in the dye vat dissolves the leuco compound on the printed area, causing its adsorption by the fiber. The ferrous sulfate acts not only as reducing agent, but as a resisting agent (compare *Bull. Mulh;* **1927,** 135; *Rev. Gen. Mat. Col.*, **1920,** 113; Erban, *Frb. Ztg.*, **1915,** 20).

Resists under Pad Dyeings (Short Liquors).

Zinc Chloride Process. This method was developed especially for use under sulfur color dyeings. The white resist contains 150 to 200 gm zinc chloride per kg of printing paste. Part of the zinc chloride may advantageously be replaced by manganous chloride. The printed goods are padded with the reduced vat color.

The resist effect is increased by adding potassium ferrocyanide to the dye liquor. It forms insoluble zinc ferrocyanide with the zinc chloride of the resist, thus acting as a mechanical resisting agent. The dyestuff is pasted with glycerin, and hydrosulfite and alkali added. After pad dyeing, the goods are aired for 20 to 30 seconds, washed, soured and rinsed.

Colored resists can be carried out using azo colors, basics, chrome, sulfur and vat colors (Diserens, *Rev. Gen. Mat. Col.*, **1918,** 63; also Aug., **1920,** 113).

Ludigol Process. This process has been used successfully in the past, and has been studied again in the light of the short bath methods of vat dyeing which are being developed today, such as the Pad-Steam method and Williams Unit. The fastness of the ground shades heightens interest in this process and compels preference for this style over discharge printing of direct colors.

White Resist with Ludigol

300 gm	gum arabic thickening
175 gm	Ludigol
55 gm	kaolin
390 gm	water
80 gm	zinc acetate
1000 gm	

The zinc acetate is added to form the zinc salt of Ludigol which is much less soluble than the sodium salt. Barium salts are also recommended. These salts increase the sharpness of the white.

After printing, the goods are aged four minutes, then padded in the dye vat, rinsed and washed.

Colored resists are produced by applying basic, mordant, vat and azo colors, and with Indigosol colors.

For resists with azo colors, the material is first naphtholated then printed with white resist, as above, to which Fast Red Salt has been added.

Basic colors may be fixed with tannin or zinc ferrocyanide. The print paste contains Ludigol, basic color and tannic acid. After steaming and dyeing, the goods are treated with tartar emetic.

L. Diserens developed a method by which the basic color is printed with tannic acid and zinc acetate, using resorcin to prevent precipitation of the color lake (*Rev. Gen. Mat. Col.*, **1917,** 14; **1918,** 63). The formula for printing is as follows:

30 gm	basic dyestuff
100 gm	resorcin 1:1 or glycollic acid 1:3
180 gm	water
150 gm	Ludigol
300 gm	gum thickening
120 gm	tannin 1:1
120 gm	zinc acetate or zinc lactate
1000 gm	

The treatment in tartar emetic is unnecessary. The printed fabrics are aged, immediately padded in the vat dyestuff solution, acidulated and rinsed.

Indigosol dyestuffs give interesting colored resists under vat dyeings. The process is based on the principle of using the manganese salt of *m*-nitrobenzene sulfonic acid as resisting agent. This salt is much less soluble, even at elevated temperatures, than the corresponding sodium salt. The trade name is Reservol B (*G.P. 548,202*). It can also be prepared for use in the print formula as follows:

I.	200 gm	Ludigol
	300 gm	hot water

II.	220 gm	manganous chloride
	250 gm	hot water

Mix II with I. The manganese salt settles out on cooling in the form of fine crystals, which are filtered and pressed. The yield is about 375 gm of a 66 to 70% paste. When added to the print paste it acts as an acid oxidizing agent, and promotes the development of the Indigosol.

Resist Paste

50 gm	Indigosol dyestuff
50 gm	Durit O
145 gm	water
510 gm	gum thickening
25 gm	$NaClO_3$ 1:3
20 gm	ammonium vanadate 1:1000
200 gm	paste of manganese *m*-nitrobenzol sulfonate
1000 gm	

The fabrics are printed and dried, then blotched with vat color, dried and aged 5 minutes in the rapid ager. The development of the Indigosol colors is brought about by a 2-second passage through cold solution of 5 gm of sodium nitrite and 20 gm of sulfuric acid 66° Bé per liter, skying 20 seconds, rinsing and soaping.

Vat colors can be printed as resists under vat color dyeing by *G.P. 272,685.* It was observed that certain vat colors can be reserved by nitro compounds, while others can be fixed in their presence. In this way, for example, Indanthrene Yellow resists can be produced under Indanthrene Blue. The printing formula is as follows:

150 gm	Indanthrene Yellow R paste
550 gm	gum tragacanth
75 gm	Ludigol
50 gm	glucose
175 gm	water
1000 gm	

After printing, the goods are overprinted by means of blotch roller with Indanthrene Blue, sulfoxylate formaldehyde and alkali, or padded with the paste in a two-roll mangle, aged, washed and soaped. (Haller, *Bull. Mulh.*, **1927,** 135).

The use of Colloresin DK as thickening agent for the resisting vat color is described in *G.P. 520,519* (I.G.—Gossler).

Vat dyes have been extensively used as colored discharges in other ways. They are used for their outstanding fastness properties: as colored alkaline resists in the tannic acid-tartar emetic style under basic colors; as colored discharges of mordant dyeing, particularly for dyed Alizarine Red; as color discharges on azo dyeings on β-naphthol or Naphthol AS, also for Variamine Blue style; as color discharges on substantive dyeings; as colored resists under aniline black; as resists under Indigosols; as resists under sulfur colors.

DYEING

Dyeing with Indigo

It is not intended to give here the complete details of the indigo dyeing processes, as this style has been almost completely replaced by more modern dyeing methods. There have been few additional researches conducted on the style in recent years. However a summary of the known processes with corresponding references will be given to complete a survey of the field of vat dyeing.

References:

Haller and Glafey: "Chemical Technology of Cotton" in Herzog, "Technology of Textile Fibers", p. 111 ff.

Reinking: "The Oldest Description in the Field of Vat Dyeing", *Mell.*, **1925,** 349; also "The First Appearance of Indigo in Europe", *Mell.*, **1924,** 187; also *Mell.*, **1929,** 733.

Hackl: "New Methods in Dyeing & Printing", *Mell.*, May, **1930,** 383; July, **1930,** 530.

Badische A.S.F.: "Indigo Rein", 1909.

Haller: *Frb. Ztg.*, **1912,** 259; *Mell.*, **1922,** Report of Innsbruck Congress of 1922.

Perndanner, Hackl, Bartl: "Chemistry of the Hydrosulfite-Glucose Vat", *Mell*, Jan., **1930,** 42.

Leupin and Hartmark: "Studies of Indigo and Wool-Dyeing with Indigo", *Mell.*, **1943,** 394.

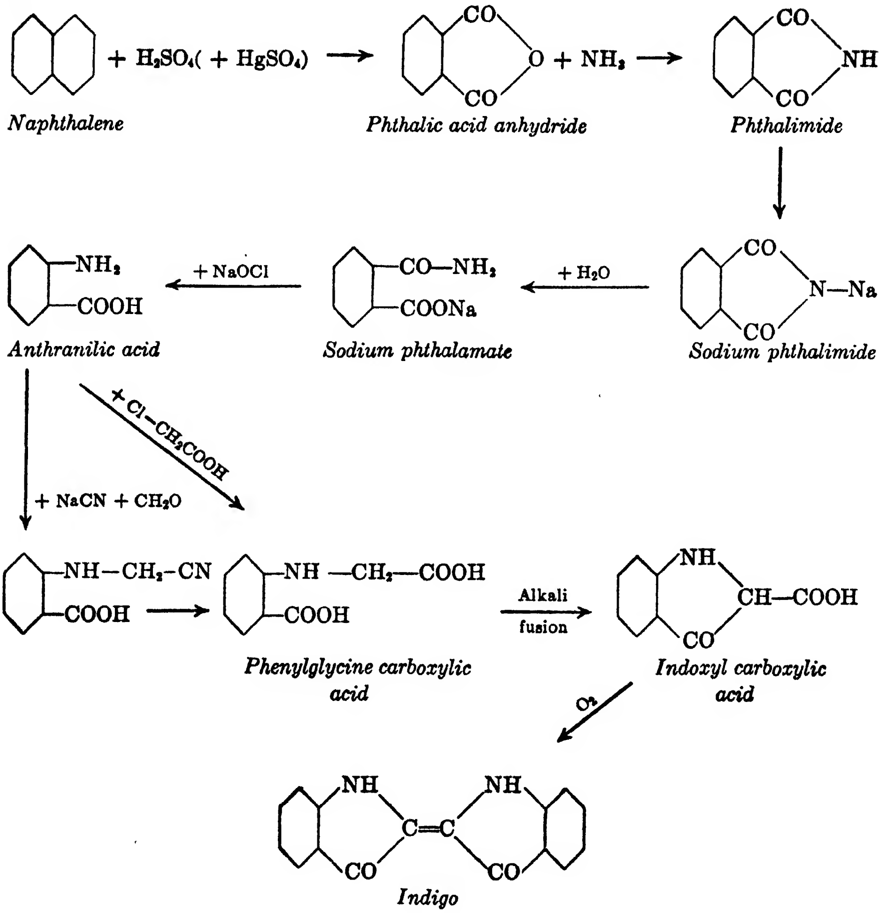
Indigo is the oldest representative of the vat dyestuffs. The dyeing property of natural indigo was recognized thousands of years ago. The dye has been employed in all parts of the world and has been used in great quantities in the past.

Indigo was first produced synthetically by von Baeyer in 1880. Its manufacture on an industrial scale was begun ten years later, and its successful production must be credited to such chemists as Heumann and Knietsch of Badische A.S.F., and to Sandmeyer of Geigy, whose very ingenious method was invented at the beginning of the 20th century.

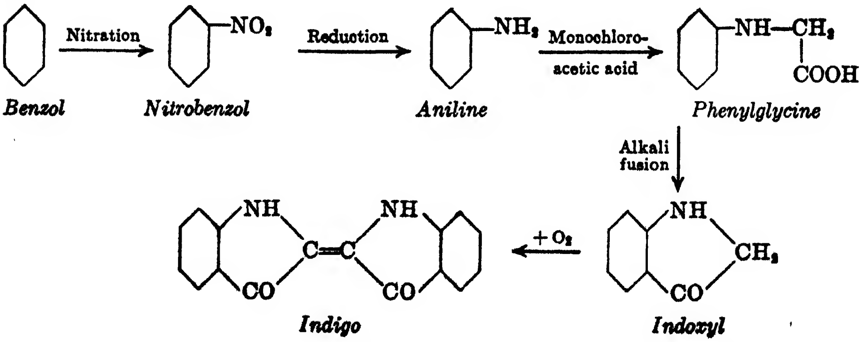
A short schematic survey of these important methods is given:

Synthesis of Badische A. S. F. (Heumann)

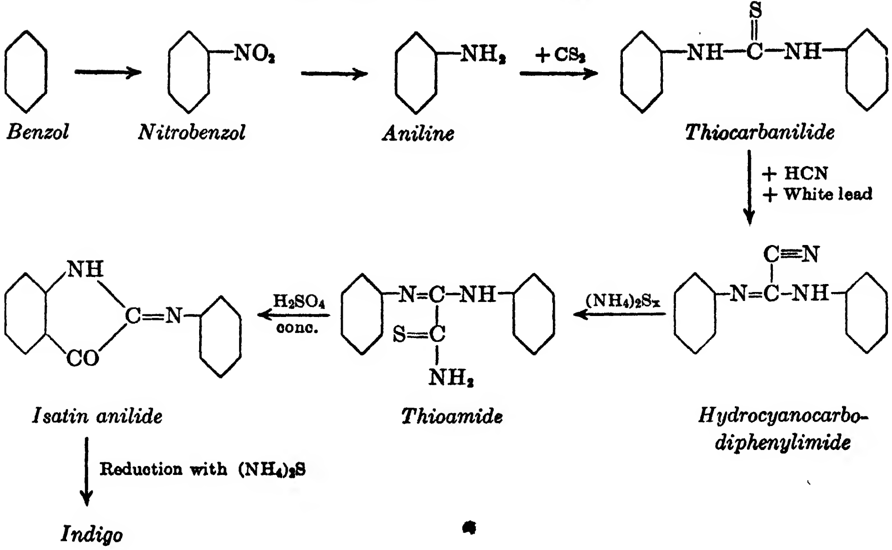
(1)



(2)



Synthesis of Sandmeyer (Geigy)

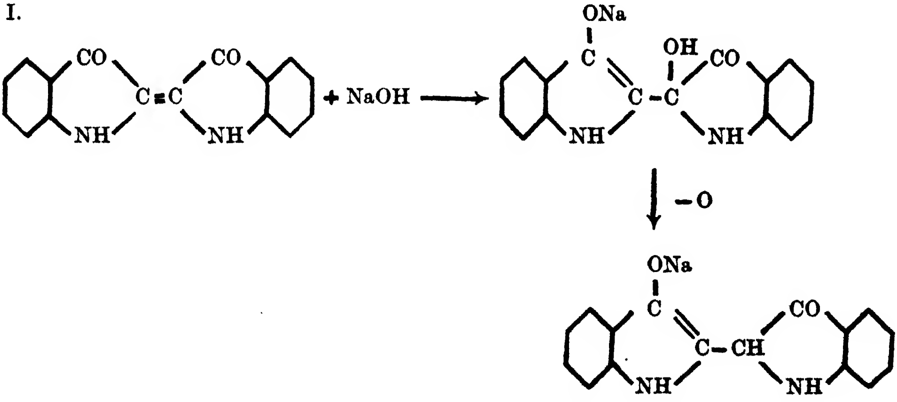


Indigo is transformed by reduction into a yellow-white compound, leuco-indigo, which has two more hydrogen atoms than the blue indigo.

The dyestuff forms a sodium addition compound in the vat. Two salts can be formed.

The first salt (I) has good solubility, the second (II) is less soluble.* Dyeing is carried out in the standing vat, or on the continuous machine.

I.



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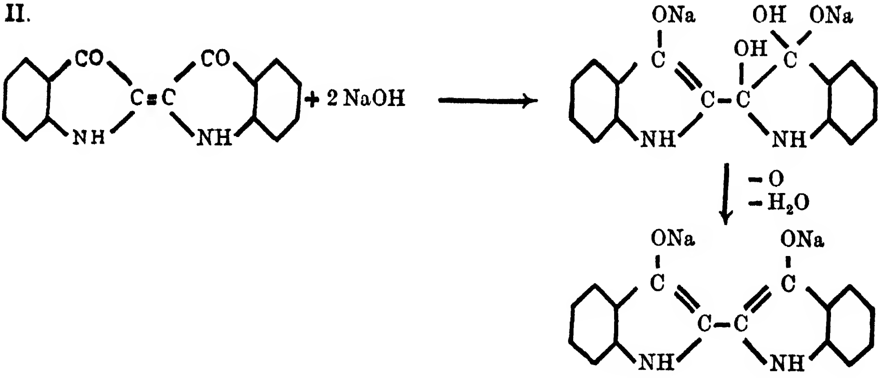
* Binz and Runge, *Z. f. angew Chem.*, **1902**, 627; *G.P. 158,625, 219,732.*

II.



The dye baths can be classified according to their composition:

(1) Zinc-lime vat: indigo, zinc powder and lime.
(2) Copperas vat: indigo, ferrous sulfate and lime.
(3) Hydrosulfite vat: indigo, sodium hydrosulfite and caustic soda.
(4) Hydrosulfite-glucose vat: Candit V and indigo
(5) Fermentation vat: indigo, sugars, soda ash and lime.
(6) Zinc-bisulfite: indigo, zinc dust and sodium bisulfite.

Zinc-Lime Vat. This vat is based on the chemical reaction of zinc with slaked lime, which forms calcium zincate and hydrogen as in the equation:

$$Zn + Ca(OH)_2 = CaZnO_2 + 2H$$

Nascent hydrogen reduces the indigo to leuco-indigo which dissolves in the excess of lime. Actually, the reaction does not proceed in such a simple manner, observation pointing to a more complicated chemical process.* The dye bath is made up as follows:

200 kg indigo 20% paste
45 kg zinc powder
100 kg lime

to 2000 liters

Caustic soda can be used in place of the lime.

Copperas Vat. The reduction agent is ferrous sulfate, the reducing properties of which have already been referred to on page 90, and which Jeanmaire employed for printing vat dyes.

The reducing action of ferrous sulfate in an alkaline medium is explained by the following equations

$$FeSO_4 + Ca(OH)_2 = Fe(OH)_2 + CaSO_4$$

$$2Fe(OH)_2 + 2H_2O = 2Fe(OH)_3 + 2H$$

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* *Z. f. angew. Chem.*, 1899, #21 and 22.

The ferrous hydroxide transforms indigo to leuco-indigo, while it is itself oxidized to ferric hydroxide.

Stock Vat

25 kg indigo 20% paste, *suspended in*
45 l water at 60°C
Add:
30 kg lime, previously slaked
Add:
20 kg ferrous sulfate, *dissolved in*
80 l water at 60°C
Dilute to 250 l

Hydrosulfite Vat. This method is particularly suited for machine dyeing.

Candit V. This product can be used as reducing agent in dyeing indigo. This method and the following (Fermentation Vat) are the only ones operating at elevated temperatures. The affinity of leuco-indigo for the fiber decreases substantially at higher temperatures. Several addition products, such as glue and Tetracarnit, have been recommended for improving the yield of the color (Haller, *Mell.*, **1926**).

Fermentation Vat. This process was employed principally in Asia (Japan, China, India) and in Asia Minor. It was not taken up in Europe, with the possible exception of Russia. The reducing agent is hydrogen generated by bacterial fermentation of carbohydrates in an alkaline medium. According to the country in which this vat process was operated, the following were used. Reducing agents: bran, flour, molasses, bread, dates and other fruits containing sugar, henna leaves, raisins, madder; Alkaline agents: lime, potash, wood ashes, soda ash, urine, naturally occurring soda, called Illig or Kallia in Syria and Persia, Calager in the Caucasus.

Example of Vat

9 kg	indigo 20% paste
3 kg	potash
15 kg	decoction of bran

The bran is boiled with 100 liters of water, then strained through a sieve, and added to the vat, which must be maintained at 50°C. Fabrics dyed in this way have a peculiar odor, probably caused by the formation of indol.

Zinc-Bisulfite Vat. The zinc powder-sodium bisulfite vat differs very little from the hydrosulfite vat, but is accompanied with various complications, such as formation of precipitates, etc.

Another method of dyeing indigo is described in *G.P. 692,623*: The material, cotton or rayon, is padded with leuco-indigo in alkaline, neutral or acid solution, either with or without dispersing or wetting agents, thereupon treated in alkaline reducing bath for the purpose of fixing any partly reoxidized indigo. In this way, deep blue shades of indigo are obtained, of high degree of levelness and penetration, and without bronzing.

Dyeing of Wool with Indigo

Before the invention of hydrosulfite, indigo was dyed by the fermentation vat. The reduction is carried out by fermentable substances which were added to the dye vat together with an alkali and the dyestuff. For fermenting, bran, woad, molasses or madder was used, and for the alkali, potash, lime or soda. Dyeing is carried out at 50°C. The method required strict supervision. It was eagerly replaced by the zinc bisulfite vat, and by the hydrosulfite vat, in turn, as these processes were discovered.

A typical dye vat is given here.

Stock Vat (3000 liters)
7.5 kg indigo 20% paste, *pasted with*
15. l water at 60°C
Add:
1.8 l caustic soda 40° Bé, *and*
1.5 kg hydrosulfite conc.
Reduce 1 hour at 60–70°C

The dye vat is prepared with water at 50°C containing 1 liter of ammonia and 150 gm of hydrosulfite. Glue solution (10 liters) 1:10 can be added (*G.P. 152,907*). Lastly the stock vat is added.

Slaked lime can be substituted for the caustic soda.

Dyeing with Vat Dyestuffs*

The vat dyestuffs are dyed on vegetable fibers (cotton, regenerated cellulose), seldom on wool.

Cotton is dyed as loose stock, on spools, as yarn and in the piece. Yarn, spool and stock are dyed in mechanical apparatus, the principle of which is moving liquor, stationary material.

Cotton and rayon piece goods are dyed on the padder, jig or continuously. The principle here is moving cloth, stationary liquor.

The vat colors are generally prereduced for use in mechanical apparatus. In package dyeing of cotton, as well as beam dyeing of yarns, the vat color is reduced with caustic soda and hydrosulfite. It is also possible to circulate pigment vat dyestuff, then reduce in alkaline-hydrosulfite solution.

The use of the vat colors for piece goods dyeing follows these main methods:

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* Durst, "Dyeing of Indanthrene Blue," *Mell.*, **1925**, 837; Gund, "Special Methods of Dyeing Indanthrene Dyestuffs," *Mell.*, **1943**, 401, 435, 470; Colomb, *Teintex*, **1941**, 307.

(1) Impregnation of the fabric on the padder with the unreduced vat dyestuff, then subsequently reducing on the jig (pigment pad method).

(2) Dyeing with reduced dyestuff.

(3) Padding with reduced vat color, then passing through booster solution containing alkali, hydrosulfite and some dyestuff.

(4) Padding with dyestuff, potash and sulfoxylate formaldehyde, drying and ageing.

(5) The Jeanmaire process of padding vat dyestuff, ferrous sulfate, and developing in 20° Bé caustic soda at 80°C.

(6) Padding unreduced dyestuff, and either with or without subsequent drying, padding again with caustic soda and hydrosulfite, then ageing. This is the pad-steam method.

(7) Padding unreduced dyestuff and immediately passing through ultra-short wells of the Williams' unit (*U.S.P. 2,364,838*).

(8) Padding vat dyestuff, then reducing in unit in which the fabric is imposed, layer on layer, on a rotating reel. This is the Multi-lap process.

(9) Vat-acid method.

Machine Dyeing

The dyestuff is reduced in a stock vat of highest possible concentration. The dye liquor is prepared with water softener and dispersing agent, then the stock vat is added. Dyeing by reduced vat color in stock vats is based on the use of a highly concentrated stock vat which is added to the dye liquor containing a dispersing agent. Characteristic of this method is the fact that the leuco vat is more or less hydrolyzed in the dilute bath to free vat acid. In this form the affinity of the dyestuff to the fiber is suspended for the most part. The further procedure consists of transforming the dyestuff into a state of affinity by gradually adding caustic soda and hydrosulfite. This brings about better penetration of the fiber and a more complete exhaust of the dyebath.

According to the relative substantitivity of the vat dyestuff, the dyeing methods are divided into three categories, differing in the temperature of the dye bath and the quantities of the caustic soda and salts added.

(1) *High temperature and strongly alkaline:* 10–12 cc NaOH 40° Bé per liter at 60°C ("IN" method).

(2) *High temperature but weakly alkaline, with salt addition:* 3–5 cc NaOH 40° Bé per liter at 40–45°C. Glauber's salt or common salt is added during dyeing ("IW" method).

(3) *Low temperature, weakly alkaline with added salts:* Some vat colors dye best at room temperatures (20–25°C) with 3–5 cc caustic soda 40° Bé per liter, and with addition of larger quantities of salt ("IK" method).

The time of dyeing is 20 minutes to one hour. Wetting, leveling or penetrating agents are desirable additions to the dye bath, and the following have been found useful: Dekol, Nekal, Leonil, Invadin, Sandazol KB, Oranit, Neomerpin, Prestabit Oil, Avirol, Geneucol, Inferol NF, Optan, and many others.

Temperature has a great influence on the degree of wetting, the wetting action increasing with higher temperatures. It is therefore advantageous to have wetting agents which aid penetration at low temperatures. Humectol C or CX (I.G.) is particularly efficient, as well as Inferol 229 and 236.

Other dye assistants, which are leveling or retarding agents are the following: Lamepon, Peregal O, OK, Albatex PO, Repellat and Amendol. (See table at end of chapter.)

Dyeing is carried out as follows: the goods are first wet out in a liquor containing 1 to 2 cc of Peregal or Albatex PO plus 1 gm of Setamol WS per liter for 10 to 15 minutes at 75 to 80°C. Then the stock vat is added and the goods are dyed for 10 to 15 minutes. The temperature is selected for the dyestuff series employed. Partial hydrolysis of the sodium leucovat to vat acid occurs in the diluted vat liquor. The dispersing agents keep the unabsorbed and hydrolyzed portion in fine dispersion. Now sodium hydroxide and sodium hydrosulfite are added in portions to the dye liquor. In this phase of the operation the vat acid is gradually transformed to the sodium salt thus increasing the dye absorption in a continuous and uniform manner. This method aids levelness and penetration of the dye.

In the Abbot-Cox process, cotton in packages—that is, in the form of cops, cheeses or beams, loose cotton, hanks or warps—is dyed with vat colors by first impregnating with the dyestuff in pigment form followed by chemical reduction. The principle of this process lies in the exhaustion of the pigment through addition of electrolytes and the use of high temperatures during pigmentation. The dye is circulated through the packages as a fine dispersion in Dispersol VL and the temperature is raised gradually to 85 to 90°C with salt addition. The reduction is carried out in the same liquor or, in some cases where Dispersol acts as a retarding agent, in a fresh liquor (*J. Soc. Dy. & Col.*, July, **1947,** 224).

Piece Goods Dyeing

Pigment Pad Methods. The pigment pad process, or as it is sometimes called, the Prestabit Oil process, consists of padding the fabric with a suspension of the unreduced vat dyestuff, finely dispersed in the presence of a protective colloid or leveling agent, such as Prestabit Oil. The use of a dispersing agent is not as necessary today, with vat colors available in finely dispersed and stable state, as it was some years ago, when specking was a major complaint (Rupp, *Am. Dyes. Rep.*, Dec., **1946,** 651).

The fabric is batched up, or it can be dried in a hot flue dryer, then developed on the jig in a hydrosulfite and alkali liquor. Addition of some gum tragacanth to the padding liquor is advisable to promote levelness.

This method is useful for light and medium dyeings for short runs. It has been used on filament and spun rayon and rayon blend constructions, but the tension applied by the padding and jig dyeing does not give a pleasing result to eye or hand. Some of the crepe and hand of the rayons can be restored to the fabric by running the goods in rope form in beck or slack washer after the jig development (Brosnan, *Am. Dyes. Rep.*, Dec., **1946,** 648).

Preparation of the vat dye for pigment padding entails pasting the color in a manner which insures a stable suspension. A 6% gum tragacanth paste may be employed to paste up the dyestuff (*Text. Mfgr.*, **1929,** 282; *Mell.*, **1930,** 639). An addition of a wetting agent is often made, as sulfonated castor oil, Prestabit Oil or Eulysin A. Suspension of the dyestuff in fatty acid condensates of alkylolamines is recommended in *U.S.P. 2,094,608–9* (Kritchevsky). *U.S.P. 1,899,975* (N.A.C.) states that the dyeings are improved by adding alkali sulfides to the dispersion of the vat dye. *U.S.P. 1,782,122* (Du Pont—Kern—Sala) mentions alkylolamines (*e.g.*, diethylethanolamine) as dye-dispersing assistants in vat pigment padding. *G.P. 636,306* (Oranienburg) recommends pasting up the vat dyestuffs with sulfated fatty higher alcohols.

Typical padding formulas are given here:

I	II	
5	10 gm	vat dyestuff
10 cc		Eulysin A
1 gm		Nekal BX
	15 gm	Shiraz gum
——	——	

per liter

One or two passages are given on the padder at 80°C, the squeeze adjusted to give a pick-up of 75%. The fabric is batched up or dried in the hot-flue.

The jig development bath is prepared as follows:

I	II	
12 cc	12 cc	caustic soda 38° Bé
4 gm	3 gm	hydrosulfite conc.
10 gm		Glauber's salt
2.5 gm		Dekol powder
——	——	

per liter

Four to six ends are given (for rayons, 3 to 4 ends), rinsed then oxidized with 1 gm H_2SO_4 66° Bé per liter and well washed (soap, Igepon, Duponol).

In the production of pale shades with vat colors difficult to level, it is suggested to prepare the goods first with an alkaline solution of sulfite waste liquor (*U.S.P. 2,010,320*—McLoughlin).

A variation of the pigment pad method has been developed by Geigy (*F.P. 824,196*). A stock vat of the dyestuff is prepared, without any excess of alkali and hydrosulfite, and poured into a large excess of water. The shade of the leuco compound changes and a fine suspension is formed which probably contains the alkali salt of the leuco compound in a finely dissociated state. If too much alkali is used, the leuco compound precipitates in the form of flakes. By using this finely dispersed solution as padding liquor, very uniform dyeings are obtained.

Reduced Vat Dyeing. Following is an example of vat dyeing on the jig, using stock vat.

Cloth weighs 125 kg = 275 lb

The goods are entered in the greige state into the jig containing

270 l water
30 l stock vat
1 kg hydrosulfite
2½ l caustic soda 38° Bé
1 l enzyme (amylolytic)

After four ends, 1200 gm of hydrosulfite is added in two additions, and three ends more are given. Goods are rinsed, developed on three ends with

1 l acetic acid
½ l hydrogen peroxide

300 l

rinsed, soaped and rinsed.

Stock Vat

275 gm vat dyestuff fine powder
150 gm Albatex PO
1 l caustic soda 38° Bé
1 l Prestabit Oil
500 gm hydrosulfite of soda
25 l water at 60°C

total 30 l

Certain vat dyes, especially high molecular anthraquinoid dyestuffs have the drawback of forming colloidal solutions with reduced hydrosulfite and alkalis. In *B.P. 541,376* (I.C.I., 1942) it is recommended that small quantities of a condensate of ethyl chloride or iodide with hexamethylenetetramine be added, thus making the dyestuff more soluble and aiding penetration.

Reduced Vat—Booster Bath Method. While the pigment pad and jig development of vat colors yields the maximum in color fastness, it is essentially a batch process and more expensive than a continuous process. The reduced pad, continuous process of Tice (*U.S.P. 1,652,649*) is suitable for light and medium shades on long yardages of fabric. The goods are padded with reduced vat color and dyed in a bath of caustic soda and hydrosulfite.

Development in a bath of soda ash and hydrosulfite is the contribution of Wentz (*U.S.P. 2,318,133*).

In either case, the development bath, called the booster bath, must be large, to give the goods sufficient time for dyeing. Close attention to detail is necessary to achieve a color match, and long yardages are necessary to reach an equilibrium (Meunier, *Am. Dyes. Rep.*, **1945,** 206).

Sulfoxylate Formaldehyde Method. The sulfoxylate-formaldehyde method is based on the same process as direct printing by the carbonate-sulfoxylate-formaldehyde method. The dyestuff is carefully pasted up with suitable dispersing agents, thickened with a little British gum thickening, and potash and Hydrosulfite NF added. The process is suitable for light shades, but level results are difficult. After padding, the goods are dried in the hot-flue and aged with a uniform and saturated steam.

Jeanmaire Process. The Jeanmaire process, or caustic soda process, yields full, even dyeings, but a serious disadvantage is the development with strongly alkaline liquor which has a mercerizing effect on the cotton. A typical formula is given here:

10 kg vat dyestuff (*pasted with*)
10 kg dextrin solution 1:1, (*added to*)
7 kg ferrous sulfate (*dissolved in*)
19 l water
6 kg glucose (*in*)
44 l water (*and*)
2½ kg lactic acid 50%
—
total 100 l

After padding and drying, the goods are passed for 20 to 25 seconds through 20° Bé caustic soda at 80°C, well rinsed and soaped.

Pad-Steam Method. The chemists of Du Pont have found that the vat colors can be reduced in a matter of seconds in an atmosphere of live steam as compared with the lengthy reduction time required in an aqueous bath. The method is essentially a pigment padding of the vat color, followed by a chemical pad of caustic soda and hydrosulfite. From the chemical pad the cloth passes immediately into the steam chamber where the reduction takes place. The usual oxidation and soaping may be carried out in rope form on slack washers (*U.S.P. 2,415,379*, Du Pont-Vieira).

Depending on the shade, and character of the cloth, the pigment-padded goods may be dried, or run wet into the second padding. If the material is to be dried, the drying must be done evenly. It is claimed that the process may be operated economically on long or short yardages, on a full range of dyeings from light to dark shades (Meunier, *Am. Dyes. Rep.*, **1945,** 206).

Williams Unit. In this ingenious process, the vat color reduction is carried out in a very small volume of liquor. The material is padded with pigment vat dyestuff in the mangle, then passed into wells, which are narrow spaced apertures in a steam heated unit. The high speed at which the machine is run causes the fabric to carry reducing liquor along with it by centrifugal force, and the agitation of the solution, due to the passage of the fabric through the narrow sections, insures thorough penetration of the reduced vat color. The liquor carried along is returned to the emptied wells by gravity, and it is into this return flow that additions of caustic soda and hydrosulfite can be made (*U.S.P. 2,364,838*—S.H. Williams).

Reduction takes place quickly at the high temperatures of the Williams unit (approximately 210°F), with the result that migration of the vat color is minimized. Cottons and regenerated cellulose fabrics are equally well dyed (Williams, *Am. Dyes. Rep.*, **1947,** 256).

A study has been made by O. W. Clark (*Am. Dyes, Rep.* **1948,** 82) of the stability of the vat dyestuffs to reduction at high temperature, such as might be encountered in the Williams machine. He found that Vat Jade Green, Orange G, Yellow GCD, Red BN, Violet BN and Grey 2G exhibit remarkable stability, while Vat Orange 3G, Orange RRT, Orange 4R, Violet 2R, Blue BCS, Khaki 2G and Olive R change shade and strength to such an extent that their use in high-temperature reduction solution is inadvisable.

It has recently been found that certain types of dextrin have the property of protecting Indanthrene Blue BCS and BFP and other vat colors which, at high reduction temperatures, yield dull shades, particularly where the period of reduction is increased. This observation is of considerable value in the Williams machine method of developing pigment padded material at 85° to 90°C. The addition of 1 to 2 oz of dextrin per gallon in the Williams unit insures maximum fixation and brightness of these dyestuffs, and resultant normal fastness to soaping.

Multi-Lap Machine. The Multi-lap machine, an invention of the Du Pont Co. is basically, a padding mangle for applying the vat color in pigment form and a closed reducing unit in which the fabric is imposed, without tension, on a rotating reel, layer on layer. The cloth feeds in continuously while the reel is rotating through the caustic soda and hydrosulfite liquor, and leaves the machine at a 90° angle in the side. The advantages of this process are the complete relaxation of the cloth in the dyeing operation, thus making it suitable for rayons (Brosnan, *Am. Dyes. Rep.*, Dec., **1946,** 649).

Vat-Acid Method. The vat-acid process* may be considered as an improved stock-vat dyeing method. The vat dyestuff which is present in the form of an insoluble enol modification is brought into contact with the fiber in an acid medium. It is well known that the vat acids—that is, the free leuco compounds produced by neutralizing alkaline leuco-vats and substituting thereby the alkali radical with hydrogen—, can be isolated as substances relatively stable to oxidizing agents. It has been observed that in the form of the vat acid, the vat color has little if any affinity for vegetable fibers, or regenerated cellulose, in contradistinction to alkaline leuco compounds.

While the stock-vat dyeing process is characterized by a partial hydrolysis of the alkaline leuco-vat into the vat acid, the vat acid process comprises a complete liberation of the vat acids having practically no affinity for the fiber. The transformation into the vat acids results from neutralizing the alkaline vat with acetic or formic acid in the presence of an appropriate protective colloid, and of a dispersing agent.

After the stock vat has been added to the dye bath, the alkali of the bath is neutralized with acetic or formic acids, and the dyestuff converted into the vat-acid modification.

After this liquor has been dyed onto the goods and thoroughly penetrated the fiber, hydrosulfite, caustic soda and salt are added gradually to the dye bath, just as in the reduced vat-dyeing method. Further dyeing and development takes place as usual.

The procedure of vat-acid dyeing can be applied to pad dyeing as well: The goods are padded with the vat acid on the mangle, and dried in the hot-flue. The dried goods are padded in a second mangle with sodium hydrosulfite, caustic soda and Glauber's salt, and the reduction carried out in the Electro-fixer (*Elextro-fixierer*).

In many respects this method is similar to the pad-steam method. It is said the method is appropriate for light shades only.

An example of the vat-acid process is given:

Stock Vat	
1–6	gm vat dyestuff fine powder
5–10	cc caustic soda 40%
3	gm hydrosulfite
2–5	gm Setamol WS
to 300 cc	

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* Dr. J. Müller, Paper read at Meeting of I.V.C.C. in Stuttgart, Feb. 19, 1938; *Mell.*, **1940,** 80. Dr. Gund, *Mell.*, **1943,** 470 ff. *B.P. 355,363.*

Warm 3–5 min. at 50–60°C

Dye Bath

300	cc stock vat
1	gm Setamol WS
1	cc Peregal OK
650	cc water at 70–80°C
	Add:
10–20	cc acetic acid 33% *and*
50	cc water
to 1 liter	

For reckoning acid addition, one liter NaOH 40° Bé approximately corresponds to 2.5 liters of acetic acid 30% or to 0.6 liter of formic acid 80%.

Other Methods. The dyeing of spun rayon staple in the machine with vat colors brings new problems, for the swelling that takes place in water impedes penetration of the dye liquor. Special methods, particularly suitable for dyeing of spun rayon staple, have been developed to meet this problem.

A method especially adapted for regenerated cellulose fibers is described by Dr. Drapal in *Mell.*, **1940,** 294, in an article called "Das Temperaturstufenverfahren", which might be translated "Temperature-gradient Method".

Whereas the pigment pad process and the vat acid process succeed in obtaining uniform dyeings by gradual additions of sodium hydroxide and hydrosulfite to the dye bath, held at optimum dyeing temperature, the temperature-gradient method is characterized by a gradually increased temperature. The method is especially useful in dyeing colors of the "IN" type which have an unusually high affinity to the fiber at the usual dyeing temperature. The operation of the method is as follows: A bath is prepared containing:

1	gm Igepon TS or Peregal OK
1–2	cc Humectol CX
10–18	cc NaOH 38° Bé
2–3	gm hydrosulfite

per liter, cooled to 13–14°C and the stock vat added. The dry goods are handled 15 minutes in this cold bath, whereupon the temperature is raised approximately 1°C per minute. The temperature range between 20 to 35°C is critical, and care must be exercised that the temperature rise is not abrupt, but over 35°C the rise may be quicker. Dyeing is continued 15 minutes at the usual dyeing temperature over 50° and up to 70°C, after which the material is rinsed, oxidized and finished as usual.

The method gives satisfactory penetration and levelness, especially in the dyeing of spun rayon staple and blended staple yarns. Practical piece goods' experience has not been reported. (See also Gund, "Special Methods of Dyeing Indanthrene Colors", *Mell.*, **1943**, 437.)

Practical work on yarns proves this method not completely satisfactory with all types of vat colors (W. Hees, *Mell.*, **1940**, 179), and more uniformly satisfactory on cotton than on rayon yarns. The stronger affinity of the rayons for the dyestuffs in general and the higher swelling of these fibers impeding penetration of the colloidal dyestuffs, makes the process more difficult on the rayon. Dyestuffs of the "IK" and "IW" types yield satisfactory results on rayon and mixed fibers, as they can be controlled by regulation of the temperature. The higher substantivity of the "IN" dyestuffs, however, and their sensitivity to temperature changes, make their level dyeing a great difficulty.

Vat Dyeing Auxiliaries

As a matter of control, in order to regulate the high affinity of some dyestuffs and to aid in obtaining more uniform results, leveling agents may be added to the dye bath. With respect to their specific functions, these auxiliaries may be divided into two groups: (1) Those having affinity for the fiber, and (2) those having affinity for the dyestuff.

These groups act in entirely different ways. Leveling agents having affinity for the fiber are capillary-active substances. They are substantive, *i.e.*, they are absorbed by the cellulosic fiber, attaching themselves to the surface areas of the fiber, in direct competition with the dyestuff particles.* Thus the dyestuff is not immediately absorbed by the fiber, but only in longer dyeing time does the dyestuff supersede the auxiliaries on the material.

Auxiliary agents which have a substantial affinity for the fiber are the fatty alchohol sulfates and Turkey red oils, the fatty sulfonic acids and fatty acid condensates, as for example, Igepon T, Neopol T, Humectol CX and Medialan A. The last two, especially, have a decided affinity for the cellulosic fiber.

Those auxiliaries which exhibit affinity for the dyestuff, act first by attaching themselves to the dyestuff, subsequently releasing it gradually to the fiber.** Thus the dyestuff is again in competition with the auxiliary for the fiber. The absorption of the dyestuff is retarded by the action of the auxiliary, but as the dyeing time is continued and the temperature raised, as salts are added, etc., the contact of dyestuff with fiber is slowly attained, and the dyestuff gradually absorbed by the fiber.

In vat dyeing, those auxiliaries which have an affinity for the dyestuff

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* E. Valkó, *Öst. Chem. Ztg.*, **1937**, #21, 469; G. Schwen, "Probleme der Egalisierung und Durchfärbung", *Mon. f. S.K.Z.*, **1938**, #7, 374; E. Valkó, *J. Am. Chem. Soc.*, **63**, #5, 1433–37.

** Valkó, *ibid.*

have proved best, especially in the case of dyestuffs of high substantivity. Typical representatives of this group are the Peregals, also Albatex PO of Ciba. They have a definite retarding action on vat colors, regulating the speed of absorption of the color, and as such are of particular importance in dyeing of mixed vat dyes having different affinities for the fiber.

The greatest drawback in vat dyeing is the difficulty in obtaining uniformly level shades. It is this difficulty which has instigated the study and manufacture of agents which might improve the levelness and penetration of the vat colors. Some of these products aid penetration, wetting, leveling, retarding. Some of the work done in this direction is given below.

Condensates of higher carboxylic acids with protein degradation products promote leveling (*F.P. 772,585* I.G.). As examples, on the one hand, lauric, stearic, palmitic or oleic acid, and on the other, gelatin, glue, casein, etc. Similarly, *B.P. 437,528* recommends as agents which retard the dyeing process and therefore act as leveling agents, the condensates of higher fatty acids with protein cleavage products. They are believed to have an amidelike structure. As example, the product formed by reaction of oleyl chloride and a mixture of substances obtained by alkaline treatment of a glue-like by-product of rabbit skins (hat manufacture). (Compare *Aus.P. 137,321*). The chlorocarbonic acid esters of higher fatty alcohols condensed with protein degradation products, are recommended in *B.P. 425,370* (compare also *F.P. 786,391*, *B.P. 452,689*). The Landshoff-Meyer patent (*B.P. 413,016*) covers the product marketed under the name Lamepon (*Mell.*, **1935**, 62, 288). This describes condensates of higher fatty acid chlorides with proteinaceous products, and is therefore substantially identical with those mentioned above.

The Lamepons are not only vat-dyeing auxiliaries*, but excellent detergents; also protective colloids preventing damage by alkalis in dyeing wool. *U.S.P. 2,015,912* of Landshoff and Meyer also relates to the condensation of fatty acids with the so-called "protalbinic" or "lysalbinic", acids and corresponds in the main context to *B.P. 435,481* of I.G. describing condensates of higher fatty acids with polypeptides.

B.P. 295,025 (Du Pont-Kern): More uniform dyeings can be obtained, particularly with Indanthrene Blue GCD, 3G, etc., by adding substituted aliphatic amines containing OH groups, for instance, alkylol amines.

F.P. 776,146 (Ciba, 1934): The dyeing properties of the vat dyestuffs of the anthraquinoid group can be improved by adding polysaccharides (not sugars) to the dye bath. For example, to a dye bath of Cibanone Violet 2R which is a notoriously poor leveling dyestuff, especially in light

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* Schultz, Supp. Vol. II., p. 301; *Z. f. angew. Chem.*, **1933**, 668; Pattinger, *Can. Text. J.*, **1936**, #26, 39; *Chem. Zent.*, **1937**, 2457.

shades, 0.1 gm of cellulose methyl ether (of 28% methoxy content is added. Other cellulose ethers are also described, as ethyl cellulose, carboxy methyl cellulose, etc. (see also *G.P. 518,197*, *Aus.P. 131,863*—I.G.).

Similarly, *U.S.P. 2,021,932* (Du Pont) recommends the addition of cellulose ethers, which naturally must be soluble in alkaline vats. By introducing a sulfo-, carboxy-, or hydroxy group in the ether, better solubility is promoted; for example, sodium salt of cellulose glycollic acid (Colloresin V extra, Collocel, etc.).

An addition of vegetable phosphatides like lecithin, is described in *U.S.P. 2,020,496* of Am. Lecithin Corp.; also *G.P. 566,149* and *B.P. 353,873*.

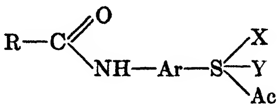
The use of sulfonated oils with the unreduced vat color is the subject of *G.P. 518,197*, that is, in the pigment-pad process. In this patent of I.G.—Poelzsch-Jaeger, flow-promoting agents are distinguished from wetting agents. Highly sulfonated oils, particularly the fatty acid sulfuric esters prepared according to *G.P. 561,715* and *614,702* (Stockhausen) have an outstanding effect.

Other additions to the pigment padding liquor are recommended in *G.P. 598,441*, *F.P. 728,808*, *G.P. 579,948* of Ciba. It was observed that wetting agents alone do not improve penetration, but that by using derivatives of dibutyl naphthalene sulfonic acids (Nekals) with emulsions of fats or oils, or alkylcelluloses, penetration is increased.

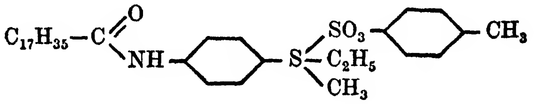
F.P. 784,276 (I.G.) discloses that vat dyeings are improved by addition of basic, alkali-resistant compounds derived from tri- or pentavalent nitrogen, pentavalent phosphorus or tetravalent sulfur, and having a hydrocarbon chain of at least six C atoms. As examples, the patent names the bromohydrate of triethylene dodecyltetramine, stearyldiethanolamines, the sulfo derivatives of oleyl ethylaniline. In a corresponding patent (*G.P. 655,443*) the above mentioned compounds are recommended as a prepare before dyeing. The goods are treated one hour at 80°C in a bath containing these basic products in order to increase the affinity of the goods for the dyes. The goods are hydroextracted after preparation, and dyed, the claim being made that deeper shades result.

G.P. 635,305 (Zittauer Masch. Fabr., 1936) sets forth the failure of the usual dyeing methods, whether those using reduced vat, or those employing the dispersed pigment pre-pad, to penetrate the intersections of cross-wound spools or bobbins. The idea advanced combines the pigment pad-dyeing method with a process already known, and called froth-dyeing: The vat dyestuff is pasted with hot water and soap and a frothing agent is added. The liquid is heated to the boil, and forced through the machine, easily penetrating the fibers. The reduction is carried out as usual in a fresh liquor with alkali and hydrosulfite.

F.P. 811,760 (I.C.I.), corresponding in the main to B.P. *464,110*, recommends as auxiliaries in vat dyeing tertiary sulfonium salts of the general formula

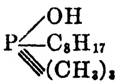


in which R is a higher aliphatic radical, Ar is an aromatic group, Y and X are lower alkyl radicals, and Ac is an acid group. As example, the *p* toluolsulfonate of *p*-stearylamide phenylmethylethyl sulfonium

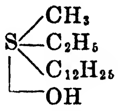


or the corresponding lauryl amidophenyl compound. Similarly, *F.P. 817,786* and *B.P. 470,346* suggest the use of quaternary ammonium compounds for aiding dye absorption. Such compounds are formed from esters of alkyl aminobenzoic acid (as cetyl ester of diethyl aminobenzoic acid) with alkylating agents such as methyl sulfate.

B.P. 435,443 and *435,444* also mention the high substituted phosphonium or sulfonium compounds, as



or



Trimethyl octyl phosphonium hydroxide *Methylethyldodecyl sulfonium hydroxide*

In *F.P. 782,143*, quaternary ammonium compounds with fatty acid radicals are recommended as vat-dyeing assistants, and because of their strong dispersing action, also as stripping agents.

The yield of vat dyeings is increased if the goods are treated before dyeing with quaternary ammonium bases or with phosphonium or sulfonium bases, according to *B.P. 448,272*. Especially recommended are heterocyclic bases such as pyridinium compounds.

Besides those already mentioned, there are many other patents advocating the cationic properties of phosphonium, sulfonium, and nitrogen compounds for increasing the yield of vat colors. A further enumeration would be repetitious.

B.P. 440,983 (I.C.I.) aims at producing stable colloidal solutions of vat dyestuffs by use of the alkali-destruction products of wool by-products or glue. The destruction is carried to a definite point, at which it is stopped by adding sulfuric acid. The pH of the product is adjusted to 10 before adding to the vat color.

A number of patents of De Carp's Garnfabriken (*G.P. 661,136* Zahn; *F.P. 811,549; S.P. 192,555; B.P. 467,662*) explain a novel way of vat dyeing. The vat is made up with a relatively large amount of alcohol or other water-miscible solvent. The material is dyed with this solution, then with the vat color in water, and finished as usual. The method, which possibly gives uniformity by the wetting-out action of the alcohol, is recommended for machine dyeing.

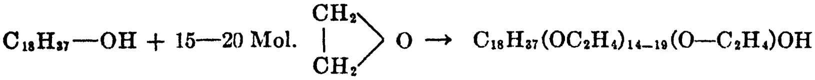
For the protection of light and delicate fabrics, which would suffer loss in tensile strength by repeated passage over rollers, the use of hydroquinone is proposed in I.G. patents *G.P. 644,069, U.S.P. 2,115,317*, and *B.P. 461,752*. The hydroquinone, which readily changes to quinone, exerts a kind of buffering action. In one case it was shown that a lawn fabric which lost 57% in tensile strength, was held to a loss of 0.3% in strength under otherwise identical conditions.

For improving the level dyeing of vat colors, Sandoz recommends (*F.P. 822,739*) aliphatic polyamines, which are prepared by condensing glycerin dichlorohydrin with ammonia or with primary, secondary or tertiary amines. The examples name condensates of one mole of glycerin α-γ-dichlorohydrin with two moles of ammonia. Leveling is promoted by the retarding effect of the compound. For the same reason, the products can be used for stripping vat and sulfur color dyeings (*U.S.P. 2,155,135*, Sandoz-Kartaschoff).

Preparation of heavy goods before dyeing, using sulfite waste liquor or glue solution, is suggested in *G.P. 561,482*.

The following patents relate to the manufacture of the Peregals O and OK* which are also discussed in the following section on Stripping of Vat Color Dyeings: *F.P. 713,426, 713,427, 717,427, 727,202, 752,831, 762,839; B.P. 346,550, 367,420, 409,336, 443,559; G.P. 548,201, 636,305.*

Peregal O is a 15% solution of Emulphor O, which is a condensation product of cetyl or stearyl alcohol with 15 to 20 moles of ethylene oxide, as in the equation



$$C_{18}H_{37}\text{—}OH + 15\text{—}20\ \text{Mol.}\ \left.\begin{array}{l} CH_2 \\ | \\ CH_2 \end{array}\right\rangle O \rightarrow C_{18}H_{37}(OC_2H_4)_{14-19}(O\text{—}C_2H_4)OH$$

Emulphor O is a whitish solid, readily soluble in water to a clear, yellowish solution. It exhibits wetting and foaming properties, has a defi-

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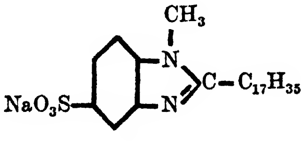
* Schöller, *Mell.*, **1934**, #15, 357; *Mell.*, **1937**, #18, 234; Rudolf, *Z. f. ges. Tex. Ind.*, **1934**, #37, 385; Patel, *Am. Dyes. Rep.*, **1934**, #23, 505, 521; Köster, *Mell.*, **1935**, #16, 271; Stierwaldt, *Mell.*, **1926**, #17, 50; Volz, *Z. f. ges. Tex. Ind.*, **1936**, #39, 149; Kosche, *Z. f. ges. Tex. Ind.*, **1936**, #39, 60; Schwen, *Text. Mfr.*, **1936**, #62, 153; Hasse, *Mell.*, **1937**, #18, 456, 527, 672, 1004; Schwen, *Mell.*, **1933**, #14, 22; *D.F.Z.*, **1933**, #69, 145.

nite effect on the affinity of direct colors and leuco-vat compounds, and is an outstanding leveling agent.

The product has the property of attracting and accumulating the leuco compounds, forming aggregates, thus retarding the speed of absorption of vat dyestuffs.

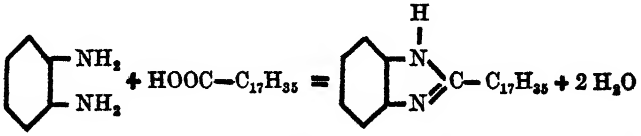
When larger quantities of Peregal O or OK are employed, the retarding action is so marked that part of the dyestuff is prevented from dyeing the material. This property can be used for stripping vats. In a blank vat containing Peregal O or OK a vat color dyeing can be more or less completely stripped.

Albatex PO (Ciba) acts in similar fashion to Peregal O and OK. According to Chwala this product is a high molecular benzimidazol sulfonate, with added alkyl cellulose and polyvinyl alcohol for increased effect.* The products of sulfonation of the benzimidazols are described as leveling agents which are able to retard the dyestuff absorption (*F.P. 778,476, U.S.P. 2,053,821, B.P. 398,150*—Ciba). In *G.P. 678,131*, Ciba describes dispersing agents for vat dyeing, namely, sulfonic acids of cyclic amines, compounds such as cetylaniline sulfonic acid, addition products of dimethyl sulfate on methylcetylaniline and the sulfonic acid of benzyldodecyl methylamine. All of these compounds have a retarding action on dyestuffs which otherwise have high affinity for the fiber. This patent, which probably corresponds to the *F.P. 778,476* above, covers, among other products, the auxiliary Albatex PO. It comprises quite generally dispersing agents containing eight C atoms, one sulfo or sulfinic group and a basic nitrogen. Examples given are benzimidazol derivatives such as sulfonated N-methyl-μ-heptadecylbenzimidazol or the methyl sulfate of heptadecylphenyl dimethyl ammonium:



N-Methyl-μ-heptadecylbenzimidazole sodium sulfate
(Ultravon K)

This compound is made by reacting higher fatty acids with *o*-phenylenediamine, and subsequent sulfonation of the intermediate:



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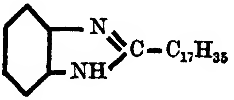
* *F.P. 774,018, 776,146, 778,476, 778,833; G.P. 678,131; U.S.P. 2,053,821; B.P. 398,-150, 441,296;* Landolt, *Mell.*, 1936, #17, 650.

These products are sold under the name of Ultravon by Ciba, and are recommended as leveling and stripping agents, and as detergents. Graenacher reviews the constitution of the Ultravons in *Bull. Fed.*, **1938,** 268, and defines them as compounds having a long hydrocarbon chain of over eight C atoms linked to the nuclear carbon atom of an imidazol ring, as:



In *F.P. 778,833*, Ciba suggests adding polyvinyl alcohol or its derivatives (1 to 4%) to retard the absorption of vat dyes in dyeing.

Another leveling and retarding agent is disclosed in *B.P. 435,431*, and *G.P. 673,158*, *F.P. 770,235* (Böhme). By adding cation-active auxiliary agents (organic bases substituted with fatty radicals) to the dye bath, a marked decrease in affinity results, while anion-active agents (fatty alcohol sulfonates) weaken this effect and are even able to counteract it. The method suggested consists of adding cation-active agents to retard the absorption, and to control the speed of the dyeing process by gradually adding the anion-active products. The patents cover the cationic component, Repellat KS, which is, for example, lauryl pyridinium sulfate

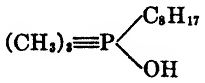
and the anionic component, Amendol, a fatty alcohol sulfate. Repellat retards the dyeing process, while Amendol, applied with the Repellat, accelerates the absorption of the color.

F.P. 716,444 and *S.P. 149,067* describe the addition of aromatic or hydroaromatic sulfonic or carboxylic acids, excepting the salts of benzylsulfanilic acid. This reference to compounds like dimethyl metanilic or sulfanilic acid salts has already been mentioned in discussing the use of hydrotropic compounds in pasting vat dyestuffs, and as additions to print pastes.

Other products already referred to in preparation of vat printing paste can be advantageously used in the dye bath. *G.P. 562,282* and *562,889* suggest addition of condensates of urea and aldehyde-ammonia to the dye bath, or to use for the same purpose the reaction product of ethylene oxide and albumen, for example, ethoxycasein. *U.S.P. 2,006,557* (Du Pont) contains a formula for producing stable emulsions as wetting agents in vat-dyeing processes: Nekal is mixed with Turkey red oil and with products obtained by the catalytic hydrogenation of carbon monoxide. The use of cresol is mentioned in *G.P. 589,508* (Oranienburgh-Lindner) which describes a dyeing method employing reduced vat colors admixed with fatty alkyl sulfates and cresol.

Haller studied the effect of an addition of glucose to an Indanthrene vat (*Mell.*, **1928**). It has already been explained that the effect of glucose in a hydrosulfite vat may be the formation of a stable reaction product of hydrosulfite and glucose. Haller considered this complex body to be an addition-compound having the formula, $C_6H_{12}O_6 \cdot NaHSO_2$, and the Chem. Fabr. Pyrgos brought this chemical on the market under the name Candit V (Hackl *Mell.*, July, **1930,** 530 and May, **1930,** 383). It was originally intended for use in the indigo vat. The corresponding zinc salt was also prepared and marketed, and found superior to sodium hydrosulfite. In working on the continuous range or on the jig at temperatures of 75 to 80°C it permits an improved yield in color value. (See the work on chemical reactions taking place in the hydrosulfite-glucose vat by Perndanner, Hackl, Bartl, in *Mell.*, **1930,** 42 and 533.)

Long-chain substituted amines, for example, laurylamine, or ethoxy derivatives, are recommended as leveling agents in *B.P. 436,942*, also amines containing di- or triethylene glycol groups, as dodecyl monoethanolamine. The corresponding *G.P. 739,860* was published in 1943, although application was made over nine years before. This patent lists a great number of leveling agents, among them the reaction product of 20 moles of ethylene oxide on one mole of dodecyl monoethanolamine, further, higher molecular aliphatic polyamines, such as dodecyl ethylenediamine, also ethoxyamines as dodecyl monoethanolamine or oleyl diethanolamine. Also mentioned are condensates of fatty acids and amines, for instance, the amide from coconut fatty acid and triethylenetetramine, and aromatic polyamines, such as conversion products of polyglycols and of halogenated parafins with ammonia or amines. The following compounds are particularly noted: dodecyltrimethyl ammonium bromide, dimethylphenylbenzyl ammonium chloride (Leucotropes) and trimethyloctyl phosphonium hydroxide



$$(CH_3)_3{\equiv}P\begin{matrix} \diagup C_8H_{17} \\ \diagdown OH \end{matrix}$$

The following example is given: A viscose rayon cloth is dyed in an alkaline hydrosulfite vat with 1 % Indanthrene Brilliant Violet 2R double paste, with addition of 0.5 gm of a mixture of sulfonated castor oil 0.45 gm) and trimethyldodecyl ammonium bromide (0.05 gm) per liter. The resulting dyeing is more uniform.

It has been established that dyeing of vat dyes can be carried out under particularly favorable conditions when water-soluble or water-dispersible basic compounds are added which are stable to alkalis. Such compounds are derived from tri- or pentavalent nitrogen, from pentavalent phosphorus or tetravalent sulfur, and containing an aliphatic, cycloaliphatic or aromatic radical of six or more C atoms.

An invention of R. Paschkes (Portugal) discloses an interesting idea (*G.P. 747,861*—I.G., 1944). It has been reported above that leveling agents can be advantageously used to decrease the affinity and speed of absorption ·of the vat colors. But unfortunately the action of powerful wetting agents sometimes alters the properties of the fibers. Paschkes finds that level shades can be obtained from vat dyestuffs when cellulose in powder form is added to the vat, either before dyeing or during the dyeing operation. It is also possible to use pre-dyed cellulose in powder form as the dyestuff addition to an otherwise colorless dye bath. The colored fiber flake or powder gradually relinquishes its color to the fiber to be dyed, in the alkaline-hydrosulfite bath.

According to *G.P. 737,449* (Phrix-Lucas, 1943) level dyeings on regenerated cellulosic fabrics can be produced with anthraquinoid vat dyes, provided the material is prepared before dyeing with aluminum sulfate. Better penetration, especially at the points of intersection of the threads, is claimed. A fabric of spun and filament rayon is first treated for 20 minutes at 50°C in a bath containing 2 gm of soda ash and 1 gm of a mixture of fatty alcohol sulfate and organic solvent per liter. After rinsing, the fabric is treated for two hours in a 20% solution of aluminum sulfate at 85°C, then hydroextracted and dyed with Vat Blue GCD as usual. Excellent penetration is evidenced throughout.

Dyeing with hard water creates difficulties, in that undesirable precipitates occur which impair the dyeing results. Trouble of this kind may be avoided by adding alkali-, ammonium- or amine-salts of metaphosphoric acid to the dye bath (*G.P. 685,124*—I.G., 1932). These agents not only aid in vat dyeing, but in sulfur color and insoluble azo color dyeing, and with acetate dyestuffs.

The dyeing of linen fabrics with vat colors offers difficulties. More uniform results are obtained by intermediate drying, after padding with the vat color in pigment form. Development is best carried out in the jig (*Text. Mfr.*, **LXI**, 722, 76, also *Dyer*, **LXXIV**, 486).

Vat Dyeing of Animal Fibers

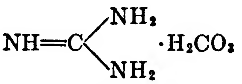
Most of the patents relating to vat dyeing of animal fibers aim at decreasing the dangerous alkalinity of the dye bath. Some are here briefly outlined.

The addition of boric acid to the vat (*B.P. 340, 267*—Morton), substitution of the boric acid with compounds such as resorcinol, phenol or other buffer substances (*B.P. 354,777*), and the use of alkali borate instead of boric acid in carefully controlled amounts to regulate the pH between 8 and 13 (*B.P. 390,513*, Morton-Harris) are suggested.

Phosphates, particularly trisodium phosphate, are recommended in *B.P. 388,044* (I.C.I.).

In *U.S.P. 1,964,934* (IG-Wallis, Virck) magnesium salts or hydroxide are suggested, together with protective colloids such as sulfite cellulose waste liquor. In a similar disclosure (*G.P. 691,196*) it is noted that the protective action of the sulfite liquor is improved by the addition of salts of Mg, Al, Cr or Zn.

G.P. 479,344 recommends the addition of triethanolamine or pyridine, as partial substitution for the alkali of the vat. In dyeing animal fibers it is suggested in *G.P. 659,493* (I.G.—Krist) that guanidine carbonate be added to the amount of alkali just necessary for preparing the stock vat, thus avoiding excess alkalinity. The method is especially intended for those vat dyestuffs not belonging to the indigoid group



$$NH{=}C(NH_2)_2 \cdot H_2CO_3$$

Guanidine carbonate

This compound can be prepared according to Merck's *G.P. 458,437*.

The use of alkali polyphosphates in place of caustic alkali is suggested in *G.P. 669,800* (Chem. Werke Albert). These polyphosphates are characterized by a $Na_2O:P_2O_5$ ratio of 3:2, 5:3, 6:5, etc. Thus they stand in this respect between the metaphosphates (ratio 1:1) and the pyrophosphates (ratio 2:1). They are indifferent to the alkaline earths, and similar to the product known as Calgon.

F.P. 857,904 (Cortaulds, Ltd) describes a process of preparing the stock vat with alkali and hydrosulfite as usual, then neutralizing the excess of sodium hydroxide with carbonic acid, added in the form of sodium bicarbonate. The dye bath is prepared as follows: 0.1 gm Indanthrene Golden Yellow RK double paste is dissolved by adding 2 gm NaOH 17° Bé and 0.6 gm hydrosulfite powder at 60°C and made up to 400 cc with water. As soon as the dyestuff is completely dissolved, 2.4 gm. of dry sodium bicarbonate are added. Wool or cellulose acetate fibers are dyed in this bath at 60 to 70°C for 45 minutes.

Vat dyeing of wool in ammoniacal solution in the presence of protective colloids is described in *D.F.Z.*, **#21,** 23. Another reference is a study in *Öst. W.u L. Ind.*, **#55,** 363 (Kraus) concerning vat dyeing in the presence of protective colloids and leveling agents such as Dekol, Nekal AEM, Prestabit Oil, etc. Dyeing of woolen piece goods with vats is described in *Am. Dyes. Rep.*, **1943,** 31 (Derby) and 33 (Linberg).

A process of dyeing wool with the vat acid in the presence of amines is the subject of *G.P. 745,858* (I.G.—Joachim). The vat acid is prepared by pouring the concentrated stock vat into a dilute acid solution containing dispersing agents such as naphthalene-2-sulfonic acid-formaldehyde or glue.*

The use of amines with the vat-acid process is more completely described in *B.P. 355,363*, the amines fully stabilizing the dye bath.

The stock vat is prepared as follows:

2 parts dyestuff
2 parts lime solution 1:10
2 parts sodium hydrosulfite
12 parts caustic soda 38° Bé cut 1:5
—
to 60 parts with water
Heat to 55°C

The dye bath is prepared with:

2 parts stock vat
2 parts sodium hydrosulfite
1.5 parts acetic acid 50%
0.5–1 part triethanolamine

and brought to volume.

The dyebath has a pH of 6.2. The goods are dyed 10 minutes, then developed with acid and perborate. An equal amount of diethanolamine, pyridine or guanidine can replace the triethanolamine.

Vat Dyeing of Acetate Cellulose

The dyeing of acetate cellulose fibers with vat colors involves a change in the fiber. Even small amounts of alkali attack the fiber and dyeing with vat colors entails a surface saponification (deacetylation).

Ever since acetate cellulose appeared as a permanent article, chemists have been busy trying to solve the problem of applying fast vat colors in dyeing, and as the fiber has been widely used in the textile field, both alone and in combination with other fibers, the interest in achieving fast colors has increased. While the theoretical solution of the problem has been found, practical results have not been eminently satisfactory. Research work has lagged, no doubt because the special acetate dyestuffs have given satisfactory fastness in the trade.

Since the dyeing of acetate rayon with vat dyestuffs requires an alkaline dye-liquor, and since the fiber is so reactive to alkalis, there will be danger

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* An older patent of Badische A.S.F. (*G.P. 152,907*) recommended ammoniacal indigo vats for dyeing wool. Ammonia alone does not sufficiently dissolve the leuco-vats but addition of glue or other protein product yields good dispersion.

of saponification. Even though this saponification is only partial and quite unimportant with respect to the strength of the fiber, it is only with a very minimum of saponification that threads for resist effects can be prepared which will not be dyed in subsequent cross-dye baths.

Clavel proposed as early as 1921 (*F.P. 542,940*) to dye acetate cellulose with vat dyestuffs in a dye bath of such low alkalinity that saponification could be practically eliminated. For this purpose he made up stock vats with soda ash as alkaline agent, adding them to ammoniacal dye baths containing buffers such as chlorides of alkaline earth metals, or protective colloids such as gelatin, glucose, starch or broken soap. Later other protective colloids were recommended, particularly sulfite cellulose waste liquor (*B.P. 214,320*—Clayton, 1923), certain anthraquinone derivatives (*B.P. 214,212*), and hydroxyaromatic compounds or their sodium salts (*B.P. 252,208*—1925 and *B.P. 263,437*—1926). Although these patents have been available for many years, the processes have not enjoyed any substantial success in the practice.

Other attempts to avoid saponification include dyeing with vat acids obtained, for instance, by neutralization of the alkali with sodium bicarbonate, or with boric acid. The action of the alkali necessary in the subsequent reduction can be minimized by holding the temperature below 5°C. Other references recommend converting the dyestuff to the leuco compound with organic bases instead of caustic alkalis, and another, to reduce in a non-aqueous bath.

Rhodiaceta suggests in *F.P. 765,960* (1934) using magnesium hydroxide as alkaline agent. It is but sparingly soluble, but sufficiently alkaline to replace sodium hydroxide or carbonate. There is a minimum of deacetylation. The following will serve as an illustration of the method.:

50 gm Indigo N2B (Kuhlmann-Francolor)
250 gm sodium hydrosulfite
250 gm magnesium hydroxide

are dissolved in five liters of water at 60°C while stirring 15 minutes. This stock vat is charged into 50 l of dye bath. One kg of acetate cloth is dyed one hour at 75°C, after which it is well rinsed and developed in sodium perborate solution at 30 to 60°C.

It has also been found possible to work in a vat of reduced alkalinity in the presence of soap, ammonium carbonate and hydrosulfite (*B.P. 274,550*), or the leuco compounds can be applied in the form of suspensions or dispersions (*F.P. 697,523*) or the acetate can be dyed in a slightly alkaline bath using an excess of hydrosulfite (*F.P. 542,940*). Another solution is disclosed in *B.P. 444,953* (Dreyfus), wherein the alkali content is reduced by forming the zinc-enolates of the vat dyestuffs. In order to avoid too rapid reoxidation it is suggested to dry the fabrics in a current of carbon dioxide or under reduced pressure.

U.S.P. 1,978,786 (Celanese Corp.) relates to vat dyeing of acetate rayon and some interesting details are disclosed regarding the temperature of operation. The amount of alkali is reduced by partially substituting the caustic alkali with trisodium phosphate, as practiced in wool dyeing. Certain indigoid vats can be dyed with magnesium hydroxide. In dyeing a mixture of viscose and acetate rayons, the viscose can be dyed at 10°C with vat colors in order to avoid saponification of the acetate portion. The latter is thereupon dyed with acetate dyestuffs.

The following formula illustrates the ammoniacal bath process which has had some success:

The bath is prepared as follows:

1.5 gm Prestabit Oil NA
3 cc NaOH 38° Bé
3 gm sodium hydrosulfite
5 cc ammonia 20° Bé

The entire quantity of sodium hydrosulfite and part of the hydrosulfite are used for preparing the stock vat, which is added to the dye bath containing the ammonia. Dyeing is carried out at 40 to 60°C for $\frac{1}{2}$ to $\frac{3}{4}$ hour, after which the material is rinsed and oxidized (with 2 cc of sulfuric acid 66° Be per liter) and washed.

The following vat dyestuffs are suitable for this process:

Ciba Yellow G
Cibanone Yellow GC
Indanthrene Yellow G
Indanthrene Scarlet B
Indanthrene Brilliant Pink R
Ciba Violet B
Brilliant Indigo 4B
Ciba Brown 2R
Algol Black B
Indanthrene Brilliant Blue 3G

The Societa Rhodiaceta in Lyon (P. Joly, *Teintex*, **1944**) made a series of experiments for the purpose of determining the influence of the temperature and concentration of alkali on the saponification of acetates. It was found that no danger of saponification exists even on warming the vat to 80°C, provided that the concentration of alkali does not exceed 1.12 cc of NaOH 36° Bé per liter. As far as stability of the vat is concerned, sodium hydroxide is preferable to all other alkaline agents. Considering that a substantial part of the alkali is used in forming the sodium salt of the leuco compounds, it was concluded that the dye bath should contain 1 to 2 cc of NaOH 36° Bé per liter, depending on the depth of shade to be dyed. The method recommended by Rhodiaceta is therefore as follows:

The dyeing is carried out in soft water, in a 50:1 liquor ratio. According to the individual dyestuffs used and the depth of color desired, the dye bath contains as maximum concentrations per liter, including the quantities used to prepare the stock vat:

2–3 gm sodium hydrosulfite
1–2 cc caustic soda 30° Bé
0.5 gm Setamol WS

These quantities suffice when the material is dyed under the surface of the liquor in order to keep the alkalinity and reducing action constant. The condition of the bath can be ascertained by testing with paper impregnated with Solanthrene Yellow J.

In skein-dyeing the procedure is as follows: The pre-wetted skeins are suspended on U-shaped rods, so that the material is constantly beneath the surface of the liquor, and dyed 15 minutes at 60°C. The bath is heated to 80°C and dyeing continued for one hour at this temperature. The goods are constantly turned. The skeins are hydroextracted immediately on removing and rinsed 5 minutes at 25°C in a bath containing

0.2 gm hydrosulfite of soda
0.5 gm Peregal O

per liter, then in a bath of 0.5 Peregal O only, whereupon the skeins are treated in an oxidizing bath of

2	cc hydrogen peroxide 100 vol.
0.5	gm sodium bicarbonate
0.5–1	gm Peregal O

per liter. The pH of this bath is kept at about 8.5.

It is interesting to note that the recommended high temperature of 80°C is without detriment to color yield, or to the tensile strength of the acetate yarn.

Pigment-pad dyeing with vat colors on cellulose acetate with drying at 90°C and subsequent development in weakly alkaline hydrosulfite solution is suggested in *B.P. 578,212* (Brit. Celanese, 1946).

Vat dyeing of acetate cellulose is carried out only in special cases because the process is rather complicated and because the fastness properties of the dyestuffs are in general inferior as compared to cotton or viscose rayon. For most purposes the acetate dyestuffs are sufficiently fast.

Mixed fabrics of acetate cellulose and cellulosic fiber can be dyed with vat dyestuffs, leaving the acetate white (J. Rolland, *Rev. Gen. Mat. Col.*, Nov., **1934**). According to *F.P. 633,505* (I.G.), acetate can be reserved by treating the material in a hot dye bath with high molecular aldehydes or ketones. The application of sulfonated phenols such as *m*- or *p*-cresol sodium sulfonates for the same purpose has been described in *G.P. 256,277*.

For dyeing cellulose fibers leaving acetate white, Rhodiaceta recommends the following formula:

20 gm vat dyestuff
6 gm caustic soda 30° Bé
2 gm hydrosulfite of soda
2 gm dextrin
4 gm Dekol or Cellex

per liter. The dyestuff is reduced in a stock vat of one-tenth of the volume of the dye bath, using the entire hydrosulfite amount and a third of the alkali. After reduction of the dye (15 minutes at 65°C), the stock vat is added to the dye bath at 20 to 25°C. The material is thereupon dyed, oxidized and washed.

The anthraquinoid vat dyestuffs leave acetate cleaner than the indigoid vats. With very few dyes, however, can a pure white be obtained.

Good white acetate reserves are claimed with short-liquor dyeing methods, such as the pad-steam process, and with the Williams unit.

According to *B.P. 450,868*, *U.S.P. 2,116,553*, *F.P. 801,131* (I.C.I.) vat dyeings, as of indigoid dyestuffs, and also chrome color dyeings can be obtained with improved fastness properties, by a treatment with glycerides of higher fatty acids. By these compounds are meant not the triglycerides of fatty acid but water-soluble compounds having free OH groups, formed by condensing relatively small amounts of fatty acid with excess glycerin in the presence of alkalis.

Vat Dyestuffs Injurious to Textiles

Some vat dyestuffs are known to cause an accelerated deterioration of the fabric under the influence of light. This fact was brought under scrutiny after numerous complaints had been received concerning vat-dyed fabrics, particularly drapery and upholstery materials (R. Kling, *Öst. W.u.L. Ind.*, **1934,** 95).

Systematic investigation has been carried out on this subject. The following references are pertinent: F. Scholefield and Goodyear, *J. Soc. Dy. & Col.*, **1929,** 175. Scholefield, *J. Soc. Dy. & Col.*, **1945,** 245. *Mell.*, Nov., **1929,** 867; *J. Soc. Dy. & Col.*, **1928,** 268. Landolt, *Mell.*, **1929,** 533; **1930,** 937; **1933,** 32. C. M. Whittaker, *J. Soc. Dy. & Col.*, **1933,** 9. *Helv. Chim. Acta*, **20** (2) 880 (1937). Brear and Turner, *J. Soc. Dy. & Col.*, **1945,** 273.

It was observed by Scholefield and Goodyear that yellows, oranges and some brown and red vat dyestuffs caused destruction of the substrate (cotton) by the formation of oxycellulose under the influence of light. Moreover, in applying mixtures of yellow or orange with blue vat colors on cotton, the fastness to light of the blue component is imparied by the action of the yellow or orange component.

The following vat dyestuffs are denoted as injurious:

Algol Yellow WG or 1-benzoyl aminoanthraquinone
Vat Yellow GC
Indanthrene Golden Yellow FFRK and 5GK
Indanthrene Scarlet F3G
Indanthrene Golden Yellow GK or 3,4.8,9-dibenzpyrene-5,10-quinone
Vat Red B, Ciba Pink B, Algol Red 5B or 2,2′-bisoxythionaphthene indigo
Ciba Red B, BG, Indanthrene Brilliant Pink R or 6,6′-dichloro-2,2′-thionaphthene indigo
Indanthrene Red Violet RH or 5,5′-dichloro-7,7′-dimethyl-2,2′-bisoxynaphthene indigo
Indanthrene Yellow GK, Algol Yellow R, Cibanone Yellow R or 1,5-dibenzoyl diaminoanthraquinone; 1,4-dibenzoyl diaminoanthraquinone; 1,8-dibenzoyl diaminoanthraquinone
Indanthrene Orange RRK or 1,2,3-tribenzoyl triaminoanthraquinone
Hydron Yellow G or 1,2,7,8-diphthalyl carbazol

Also the vat dyestuffs of the following constitution are injurious:

4,4′-dimethyl-2,2′-bisoxythionaphthene indigo
4,4′-dimethyl-6,6′-dichloro-2,2′-bisoxythionaphthene indigo
4 methyl-6-chloro-6-methoxy-2,2′-bisoxythionaphthene indigo
4,4′-dimethyl-5,7-5′7′-tetrachloro-2,2′-bisoxythionaphthene indigo
2,1-2′,1′-bisnaphthoxythiophene indigo
1,2-1′,2′-bisnaphthoxythiophene indigo
Terephthalyl-1,1′-diaminodianthraquinone
Isoterephthalyl-1,1′-diaminoanthraquinone
1-(N)-2,5-(N)-6-anthraquinone dibenzothiazole

Landolt found that a fiber, dyed with Vat Yellow GC and impregnated with sodium hydroxide is damaged when exposed to light. It was assumed that the vat dyestuff causes the formation of hydrogen peroxide in the presence of sodium hydroxide when exposed to light rays. The hydrogen peroxide so formed acts as oxygen carrier causing the damage to the fiber. It is a known fact that wood cellulose treated with strong alkali absorbs larger amounts of oxygen from the air; and unbleached cotton from which the caustic has not been completely removed after mercerization is transformed to oxycellulose under the influence of sunlight. Vat dyestuffs act here as catalysts.

An interesting observation was made by Dr. A. Schaeffer (*G.P. 736,882*—1943) that fiber damage is prevented when vat-dyed material is aftertreated with solutions of the lower valence salts of manganese, cobalt, lead or chromium, as for instance, $Mn(NO_3)_2$, $Co(NO_3)_2$, $Pb(NO_3)_2$, $Cr(C_2H_3O_2)_2$. These salts had already been recommended for aftertreating dyeings of dithioalkylthioindigo dyestuffs on vegetable fibers in order to protect them against deterioration by light rays. The dyed material is aftertreated ½ hour at 20 to 30°C in a 1% solution of the salt, and dried.

In a later patent (*G.P. 743,221*) Dr. Schaeffer reports that fiber deterioration by above-listed vat dyes can be prevented when the dyed material is aftertreated at 30 to 40°C with sulfonamides, urea or thiourea, using 2% solutions and drying them in (cf. *G.P. 206,568*).

Stripping of Vat Dyeings

The salts of formaldehyde-sulfoxylic acid make ideal stripping agents because they destroy the major part of the dyestuffs. In general, the operation is carried out in the following manner.

The fabric to be stripped is thoroughly washed, then treated ½ to 1 hour at the boil with 5% reducing agent and 1% soda ash or 2% acetic acid. As reducing agents, the sodium or zinc salts of formaldehyde-sulfoxylic acid are employed (Hydrosulfite NF, Decrolines, etc.). The primary zinc salts of formaldehyde-sulfoxylic acid, which are soluble in water, are used for stripping vat colors on vegetable fibers, while the secondary zinc salts which are insoluble in water, are preferred for the animal fibers.

Certain difficulties are encountered in stripping vat dyes because of the reoxidation of the dyestuff in subsequent washing operations. The action of the hydrosulfite can be improved by retarding the reoxidation of the vat dye. The use of magnesium salts for this purpose is suggested in *U.S.P. 2,042,194*, *F.P. 752,831*, *G.P. 626,205*. The vat-dyed material is boiled with 12 gm of caustic soda 40° Be and 4 gm of sodium hydrosulfite per liter for half an hour, after which 10 gm of magnesium sulfate or chloride or hydroxide are added (per l) and boiling continued one-half hour. The rinse water contains some hydrosulfite.

The stripping action of hydrosulfite is also promoted by the addition of protective colloids such as sulfite waste liquor, glue or gelatin, or the degradation products of protein derivatives (the so-called protalbinates or lysalbinates) (*F.P. 752,831*).

Furthermore, the addition of monocalcium phosphate is recommended in *U.S.P. 2,046,317* (Block).

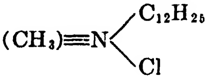
Noteworthy research work of Ciba, the I.G., and I.C.I. has resulted in the development of new compounds having high dispersing properties which are applicable not only in dyeing processes for retarding the dye absorption, but also in stripping of vat dyeings in a blank vat.

The work of the I.G. is concerned with condensates of ethylene oxide with high molecular fatty acids or alcohols, such as oleyl alcohol, lauryl alcohol and octadecyl alcohol, and also with polymerization products of ethylene oxide. The condensates of ethylene oxide with insoluble or sparingly soluble compounds having at least one reactive hydrogen atom and a hydrocarbon chain with at least six C atoms proved good stripping auxiliaries. Examples of such compounds are lauric, palmitic, ricinoleic or abietic acids. For the condensation products, the alkyl or oxyalkyl esters of these acids or their corresponding alcohols are condensed with ethylene oxide. As an example, 20 moles of ethylene oxide and one mole of octadecyl alcohol are reacted. Other compounds are formed by the reaction of these esters or alcohols with gaseous alkylene oxides at 160 to 170°C in the presence of phosphates or sulfates as catalysts.

The preparation of these products is described in the following patents: *U.S.P. 1,970,578* and *2,214,352; G.P. 548,201; F.P. 713,426-7*, *717,427*, *727,202*, *752,831*; *B.P. 346,550*, *367,420*, *409,336*, *443,559.* They are marketed under the names Peregal O and OK and Emulphor O. In a similar way, protective colloids are prepared by the reaction of ethylene oxide on starch, casein or gelatin.

The work of the I.C.I. lies in a different direction. Compounds which aid in stripping were prepared of amines or ammonium bases with long-chain hydrocarbon groups. *F.P. 752,728* (1933) *795,217*; *G.P. 605,913*, *632,066*, *632,728*, *652,347*; *B.P. 400,239*, *436,076*, *437,884*; *U.S.P. 2,003,928*, *2,019,124*, *2,052,612* describe the substances belonging to this class, such as octadecyl pyridinium bromide, cetyl trimethyl ammonium bromide, and β-hydroxyethyl-N-octadecyl morpholinium.

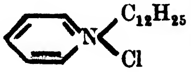
Dodecyl trimethyl ammonium chloride



$$(CH_3)\equiv N\begin{cases} C_{12}H_{25} \\ Cl \end{cases}$$

has practical use as a dispersing and leveling agent in dyeing of viscose rayon and cotton.

In a similar way, valuable textile auxiliaries are obtained by the reaction of higher alkyl chlorides with pyridine or pyridine homologs, for instance



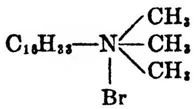
Dodecyl pyridinium chloride

which is Fixanol of the I.C.I. and similar to Repellat of Böhme. This compound behaves in dye liquors in similar fashion to Peregal O, and to Velan.

These pyridinium derivatives assist in the stripping of vat dyestuffs with the usual reagents (soda ash and hydrosulfite). They act as retarding agents in the dyeing process, preventing too rapid exhaustion and promoting a level dye operation.

According to *G.P. 632,066* (1934) the dyed goods are treated in a bath containing hydrosulfite and one of the above-mentioned ammonium compounds. On the basis of this patent, the product Decamine A, which was suitable for stripping insoluble azo dyes but less satisfactory for vat dyeings, was put on the market. Another product was developed for vat color stripping, called Lissolamine V, which is used in a manner similar to

Peregal O. According to *B.P. 400,239*, Lissolamine V is hexadecyltrimethyl ammonium bromide

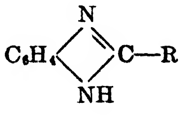


$$C_{16}H_{33}-N(CH_3)_3Br$$

(See also *B.P. 444,169*—I.C.I.)

In 1936, Seidel studied a series of auxiliary agents obtained by reacting amines with higher alkyl or acyl halides in the presence of pyridine. In the course of this work (Seidel and Brösamle, *Ber.*, **72,** # 1, 45) it was observed that the alkyl groups are not always linked directly to the nitrogen of the amino group, but that a pyridinium salt is formed, as octadecyl pyridinium bromide, which increases the solubilizing capacity of the product. By further reaction with naphthionic acid, the bromide forms the corresponding naphthionate. If these amines are linked to dyestuffs, dyeings are obtained which, while not so deep in shade, have much better wash fastness. These observations led to the use of these amines as stripping auxiliaries. The Lissolamines of I.C.I. are similar derivatives. Attention is called to the fact that despite the presence of long aliphatic chains, no water-repellent effect results. On the contrary, these products have good wetting and dispersing properties, preventing the reabsorption of the dyestuff.

Ciba patents on auxiliaries for stripping vat dyeings and relating to Albatex PO and the Ultravons, are *F.P. 778,476; B.P. 398,150; 403,977* and *441,296*; *U.S.P. 2,004,864, 2,031,037, 2,036,525, 2,335,271.* Dyestuff affinity can be reduced by adding high-molecular substituted sulfonated benzimidazols bearing a chain of eight or more C atoms in the imidazol nucleus, for instance, the sulfonates of N-methyl-μ-heptadecylbenzimidazol. The general formula is:



These substances are dispersing agents of a high efficiency, suitable as retarding agents and as stripping assistants.

According to *B.P. 398,150* (Ciba) hydrosulfite stripping effects are improved by quaternary ammonium compounds of the type, arylalkylmethyl-benzyl-N-Cl. The benzyl group must contain an HSO_3 radical. Similarly, Ciba recommends in *F.P. 727,213* the quaternary ammonium compounds obtained by the reaction of benzyl chloride on dimethylamine for the same purpose (Leucotrope). The quantities of these assistants added to the dye bath can be varied, whereby the leveling properties can be increased, as well as the stripping action. Conversely, the addition of these products to the printing paste reduces the yield, in some cases even to the effect of printing a resist.

Other products which assist in stripping will be briefly reviewed: *F.P. 778,833* and *G.P. 636,626* (Ciba) suggest the addition of polyvinyl alcohol to the alkaline-hydrosulfite stripping bath. A vat-dyed cloth is treated in a bath containing:

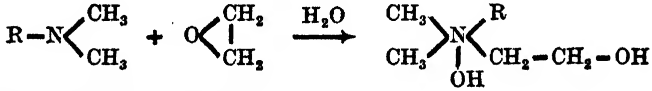
16 cc of caustic soda 30%
5 gm hydrosulfite
0.5 gm polyvinyl alcohol *in solution*

per liter at 90°C for ¾ to 1 hour.

Condensation of dimethylolurea with ethylene oxide and subsequent acylation with stearic acid produces a stripping assistant, according to *F.P. 768,732* (I.C.I.). Dimethylolurea (24 parts) and ethylene oxide (44 parts) are heated to 100 to 120°C in an autoclave with 2/*N* caustic soda while agitating. When no excess pressure is registered, 176 parts of ethylene oxide are added in small portions. 115 Parts of this condensate are then heated with 25 parts of stearic acid.

Water-soluble polypropanolamines are recommended as auxiliaries in stripping vat and sulfur color dyeings in *B.P. 497,482* (Sandoz).

Basic zinc formaldehyde sulfoxylate to which protective colloids such as sulfite waste liquor, sugar, etc., are added has been proposed as stripping assistant for vat-dyed wool. However wool undergoes chemical deterioration by the action of zinc formaldehyde sulfoxylate, even in the presence of these protective agents. Therefore *B.P. 459,209* (I.G.) suggests employing compounds generated by the action of alkylene oxides on tertiary water-soluble high substituted amines. The quaternary bases so formed are analogous to Lissolamines A and V, wetting and dispersing agents which promote the stripping operation. The reaction proceeds according to the equation:



$$R{-}N\begin{matrix}CH_3\\CH_3\end{matrix} + O\begin{matrix}CH_2\\|\\CH_2\end{matrix} \xrightarrow{H_2O} \begin{matrix}CH_3\\CH_3\end{matrix}{>}\underset{OH}{N}\begin{matrix}R\\CH_2{-}CH_2{-}OH\end{matrix}$$

Tertiary amine *Ethylene oxide*

(R = alkyl, as $C_{15}H_{31}$)

The protective action of this product can be further improved by the addition of metal salts, as Mg SO_4 or $Mg(NO_3)_2$, or cellulose sulfite waste liquor and metal oxides (MgO or ZnO), according to *G.P. 601,103, 601,196* and *B.P. 409,336*.

A definite protective action has also been observed by the use of fatty acid sulfuric esters, according to *G.P. 561,715* and *614,702* (Stockhausen) in dyeing as well as in stripping processes (*Mell.*, **1933,** 78; *Z. f. ges. Tex. Ind.*, **1929,** 619).

Animal fibers are protected by adding amino acetates or other amino acids or salts thereof, to the stripping bath according to *U.S.P. 1,990,852* (I.G.—Siefert); *G.P. 583,533*, *591,476*; *F.P. 753,141*; *B.P. 394,632*; and *S.P. 167,489*.

Water-soluble phosphonium or sulfonium compounds with aliphatic groups are recommended as stripping assistants in *B.P. 434,810*. Examples cited are dodecyltrimethyl phosphonium bromide and methylcetyl sulfonium hydroxide. The sulfonium compounds are obtained by reacting the corresponding thioethers with alkyliodide.

Classification of Auxiliaries for Vat Colors

The number of auxiliary products which have been recommended for dyeing and printing of vat dyestuff is unusually great. An exact classification of their uses is impossible, yet except for some overlapping of properties, the following may be taken as a general subdivision.

For printing, the auxiliaries fall into four classes.

(*1*) *Products having hydrotropic properties, and dispersing agents which promote leveling, or increase yield of the vats:*
Sodium benzyl sulfanilate (Dissolving Salt)
Sodium dimetanilate (Dinaton)
Cellulose sulfite waste (Dekol, Protectol)
Urea

(*2*) *Organic Solvents:*
Glycol, diethylene glycol, polyethylene glycols
Glycol ethers, as Cellosolve, Carbitol
Thiodiethylene glycol (Glyecine, Kromfax)

(*3*) *Products which are added to discharge and resist prints:*
Ether-forming compounds (Leucotrope)
Oxidizing compounds (Ludigol)

(*4*) *Assistants in development of prints:*
Oxidants, as Aktivin, Ondal

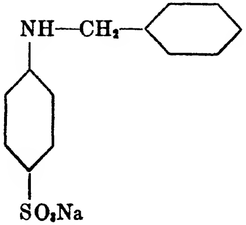
The auxiliaries for dyeing may be classified as follows:

(*1*) ***Leveling and dispersing agents:***
Cellulose sulfite waste liquor
Ethylene oxide condensates (Peregal O)
Benzimidazols (Ultravons)
Protein condensates with fatty acids (Lamepon)

(*2*) ***Pigment vat color dispersants:***
Highly sulfonated oils (Prestabit Oil, Calsolene Oil HS)
Naphthalene sulfonic acid condensates (Setamol, Tamol)

(*3*) ***Assistants in stripping of vat dyeings:***
Ethylene oxide condensates (Peregal O)
Quaternary ammonium derivatives (Lissolamines)

Table 1. Auxiliaries for Vat Dyestuffs

Name	Manufacturer	Constitution	Literature	Remarks
Solution Salt B, B new **Dissolving Salt B, B new** **Sel solvant NB, NBS** **Sel dissolvant S, B.** **Algosol** **Solvenol** **Solution Salt BN, SV, AO** **Solution Salt G** **Liovatin S** **Sel dissolvant S, SB**	I.G. G.D.C. Kuhlmann-Francolor S.P.C.M.C. I.G. I.G. I.C.I. Geigy Sandoz St. Denis	Sodium benzylsulfanilate.  White powder, soluble in water. SV = sodium dibenzylaniline sulfonate. BN = sodium benzylsulfanilate.	*B.P. 27,742* (1908) *Aus.P. 33,611* *F.P. 727,605* (1931) *B.P. 389,915* *S.P. 157,312* *Rev. Gen. Mat. Col.*, **1912**, 214; **1913**, 27 *Öst. W. u. L. I.*, **1912**, 313 Hasse, *Mell.*, **1937**, 456 *Frb. Ztg.*, **1910**, 333; **1912**, 134, 205, 436, 444; **1913**, 22, 442; **1914**, Vol. 1 and 2	Hydrotropic substance, dispersing agent and penetrating agent. Facilitates solution and reduction, promotes fixation, increases yield, levels. Used in vat printing, both in pre-reduced and unreduced formulas, in weak and strongly alkaline pastes. Particularly for starch thickenings. Addition: 30–40 gm per kg. Solution Salt SV: for vat printing on wool and silk.
Dinaton	I.G.	Sodium dimethylmetanilate.	*Seifensieder Ztg.*, **1928**, 95	Substitute for Solution Salt
Liovatin FL	Sandoz	Thick liquid. An aliphatic boric acid ester, probably glycerin boric acid ester.	*B.P. 367,240; 367,249* *Rev. Gen. Mat. Col.*, **1936**, 349 *B.P. 508,554* (1939) *G.P. 713,902* *F.P. 863,256*	In vat color printing facilitates reduction and increases depth of prints. Added to print paste, especially those made with carbonates. Recommended particularly for Sandothrene Orange NJ dbl. pst.
Débécuvol A	L.Z.J.	Probably triethanolamine salt of benzylsulfanilic acid.		Dispersing agent for vat printing to improve yield.

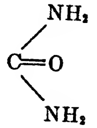
Ursin D	Fett- & Oel-Chem. Werke	Solvent mixture of glycol, glycerin and urea.		Vat color auxiliary.
Nekal B, A, AEM **Nekal BX**	G.D.C., I.G. G.D.C.	Alkylated aromatic sulfonic acid, as butyl or isopropyl naphthalene sulfonic acid.	*U.S.P. 1,737,792* (1930) *U.S.P. 1,843,420* (1932)	Emulsifying agents. Used for wetting and penetration.
Dekol **Protectol I pdr.** **Protectol II pdr.** **Unisol NS, N, NDL** **Levana** **Cellex pdr.** **Sulfitablauge pdr.** **Lomar AJ**	I.G., G.D.C. I.G., G.D.C. I.G., G.D.C. Kuhlmann-Francolor Sandoz Ciba Ciba J. Wolf	Dark brown liquid or grey powder, readily soluble in water, with characteristic odor. Made from sulfite-cellulose waste liquor. Active ingredients: sodium lignin sulfonates.	*F.P. 681,566* (Ciba) *G.P. 229,191* (Badische A.S.F.) *G.P. 313,840* *Frb. Ztg.*, **1911**, 45, 358 *Z. f. ges. Tex. Ind.*, **1911**, 23; **1934**, 400 *Bull. Fed.*, **#1**, 133 *Mell.*, **1921**, 353; **1927**, 534; **1930**, 532, 610; **1937**, 739; **1932**, 485, 546 *S.P. 148.451*	Unisol and Dekol are brown liquids which have good dispersing properties in water solution. Stable to the earth alkalis. Protect animal fibers from attack by alkalis. Uses: in vat printing 40–50 gm per kg; in vat dyeing; for preparation of vat dyestuff pastes and fine powders in combination with hydrotropic and dispersing agents; in dissolving naphthols; in wool dyeing; in wool degreasing and as protective agent for wool.
Intensifier CIBA	Ciba	Urea.  White crystals, soluble 1:1 in water.	*F.P. 731,270; 681,566* *U.S.P. 1,835,926* *G.P. 570,583* (1929) *Mell.*, **1937**, 275	Hydrotropic substance with solvent action. Auxiliary in vat printing, where the yield is considerably increased. Addition: 60–100 gm per kg. The addition is made to the warm gum thickening.

Table 1. Auxiliaries for Vat Dyestuffs (*Continued*)

Name	Manufacturer	Constitution	Literature	Remarks
Peregal O, OK **Emulphor O** **Rexan O** **Emulsifier L34A**	I.G., G.D.C. I.G., G.D.C. Dexter J. Wolf	Condensation products of ethylene oxide with higher fatty acids or alcohols, as lauryl or octadecyl alcohol. Peregal O is said to be a solution of Emulphor O. Peregal OK is a corresponding quaternary compound.	*B.P. 346,550; 367,420; 409,336; 443,559* *F.P. 713,426–7; 717,427; 727,202* (1931); *752,831* (1932) *G.P. 548,201; 636,305* *Rev. Gen. Mat. Col.*, **1934**, 153 *Tiba*, **1934**, 11 *Bull. Fed.* I, 244–5 *Mell.*, **1933**, 22 *D.F.Z.* **1933**, 145 *U.S.P. 1,959,930* (1934); *1,970,578; 2,069,336* (1937); *2,214,352*	Readily soluble liquid, nonionic. Active dispersing agent, retards the exhaust of vat dyes, and so aids in leveling. In higher concentrations it more or less hinders the dye absorption. Used as auxiliary in stripping of vat and naphthol dyeings.
Albatex PO	Ciba	Derivative of benzimidazole sulfonate.	Landolt, *Mell.*, Fr. ed. **1936**, 650 *Bull. Fed.*, I, 514 Egger, *Mell.*, **1937**, 651 *Rev. Gen. Mat. Col.*, **1935**, 349 *F.P. 776,146; 778,476; 778,853*	Thick liquid, readily soluble in water. Very active leveling and penetrating agent. Produces no precipitate with vat colors. Used as stripping assistant for vat and naphthol dyeings.
Solopol W, W conc. **Solopol PW, PW conc.**	Stockhausen Stockhausen	Yellow brown liquids, soluble in hot water. Similar in constitution to Peregal O.	*Seide-Kunstseide*, **1937**, 200	Leveling and dispersing agents. Used in the dye bath.
Tinegal T	Geigy	Aromatic fatty acid sulfonate. Brownish paste.		Leveling agent for dyeing, especially in vat dyeing. Softens the fabric when used in the dye bath.

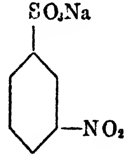
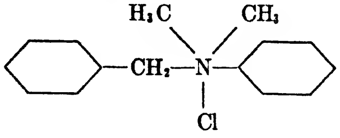
Lissolamine V **Decamine (replaced by above)**	I.C.I. I.C.I.	Quaternary ammonium compound, especially pyridinium derivatives. Original patent indicates octadecyl pyridinium bromide or hexadecyltrimethyl ammonium bromide. Light grey paste giving milky solution of slightly acid reaction.	*B.P. 400,239; 426,076; 437,884* *F.P. 795,127; 771,349; 748,510* (1932); *752,728* (1933) *G.P. 605,913; 632,066; 632,728; 652,347* *U.S.P. 2,003,928; 2,019,124; 2,052,612* *Rev. Gen. Mat. Col.*, **1933**, 465; **1934**, 153 *Tiba*, **1933**, 935 *Rev. Chem. Ind.*, **1933**, 305	Water-miscible paste. Powerful dispersing agent. Used for stripping vat color dyeings in alkaline hydrosulfite baths.
Hydrolux	Warwick Chem.	Compound formed from glucose and alkali sulfites or bisulfites. Also bisulfite-acetone dissolved under pressure with glucose and alkali.	*U.S.P. 2,201,010* (Parini) *U.S.P. 2,201,042* (Katz)	Stabilizing effect on sulfoxylate formaldehyde. Used to improve white discharge with Hydrosulfite NF, and recommended also in vat color printing.
Sitol **Nacan** **Ludigol** **Solidol N** **Mattenol** **Revatol S** **Albatex BD** **Reserve Salt G** **Sel Réserve O** **Resist Salt** **Retardit**	Du Pont N.A.C. G.D.C., I.G. Kuhlmann S.P.C.M.C. Sandoz Ciba Geigy St. Denis I.C.I. Onyx	*m*-Nitrobenzol sodium sulfonate.  White powder, readily soluble. The calcium salt is also made. Analogous naphthalene and anthracene derivatives used for same purposes.	*G.P. 210,682; 211,526* Hasse, *Mell.*, **1937**, 456 *Mell.*, **1937**, 532	Resisting agent under vat and sulfur colors, and under hydro discharges. Uses: resist under vat dyeing; protection against facing of dyed grounds in discharge printing; as pad after printing to lift doctor streaks; as protective addition to colors (as Rapidogen) printed alongside vats. As resist under all-over vat print patterns. In kier boiling.

Table 1. Auxiliaries for Vat Dyestuffs (*Continued*)

Name	Manufacturer	Constitution	Literature	Remarks
Reserve Salt K	Kalle	*o*- or *p*-Nitrotoluol sodium sulfonate.		Uses: same as Ludigol
Reservol B, BC	I.G.	Ca, Zn or Mn salt of *m*-nitrobenzol sulfonate or or *m*-nitroanthracene sulfonate.	*G.P. 548,202* *Mell.*, **1931**, 283	White powder, difficultly soluble in water. Used as resist under vat colors. Its poor solubility is an advantage, minimizing staining of the whites.
Candit V (1928)	Pyrgos	Glucose-sodium sulfoxylate, $C_6H_{12}O_6 \cdot NaHSO_2$ (Haller & Solbach). White paste, neutral, stable to Ca but not to acids. According to Hetzer: zinc-sodium-glucose hydrosulfite (*Färb. Kal.*, **1944**, 325).	*G.P. 529,617* Hackl, *Mell.*, **1930**, 383, 533 *Mell.*, **1929**, 41, 630, 717; **1930**, 42 *Tiba*, **1930**, 963 Pomeranz, *Mell.*, **1930**, 286	Reducing agent for the indigo vat, increasing its stability. Used in vat dyeing, on the jig and continuous machine. As addition to indigo discharge (Haller).
Leucotrope O **Metabol O** **Discharge Salt O** **Addol O** **Leucofixe NJ** **Leuco SO** **Leucophenine O** **Reduzin NS**	G.D.C., I.G., J. Wolf I.C.I. Ciba Geigy Kuhlmann-Francolor Soc. Dériv. Soufre Rohner Sandoz	Dimethylphenylbenzyl ammonium chloride (Reinking, 1909).  Grey green powder, easily soluble in water.	*G.P. 231,543* (1909); *184,381; 229,023* *F.P. 414,937* *Frb. Ztg.*, **1910**, 243, 309, 374; **1911**, 103, 227, 237, 406, 465 *Frb. Ztg.*, **1912**, 211, 236, 309, 334, 374 *Chem. Ztg.*, **1937**, I, 725	Capable of combining with leuco-vat colors. Used for yellow discharge on indigo, resists under all-over vat print patterns.

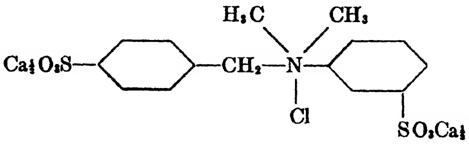
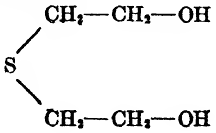
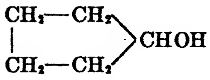
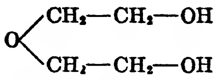
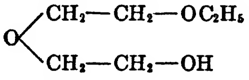
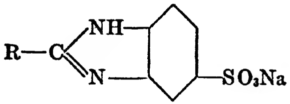
Leucotrope WX **Leucotrope W** **Leucophenine NB, NB conc.** **Metabol WS** **Discharge Salt W** **Addol W ex. conc.** **Leuco SW** **Reduzin S** **Sel Réserve W**	G.D.C., I.G. J. Wolf Kuhlmann-Francolor I.C.I. Ciba Geigy Soc. Dériv. Soufre Rohner St. Denis	Sodium or calcium salt of dimethylphenylbenzyl ammonium disulfonic acid (Reinking, 1909).  Yellow powder, soluble in water.	*G.P. 235,879; 235,880; 240,513; 246,252; 246,519; 247,099; 247,100; 247,101; 249,542–3; 250,084* *F.P. 413,554* Reinking, *Frb. Ztg.*, **1910**, 243; **1912**, 250, 309; **1913**, 45 Bude, *Frb. Ztg.*, **1912**, 470; **1913**, 103 *Rev. Gen. Mat. Col.*, **1913**, 54	Capable of combining with leuco-vat colors, forming a benzyl ether which is stable in air and soluble in alkali, and which can be removed in hot silicate bath. Used in white discharges and resists of vat colors.
Glycine A **Kromfax Solvent** **Brecolane NCI** **Dehapan GB** **Lyogen TG** **Neocotone Solvent II** **Tinosol Solvent A**	G.D.C., I.G. C.C.C.C. Kuhlmann-Francolor D. & H. Sandoz Ciba Geigy	Thiodiethylene glycol.  (B.p. 282°C) Syrupy liquid of sweet, pungent odor, miscible with water.	*G.P. 339,690* *B.P. 147,102; 427,058* (D. & H.) *F.P. 711,869; 713,460* *S.P. 159,928*	Solvent. Hygroscopic agent. Used to paste up vat dyestuffs. Aids leveling, increases depth and brightens shade.
Débésol B	L.Z.J.	Mixture of high-boiling solvents.		Hygroscopic agent for printing vat colors.
Hystabol D	Böhme F.C.	Solvent mix of polyglycols and tetrahydrofurfuryl alcohol. 	*Aus.P. 139,111; 139,845* *S.P. 165,151* *U.S.P. 1,967,656* *F.P. 744,251* (Böhme F.C.) *Mell.*, **1934**, 516	Dispersing agent. Excellent solvent action. Used as addition to vat color printing pastes to improve yield and levelness.
Irgasol	Geigy	Solvent based on ethylene glycol and ethylenechlorohydrin.	*F.P. 587,269* *G.P. 386,032* and *400,684* Geigy	Solvent for vat dyestuffs. Used as addition to print pastes.

Table 1. Auxiliaries for Vat Dyestuffs (*Continued*)

Name	Manufacturer	Constitution	Literature	Remarks
Diethylene glycol **Brecolane NDG** **Polyglycol**	C.C.C.C. Kuhlmann-Francolor I.G.	Colorless liquid, miscible with water. Hygroscopic agent.  (B.p. 245°C; Sp.Gr. 1.1212)	*U.S.P. 2,047,650* (Du Pont) *G.P. 340, 552; 391,007* (I.G.) *B.P. 366,910; 427,058* *S.P. 157,912-3*	Very hygroscopic solvent. Used to paste up vat colors, and to prevent their drying out and freezing. Improves yield and penetration of vat prints.
Carbitol	C.C.C.C.	Monoethyl ether of diethylene glycol. Colorless liquid, miscible with water.  (B.p. 200°C; Sp.Gr. 1.020)	*U.S.P. 1,696,874; 1,750,061; 1,732,856*	Excellent solvent for vat colors in dyeing and printing.
Fibrit D **Durit O**	G.D.C., I.G. Carbic	Solvent mixture of glycols and polyglycols. Fibrit D is 80% ethyl ether of triglycol and 20% glycol.	*G.P. 340,552; 391,007* *U.S.P. 1,967,656* *S.P. 157,912-3; 165,151* *Aus.P. 139,111; 139,845*	Solvent for pasting up vat colors, and to aid levelness in printing.
Geneucol M	A. Th. Böhme	Sulfonated oil.		Used like Prestabit oil.
Ultravon F, FA **Ultravon W, K**	Ciba Ciba	Benzimidazole derivative.  (Graenacher)	*F.P. 774,018; 778,476* *B.P. 398,150; 441,296* Ranshaw, *Dyer*, **1937**, 579 *Bull. Fed.*, Sept., 1938 *Mell.*, **1935**, 749; **1936**, 85 *Z. f. ges. Tex. Ind.*, **1935**, 646 *U.S.P. 2,053,822; 2,004,864; 2,036,525; 2,043,164; 2,335,271*	Neutral detergents, stable to hard water as well as acids and alkalis. K: for use at high temperatures. W: for use in vat dyeing, as well as in naphthol and direct color dyeing.

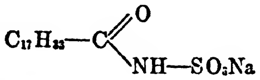
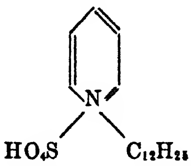
Peregal KB	G.D.C., I.G.	Compound of polyethylene polyamine and ethylene chloride.	*J. Soc. Dy. & Col.*, Dec. 1946	Dye-bath assistant.
Humectol C, CX	I.G.	Sodium fatty acid amide sulfate.  $C_{17}H_{33}-C(=O)-NH-SO_3Na$	*F.P. 693,620* *U.S.P. 1,932,176* *Mell.*, **1937**, 155	For machine dyeing, especially with vat colors. As addition to dye bath in pigment pad method.
Inferol NF, NFK **Inferol 229, 236**	A. Th. Böhme (1933) A. Th. Böhme (1933)	Fatty alcohol sulfonates.		Cold dyeing assistant.
Pentazikon TI, TS	Baumheier	Highly sulfonated alkyl aromatic compounds.	Rordorf, *Kunstseide*, **1936**, 201	Penetrant, also detergent for washing vat prints. TS: for sulfur color dyeing.
Repellat KS	Böhme F.C. P.C.M.R.	Laurylpyridinium sulfate. 	*B.P. 425,431* (Böhme F.C.) *G.P. 673,158* *S.P. 173,257; 183,676* *Aus.P. 154,886*	Leveling agent for vat dyes. Retards exhaust of vat colors on cotton.
Amendol	Böhme F.C. P.C.M.R.	Fatty alcohol sulfonate.	*B.P. 455,431*	Used in conjunction with Repellat KS to promote exhaust of vat colors.

Table 1. Auxiliaries for Vat Dyestuffs (*Continued*)

Name	Manufacturer	Constitution	Literature	Remarks
Prestabit Oil G, GA	Stockhausen	Alkali salt of fatty acid ester sulfonate.	*G.P. 551,751; 614,702; 656,000* *Mell.*, **1928**, 799; **1930**, 610; **1931**, 196 Steitz, *Z. f. ges. Tex. Ind.*, **1932**, 27; **1933**, 36, 210 Friedrich, *Mell.*, **1933**, 78; **1935**, 736 Arnold, *Text. Mfr.*, **1935**, 76 Nelson, *Dyer*, **1935**, 74, 486 *Am. Dyes. Rep.*, **1946**, 684	Liquids of slightly acid reaction, stable to metal salts. KG: stable to strong caustic solutions. Good wetting and penetrating properties. Used in the mercerization of cotton. G: dyeing and wetting oil of high stability. Used in vat dyeing. V: penetrating agent for the pigment pad method. NRT: especially for machine dyeing. Prevents bronzing of sulfur dyeings. MA: dispersing and wetting agent for strongly alkaline baths. Z: wetting agent.
Prestabit Oil V, S, NRT, MA	Stockhausen	Alkali salt of fatty acid ester sulfonate and solvents.		
Prestabit Oil Z	Stockhausen	Fatty acid ester sulfonate.		
Prestabit Oil KG, W310, K spec.	Stockhausen			
Prestabit Oil V new	G.D.C.			
Maxitol	Dexter			
Apasol	J. Wolf			
Oleonat D, EW, N	Pfersee	Highly sulfonated oils, stable to Ca and Mg salts		As addition to dye bath, and as detergent in washing prints.
Tergitol 4, 7	C.C.C.C.	Amine salts of high molecular secondary alkyl sulfates.	*U.S.P. 2,088,014; 2,088,017–21*	Penetrants and dispersing agents. Used in padding, especially pigment vat padding.
Protolene	Dexter	Sulfonated isopropyl ester of oleic acid.		High-speed wetting agent. Withstands high temperatures.

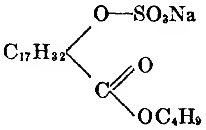
Avirol AH, AH ex. **Avirol AH extra** **Sandozol KB, KBN** **Oloran B7** **Tibalene NAM** **Immersol S, SG** **Astrolane** **Puropol Oil S, A, NB**	Böhme F.C. P.C.M.R. Sandoz Oranienburg Kuhlmann-Francolor St. Denis S.P.C.M.C. Simon-Dürckheim	Sulfonated castor oil esters, for example, sulforicinoleates of amyl or butyl alcohol.  By esterification of the COOH group with different alcohols.	*F.P. 677,526; 677,527* (1929) *F.P. 698,637* (1930); *702,626* (1930) Nopitsch, *Mell.*, **1928**, 136, 241 Kling, *Mell.*, **1928**, 48, 111; **1931**, 112 Hüttenlocher, *Mell.*, **1927**, 538 *Z. f. ges. Tex. Ind.*, **1930**, 38 Landolt, *Mell.*, **1928**, 759; **1935**, 62, 134, 288 *Mell.*, **1926**, 841; **1928**, 913; **1930**, 381, 610, 788 Bertsch, *Mell.*, **1930**, 779 *Rev. Chim. Ind.*, **1931**, 172 *Seifensieder Ztg.*, **1928**, 372, 405; **1932**, 45–7	Excellent penetrating agents of good stability to Ca and Mg salts. Used as pasting agents and dye-bath auxiliaries, for vat colors, naphthols, direct colors, etc.
Tamol **Setamol WS** **Blancol conc. pdr.** **Lomar PW** **Diastersol NDS** **Dispergine**	Röhm & Haas I.G. G.D.C. J. Wolf Kuhlmann Francolor	Sodium salt of the condensation product of β-naphthalene sulfonic acid and formaldehyde. Tamol is the sodium salt of disulfodinaphthyl methane.	*Mell.*, **1928**, 779 *Mell.*, **1932**, 220	Dispersing agent. Used in the vat acid method. Also in dyeing wool with white silk effects.
Calsolene Oil HS	I.C.I.	Highly sulfonated oil, stable to acids and hard water.		Penetrating agent, especially on heavy-woven fabrics.
Tinopol Oil BH, NE **Triumph Oil supra**	Geigy Zschimmer & Schwarz	Highly sulfonated oils.		
Neberon BA, S, BF	Chem. Fabr. Schmitz	Sulfonated oil derivatives.		As addition to dye bath.

Table 1. Auxiliaries for Vat Dyestuffs (*Continued*)

Name	Manufacturer	Constitution	Literature	Remarks
Eulysin A	I.G. (1928) G.D.C.	Alkylated naphthalene sulfonic acids and amines.	Hetzer, *Tabellen*, 55 Nüsslein, *Mell.*, **1935**, 49 Prasse, *Mell.*, **1936**, 334 Stierwaldt, *Mell.*, **1936**, 500 Schwen, *Text. Mfr.*, **1936**, 153 Hasse, *Mell.*, **1937**, 456	Leveling agent in dyeing yarn in cops, spools, etc. Pasting agent for vat and sulfur colors. For use in vat pigment pad method. Improves crocking and smearing of sulfur color dyeings.
Tibalène NED	Kuhlmann-Francolor			Prevents lime soap formation. Dispersing agent for vat colors in dyeing.
Ondal d.c. **Ondal A**	Böhme F.C. P.C.M.R. Du Pont	Phosphoric acid ester of higher fatty sulfated alcohol (as lauryl) mixed with perborates. Typical mixture consists of Gardinol WA, sodium perborate, and tetrasodium pyrophosphate.	*G.P. 594,806; 589,778* *B.P. 425,804* *S.P. 183,447* *Z. f. ges. Tex. Ind.*, **1936**, 133; **1937**, 178	Combination washing and oxidizing agent for vat prints. Stabilizer for peroxide bleaching.
Igepal C conc., B conc., M conc. **Uniperol**	I.G., G.D.C. I.G.	Produced by condensation of phenolic compounds with ethylene oxide. Higher fatty radicals with short hydrocarbon side chains connected with ether oxide bridges. Completely stable to hard water ions and metal salts.	Basic patents: *B.P. 471,483; F.P. 823,454* Nüsslein, *Mell.*, **1937**, 248 Chwala and Martina, *Mell.*, **1937**, 999 *Z. f. ges. Tex. Ind.*, **1943**, 1194 Hetzer, *Mell.*, **1943**, 177 *J. So. Dy. & Col.*, **1946**, 322 *U.S.P. 2 2.3,477* *F.P. 823,454* (*Chem. Abs.*, **1938**, 5414)	Soluble in water, excellent stability against hard water and metal salts. Washing agent for development of vat dyeings.
Leukotex PS	Zschimmer & Schwarz	Based on perborates.		For oxidizing vat colors.

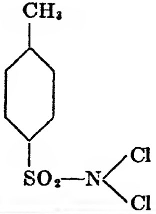
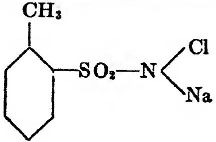
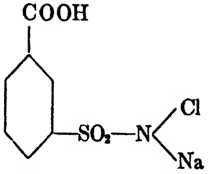
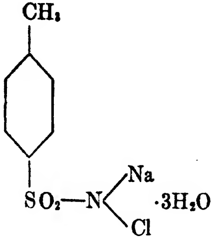
Lamepon A	Landshoff & Meyer	Polypeptidoleylamide.	*U.S.P. 2,015,912*	Leveling agent for vat dyeings.
Maypol	Maywood Chem.	By condensation of fatty acid chlorides with proteinaceous products.	*B.P. 413,016; 435,481* (Landshoff and Meyer) *F.P. 772,585* *Mell.*, **1933**, 424	Emulsifying and dispersing agent. For washing vat and sulfur dyeings.
Colloresin D, DK	I.G., G.D.C.	Cellulose ether.	*G.P. 495,712; 525,182*	Thickening agent, soluble in cold, insoluble in hot water.
Cellosize WS	C.C.C.C.	Hydroxyethyl cellulose.	Scholl, *Mell.*, **1935**, 155,444	Used in printing vat colors and naphthol dyestuffs, especially screen, block and novelty printing.
Carboxymethocel	Ciba	Cellulose glycollate.	Kerth, *Mell.*, **1935**, 794	
Methocel	Ciba	Methyl cellulose ether.	*Mell.*, **1927**, 1047; **1928**, 666 *Mell.*, **1937**, 378	
Deceresol OS, OT	Am. Cyanamid Co.	Alkyl aryl sulfonates.	*U.S.P. 2,028,091; 2,200,750; 2,391,830; 2,391,831*	Emulsifying and wetting agents.
Deceresol AS, AY, MA	Am. Cyanamid Co.	AY: diamyl sodium sulfosuccinate. OS: isopropyl naphthalene sodium sulfonate. OT: dioctyl sodium sulfosuccinate.		Very effective in reducing surface tension.
Peraktivin	Pyrgos	Toluol dichlorosulfoamide. 		White powder, with strong odor of chlorine.
Chloramine TO	Pyrgos	Isomeric *ortho* derivative of Chloramine T. 		

Table 1. Auxiliaries for Vat Dyestuffs (*Continued*)

Name	Manufacturer	Constitution	Literature	Remarks
Chloramine BX	Pyrgos		Thiebaud, *Teintex*, **1937**, 366 Feibelmann, *Mell.*, **1931**, 263 Hausner, *Mell.*, **1932**, 268	
Aktivin	Pyrgos	Sodium salt of *p*-toluol chlorosulfonamide.  White powder, readily soluble in water, salt and alkaline solutions.	*G.P. 390,658; 422,076; 423,464; 443,013; 461,637; 462,199; 504,997; 530,894; 559,250; 563,887* *F.P. 610,985* *B.P. 241,579; 241,580* Feibelmann, *Chem. Ztg.*, **1924**, 297; *Mell.*, **1926**, 47, 144; **1927**, 714; **1931**, 263 *Mell.*, **1927**, 172; **1929**, 240; **1930**, 610 Herbst, *D.F.Z.*, **1934**, 395 Bonnet, *Teintex*, **1937**, 95, 158 Kosche, *Z. f. ges. Tex. Ind.*, **1933**, 578; **1932**, 168 Heermann, *Mell.*, **1924**, 181 Haller & Hobmann, *Mell.*, **1926**, 739	Oxidation agents which act in neutral solution, more energetically in acid solution. Recommended for oxidizing vat prints and dyeings. Mildly active, without damage to the fiber.
Aktivin S, S spec.	Pyrgos			
Aktivin	Heyden U.S.A.			
Chloramine	S.P.C.M.C.			
Chloramine	Heyden			
Chloramine T	Rhône-Poulenc			
Peralbine NBA	Kuhlmann-Francolor			
Mianin	Fahlberg-List			
Chlorine C	St. Denis			
Chloramine T	Monsanto			
Perburanil	Bauer-Gaebel	Sodium pyrophosphate.		For developing vat dyeings.

Chapter II

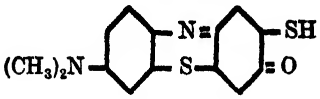
Sulfur Dyestuffs

Sulfur colors* are dyestuffs obtained by the chemical action of alkali sulfides or sulfur, or both, on various organic compounds.

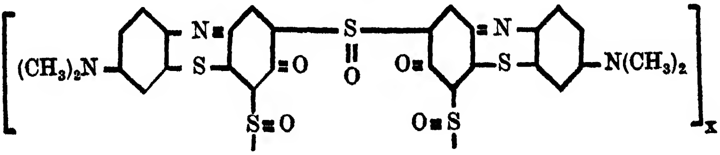
The first dyestuffs of this group were Cachou de Laval (Croissant and Bretonnière, 1873), produced by melting sulfur and sodium sulfide with organic substances such as sawdust, blood, peat, etc., and Vidal's Black (Vidal, 1893) made by melting benzene and naphthalene derivatives, especially *p*-amino- and dinitrophenol with sulfur and sodium sulfide (*G.P. 99,039*; *Frdl.*, # **5**, 439).

Immedial Black, a valuable sulfur dyestuff was prepared in 1897 from dinitrohydroxydiphenylamine (Kalischer, Cassella). The important Sulfur Black T followed in 1899, obtained from 2,4-dinitrophenol or dinitrochlorobenzol.

In the following years the number of sulfur dyes has grown tremendously, and the textile industry has a rich selection of brown, blue, green, orange and yellow shades in this group. In 1900 Weinberg and Herz, of Cassella, produced sulfur blues from indophenols and indamines, especially Immedial Pure Blue from 4-dimethylamino-4-hydroxydiphenylamine. According to Norton, Jones and E. Reid (*J. Am. Chem. Soc.*, **1932,** # 54, 4393), Immedial Pure Blue has the following constitution:



Keller and Fierz-David (*Helv. Chim. Acta*, **1933,** # 16, 585; *Chem. Zent.*, **1933,** 1188, 1289) assign the following construction to this dyestuff:



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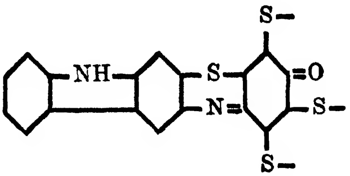
* Otto Lange, "Die Schwefelfarbstoffe"; F. Mayer, "Chemie der organischen Farbstoffe", J. Springer, Berlin, 1934; Cain and Thorpe (Thorpe and Linstead), "Synthetic Dyestuffs", Griffin, London, 1946.

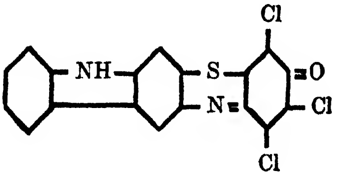
Pure yellow shades were obtained in 1903 by sulfurizing *m*-toluylene diamine (Immedial Yellow, Weinberg of Cassella) and, green dyes were produced, using copper salts.

A discovery of great importance was made by Haas and Herz in 1908, when they prepared the fast Hydron Blue using carbazole quinonimines. This was no doubt the most important finding in the field of sulfur colors, as Hydron Blue has much greater fastness to chlorine than other dyestuffs of the sulfur group.*

Hydron Blue R (Ciba Blue RH, 2RH, 3RH of Ciba, Thio-Tinon Blue of Geigy, Sandone Blue RG of Sandoz, etc.) corresponds to the general formula:

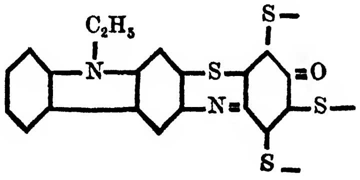


The dyestuff is prepared from 3-amino-carbazole, which is converted into the *o*-mercaptan and condensed with chloranil (tetrachloroquinone). The compound



is so obtained, the Cl atoms of which can be readily replaced by sulfur.

Hydron Blue G, also of Cassella (Schober, *Mell.*, **1925**, #6, 499; *G.P. 222,640*, *224,590*) has the constitution:



Sulfur dyestuffs possess good fastness to soaping, to light and to crocking. Despite their relatively poor fastness to chlorine, they are important for dyeing heavy cottons, especially in full and medium shades. However, it

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* Bernasconi, *Helv. Chim. Acta*, **1932**, #15, 287; A. von Weinberg, *Ber.*, **1930**, 119; Keller and Fierz-David, *Helv. Chim. Acta*, **1923**, #16, 585; *G. P. 224,591*; Schober, *Mell.*, **1925**, 449.

can be said that their usage was most widespread in the years preceding the First World War. Since that time it appears that the interest in this group has waned, as few inventions have been published in this field. The Indo Carbon Blacks are an exception. These fast colors were introduced in 1926 and are particularly recommended for printing purposes.

The sulfur colors are brought out under various trade names, some of which are listed here.

Eclipse	Geigy	*Sulfur*	N.A.C. and Francolor
Calcogene	Calco	*Auronal*	ter Meer
Pyrogen	Ciba	*Sulphol*	J. Robinson
Sulfogen	Du Pont	*Sulphast*	Williams
Thional	Sandoz	*Thio-Tinon*	Geigy
Thionol	I.C.I.	*So-dye-sul*	Southern D.C.
Thionine	L.B.H.	*Suldura* *Sulfatone*	Y.D.C.
Immedial *Katigen* *Hydron* *Indo Carbon*	G.D.C. I.G.		

As a group, the sulfur colors do not offer the complete color scale. Bright reds, and shades near the red, are still missing.

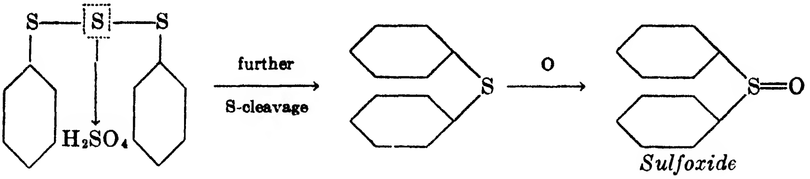
A more recent innovation in sulfur dyeing is the advent of sulfur leuco dyes. These dyestuffs, known as Immedial Leuco dyes of the I.G. and Eclipsol dyes of Geigy, deserve special mention because they offer greater ease in handling. They are pre-reduced, stable compositions, readily soluble in water without the addition of sodium sulfide. They require only cold water for solution, and have good affinity at low temperatures (25 to 30°C).

The valuable fastness properties of the sulfur dyestuffs can be explained by their insolubility in water and their chemically inert nature. The sulfur colors are more easily reduced and vatted than the vat dyestuffs. It has been found that sulfur in the form of the disulfide radical (—S—S—) has the property of combining different compounds. By reduction and vatting, the disulfide group is transformed into the hydrosulfide group (—SH).

The sulfur colors are capable of developing sulfuric acid by autooxidation. This may happen to the dyestuff paste or powder, as well as to the dyestuff on the fiber, in which case the fiber is attacked and weakened. The sulfur atoms which are bound by secondary valences, or by adsorption or addition linkages, are most readily oxidized. Heat and humidity act as accelerators, as well as copper or iron salts.

To combat this condition, it has been recommended to aftertreat the dyeings in a bath of sodium acetate or sodium formate.

According to Möhlau and Erdmann, there are polysulfide bridges from which the sulfur may be split off and oxidized, as follows:



PREPARATION OF PASTES AND FINE POWDERS

According to *U.S.P. 2,091,417* (I.G.—Schick, Kohl) and *G.P. 641,039* and *641,278*, sulfur dyestuff pastes can be prepared by mixing the dry color with sodium sulfide, a salt of an organic acid (as sodium formate) and a salt of a phenol sulfonic acid. The paste is almost completely unaffected by atmospheric oxidation. The reduction of sulfur colors for the manufacture of highly concentrated pastes is carried out by using sodium sulfide in an excess so as to provide sufficient quantities for the solution of the color in the dye bath (*B.P. 429,350*). The reduction is carried out at temperatures (50 to 80°C) below the boiling point of the liquid.

The method outlined by I.G. in *B.P. 419,817* of mixing the dry sulfur powders with alkali sulfide and a hygroscopic agent such as phenolsulfonate or potassium thiocyanate refers to micro powder brands rather than to pastes. These micro powders are stored with a protective layer of felted wrapping.

The principal application of sulfur dyestuffs is in dyeing. The use of these colors in printing has been largely confined to the production of resist effects. This style was carried out in Russia before the first World War with great success; details of the method are just being published.

DYEING AND PRINTING WITH SULFUR DYESTUFFS

Dyeing*

Most of the sulfur dyestuffs are absorbed by the vegetable fiber in the form of their colloidal leuco compound. In this respect they are similar to the vat dyestuffs.

On the other hand, they resemble the substantive colors insofar as their fastness is improved by an aftertreatment with metal salts. They can be regarded as occupying a position between the vats and the direct colors (Biltz, *Ber.*, **38,** 2963 ff.; *Chem. Zent.*, **1905,** #11, 525; Friedländer, *Z. f. angew. Chem.*, **1906,** 615).

Sulfur dyes can be dyed on cotton raw stock, on yarns and in the piece.

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* Matos, *Text. Mfr.*, "Dyeing of Cotton with Sulfur Colours," **1912,** 131; Hetzer, *Z. f. ges. Tex. Ind.*, **1912,** 9; A. Busch, *Z. f. ges. Tex. Ind.*, **1917,** 630; Pomeranz, *Z. f. ges. Tex. Ind.*, **1917,** 162; Hofmann, *Frb. Ztg.*, **1917,** 197.

Piece goods are dyed on the pad, jig or continuous range, while raw stock and yarns are dyed in machines with stationary material, flowing liquor. Yarn wound on tubes or in packages are dyed in pressure type or vacuum type apparatus, the dye liquor being forced through the yarn (Obermaier, Haubold, Zittauer, Thies). When dyeing skeins, the skeins may be moved during dyeing, but the liquor should circulate also (Smith-Drum).

At first the dyeing of sulfur colors presented difficulties, because of the rapid oxidation of the dye liquor carried into the air. This led to the construction of under-water jigs. The oxidation of the individual sulfur leuco compounds varies within wide limits. Many of the leuco compounds remain unoxidized on the fiber for some time, while on the other hand, there are many sulfur colors which draw directly from the dye bath and require no further oxidation.

Various methods have been proposed to minimize the atmospheric oxidation during dyeing:

F.P. 329,432: Use of sodium bisulfide or polysulfides (Na_2S_7) instead of sodium sulfide.

G.P. 129,281: Alkali hydrosulfides (NaHS) instead of sodium sulfide Na_2S.

G.P. 130,848, 197,892: Use of ammonium salts (Katigen Intensifier) as oxidation retardants.

G.P. 117,732: Replacement of sodium sulfide by salts of trithiocarbonic acid which are excellent solvents for the dyestuff and prevent dyestuff adhering during rinsing process.

G.P. 213,455: Addition of sodium bicarbonate to prevent oxidation of sodium sulfide.

G.P. 220,169: The addition of sodium bisulfite for the same reason as above.

German application K. 33,600: Use of arylmercaptans, thiophenols, thionaphthols or thiocresols which protect the sulfur dyestuffs from premature oxidation, as they are themselves more readily oxidized than the dyestuff.

Preparation of Dye Bath. The dyestuff is first dissolved by adding the necessary amount of sodium sulfide, which dissolves the color by reduction. Common salt and Glauber's salt are used for promoting the absorption of the dyestuff. The sulfur dyestuffs are relatively cheap and are generally used for the mass production of textiles, the price of which is dictated by sharp competition.

"Bronzing" is one of the numerous defects encountered in dyeing sulfur dyestuffs in dark shades. This can be counteracted by the addition of 2 gm of Trilon B per liter of dye liquor. It is further suggested that dyeings of Hydron Blue or Carbon Black having this defect can be cleared by treating the material on the jig at 60°C with a bath containing 2 gm of

Trilon and 30 gm of sodium sulfide per liter, then rinsing with 2.5 gm of Dekol and 3 gm of sodium sulfide per liter at 50°C, finally rinsing in cold, then hot and again in cold water.

Dyeings of sulfur colors are sometimes apt to exhibit poor fastness to crocking. So it is advisable to add certain auxiliary agents to the dye bath, as Medialan or Eulysin A. These products are not only good pasting-up, but also efficient leveling agents.

Immedial- or Katigen-Intensifier, ammonium chloride or ammonium carbonate (Erban and Mebus, *Chem. Ztg. Rep.*, **1907,** 220) can be employed for improving uniformity and yield of the sulfur colors. Dextrin, glucose and Turkey red oil promote penetration and leveling, and increase the color yield.

Temperature. Most of these dyestuffs can be dyed at temperatures near the boiling point, or relatively cold. In general, dyeing is carried out at 70 to 80°C, or, for light shades, at 60 to 70°C. The use of low temperatures for dyeing was promulgated (in Germany) during the second World War, and was found satisfactory for sulfur colors (Schumacher, *Mell.*, **1943,** 231; Käster, *Mell.*, June, **1943,** 265).

Low-temperature dyeing is generally regarded as 40 to 45°C dye-bath temperature. This means that dyes must be selected which are absorbed in this range. It is well-known that many of the sulfur dyes, particularly among the red-browns, violets, blues and greens, yield brighter dyeings at 50 to 60°C.

Many of the Immedial leuco dyes have a fair affinity for cotton fibers at temperatures as low as 30°C. For staple rayon fibers it has been suggested to dye at the slightly higher temperatures of 40 to 50°C in order to obtain better color yield. Besides the Immedial leuco dyes, sulfur colors of a wide color range can be selected which exhaust at low temperatures, for example Immedial Yellow GG, Immedial Brilliant Blue CLB extra, Immedial Green GG extra, Indo Carbon CL conc., etc.

Aftertreatment. Aftertreatment is suggested as follows: With hydrogen peroxide and dilute alkalis, to increase fastness to washing (*G.P. 110,367, F.P. 350,096*). With sulfites, to improve the brilliance of shade (*F.P. 325,462*). With thiosulfate, to improve the fastness to light and to storage (*F.P. 295,190, G.P. 140,541, 141,371*; see also Müller, *Chem. Ztg. Rep.*, **1921,** 104). With sodium fluoride or potassium fluoride, to prevent oxidation in storage (*U.S.P. 1,953,908-9,* Du Pont).

With metal salts: Sulfur colors form insoluble lakes with metal salts, increasing fastness to washing and to light.

(1) Aluminum, chrome, nickel or cobalt salts (*G.P. 114,266, 114,267. 124,507*).

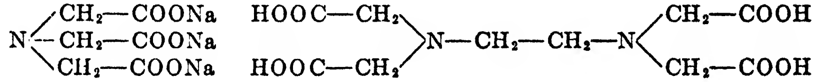
(2) Chrome-oxide salts (chrome alum) (*G.P. 127,465*).

(3) Chromium bisulfite (*G.P. 131,261*).

(4) Chromates with sulfuric acid, or copper sulfate and sulfuric acid (*G.P. 112,799*).

(5) Nickel salts (*G.P. 213,582*; see Eppendahl, *Frb. Ztg.*, **1911,** #22, 166).

After the dyeing operation, the sulfur colors are fixed by oxidizing with atmospheric oxygen, either by hanging the dyed cloth in the air, or by rinsing in running water. Uneven dyeings often occur when deposits of oxidized dye particles form on the surface of the cloth. Some dyes show this troublesome characteristic more than others, and to such a degree that uniform shades are well nigh impossible. According to *G.P. 743,992* (I.G.), this disadvantage can be obviated by the addition of salts of aminocarboxylic acids to the dye bath. The reoxidation of the leuco compounds proceeds rapidly and uniformly, preventing an accumulation of surface dye. As an example, the patent mentions the salts of trimethylamine tricarboxylic acid and ethylene bis-iminodiacetic acid:



$$N(CH_2{-}COONa)_3 \qquad (HOOC{-}CH_2)_2N{-}CH_2{-}CH_2{-}N(CH_2{-}COOH)_2$$

These products are marketed under the names Trilon A and Trilon B (see Table 2, page 174).

Sulfur color dyeings on cotton and mixed fabrics can be improved by addition to the dye bath of condensates of the Lamepon type (*G.P. 647,773*). The advantages gained are a retarding of the dyestuff adsorption, increasing levelness, and a retarding of oxidation, insuring good penetration and resulting in a finely dispersed reoxidized dyestuff. Any particles adhering to the fabric surface after oxidizing remain in a colloidal state and can readily be removed in subsequent rinsing.

Two references in *Chem. Zent.*, **1937,** II, 3234 (Koshin and Matwejew) disclose that losses in the rinsing process can be avoided by an aftertreatment with magnesium salts. These salts combine with the leuco sulfur dyestuff, producing insoluble salts, and magnesium hydroxide, formed by hydrolysis, further aids by abrading superficially adherent particles. Probably there is also a favorable neutralizing action of any sulfuric acid generated.

Stability of the sulfur color against oxidation in the dye bath can be achieved by using a mixture of equal parts of sodium sulfide and sodium hydrosulfide instead of the usual mixture of sodium sulfide and sodium carbonate (*U.S.P. 2,120,415–6*, So. Dye. Corp.). In this way the pH of the dye bath is reduced to a minimum. The chemical mixture can be made by dissolving sodium hydrosulfide and adding alkali to the desired pH. Clear, highly concentrated sulfur dyestuff solutions, of good stability to atmospheric oxygen, can be manufactured by this method.

G.P. 657,820 (Landshoff and Meyer) deals with the problem of uniformly dyeing mixed fiber materials, such as wool and cotton or rayon staple. The method suggests the addition of protective colloids, such as condensates of the Lamepon type, by lowered content of alkali sulfide and by employment of lowest possible temperature (25°C) in order to protect the wool fiber.

Practical Formulas. The following formulas are given for dyeing:

(*1*) *Hydron Blue on Moleskin for Workmen's Suiting.* One roll of two pieces = 80 kg. The boil-off, dyeing and development are to be carried out on the jig. The goods are first quetsched with 5 gm of Biolase and ¼ gm of Igepal C per liter at 70°C, and batched up for 3 to 4 hours, then put on the jig.

One end in running water; two ends in boiling water; four ends in 5 gm $NaOH$ 38° Bé per liter at 90°C. Without rinsing, the pieces are put into the dye bath:

Dye Bath	Stock Vat
170 l water at 70°C	1200 gm Hydron Blue R
30 l stock vat	1500 gm sodium sulfide
	500 gm soda ash
	3 l $NaOH$ 38°Bé
	150 gm Albatex PO (700%)
	500 gm Laventin HW
	to 30 l

Two ends at 70°C; add 2 kg sodium hydrosulfite. Three ends at the boil; add ½ kg sodium hydrosulfite. Three ends at the boil; rinse. Develop at 40°C with 1 liter of acetic acid and ½ liter of hydrogen peroxide 40% in 200 l water. Rinse well, and dry.

(*2*) *Dark Brown with Sulfur Colors on Jig.* The greige goods are entered directly into the dye liquor.

Dye Bath	Stock Vat
200 l water at 70°C	200 gm Immedial Brown BR extra
½ l Etingal A	300 gm Immedial Carbon B
30 l stock vat	1000 gm soda ash
	1200 gm Na_2S
	125 gm Albatex PO (700%)
	200 gm Laventin HW
	to 30 l

Two ends at 70°; add 6 kg sodium sulfate. Four ends at 70°; rinse. Three ends for development at 40°C with 1 l acetic acid and ½ l hydrogen peroxide in 200 l water. Rinse well.

Dyeing on Wool and Silk. The sulfur dyes are not important for dyeing wool. The majority of them have little or no affinity for the wool fiber, a few, however, especially among the blues, can be fairly well applied (*G.P. 109,856*, *197,165*; see also Levinstein, *J. Soc. Dy. & Col.*, **#23**, 296; *B.P. 3,492*, 1903).

Sodium sulfide is likely to damage wool, by its strongly alkaline nature, and by the extensive chemical and mechanical changes it produces in the structure of this valuable fiber. It has been observed that fiber damage can be greatly lessened, however, by adding tannic acid or glucose to the dye bath (*G.P. 161,190*). Other substances such as blood albumen and sodium bisulfite, also have a favorable influence (*G.P. 224,017*). Wool pretreated with formaldehyde is far less sensitive to alkalis, according to Kann (*G.P. 144,485*, *146,845*; *B.P. 25,971*, 1906; *U.S.P. 904,752*, Cassella-Böhler).

Dyeing of silk with sulfur dyestuffs is of no more importance than dyeing of wool. Natural silk is likewise very sensitive to the action of sodium sulfide, and can be dyed with sulfur colors only in the presence of protective colloids like glue. Dyeing can be carried out in the presence of sodium lactate or formate (*G.P. 173,685*) or glucose (*G.P. 161,190*). Ammonium sulfide can replace sodium sulfide (*G.P. 138,848*). Sodium bisulfite and Diastafor have been recommended in *G.P. 199,167* and *210,883*, respectively, as dye-bath assistants.

Printing

Sulfur dyestuffs, as already noted, are but rarely employed in application printing. The printing paste is composed of thickening agent, dyestuff and a reducing agent. Sodium sulfide cannot be used when printing on copper rollers, because the rollers would become unserviceable within a short time by reason of the destructive action of the sodium sulfide. Instead, glucose can be used as reducing agent with an alkali. It is also necessary to select the dyestuff from special printing brands which are relatively free of polysulfides.

Attempts have been made to use a reducing agent of sodium sulfide with formaldehyde, especially in Russia (*G.P. 164,506*). It is possible to use the regular sulfur colors, binding free sodium sulfide by the addition of formaldehyde (20 to 50 cc per kg).

Hydron Blues are sometimes printed, employing the formula for slightly alkaline pastes, and pre-reducing the dyestuff. Special types which are suitable are Hydron Blue R or G 20% paste for printing. The dyestuff is especially prepared in a finely dispersed state. It is recommended that Solution Salt be added to improve the yield in full color prints (Lichtenstein, *Frb. Ztg.*, **1912** and **1913**; *Öst. W. u. L. Ind.*, **1912**, **#15**, 313; Haller, *Frb. Ztg.*, **1914**, 8, 26).

Of special importance for application printing is Indo Carbon CL fine for printing (G.D.C., I.G.). This dyestuff is easily fixed in the rapid ager, the black is full and deep and the fastness corresponds to that of the vat dyestuffs (A. Kertess, "Report on Sulfur Black and Indo Carbon," *Mell.*, 1927, 56).

The sulfur colors can be printed with glucose and caustic soda. The formula is given here for a special application which was successfully carried out in printing cotton velour on wrought iron rollers.

100 gm Katigen Green 2BF conc.
60 gm glycerin
115 gm water
70 gm potassium carbonate
35 gm potassium hydroxide
120 gm glucose
450 gm British gum thickening
50 gm Rongalite C

1000 gm

Prints are aged five minutes, rinsed cold, oxidized with perborate and acetic acid, and washed.

According to *G.P. 682,799* (I.G., 1935) faults occurring in the application of the usual printing pastes can be avoided by adding Medialan A (oleylmethyl aminoacetic acid). Medialan A may be used alone, or preferably with sulfite waste liquor or sodium pyrophosphate.

The Berthold patent (*G.P. 628,303*—I.G., 1931) may be mentioned again, as the assistants noted are applicable in sulfur color printing. The print paste assistants are sulfur compounds of anthraquinone derivatives, and the examples given are anthraquinone-2-mercaptan or the thiocyanate of anthraquinonyl chloride. In the corresponding *B.P. 378,533* it is emphasized that the sulfur colors are fixed more readily and give a better color yield.

The Eclipsol colors of Geigy are sulfur dyestuffs which dissolve without the addition of sodium sulfide. The following formula is recommended for their application:

50–60 gm dyestuff
40 gm urea
330 gm water
500 gm textile gum
50 gm soda ash
20 gm Tinopol oil NP

1 kg

After printing, age five minutes and develop in a bath containing 3% hydrogen peroxide (30%) and 5% acetic acid 6° Bé at 40°C for 5 minutes, and soap well. The addition of 5 gm of Hydrosulfite NF per kg of print paste increases the dye yield. In using these colors for dyeing with Glauber's salt and soda, as with substantive colors, poor results are obobtained, but by adding sodium hydrosulfite after one hour's dyeing time at 40°C and continuing the dyeing 20 minutes more at 60°C, the brightness and depth of shade are considerably improved.

Discharge and Resist Prints*. The sulfur colors do not lend themselves to white discharge style. While a chlorate discharge can be used, the white is not satisfactory and little interest is evidenced for the process. The discharge with aluminum chlorate is sometimes practiced. (Haller, "Chem. Technologie der Baumwolle," p. 327; Erban, *Chem. Ztg.*, **1910,** 596; Elbers, *Z. f. Frb. Ind.*, #3, 99; *B.P. 16,170*-1901; *Chem. Ztg. Rep.*, **1907,** 56; *Frb. Ztg.*, **1904,** 85).

200 gm	British gum
70 gm	water
560 gm	aluminum chlorate 25°Bé
150 gm	sodium chlorate
20 gm	potassium ferricyanide
1000 gm	

Badische A.S.F. recommends the following process (*G.P. 246,519*). Fabrics dyed with sulfur colors are padded with a solution of Leucotrope W (150 gm per l) and printed with:

70 gm	zinc oxide
70 gm	glycerin
40 gm	anthraquinone
100 gm	Rongalite CL
115 gm	Leucotrope W
150 gm	water
455 gm	alkaline thickening
1000 gm	

After ageing 5 to 6 minutes, the goods are boiled in a 1% silicate solution.

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* References:

Badische A.S.F., *G.P. 246,519*, "Method Using Rongalite CL."

Cassella-Bayer, *F.P. 311,644*—1901; *F.P. 317,145; Rev. Gen. Mat. Col.*, **1902,** 294; *G.P. 130,628; B.P. 12,540*—1901; *F.P. 387,516; G.P. 153,146.*

Baumann-Thesmar, *Z. f. Frb. Ind.*, **1908,** 125; *Frb. Ztg.*, **1909,** 320.

Scheunert-Frossard, *Bull. Mulh.*, **1927,** 163 (Sealed communication of 1907).

Kielbasinsky, *Frb. Ztg.*, **1912,** 232.

L. Diserens, *Rev. Gen. Mat. Col.*, **1918,** 63; **1917,** 141.

N. Wossnessensky, *Bull. Mulh.*, **1928,** 657.

Cassella, *G.P. 223,682*—1908; *Frb. Ztg.*, **1908,** 126, 225, 394; "Buntreserven mittels Chromfarbstoffen".

Kalle, *G.P. 210,682.*

Fleischer, *Bull. Mulh.*, **1927**; Report Comm. Chem., Feb. 2, 1927.

White and colored prints can be obtained practically on sulfur dyeings only by resist methods. This style had a great success in Russia, replacing the discharge style on substantive grounds colors. Cassella found in 1901 that certain metal salts prevent the fixation of the sulfur dyes.* The method was practiced extensively by Hübner, Zündel and Prochoroff in Moscow, who brought out a line of white and colored resists under sulfur colors in 1906 (Scheunert and Frossard, *Bull. Mulh.*, **1927,** 163).

The print paste contains zinc chloride or zinc sulfate which acts as an excellent resist; the thickening agent is Indian or Senegal gum, which in itself may be considered a mechanical resist. After printing and drying, the goods are padded with a three-roll padder, the trough having a capacity of 50 to 60 liters at 40 to 50°C, then aerated, acidulated and rinsed in cold running water. The dye liquor is prepared by dissolving the dyestuff with sodium sulfide. Baumann and Thesmar (*Z. f. Frb. Ind.*, **1908,** 123) used dye baths containing sodium sulfide and sodium hydrosulfide or glucose and sodium hydroxide.

White Resist (*Morosoff Plant Formula*)

250 gm Senegal gum thickening
500 gm zinc chloride 42°Bé
100 gm kaolin
20 gm rape seed oil
130 gm gum thickening

1000 gm

The resist effect can be considerably improved by precipitating insoluble salts on the fiber. For example, potassium carbonate or potassium ferrocyanide is added to the dye liquor, using 25 to 30 gm per liter. The precipitated zinc carbonate or ferrocyanide forms an insoluble membrane which prevents seepage from the dye liquor (Kielbasinsky, *Frb. Ztg.*, **1912,** 232).

L. Diserens obtained (1917) excellent results by adding aluminum salts to the printing paste, and sulfoleates, ricinoleates or olate soap to the dyeing liquor. These compounds produce aluminum soaps on the fiber, and being water repellent, prevent penetration of the dye liquor at the printed areas. White resists of great clarity result.

Colored resists can be obtained with azo colors, formed on the fiber, or with basic, chrome mordant or vat colors. In the case of the azo colors, the thickened diazo solution is printed with zinc chloride on pre-naphtholated fabrics. (Aubert, *Bull. Mulh.*, **1909,** 476). The goods are aged two minutes, dyed and finished as usual.

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* *F.P. 311,644, 317,145, 387,516; G.P. 130,628, 153,142; B.P. 12,540* and *21,272*—1901; *Frb. Ztg.*, **1909,** 301; **1908,** 422.

Basic color resists were produced on a large scale by the Russian firms of Zündel and Prochoroff in Moscow, Konschin in Serpoukhoff and Kouwaieff in Iwanowo-Wosnessensk. The difficulty of mixing basic dyestuff, zinc chloride and tannic acid in the same print paste can be circumvented in several ways.

(1) By preparing the goods with potassium ferrocyanide and printing the basic color together with zinc chloride. The zinc ferrocyanide formed *in situ* is a mordant for the dyestuff. The fastness is improved (Fleischer, *Bull. Mulh.*, **1928,** 125) by adding zinc tungstate and tartaric acid. It is reported that fiber damage may occur, a difficulty which may be avoided by combining the tungstate with the ferrocyanide solution.

(2) By printing the basic color with zinc chloride and tartar emetic on a tannic acid prepare.

(3) By using resorcin with aliphatic acids to prevent the precipitation of zinc tannate. This method was proposed by L. Diserens in *Rev. Gen. Mat. Col.*, **1918,** #258, 63, and the following print paste is recommended:

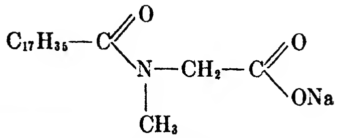
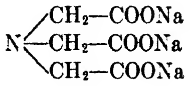
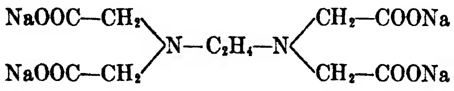
30 gm	dyestuff
50 gm	glycerin
150 gm	resorcin 1:1 *or* glycollic acid 1:3
280 gm	gum thickening
300 gm	zinc chloride crystals
50 gm	kaolin
120 gm	tannin-acetic 1:1
20 gm	rape seed oil
1000 gm	

Other proposals have been made favoring the use of resorcin, but in the form of its formaldehyde condensate (Frossard and Mouette, *Bull. Mulh.*, **1924,** 278; von Favre, Wossnessensky, *Bull. Mulh.*, **1938,** 657; Report of Comm. for Chemistry, June 3, 1938, *Bull. Mulh.*, **1938**; Gandourine, *Bull. Mulh.*, **1928,** 367).

L. Diserens offers formulas for printing vat colors as resists, using ferrous sulfate or zinc salts together with vat dyestuff on soda-prepared goods (*Rev. Gen. Mat. Col.*, **1920,** #284, 114). The dye liquor for the mangle is prepared as follows:

10–60 gm	sulfur dyestuff
30–90 gm	sodium sulfide crystals
20 gm	soda ash
2 gm	Turkey red oil
per liter	

Table 2. Auxiliaries for Sulfur Dyestuffs

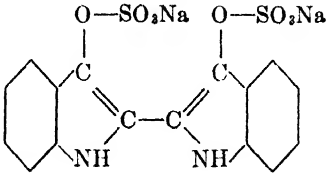
Name	Manufacturer	Constitution	Literature	Remarks
Medialan A **Medialan A pdr.** **Medialan AL**	I.G. I.G. I.G.	Sodium salt of oleyl sarcoside, or *n*-oleyl methylamino acetic acid.  AL: type A plus solvent.	*G.P.* *635,522* *B.P.* *459,039; 461,328; 456,142; 455,310* *F.P.* *789,004* *Mell.*, **1937**, 296 Nüsslein, *Mell.*, **1937**, 248	Good stability to hard water and acids. Washing and dispersing agents. Recommended in dyeing of sulfur colors, and washing of vat prints.
Trilon A	I.G. (1938)	Sodium salt of nitriloacetic acid, or sodium salt of aminotrimethyl carboxylic acid. 	*B.P.* *474,518* *S.P.* *190,986* *F.P.* *811,938* Chwala, "Textilhilfsmittel," 1st ed., p. 81 Schultz, "Farbstofftabellen," 2nd ed. Sup., p. 295	White powder, easily soluble in water. Water softener. Salts of Fe, Ca, and Mg are rendered harmless, the amounts necessary being: for each degree hardness, 0.12 gm Trilon A or 0.16 gm Trilon B per liter.
Trilon B	I.G. (1938)	Sodium salt of ethylenediamine tetramethyl carboxylic acid. 	Hasse, *Mell.*, **1937**, 456 Metzger and Röhling, *Mell.*, **1937**, 644 *D.F.Z.*, **1937**, 583; **1938**, 141	Recommended in ***G.P.* 743,992** (I.G. 1944) for dyeing sulfur colors.

Chapter III

The Indigosols[*]

The Indigosol dyestuffs were invented and developed by Dr. M. Bader[**] in 1921. They are the sodium salts of disulfuric acid esters of indigoid or anthraquinoid leuco-vat dyestuffs.

The first representative of this group made by Dr. Bader was the sodium salt of the disulfuric acid ester of leuco indigo itself (Indigosol O):



The manufacture of this product was achieved by esterification of the corresponding phenol with chlorosulfonic acid in the presence of pyridine.

Very possibly the development of the Indigosols to their present status required a tremendous amount of work in their manufacture as well as in their application, thus delaying their introduction in the practice. However, the final results should give full satisfaction to the inventor and to the manufacturers. Systematic research, continued over many years, has been necessary to solve the many scientific, practical and economic problems which the production of these dyestuffs entailed. The Indigosols have found their way into many different styles because of their versatility. They can be combined with the insoluble azo colors, thus providing chem-

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[*] Trade names: Algosols (G.D.C.), Indigosols (Carbic, D. & H.), Soledons (I.C.I.), Anthrasols (I.G.), Tinosols (Geigy), Cibantines (Ciba), Sandozols (Sandoz).

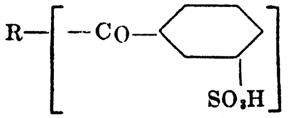
[**] M. Bader, "Dérivés de l'Indigo", *Chim. Ind.*, **1924**, 449. Ch. Vaucher and M. Bader, "L'Indigosol DH en teinture et impression", *ibid.*, 455; M. Bader, "Chimie et Coloristique des Indigosols", Report to the Swiss section of the I.V.C.C., May 2, 1937, *Bull. Fed.*, Sept., **1937**, 169; T. Voltz, 1933 Yearbook of Höhere Chemieschule, Mulhausen; Caberti, "Les Indigosols", *Rev. Gen. Mat. Col.*, **1934**, 185; Torinus, "Druckverfahren für Indigosole", *Mell.*, **1935**, **#**16, 327; Friedländer, *Mell.*, **1925**, 916; August, **1926**, 696; September, **1926**, 781; Rittner and Gmelin, *Mell.*, **1927**, 530; G. Martin, *Rev. Chim. Ind.*, **1934**, **#** II; Bell, *Z. f. angew Chem.*, **1924**, 670; Schreiner, *Mell.*, **1924**, 670; **Tagliani**, *Mell.*, **1925**, 107; Wiltshire, "Soledon Dyes on Knitted Goods", *J. Soc. Dy. & Col.*, October, **1946**, 313.

ists and colorists with a large choice of clear bright shades, which are readily available and applicable within the limits of normal mass production.[*]

The uncontested success of these dyestuffs lies in their manysided usefulness. They can be used in application printing alongside the Rapidogens and as complements of these colors; in the resist print style they offer the possibility of producing fast prints under aniline black and under Variamine Blue. It is possible to carry out dyeing effects which could not otherwise be obtained, for example, by printing vat color resists under Indigosol dyeings, thus actually resisting vat dyes with vat prints. Finally, a method was made available for dyeing light shades, level and well penetrated, which had always posed a serious problem with the true vat dyestuffs.

A series of dyestuffs of similar constitution was brought out a few years late (1924) by the Scottish Dyes Co. Ltd., under the name "Soledon" (*G.P. 563,958; Frdl.,* # 18, I, 1513.) They are likewise ester salts of leuco indigoid or anthraquinoid vats, but produced by another and simpler method,[**] as the phase of isolating the leuco compounds is avoided. The dyestuff powder is suspended in a tertiary base, such as pyridine, and a metallic powder (as Cu, Zn, Fe, Al) is added while vigorously agitating. Chlorosulfonic acid is charged into the cooled mixture which is warmed to 50 to 60°C. The reaction products are diluted, and after neutralization, are allowed to crystallize.

After the appearance of the Indigosols on the market, other methods of manufacturing them were sought, but except for the Soledons, no others were commercially successful. One class of solubilized vat dyestuffs, however, deserves mention. These are obtained by reacting indigoid or anthraquinoid vat dyestuffs with *m*-sulfo-benzoylchloride, yielding compounds of the general formula



wherein R denotes the dyestuff radical. In contradistinction to the Indigosols which are developed by an acid oxidation, these benzoyl-*m*-sulfonates

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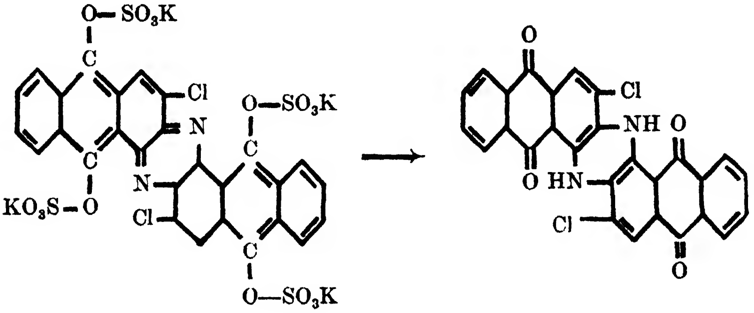
[*] Patents which relate to the preparation of Indigosols are as follows: *G. P. 410,972; 418,487; 428,241; 431,250; 431,501; 433,146; 433,736; 435,787; 436,176; 441,371; 465,971; B. P. 186,057; 202,630; 202,632; 203,681; 212,546; 213,546; 218,649; 220,649; 220,964; 231,189; 234,829; 237,295, 260,303; 267,952; U. S. P. 1,575,958; 1,639,206; 1,668,392.*

[**] This process of Scottish Dyes was first used by Durand and Huguenin who owned the Bader patents. Later on however, an agreement was reached, because I.C.I., who had meanwhile taken over management of Scottish Dyes, developed new and different methods for preparing some of the Indigosol dyes, particularly Indigosol Blue IBC, which were not mentioned in the D. & H. patents. It might be concluded therefrom that the dyestuffs marketed under the name Soledons correspond to the Indigosols of D. & H.

are developed by an alkaline oxidation (*U.S.P. 1,903,870–1*, I.G., Mieg-Heidenreich).

Several vat dyestuffs, particularly Indanthrone and Flavanthrone, are difficult to convert into sulfates, and the method of preparing the Indigosol analogous to Indanthrene Blue BC was not discovered until 1927. Eventually in 1932 Indigosol Blue IBC appeared on the market. It is a potassium tetrasulfate derived from 3,3′-dianthrahydroquinonazine (*G.P. 470,809*, *476,811*, *579,327*, *580,013*, *580,534*, *584,718* of the I.G.; and *G.P. 547,083* and *574,190* of Scottish Dyes). It corresponds to the formula



Indigosol Blue IBC *Indanthrene Blue BC*

and is obtained by oxidizing potassium sulfate of 3-amino-2-chloroanthraquinone (Bader, *Bull. Fed.*, Sept., **1937**).

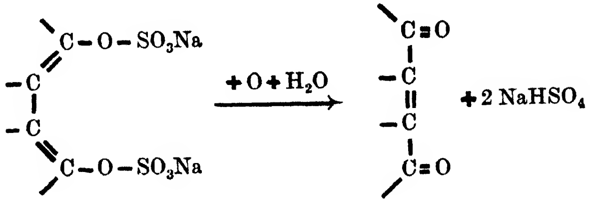
Up to the time of this dyestuff's appearance, the valuable properties of the Indanthrene Blue BC could not be obtained with the Indigosol series.

It was observed that although paste-form dyestuffs of the Indigosols of the anthraquinone series containing alkali carbonates were relatively stable, powder-form dyestuffs prepared by drying and grinding these pastes decomposed in storage. *U.S.P. 2,122,113* (D. & H.-Ratti) recommend the addition of dextrose, urea or sulfite waste liquor to the alkaline filter-cakes before drying, and drying under reduced pressure, and finally grinding. In this way the powders are fairly resistant to the influence of the atmosphere.

There are about thirty individual Indigosol dyestuffs, most of which are listed in Table 3 on page 180. Besides denoting the vat color from which each dyestuff is derived, the table subdivides the Indigosols into five groups according to their relative affinity for cellulose fibers. The first group has poorest affinity; the last group the best affinity (*Bull. Fed.*, Sept., **1937**; also Durand and Huguenin, "The Indigosols," Vol. **I**, p. 199, 2nd ed.).

The principal characteristic of the Indigosols is their ability to form the original dyestuff readily. This regeneration is almost quantitative in acid oxidizing baths. The chemical processes involved are hydrolysis of the ester and reoxidation of the leuco compound to the vat dyestuff.

The conversion of the Indigosol into the original vat dyestuff can be explained by the following schematic equation:



The thioindigoid Indigosols are the most difficult to reoxidize. Chromic acid, nitrous acid, chlorates of sodium, ammonium and aluminum, ferric chloride, and copper and iron salts of organic acids can be employed as oxidation agents.

The principal field for the Indigosols is in printing. These dyestuffs permit the creation of a great number of styles in application printing, as well as in resist and discharge printing. They are readily applicable alongside Rapidogens, Rapid Fast Colors, mordant and vat dyestuffs and on naphtholated goods with Fast Color Salts. The Indigosol resists under aniline black and Variamine Blue have enjoyed notable success.

The demand for Indigosols for dyeing purposes has also increased in recent years. The reasons here are the simplicity of application and their extraordinary leveling properties. They yield fuller dyeings than the vat colors in pale shades and are especially adaptable for dyeing fabrics of tightly woven construction. The use of Indigosols in dyeing is generally restricted to light shades. The introduction of the sulfo group into the dyestuff molecule has rendered the dye soluble in water, but in most cases has decreased the substantivity (affinity for cellulose) in comparison to that of the analogous leuco-vat dyestuff.

PRINTING AND DYEING METHODS WITH INDIGOSOLS

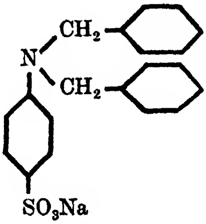
The printing of the Indigosols offers few difficulties. The advantages of the Indigosols over vat colors lie in the omission of the vatting operation with all its irregularities, and in the omission, in many cases, of the ageing process, which, as we have seen, can cause such great variations in yield.

In general, it can be said that starch-tragacanth gives the best yield in printing Indigosols. Starch-dextrin mixtures have also been recommended, especially for rayon fabrics. Other thickeners have also been proposed, especially during shortages of corn, wheat starch, and tragacanth gum as befell in Europe in the last war. Tragu S was used for tragacanth, and potato starch for corn starch, while Colloresin V extra or Colloresin MB was often used in combination with the other substitutes. Solvitex thickening (Scholten) was used for Indigosols as well as Rapidogens.

Other gum thickenings which have been used to good advantage are Keltex gum (Keltex Co.) Algin, Carboxy methocel, Tragasol and RPG gum (Arnold-Hoffman).

Most of the Indigosols are readily soluble, with the exception of Indigosol Brown IRRD. The yield of the printing pastes is generally improved by adding special solvents. Glycol, and its derivatives, diethylene glycol, Cellosolve, thiodiethylene glycol, etc. are recommended for dissolving these dyestuffs (*B.P. 298,088*—D. & H.; *G.P. 504,076*). Prints with these solvents are fuller and more uniform (*B.P. 427,058*—D. & H.; *Mell.*, **1935,** 327). Products of the trade particularly useful for dissolving the Indigosols are Dehapan O and GB (D. & H.), Glyecine A (G.D.C.) Debesolvol IND (L.Z.J.). Prints are likewise improved by adding to the paste urea, phenol and certain alcohols, as furfuryl alcohol (*F.P. 769,171*). Durit FA is furfuryl alcohol (D. & H., Carbic).

The depth of color of many Indigosols, especially Brown IRRD and Grey IBL, is increased by the addition of urea alone (*U.S.P. 2,029,351*). Another product which increases the color yield, and at the same time aids the solubility is dibenzylsulfanilate of sodium (*B.P. 421,066* of the I.C.I.). This product is marketed under the name Solution Salt SV. It has the formula:



According to *F.P. 754,235* and *B.P. 422,549* of D. & H., the triethanolamine salts of some Indigosols are more readily soluble than the corresponding sodium salts, and therefore especially recommended for printing. They are manufactured by reacting the sparingly soluble pyridine salts of the sulfuric acid esters of the leuco-vat dyestuffs with triethanolamine. *U.S.P. 1,954,702* (Du Pont) recommends a similar procedure. A favorable result can be obtained by pasting up the Indigosols, with 20 gm of triethanolamine per kg of print paste. Another step toward better solubility has been proposed in *B.P. 401,137* (D. & H.), wherein the lithium salts are recommended over the sodium salts.

Additions of heterocyclic substituted nitrogen bases are suggested in *B.P. 428,701* and *F.P. 764,012* (I.G.). Examples given are the trihydroxyethyl ether of triethanolamine, or the product of the action of ethylene oxide on pyridine. The solubility of some Indigosols is improved by such additions, and better yields are claimed.

In Table 3, below the ease of oxidation of Indigosol Green IB is noted. The stability of print pastes containing this dyestuff can be improved by adding certain auxiliaries such as thiophenol, thioglycollic acid

Table 3. Indigosols

Substantivity	Name	Oxidizability	Equivalent Vat Color	Constitution
I poor	Indigosol Blue IBC	easy	Indanthrene Blue BC	3,3'-Dichloroindanthrone. The Indigosol is the potassium tetrasulfate of dichlorodianthradihydroquinonazine)
	Indigosol O	easy	Indigo	Bis-indol-2,2'-indigo
	Indigosol OR	easy	Indigo R, Indigo Ciba R	5-Monobromoindigo
	Indigosol Printing Blue IGG	easy	Indanthrene Printing Blue GG	Substituted naphthalene indolindigo
	Indigosol Red Violet IRH	slow	Indanthrene Red-Violet RH (Helindone Red 3B)	5,5'-Dichloro- 7,7' -dimethyl thioindigo
	Indigosol Brilliant Pink 13B	slow	Indanthrene Brilliant Pink 3B	Halogenated thioindigo
	Indigosol Pink IR extra	slow	Indanthrene Brilliant Pink R extra	6,6'-Dichloro-4,4'-dimethyl-2,2'-bis-thionaphthenindigo (Herz)
	Indigosol Scarlet HB	slow	Helindone Scarlet B	Mixture of Pink R and Orange R
II fair	Indigosol Orange HR	easy	Helindone Orange R	6,6'-Diethoxythioindigo
	Indigosol Red HR	slow	Helindone Red R	Halogenated thioindigo
	Indigosol Scarlet B	easy	Indanthrene Scarlet IB	6-Monoethoxy-4'-methyl-6 -chlorothioindigo
	Indigosol Brown IRRD	easy	Ciba Brown G, Indanthrene Brown RRD	Dibenzothioindigo
	Indigosol Printing Violet IRR	easy	Indanthrene Violet RR	Oxythionaphthene indolindigo
III good	Indigosol Golden Yellow IGK	easy	Indanthrene Golden Yellow GK	3,4,8,9-Dibenzpyrenquinone-5,10
	Indigosol Printing Violet IBBF	slow	Indanthrene Violet BBF (Hydron Violet BBF)	Halogenated oxythionaphthene indolindigo
	Indigosol AZG	slow	Alizarine Indigo	Anthracene indolindigo

Table 3. Indigosols (*Continued*)

Substantivity	Name	Oxidizability	Equivalent Vat Color	Constitution
IV strong	Indigosol Golden Yellow IRK	easy	Indanthrene Golden Yellow IRK	Dibromo derivative of Golden Yellow GK
	Indigosol Brown IBR	easy	Indanthrene Brown BR	
	Indigosol O6B	slow	Indigo 6B	Hexabromoindigo
	Indigosol O4B	slow	Indigo 4B (Ciba Blue 2B)	Tetrabromoindigo
	Indigosol Olive Green IB	easy	Indanthrene Olive Green B	
	Indigosol Green AB	slow	Alizarine Indigo Green B	Halogenated naphthalene indolindigo
V very strong	Indigosol Brilliant Green IB	easy	Indanthrene Brilliant Green B, Caledon Jade Green B	Dimethoxydibenzanthrone
	Indigosol Grey IBL	easy	Indanthrene Printing Black BL	Benzoxythionaphthene indolindigo

and thiodiethylene glycol (*B.P. 452,018*, I.G.). The Indigosol brands which tend to decompose in the print paste—by which are meant the derivatives of the benzanthrones—may be stabilized by adding mercaptan derivatives, according to this reference.

In 1944, Durand and Huguenin offered a new group of Indigosol dyestuffs of particular advantage for the printing industry. The first representative of this group, Indigosol Brown IRRD Supra powder, is characterized by its solubility, being much better than the regular Brown IRRD, and not salted out with electrolytes. The older type is not adapted for printing purposes, giving satisfactory results only with the bichromate process, while the newer Supra type can be applied by all printing methods without trouble.

In the following paragraphs the several methods for printing Indigosols will be discussed. The development of the Indigosols, depending on the process used, is carried out by an appropriate wet process, or by a steaming process.

Development by Wet Processes in Printing

The wet development methods may be divided as follows:

(1) Bichromate
(2) Chromate
(3) Nitrite
(4) Ferric nitrate
(5) Cupric sulfate (of little importance)

(6) Durit ADF (neutral chromate)
(7) Ferric chloride

All of these methods consist of treating the fiber, which has absorbed the dyestuff, with an acid solution. The oxidizing agent may be applied with the color, or in other cases, with the acid treatment.

Bichromate Method. The Indigosol color is dissolved with appropriate solvent, and thickened, then printed. The prints are dried well, then developed for 2 seconds in a bath containing 8% sulfuric acid 66° Bé and 3% sodium bichromate at 35°C, quetsched, skyed 20 seconds, rinsed and neutralized. A short steam passage before the wet treatment improves the yield.

Indigosol Blue IBC and Indigosol Printing Black IB cannot be developed by this method.

The bichromate developing, as well as the nitrite process, has a yellowing effect on rayon and natural silk. According to *G.P. 679,767* and *F.P. 835,854* (D. & H.) this can be prevented by adding to the acid oxidizing bath some readily oxidizable substance such as *p*-amidophenol, hydroquinone or resorcin. The addition must be carefully controlled, as an excess can result in an incomplete development of the Indigosol dyestuff.

Chromate Method. This is a variation of the bichromate method. Instead of bichromate in the developing bath, neutral sodium chromate is added to the print paste. According to the chromate method, the print paste is composed of the Indigosol dyestuff, appropriately dissolved and thickened, plus 75 to 120 gm of neutral chromate solution 1:2 per kg. The color is developed in an acid bath containing

25 cc	sulfuric acid 66°Bé
30 gm	oxalic acid
50 gm	Glauber's salt

per liter. It is possible, on the other hand, to fix the Indigosol prints by an acid ageing alongside Rapidogen prints; in this case no acid developing bath is necessary. All of the easily oxidizable Indigosols (Golden Yellow IGK, Green IB, Brown IBR, Scarlet IB, Grey IBL) can be fixed by this method. This is of special importance when using overlapping prints.

The print paste is prepared by the following type formula:

80 gm	Indigosol Brown I3B
100 gm	urea
20 gm	Dehapan GB
205 gm	hot water
500 gm	neutral starch-trag. thickening
75 gm	neutral sodium chromate 1:2
20 gm	soda solution 10%
1000 gm	

The development is carried out in the sulfuric-oxalic acid bath at 35°C for 8 seconds; rinsing and soaping follow.

Nitrite Method. This is the most popular of the wet development processes. A short ageing preceding the acid bath improves the results. The fabric is printed with Indigosol and solvent, plus thickener and sodium nitrite (10 to 15 gm per kg), and the prints developed in a continuous passage through a bath containing 20 cc of sulfuric acid 66° Bé per liter at 65 to 70°C for 2 to 20 seconds. When using short development baths (2 to 6 seconds) a skying is necessary before rinsing. This method was worked out by Dr. H. Perndanner (*Mell.*, **1925**, 32). The print paste stability is improved by the addition of 20 gm of sodium naphtholate per kg.

Dr. Tagliani and Dr. Krähenbühl changed the method slightly for certain Indigosols, particularly Indigosol O (*Mell.*, **1925**, 107). It was observed that the reoxidation of Indigosol O to the vat dyestuff can be brought about by the action of easily dissociating organic salts of organic acids, by simply drying or ageing the nitrite print pastes. For salts of organic acids, the oxalates, glycollates, lactates are preferred. The development can also take place in acid ageing.

Tagliani's Formula

30 gm	Indigosol O
135 gm	water
5–35 gm	sodium nitrite
200 gm	ammonium lactate 21°Bé
600 gm	gum thickening
1000 gm	

Durand and Huguenin suggest (*G.P. 696,268*, Aug., 1937) the use of developing baths containing organic acids besides the usual mineral acids, at temperatures between 75° and 90°C.

The oxidation proceeds in a gentle manner, avoiding any fiber damage by a too rapid oxidation. The printed and dried goods are developed, without ageing, in a bath containing sulfuric acid, sodium sulfate, acetic and formic acids. Fully developed and uniform shades are obtained, not only with the Indigosols but with Rapid Fast and Rapidogen colors.

Some of the Indigosols are sensitive to overoxidation. According to *B.P. 426,073*, *G.P. 596,887*, and *F.P. 765,377* (D. & H.) it is advisable to add, for these dyestuffs, mixtures of ferrous and ferric salts, such buffering substances as stannous chloride, and titanous chloride, or nitrogen-containing compounds such as urea to the developing bath. The developing bath can contain, for example, 30 gm of sulfuric acid 66° Be, and 5 gm of stannous chloride per liter, and is maintained at temperatures between 20 to 70°C. Since the high acidity of the baths may weaken the cellulose fibers, *G.P. 570,582* (I.G.) proposes lowering the acid concentration and the temperature by adding small amounts of reducing compounds, such as sodium bisulfite or oxalic acid. Compare the patent mentioned above with *G.P. 596,887.*

The leuco-vat dyestuff esters are influenced by nitrous acid in different ways, depending on their constitution.

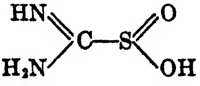
So, for example, the tetrasulfuric acid ester of 3,3′-dichlorodianthraquinonazine (Indigosol Blue IBC) is reoxidized to 3,3′-dichloro-N-dihydro-1,2,1′,2′-anthraquinonazine which, by overoxidation, is transformed into a greenish azine modification, thus dulling and greening the resulting shade. Some of the leuco-vat esters contain an amino group, as the ester of 1-amino-2-anthraquinonyl-2′,3′-anthraquinonoxazol. In this case the amino group can be diazotized by the nitrous acid.

A product of the I.G., Anthrasol Salt NO, is claimed to have the property of preventing the deleterious effect of excess nitrous acid on sensitive dyestuffs, such as Indigosol Blue IBC, Olive Green IB, and Red IFBB. Anthrasol Salt NO consists of 50% thiourea and 50% Glauber's salt.

The use of Anthrasol Salt NO is illustrated in the following printing and padding formulas.

Indigosol Blue IBC is printed by the nitrite method. The prints are well dried and aged, then developed in the open width at 60 to 80°C with 20 cc sulfuric acid 66° Be, and 4 to 8 gm of Anthrasol Salt NO per liter for 10 to 30 seconds. For dyeing, the fabric is padded with Indigosol Blue IBC and sodium nitrite, skyed 10 seconds and developed immediately in hot dilute acid bath containing 20 cc of sulfuric acid 66° Be, and 1 to 3 gm of Anthrasol Salt NO per liter, rinsed, neutralized and soaped.

The two patents *G.P. 734,399* and *734,400* (I.G.—1943) would seem to accord with the use of Anthrasol Salt NO, as it is disclosed herein that Indigosol Blue IBC is sensitive to an excess of nitrous acid, and that this disadvantage can be corrected by adding 1 to 2 gm of thiourea to the developing bath. Moreover, the compound formamidine sulfinic acid*



is particularly adapted for checking the influence of nitrous acid on sensitive Indigosol dyestuffs (*G.P. 735,094*—I.G., Hees, May, 1943).

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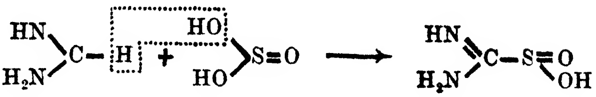
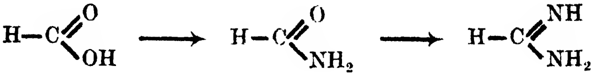
* This compound is prepared from thiourea and hydrogen peroxide. It has been recommended as a discharging and stripping agent by Du Pont in *U.S.P. 2,150,921* and *2,206,535* and by Celanese Corp. in *U.S.P. 2,248,128.*

Formamidine sulfinic acid is formed by the reaction of sulfurous acid on formamidine, according to the following equation:



Formamidine is a derivative of formic acid:



Formic acid *Formamide* *Formamidine*

As an example of the use of formamidine sulfinic acid, cotton cloth is padded with the following pad liquor at 60°C:

5 gm leuco sulfuric acid ester of 1-amino-2-anthraquinonyl-2',3'-anthraquinonoxazole
2 gm Nekal BX
2 gm soda ash
5 gm sodium nitrite
3–5 gm formamidine sulfinic acid
per liter

The color is developed in a bath containing 20 cc of sulfuric acid 66° Bé, and 1 to 3 gm of formamidine sulfinic acid per liter at a temperature of 60°C, neutralized, rinsed and soaped. Thus it is seen that in order to avoid overoxidation or diazotization of the leuco dyestuff, 3 to 5 gm per liter of formamidine sulfinic acid are added to the padding bath, and 1 to 3 gm to the developing bath.

Dyestuffs of the anthraquinonazines which are disposed to overoxidize and to change shade toward the green, can be aftertreated with a dilute alkaline reducing bath (hydrosulfite and soda) to correct the alteration of shade (*G.P. 591,410, F.P. 763,621*—D. & H.).

A new preparation for dyeing or overprinting the Indigosols is given in *B.P. 583,413*, *F.P. 891,021* (D. & H.). The dyestuffs, which may be sparingly soluble in water, are present in a finely divided state. The preparation contains a water-soluble onium compound and an organic acid amide besides the dyestuff. As onium compounds, water-soluble bases are meant, quaternary ammonium compounds, phosphonium or ternary sulfonium compounds; as amides, urea, urethane, acetamide, etc. Oxidizing agents are added to the preparation, and dyeings and prints are claimed which exhibit very good yield of dyestuff.

An interesting combination of Indigosol print and parchmentizing (transparent effect) is given in *G.P. 621,109* (Raduner-Beer). The Indigosol dyestuff is printed with nitrite and dried. The fabric is passed through the strong sulfuric acid bath of parchmentizing concentration, which develops the dyestuff in regular manner. It has been found that gum thickening resists the parchmentizing, while starch-tragacanth does not, so that it is possible to obtain colored prints with either dull or transparent effect, by the selection of the appropriate thickening agent.

Ferric Nitrate Method. This method was practiced for some years in the United States, especially in shops not equipped with a rapid ager. The Indigosol dyestuff is dissolved with Durit O and added to a paste containing neutral sodium chromate. The prints are dried, then developed at 65 to 70°C in a bath containing 40 cc of sulfuric acid 66° Bé, and 40 cc of ferric nitrate solution 47° Bé per liter, for 2 to 6 seconds. After quetsching, the goods are skyed for 30 seconds, rinsed thoroughly and passed through a bath of 7 to 28 gm of oxalic acid and 14 to 56 gm of sodium acetate per liter, rinsed, soaped and rinsed.

Copper Sulfate Method. This process is covered by *U.S.P. 1,917,101* of D. & H.—von Niederhäusern. The goods are first prepared with a copper sulfate-formic acid solution, then printed with the Indigosol print paste. It is claimed that prints of excellent fastness to soaping are obtained immediately. This method is of no practical importance.

Durit ADF Method. This process has supplanted the ferric nitrate method. The print paste contains

20 gm	Indigosol dyestuff
40 gm	urea
20 gm	Durit ADF
390 cc	water
500 gm	neutral starch-trag.
20 gm	neutral sodium chromate 1:2
10 gm	ammonium sulfocyanide 1:1
1000 gm	

The goods are printed and dried, then aged 4 to 8 minutes with acetic-formic acid. This method can be used alongside Rapidogens. Instead of acid ageing, the prints may be developed 8 seconds in a bath containing

25 cc	sulfuric acid 66°Bé
30 gm	oxalic acid
50 gm	anhydrous sodium sulfate

per liter at 35°C, then rinsed, neutralized and soaped.

Ferric Chloride Method. This process is carried out by printing the

Indigosol dyestuff, appropriately dissolved and thickened, and after drying, treating in a bath containing

30 gm ferric chloride
20 gm sulfuric acid 66°Bé
20 gm common salt

per liter at 40°C. It is apparently little used in application printing, but a modification of this principle has found use in producing colored resists with Indigosols under aniline black (*G.P. 743,461*, Oct., 1943, Scheurer, Lauth and Co. The details were worked out by Dr. Diserens and Dr. W. Hess).

Development by Steam Processes in Printing

Formulas involving steam development permit the Indigosols to be printed alongside other dyestuff groups, such as chrome mordant dyes, vats, aniline black, Rapidogens, etc. The chlorates (sodium, ammonium, aluminum) are used as oxidizing agents, and are combined with substances exerting an acid reaction in the steaming process, or with catalytically acting compounds, particularly ammonium vanadate.

There are five general methods by which the Indigosols are steam developed:

(1) Method using sodium chlorate and ammonium sulfocyanide, or sodium chlorate and ammonium sulfate.
(2) Method using sodium chlorate and Developsol (diethyl tartrate)
(3) Method using ammonium chlorate
(4) Method using aluminum chlorate.
(5) Method using ammonium nitrate

The first substances employed to split off acid in the steaming process were the ammonium salts of fixed acids, as sulfocyanide, citrate, oxalate, sulfate (*B.P. 220,694*). However, it was observed that the ammonium salts of some Indigosols are difficultly soluble, so that precipitation occurs in the print paste. Therefore a process was developed by which other agents could be used which were stable in the relatively cold print paste, but which split off acid on steaming (D. & H., *B.P. 313,407*). In other patents, D. & H. recommend the use of water-soluble organic acid esters which split into alcohol and acid in steam treatment (*B.P. 306,800; G.P. 479,678, 504,706; Aus.P. 122,467*). The Developsol (diethyl tartrate) method is based on this idea.

It should be noted here that ammonium sulfocyanide is a substance which not only produces an acid on steaming but also prevents overoxidation of the dyestuff. There are other compounds which can be used for the same dual purpose, for instance, certain sulfonic acids bearing readily oxidizable groups (as amino groups). Brighter shades are obtained by adding these compounds to the Indigosol print paste. The use of chlorides, esters or anhydrides of organic acids, particularly of sulfonic acids, instead of the ammonium sulfocyanide or diethyl tartrate, is recommended in *G.P. 531,473.* Examples given are benzene sulfonic acid anhydride, or benzene-1,3-disulfochloride.

Amine salts or fatty acid amides, such as dimethylamine hydrochloride, dimethyl- or -butylamine sulfate or oxamide, are recommended for the same purposes in *U.S.P. 2,008,966* (Rohm and Haas).

Sodium Chlorate Methods. The dyestuff is pasted up with suitable solvent, such as Dehapan O, and warmed with water until dissolved. Thickening agent is added, and the necessary amounts of sodium chlorate and ammonium sulfocyanide. When cool, ammonia and ammonium vanadate are added. It should be pointed out that this formula cannot be used with Indigosol Brown IRRD. For Indigosol Greens AB and IB, the Developsol method is better.

A typical formula for this method is:

100 gm	Indigosol Blue IBC paste
350 gm	water
490 gm	starch-trag. thickening
20 gm	sodium chlorate 1:3
30 gm	ammonium sulfocyanide 1:1
5 gm	ammonia
5 gm	ammonium vanadate 1%
1000 gm	

The prints are dried, then aged seven minutes, rinsed and soaped hot.

Smoother and deeper shades are obtained by adding alkylamine salts to the print paste (*F.P. 866,935*—D. & H.). The following formula is an example from the patent:

20 gm	Indigosol dyestuff
10 gm	urea
10 gm	phenol
20 gm	Glyecine A
40 gm	triethanolamine sulfate
270 gm	water
550 gm	neutral starch-trag.
	Heat on water bath; cool; add
30 gm	sodium chlorate 33%
30 gm	ammonium sulfocyanide 50%
10 gm	ammonium vanadate 1%
10 gm	ammonia
1000 gm	

The goods are printed and dried, aged for 8 minutes and washed.

It is necessary to wash the Indigosol prints well after developing the color in order to remove the thickening agent, which leaves a harsh hand. It is possible, however, to avoid washing by using a water-in-oil emulsion in place of gums or starches. The dyestuff solution containing all the ingredients is vigorously stirred into a water-insoluble solvent. (*G.P. 743,460*—D. & H.) The solvent may contain a cellulose ether in dissolved state. The prints are soft and pliable after ageing.

Instead of ammonium sulfocyanide, ammonium sulfate can be used. The printing paste is made according to the following formula:

50 gm	Indigosol dyestuff
80 gm	urea
140 gm	hot water
500 gm	starch-trag. thickening
70 gm	sodium chlorate 1:3
40 gm	ammonium sulfate 1:2
20 gm	ammonium vanadate 1%
1000 gm	

The prints are aged and washed as usual.

Developsol Method. This process is particularly recommended for Indigosols Golden Yellow IGK and IRK, Scarlet HB, Pink IR extra, Brown IRRD and Greens AB and IB. The dyestuff is pasted up with a solvent (such as Dehapan O or Cellosolve) and with Developsol D (Indigosol Developer D), dissolved in water and added to the thickening agent. Sodium chloride and ammonium vanadate solutions are added. The material is printed, dried, aged and washed.

A typical formula for a print according to this method is:

50 gm	Indigosol Golden Yellow IGK
50 gm	Dehapan O
40 gm	Developsol D
288 gm	water
500 gm	starch-trag. thickening
32 gm	sodium chlorate 1:3
30 gm	ammonium vanadate 1%
10 gm	ammonia
1000 gm	

Ammonium Chlorate Method. This process is described in *G.P. 668,386* by D. & H. and is one of the most recent publications in this field. The principal advantage is seen in the short ageing time. The print paste is composed of the Indigosol dyestuff, suitably dissolved, a thickening agent, ammonium chlorate solution, and ammonium vanadate. The patent also mentions the optional addition of ammonium persulfate. It will be noticed that the formula does not contain a metal salt which is a favorable circumstance, and there is no necessity for pretreatment of the goods.

It is also possible to fix the dyestuff by this method by hanging the prints 24 hours at 40 to 50°C instead of ageing. The method can be applied for dyeing as well as printing.

An example of Indigosol print by the ammonium chlorate method:

80 gm	Indigosol Scarlet IB
50 gm	Debesolvol IND
240 gm	warm water
595 gm	starch-trag. thickening
30 gm	ammonium chlorate 15°Bé*
5 gm	ammonium vanadate 1%
1000 gm	

* Ammonium Chlorate 15° Bé
I. 323 gm barium chlorate
400 cc boiling water
II. 132 gm ammonium sulfate
450 cc water
Mix I and II, filter, and set filtrate at 15°Bé

Reduction Thickening

650 gm	neutral starch-trag. thickening
10 gm	sodium chlorate 31°Bé
5 gm	ammonium vanadate 1%
225 gm	water
1000 gm	

It has been observed that some Indigosols (as Indigosol Green IB) do not develop fully when printed on delustered rayon. It is assumed that the delustering substances act as reducing agents, preventing complete development. Such prints can be brought up to shade by treating the prints with 2 to 3 gm of sodium nitrite, and 15 gm of concentrated sulfuric acid per liter after ageing, and even after ageing and washing, since the dyestuffs have a sufficient substantivity.

Another method of printing those Indigosols which do not develop properly on spun rayon fabrics is by the sodium ferrocyanide process (*F.P. 898,527*, D. & H., 1945; *F.P. 895,751*, Ciba, 1945). This method makes it possible to obtain full shades with Indigosol Green IB and Indigosol Olive Green IB. However, Indigosol Blue IBC cannot be developed by this formula. The usual catalyst, ammonium vanadate, is replaced here with sodium ferrocyanide or ferricyanide.

Printing Formula

50 gm Indigosol Golden Yellow IGK
50 gm Dehapan GB
100 gm Fixer CDH
195 gm water
500 gm starch-trag. thickening
50 gm ammonium chlorate 15°Bé
55 gm sodium ferrocyanide 1:3
——
1000 gm

Reduction Thickening

500 gm Starch-trag. thickening
400 gm water
50 gm ammonium chlorate 15°Bé
50 gm sodium ferrocyanide 1:3
——
1000 gm

After printing and drying, the fabrics are aged 5 to 10 minutes, then soaped well and rinsed.

This formula has a serious drawback in that the shades, particularly the yellows, are dulled by formation of Prussian Blue with iron ions in hard water. To eliminate this defect, the goods should be treated with a hot Calgon solution, whereby the Prussian Blue is stripped from the fabric. Fuller and brighter shades can be obtained in this way.

In *F.P. 898,527* (D. & H., 1945), the development of the shade is effectuated by oxidation in neutral or alkaline medium by potassium ferricyanide, potassium permanganate or sodium chlorite. The print is made as follows:

40 gm Indigosol dyestuff
100 gm thiodiethylene glycol
140 gm water
600 gm neutral starch-trag. thickening
100 gm potassium ferricyanide (10%)
20 gm soda ash (10%)
——
1000 gm

Prints are dried, aged and soaped.

Aluminum Chlorate Method. (*B.P. 356,577* and *G.P. 525,302*, D. & H.) This process occupies a middle position, so to speak, between the steaming procedures and the wet development. The goods must be prepared before printing, and the colors are developed by hanging the prints in dry chambers, in which respect the process is similar to the modification of the ammonium chlorate method mentioned above. The material is prepared with ammonium vanadate and tartaric acid, while the print paste contains, besides the dyestuff and thickener, aluminum chlorate solution (compare *Text. Mfr.*, **1936**, 192). The recipe is:

1 gm ammonium vanadate, *dissolved in*
200 cc boiling water
5 gm tartaric acid crys., *dissolved in*
200 cc boiling water
600 cc cold water
——

After padding and drying, the material is printed with the following print paste:

60 gm	Indigosol dyestuff
60 gm	Glyecine A
280 gm	water
550 gm	starch-trag. thickening
20 gm	tartaric acid 10%
30 gm	aluminum chlorate 25°Bé
1000 gm	

The prints are dried and cooled, then laid up overnight, and afterwards rinsed and soaped as usual. The preparation with vanadate can be dispensed with, according to later information, provided that the prints are aged to develop the colors.

The aluminum chlorate can be substituted with ammonium bichromate, using 20 gm per kg (*G.P. 541,073*, D. & H.). The colors are developed by hanging for 24 hours.

Ammonium Nitrate Method. Several of the Indigosols which are sensitive to overoxidation, as Indigosol Blue IBC, give good results when printed according to this method:

25 gm	Indigosol dyestuff
80 gm	urea
150 gm	water
585 gm	starch-trag. thickening
90 gm	ammonium nitrate 1:2
60 gm	sodium chlorate 1:3
10 gm	ammonia
1000 gm	

The prints are aged and washed as usual.

Pretreatment to Increase Substantivity

It has been shown that the affinity of the Indigosols is much lower than that of leuco-vat dyestuffs. The substantivity is lowered by the introduction of the sulfuric acid ester group. Indigosol O, for example, is an intermediate having practically no affinity for the fiber, while some of the Indigosols, on the other hand, possess varying degrees of substantivity. According to *U.S.P. 2,061,860, F.P. 777,558, G.P. 624,374, B.P. 443,588* (I.G.-Tischbein), Indigosols having low substantivity are fixed with increased yield when the goods are pretreated with substances which form insoluble compounds with the dyestuffs (*Rev. Gen. Mat. Col.*, **1936**, 514). Substances which come in question here are quaternary ammonium compounds, pyridinium bases (octadecyl pyridinium bromide), phosphonium compounds (triphenylbenzyl phosphonium chloride), or even aliphatic amines or polyamines, as polyethylene polyamine, made from ammonia and ethylene chloride.

Resists under Indigosol Dyeings*

The Indigosols occupy an important position in resist style printing. Most of them are easily reserved by alkaline agents such as zinc oxide, sodium acetate or alkali sulfites, whereby the chemical action of the acid oxidation is prevented. Since the Indigosols are developed by acid oxidation, printing of a resist of alkaline or reducing property (as thiosulfate, hydrosulfite) is generally sufficient. The principal advantage lies in the possibility of using vat dyestuffs for the resists.

Before the advent of the Indigosols, vat resists under vat dyeings were difficult to obtain, and the results were often unreliable. Reference can be made to vat color-Ludigol resists, to the metal salts resists, and to the vat color discharges with Leucotrope on vat dyeings, which have been described in Chapter I.

Prints of this same fastness can now be carried out in a much simpler manner. Various combinations are possible, as for example:

(1) Vat color resists can be printed alongside white resist and after ageing, padding with Indigosol dyestuff with sodium nitrite is carried out. The final development takes place in an acid bath. This process is easiest to perform and is most used.

(2) The cloth is first prepared with the Indigosol dyestuff and sodium nitrite. After drying, the goods are printed and aged; then the development in acid is completed.

(3) The goods are prepared with a solution of the Indigosol together with sodium chlorate and ammonium sulfocyanide or oxalate. The resist prints are then applied, and the development of both prints and ground takes place in the ager.

Details of some of the reserve methods will be given. The steps in the nitrite resist style which has given good results in practice are as follows:

(1) Printing of white and colored (vat) resists on boiled off and desized white goods.

(2) Drying.

(3) Ageing to fix vat dyestuffs.

(4) Padding in short dye liquor containing Indigosol dyestuff and sodium nitrite.

(5) Skying 10 to 15 seconds.

(6) Development in acid bath containing 20 gm of sulfuric acid 66° Bé per liter at 70°C.

(7) Rinsing, neutralizing and soaping.

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* Friedländer, *Mell.*, 1928, 697.

White Resist I

150 gm Hydrosulfite NF
560 gm Senegal or Shiraz gum
100 gm Titanox 1:1
40 gm egg albumen 1:2
150 gm water
——
1000 gm

White Resist II

200 gm sodium thiosulfate
100 gm water
500 gm gum arabic paste
200 gm fish glue 1:1
——
1000 gm

Vat Color Resist

100 gm vat dyestuff
30 gm glycerin
500 gm starch-British gum thickening
120 gm potash
150 gm Hydrosulfite NF
100 gm water
——
1000 gm

For faultless results, the goods should be padded immediately after ageing. If the goods are laid up for any time after ageing, they should be can-dried before padding. Practical experience seems to point to the fact that the resist effect is brought about as much by the decomposition products of the Hydrosulfite NF as by the alkali present, and that the resist effect decreases rapidly when air has access to these decomposition products. The prints are padded on the mangle to the nip with the printed side down, in order to prevent the pad liquor from washing off the print, and to prevent the prints picking off on the dry, upper roller.

Pad Liquor

5–10 gm Indigosol dyestuff
100 gm trag. gum 6%
10 gm turpentine or Tergitol #4
10–15 gm sodium nitrite
——
per liter

The nitrite method is generally used for resists under light shade dyeings. The Indigosols which are most used for this style are

Indigosol Golden Yellows IGK and IRK
Indigosol Scarlet IB
Indigosol Browns IRRD and IBR
Indigosol Blue IBC
Indigosol Green IB
Indigosol Grey IBL

Resists under fuller shades are generally obtained by padding the white goods with Indigosols using the chlorate formula, drying and printing with the resists. By this method the less substantive Indigosols may be employed, which are easily reserved in the chlorate steam process.

White Resist

200 gm	textile gum
400 gm	starch-trag. thickening
100 gm	Hydrosulfite NF
50 gm	Leucotrope W conc.
100 gm	zinc oxide 1:1
50 gm	soda ash
100 gm	water
1000 gm	

Padding Solution

30 gm	Indigosol O4B
25 gm	Glyecine A
300 gm	water
60 gm	gum trag. 6%
40 gm	sodium chlorate 1:2
15 gm	ammonium vanadate 1%
per liter	

The goods are padded and dried, printed with the resists, dried, aged and well washed.

It has been observed however that vat color resists under dyeings of Indigosol Blue IBC are dull because the presence of Hydrosulfite NF does not permit a complete reserve effect of this dyestuff. This problem has been solved by the development of the product Reservol BC which enables a clear and full resist effect. With this product it is possible to obtain the same colorings as by the well-known Indanthrene Blue RS dip style.

The colored resists, to which Reservol BC has been added, are printed on white goods, aged, then padded with an Indigosol Blue IBC solution prepared according to the chlorate method, dried in the hot flue and aged again to develop the Indigosol dyestuff (Pamphlet N 1825, I.G., July, 1939).

White Resist

400 gm	textile gum
100 gm	zinc oxide 1:1
295 gm	water
80 gm	soda ash
75 gm	caustic soda 38°Bé
50 gm	Ludigol 1:1
1000 gm	

Stock Resist

100 gm	starch-trag. thickening
200 gm	British gum 2:3
50 gm	water
30 gm	glycerin
60 gm	zinc oxide
80 gm	soda ash
	Heat to 60°C; add
100 gm	Reservol BC
	Cool; add
30 gm	caustic soda 38°Bé
650 gm	

Vat Color Resist

100–200 gm	Indanthrene dyestuff
650 gm	stock resist
90 gm	Hydrosulfite NF
20 gm	caustic soda 38°
30–130 gm	water or thickening
1000 gm	

Indigosol Blue IBC Padding Liquor

50 gm	Indigosol Blue IBC
20 gm	Glyecine A
500 gm	water
45 gm	sodium chlorate 1:2
2 gm	ammonia
35 gm	ammonium oxalate
200 gm	gum trag. 6%
40 gm	ammonium vanadate 1%
20 gm	Ludigol
1 liter	

The goods are printed, aged, padded with the printed side down, dried and aged again 3 minutes, oxidized and washed.

Indigosol dyeings can also be resisted by Rapid Fast and Rapidogen dyestuffs. These dyestuffs, being printed in alkaline pastes resist the Indigosols in the same manner as the vat dyes. This resist style can be carried out either according to the nitrite or chlorate steam method. In the latter event, the resist prints can be developed either in two separate stages or in one operation. The two-stage method consists in first padding with the Indigosol dyestuff (using the sulfocyanide or Developsol method), drying, printing the Rapid Fast color resist, ageing to develop the ground, and finally treating the goods in an acid bath to develop the resist color. The same results can be obtained in one operation. The padding liquor contains a relatively higher amount of acid salt, which, when aged, releases enough acid to develop the Rapid Fast or Rapidogen dyestuff.

Finally, it is also possible to resist the Indigosol paddings with vat colors alongside Rapidogen colors, whereby a full line of fast, bright resist effects may be produced.

Indigosol Brilliant Green IB (the ester salt of Indanthrene Brilliant Green B) and Indigosol Olive Green IB, are very substantive to the vegetable fibers, and are difficult to resist cleanly. Other Indigosols, of varying substantivity, such as Indigosol Blue IBC and Brown IRRD, also give trouble. Considerable research work has been done by Durand and Huguenin and by I.C.I. to obtain pure white effects in these cases.

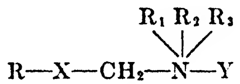
In *U.S.P. 2,090,890*, *F.P. 785,532*, *G.P. 636,208* and *B.P. 433,865* (I.C.I.), pyridinium derivatives are recommended as resist agents. A paste containing 50 gm of benzyl pyridinium chloride per kg, suitably thickened, is printed on white goods, then padded with Indigosol color and nitrite (as example, Soledon Jade Green), dried and developed in sulfuric acid (*Rev. Gen. Mat. Col.*, **1937**, 428; **1936**, 211). According to the British patent mentioned above, quaternary ammonium compounds act as a resist, without alkaline or reducing agents. Besides the pyridinium or chinolinium compounds, there are other ammonium compounds which give better results, for example Leucotrope (dimethylphenylbenzyl ammonium chloride) printed together with potash and sulfoxylate formaldehyde (*B.P. 440,573*—I.C.I.). Similar resist pastes are described in *U.S.P. 2,182,140* (E. Tschan).

The patents *F.P. 789,925*, *G.P. 636,823*, *B.P. 441,330* granted to I.C.I. belong to this same subject. The resists under Indigosols (or Soledon Jade Green) contain phosphonium or sulfonium compounds with long hydrocarbon chains, as for example, cetyl trimethyl phosphonium bromide, the methyl sulfate of dimethyl cetyl sulfonium, etc. (*Rev. Gen. Mat. Col.*, **1936**, 388 and **1938**, 22).

Quaternary bases are also mentioned in *G.P. 626,686*, *F.P. 788,336* and *B.P. 445,224* (D. & H.) as resisting agents. The print paste contains, besides soda ash, benzylphenyl ammonium chloride or triphenyl ammonium methyl sulfate (*Rev. Gen. Mat. Col.*, **1937,** 38).

Colored resists under Indigosol dyeings are produced with Rapid Fast and Rapidogen colors together with quaternary ammonium bases, according to *G.P. 627,068* (I.C.I.). The paste is printed first, the print developed in the acid ager and the goods are then padded with the Indigosol solution (*Rev. Gen. Mat. Col.*, **1936,** 125).

A progressive step in the production of resists under Indigosol dyeings is taken in the *B.P. 491,931* of the I.C.I. In this patent quaternary bases are described wherein the N atom is linked to a high-molecular fatty chain by a bridge, generally formed by an amino group. As a schematic formula the following may be given



$$R{-}X{-}CH_2{-}\overset{R_1\ R_2\ R_3}{N}{-}Y$$

where R, R_1, R_2, R_3, are alkyl groups, X is amino and Y an acid radical. For example, stearyl amidomethyl pyridinium chloride. The resisting effect of the quaternary compounds, already mentioned, is increased by the combination with the high-molecular fatty chain, very probably by the mechanical formation of a film on the fiber's surface, analogous to the water-repellent finish of Zelan. This patent also mentions the possibility of forming colored resists using Rapid Fast dyes.

The general idea of using a water repellent film as resist has been developed further in *B.P. 489,235* and *492,157* (I.C.I.). In these patents the reaction of aliphatic or aromatic isocyanates on the vegetable fiber is described as having an immunizing effect, by which reaction the cellulose no longer has affinity for direct colors, but does acquire an affinity for acetate dyestuffs. This method can be carried over to the technique of resist printing of Indigosols, as a cellulose fiber may be printed with an emulsion of a high-molecular isocyanate (for example, heptadecylisocyanate), ageing and padding with Indigosol dye and nitrite. Very good white resists and colored resists with Rapid Fast colors are obtained.

The action of resisting Indigosols with cationic products is one of precipitation of the Indigosol. The sulfuric acid esters of the leuco-vat dyestuffs yield colorless precipitates with these ammonium bases. The precipitates are not attacked by alkalis and the original dyestuff can not be recovered from these precipitates formed on the printed areas. The fabrics must be soaped very energetically to remove these resinous complexes from the fiber. However, this operation can be avoided by replacing the cationic quaternary compounds with water-repellent compounds wherein the aliphatic chain is linked to the nitrogen atom by a sulfur or oxygen bridge (*F.P. 836,079*, I.C.I.).

A water-repellent film is formed on the printed areas which prevents the penetration of the pad liquor into the cloth. An example of this effect is brought about by the use of stearyl methyl pyridinium chloride. The prints are handled in the same manner as in the application of Zelan. The fabrics are first dried at low temperatures in order to prevent premature decomposition, then heated to 110°C.

The principle of imparting water repellency to printed areas for local resist effects is extended in *F.P. 836,146*, I.C.I. An emulsion of a high-molecular alkali isocyanate; for example, heptadecylisocyanate is printed on white cotton. As in the Zelan process, it is essential to dry at lower temperatures, then to carry out the second part of the reaction, or curing, at elevated temperatures. The fabric becomes hydrophobic at the printed portions, and the prints act as mechanical resists. Colored resists can be made with vat dyestuffs, while the ground can be dyed with substantive colors, or Indigosols. A resist is prepared, for example, with Flavanthrene paste containing heptadecylisocyanate. This resist can also be printed on fabrics prepared with naphthol, then developed with diazo solution, and under chrome mordant dyeings.

In a different way, resists can be made using inorganic acid salts, as chromium alum, potassium alum, iron ammonium alum, aluminum sulfate. These salts form insoluble precipitates with the Indigosols, and can be removed in the soaping (*U.S.P. 2,074,197*, I.C.I.).

Organic salts can also be used as resists. *U.S.P. 2,090,890* (I.C.I.) lists the following: aniline salt, benzyl pyridinium chloride, octadecyltrimethyl ammonium chloride, and other sulfonium and phosphonium compounds.

The use of proteinaceous substances as mechanical resists, is recommended in Durand and Huguenin's *F.P. 793,279*, *G.P. 636,995* (1935). Glue, gelatin and other albuminoid substances are used to augment the chemical resists of the print pastes (*Rev. Gen. Mat. Col.*, **1937,** 123; **1938,** 23). These patents apparently protect the product Reserve X (D. & H., Carbic), Reserve T (Geigy) and Soledon Resist A (I.C.I.). The print paste contains, besides the Reserve X, some gum thickening and either sodium bisulfate or sodium thiosulfate. Additions of soda ash and Leucotrope O are recommended. In printing easily penetrated sheer fabrics the alkaline pastes, containing for example, sulfoxylate formaldehyde, give irregular results. In such cases the acid salt resists are superior. The following print paste is suggested:

50 gm	sodium bisulfate
130 gm	water
200 gm	textile gum
500 gm	Reserve X 2:3 water
20 gm	Leucotrope O
100 gm	titanium dioxide 1:1
1000 gm	

The printed cloth is dried well, and in the event that vat colors are printed alongside, is aged 5 minutes, padded on the mangle with Indigosol dyestuff and sodium nitrite, and developed in sulfuric acid solution. The method is described in Durand and Huguenin's manual, 2nd ed., p. 129.

Additional details have been contributed by Nestelberger in *Mell.*, July, **1938,** 590. The resists should be printed on the white cloth, rather than on the padded cloth. A mixture of glue and textile gum is prepared, and some urea or resorcin added during the cooking in order to avoid gelling. The print paste is prepared by adding to this thickener, soda ash, sulfoxylate formaldehyde and Leucotrope W. Vat dyestuffs can be added for colored effects. Where Rapidogens are used for colored resists, the print paste should be altered, and thiosulfate and zinc oxide employed with the thickeners.

Resists of Indigosols under Indigosol dyestuffs have been successfully prepared (*G.P. 645,469, B.P. 469,843* and *F.P. 803,590* of D. & H., 1936). The resist contains Indigosol dyestuff, nitrite, phenol, urea and zinc oxide. The goods are printed and dried, padded with Indigosol color with nitrite and developed without intermediate drying in a bath containing 20 cc of sulfuric acid 66° Bé per liter at 70°C. Thereupon the fabrics are rinsed, neutralized, soaped and rinsed. It is claimed that all Indigosol dyes can be used in the printing and dyeing, whereas previously it had not been possible to obtain resists containing difficultly oxidizable Indigosols under the readily oxidizable types.

A metal salt precipitate is recommended as resist in *B.P. 393,381* (Bleacher's Assn.). A metal salt, such as copper sulfate, suitably thickened, is printed on white cloth. The padding liquor contains, besides the Indigosol dyestuff, a substance capable of forming a precipitate with the copper sulfate, for example, potassium ferrocyanide (*U.S.P. 2,298,147*). The Indigosol dye cannot penetrate the insoluble film so produced, it is oxidized in the ageing process by the action of the copper sulfate on the printed portions, and is removed later on as an insoluble and unfixed precipitate. The mechanical resist effect is enhanced by the addition of aluminum acetate. Locust bean gum is the thickening agent. The inventors claim that satisfactory resists under Indigosols are obtained even with those types where the usual alkaline resists fail (compare the Parker Schwabe patents: *B.P. 386,365, 421,466; U.S.P. 2,031,546; G.P. 629,895, 638,755, 642,581; Rev. Gen. Mat. Col.*, **1938,** 103, 225).

Indigosol resists under Variamine Blue and aniline black will be discussed under the corresponding dyeing processes.

Some Indigosols can be printed with discharge pastes containing sulfoxylate formaldehyde and Leucotrope, without detriment to the shade. It is therefore feasible to print colored discharges with Indigosols on dischargeable vat dyes or azo colors. The Indigosol is printed and aged, and thereupon developed in an oxidizing liquid, while the benzyl ether of the leuco-vat is removed in an alkaline bath (*Rev. Gen. Mat. Col.*, **1933,** 312, 338).

An example of discharge paste of this process is as follows:

50 gm	Indigosol Green IBA paste
50 gm	Dehapan O or Debesolvol IND
350 gm	British gum thickening
150 gm	soda ash
150 gm	Hydrosulfite NF
150 gm	Leucotrope W
100 gm	zinc oxide 1:1
1000 gm	

Dyeing with Indigosols

The Indigosols have undoubtedly had less success in dyeing than in printing. They are used to produce light and medium shades where fastness and levelness are required, and are particularly suitable for special mixed fabrics, containing wool or mohair. Full shades are more economical with vat dyestuffs (see also C. Dierkes, *Allg. Tex. Z.*, **1944,** 149–151; *Mell.*, **1944,** 248; P. Colomb, *Teintex*, **1942,** 255).

The most important advantage of the Indigosols is the uniformity and levelness of the dyeing. The accepted dyeing technique for these dyestuffs is on the padder, because of their low substantivity. This dyeing method in a concentrated and short bath gives the best results, although they can also be dyed on the jig or in a continuous vat.

The composition of the pad liquor is very simple. In general, no leveling agents are needed, but for speedy wetting-out of the fabric some auxiliary like Nekal BX or Tergitol is recommended. The nitrite and bichromate processes are most often employed.

When padding Indigosols there is some substantivity and depletion of dye-liquor strength. This varies with different types, so that the concentration of feed liquor is difficult to determine. For this reason an especially constructed mangle is used. This is particularly true in America. The goods to be padded are conveyed directly to the nip of a two-bowl padder, both rollers being rubber and not covered. In order to insure thorough penetration and uniformity of back and face, the lower roller dips into a trough of the pad liquor, while the pad liquor is also discharged through a perforated pipe at the nip and onto the face of the cloth, thus forming a dam or well before the nip. Thus the cloth is impregnated simultaneously from above and below. The pad liquor is circulated continuously with the feeding tank liquor, by which precaution there is no loss in strength by the substantivity of the dyestuff. The circulation is controlled to maintain a definite level in the padding trough.

A survey of the different dyeing methods follows:

Nitrite Process. Following is an outline of the steps in this process.

Preparation of the Pad Liquor. The dyestuff is first pasted with a solvent (Cellosolve, etc.), water added while stirring, and the bath warmed until the dye is completely dissolved. A wetting agent may be optionally added, as Invadin N or Nekal BX. Finally the required amount of sodium nitrite together with about 1 gm of soda ash per liter are added. The solution is brought up to volume and heated to 50 to 60°C. It is often the practice to add gum tragacanth solution, or a suitable substitute gum, to give a little viscosity to the solution.

The quantity of nitrite to develop the Indigosol must be adjusted to the special conditions and to the depth of color. For the average Indigosol color 5 to 15 gm of sodium nitrite per liter pad liquor is necessary, but for Indigosol Red IFBB 0.2 to 2 gm are sufficient.

Padding Operation. The bleached, desized and dried fabrics are padded, and expressed to about 100% pick-up on the weight of the cloth. When using the three-bowl mangle, it is necessary to compensate for the affinity of the Indigosol by first feeding a somewhat weaker dye liquor (for instance 25 liters of stock solution diluted with 4 to 7 liters of water), then feeding the full strength stock solution. Care must be taken to maintain the level of the liquid during the entire passages. After padding, the goods are aerated or skyed for 7 to 15 seconds. This is to improve penetration and levelness.

Development. The dyeing is developed in dilute sulfuric acid (20 cc of concentrated sulfuric acid per liter) at 70 to 80°C. The time of development is 2 to 4 seconds, so that a small tank can be appropriately used. However, to insure complete fastness, an air passage of about 20 seconds should be given after the developing operation. If the air passage cannot be carried out, the time of developing must be lengthened to 10 seconds.

An addition of 2 to 3 gm of Anthrasol Salt NO per liter to the developing bath has proved effective in preventing overoxidation of sensitive dyes like Indigosol Blue IBC.

The developing liquor is sharpened with 1 liter of 25% sulfuric acid after each 200 meters of cloth, or it can be fed gradually with a 4% sulfuric acid solution to replace liquid lost by carryover.

The modern Indigosol dyeing unit consists of a continuous range, the padder, skying, developing tank, skying and rinsing and soaping compartments being in tandem. Colomb (*Teintex*, **1942**, 255) describes a developing tank of very short liquor. It consists of a V-shaped trough fed from a raised reservoir with warm sulfuric acid solution. The acid is supplied by two distributing pipes which feed the trough on both sides below the level of the dye bath. The trough is narrow, carrying only 12 to 15 liters for fabrics of 0.8 meter or 20 liters for fabrics of 1 meter width. The bath is kept at constant temperature by surrounding water bath.

The fabric is in contact with the acid of the trough for a short time only. This necessitates a relatively quick renewal of the acid in the trough. The acidified pieces must then be skyed to complete the development, after which they are rinsed, then neutralized in a solution of 2 gm of soda ash per liter, and washed. The neutralizing bath is replenished with a 4% soda ash solution (1 liter per 200 meters of cloth).

When medium or dark shades are handled, it is advisable to dry after the padding operation, and develop later. This drying process should be carried out in a hot flue, or on the enclosed frame. Festoon drying devices in hot-air chamber are also successful. When drying on the tenter frame, care must be taken that the hot air supplied is evenly distributed on both sides of the fabric. Direct light rays, moisture and acid fumes must not be allowed to have access to the dried goods.

Bichromate Process. This method is similar to the nitrite method, differing from it only in that the oxidizing agent (bichromate) is not added to the dye liquor but to the developing bath. Thickening agents should be used with the dye liquor only when levelness cannot otherwise be obtained, and only if the thickener has no reaction with bichromate solutions.

Dye Bath

0.1–8 gm	Indigosol dyestuff
500 gm	water at 60–80°C
6–8 gm	wetting agent
50–150 gm	gum trag. 6%
1000 gm	

Developing Bath:

	For light shades *0.1–3 gm dyestuff*	*For medium shades* *3–10 gm dyestuff*
Sodium bichromate	10 gm	20 gm
Sulfuric acid 66°Bé	30 cc	40 cc
	per 1	per 1

The dyeings are developed for 1 to 3 seconds at 35°C, and skyed. Or they may be treated 6 to 10 seconds in the continuous box. The shades obtained by this process are not as bright as those produced by the nitrite process, probably because of overoxidation.

Many special apparatuses for dyeing Indigosols have been constructed, for instance, the Fibe machine of F. Benninger in Uzwil, Switzerland (*G.P. 464,714*—Fischer), the principal advantage of which lies in the lack of tension on the fabric running through, the Haubold dyeing machine (Chemnitz), the four-roller dye mangle of the Zittauer Maschinenfabrik and the open-width dye box "Anti-Mousse" of A. Deck in Mulhouse. Details of these machines may be found in the manuals of Durand and Huguenin as well as in Stierwaldt's article in *Mell.*, Jan. 1936, 50–1.

The steam process with sodium chlorate is rarely used for plain shades, as it is more troublesome than the wet oxidation method.

The ferric chloride process can be applied for plain dyeings of the Indigosols. The process has been studied by Fairweather and Thomas (*U.S.P. 1,886,947*—I.C.I.), and they recommend adding some ferrous salt to the dye bath, or some salt of a weak acid, which will form a double salt with the ferric salt of the development bath. Overoxidation is avoided in this way.

G.P. 568,003 and *U.S.P. 1,826,352* (Scottish Dyes) suggest padding the fabric in a solution containing the Soledon (Indigosol) dyestuff plus sodium nitrite and sulforicinoleate. The goods are aged, without intermediate drying, in customary ager and developed as usual in warm acid bath. Full, well-penetrated dyeings are claimed (*Rev. Gen. Mat. Col.*, **1936,** 157).

The addition of a wetting agent in the padding liquor has been recommended. It should be noted that a wetting agent which creates a foam during the padding operation should be avoided.

The affinity of Indigosol Blue IBC for vegetable fibers can be considerably increased by adding salt to the pad liquor. A very small amount of an organic acid is recommended in *G.P. 627,276* (D. & H.—1934) together with the salt.

The individual Indigosol dyestuffs react differently with acid oxidation agents. While some of them require an energetic action there are others which tend easily to overoxidation. Difficulties occur therefore when types have to be mixed which react differently. It has been found that Indigosols of different reaction types can be blended and developed together provided that the developing bath contains a compound which is easily reacted on by oxidizing compounds (*B.P. 503,699*, D. & H., *F.P. 834,113*, *Aus.P. 155,312*). The patents mention pyrocatechol and hydroquinone as examples, also 1,4-naphthohydroquinone and pyrogallol, but *m*-dihydroxy compounds like resorcinol are explicitly excluded. The products recommended here are buffers, reacting with oxidants and combining with oxygen, but releasing it again slowly.

This subject was studied by A. G. Hall (*Am. Dyes Rep.*, **1940,** 58–60, 68–71) and the chemical constitution, manufacture and dyeing methods of Indigosols reviewed. Hydroquinone is shown to have a particularly good influence in the problem of overoxidation, when added either to pad liquor or printing paste. Other buffering substances are copper and ammonium cyano-compounds, thiodiethylene glycol, thiourea, aromatic *o*- or *p*-dihydroxy or *o*- and *p*-hydroxy amino compounds.

Another method of preventing overoxidation is by the addition of metallic reducing compounds such as stannous chloride or titanous chloride to the oxidizing development bath.

The fastness of dyeings made with Indigosol dyestuffs can be increased by preparation of the goods with cationic substances, according to *F.P.*

777,558 (I.G.). The cationic products given as examples include octadecyl pyridinium bromide and triphenyldichlorobenzyl phosphonium chloride.

Pad Jig Dyeing. The methods enumerated above refer to a continuous range padding, skying, and development. It should be brought out here that development may also be carried out on the jig. The following formula is typical of such procedure. The padding liquor contains

5 gm Indigosol Blue IBC
1 gm Nekal BX
3 gm hydroquinone
10 gm sodium nitrite
—
per liter

The fabric is padded at 50 to 60°C with this liquor, and preferably dried in the hot flue. The color is then developed on the jig in a 2% sulfuric acid bath, one or two ends being sufficient; it is then rinsed and soaped.

Jig Dyeing. The entire dyeing of Indigosols may be carried out on the jig. The dyeing is generally done in a cold, or cooling bath, with additions of Glauber's salt to exhaust the color. After rinsing, the development is brought about in a bath of 20 cc of sulfuric acid 66° Be, and 1 gm of sodium nitrite per liter at 20 to 70°C, depending on the type of color.

Box Dyeing. This method can be utilized for knitted fabrics or for skeins, and depends on the action of Unipan A (D. & H., Carbic). The dyestuff is added in small portions, then Glauber's salt is added and the dyeing continued. Finally ½ to 1 gm of sodium nitrite and ½ to 1 gm of Unipan A are added per liter of dye liquor. Sulfuric acid is added in very small quantities during the time the absorbed dyestuff is developed.

Cellulose sulfite waste liquor (Dekol, Cellex, etc.) used in amounts of 1.5 to 2.5 gm per liter has a favorable effect in dyeing the Indigosols in the one-bath methods. The action is one of a protective colloid, keeping oxidized particles in suspension and avoiding blotches.

Dyeing Rayon in the Spinning Mass. A new application for Indigosol dyestuffs has been discovered by H. Dosne. He found a method of dyeing viscose and acetate cellulose in the spinning mass and was able to apply it on an industrial scale (*U.S.P. 2,041,907, F.P. 760,350, 775,096, G.P. 623,118, 624,170, B.P. 403,049, S.P. 173,686, Holl. P. 38,311;* compare *Rev. Gen. Mat. Col.*, **1937,** 328). In this process the Indigosol and sodium nitrite are incorporated in the viscose, while the color is developed in the same acid bath in which the spun thread is precipitated. It is feasible to add the Indigosol to the viscose in this way, since the solutions are alkaline and the dyestuff is stable in this condition. The *F.P. 775,096* suggests charging the finely ground Indigosol into the viscose without previously dissolving it. This process was introduced on an industrial scale in France, the product being sold under the name "Strascolor" (fil de Strasbourg).

A comparable method for acetate cellulose is recommended in *G.P.*, *637,829*, Dosne. The Indigosol is dissolved in dioxan, diethyl oxide, or other glycol or ether, and added to the acetone solution of the cellulose acetate, (or to the alcohol-ether solution of nitrocellulose). The solutions are extruded as threads, and the color developed in an acid bath. The principal difficulty of this method lay in the diminished concentration of the spinning mass. It was therefore proposed in *G.P. 647,418* (Dosne, 1934) to add the finely powdered Indigosol directly into the spinning mass, solution being automatically attained after three hours.

Indigosols on Wool and Silk

Printing on Wool and Silk. The Indigosols are generally printed on the animal fibers by the chlorate steam process. In order to obtain a good yield on wool, it is necessary to chlorinate the fabric before printing, as only fair results can be expected on unchlorinated wool. The following formula is typical of the chlorate method used for wool: (*Bull. Fed.*, **I**, 134, 529; *Aus. P. 124,716*, D. & H.)

60	60	gm Indigosol dyestuff
30	30	gm Cellosolve or Glyecine A
180	135	gm water
500	500	gm British gum thickening
100	125	gm sodium chlorate 1:2
30	—	gm Developsol D
—	40	gm ammonium sulfocyanide
100	100	gm ammonium vanadate 1:1000
0	10	gm ammonia
1000 gm		

The printed fabrics are first aged 5 minutes in the rapid ager, then steamed half an hour in the cottage steamer, rinsed and washed warm.

Improved results are obtained by first printing the Indigosol dyestuff with gum and ammonium sulfocyanide, steaming, and developing in an acid oxidizing bath (*F.P. 745,781; B.P. 413,713*, I.G., 1922; *G.P. 574,940*, I.G.—Sommer—Torinus). The process is distinguished by the fact that the fixation of the dyestuff is carried out in two separate steps: the first consisting of absorption of the Indigosol dyestuff by the fiber and the second consisting in development in acid oxidation (*Bull. Fed.*, **I**, 528). The formula follows:

50 gm	Indigosol Scarlet IB
80 gm	glycerin
50 gm	Glyecine A
30 gm	water
200 gm	ammonium vanadate 1%
550 gm	British gum thickening
40 gm	ammonium sulfocyanide
60 gm	sodium acetate crystals
1000 gm	

Reduction Thickening	
550 gm	British gum thickening
50 gm	glycerin
50 gm	ammonium vanadate 1%
40 gm	ammonium sulfocyanide
310 gm	water
1000 gm	

The printed goods are dried and aged 10 minutes, then developed by treating 25 seconds in a bath containing 30 cc. of sulfuric acid 66° Be, and 30 gm of sodium chlorate per liter at 90°C, rinsed and soaped.

The print paste contains an acid-forming salt but no oxidation agent. Thus, during the ageing, the free Indigosol acid is released which is absorbed by the fiber. An oxidizing agent, if present, would have the effect of producing the vat dyestuff immediately, which cannot be absorbed by the wool fiber. Good results are obtained by carrying out the development only after ageing, and preferably on chlorinated wool fabrics. In this process chloramines are formed which might develop the dyestuff prematurely during ageing, for which reason an addition of sodium acetate to the print paste is advisable.

According to Durand and Huguenin's *G.P. 486,174*—1927 (compare *B.P. 296,648*, I.G., 1928), it is possible to develop the Indigosols with persulfate together with an inorganic acid. This process has some importance for production of colored discharge effects on wool. The woolen goods are printed with a paste containing Indigosol dyestuff and a reduction discharge agent, aged, and aftertreated with persulfate bath containing some free acid (*G.P. 504,628*, D. & H.).

The fastness to crocking of Indigosol prints on wool is not good, especially for pinks and scarlets. The use of pyridine has a good effect on the crocking fastness and on the color yield (*Text. Rec.*, May, **1935**). Better penetration results by the addition of pyridine (*U.S.P. 1,926,601*—Heberlein-Kundert; *Bull. Fed.*, **II**, 111). The addition of a pyridine base, an alcoholic phenol solution and a mild oxidizing agent to the print paste, and development in dilute acid are recommended.

The fastness to crocking can also be improved by an aftertreatment with auxiliaries of the Sapamine type, as claimed by Durand and Huguenin (*G.P. 516,669*). The Sapamines are cation-active compounds formed by substitution of fatty acid radicals in ethylene diamines, and exert a detergency effect in acid solution similar to soap in an alkaline solution. Thus the name Indigosol Soap SP for Sapamine.

Dyeing on Wool and Silk. The difficulty in dyeing wool with Indigosols lies principally in their poor fastness to crocking. The dyeing of wool is generally restricted to the blues, Indigosol O and OR, and is carried out on the dye box. In the first stage of dyeing, the dyestuff is absorbed by the fiber, the dye bath containing, besides the Indigosol color, some formic acid, sulfoxylate formaldehyde and Glauber's salt. The reducing agent prevents premature oxidation. In the second stage, the absorbed dyestuff is developed by sodium nitrite and sulfuric acid, the chemicals being added in small increments.

The Indigosols have the property of dyeing the animal fiber at low temperatures provided that an alkaline agent and a reducing compound are added to the dye liquor. The color is thereupon developed in an acid oxidizing bath containing persulfate and sulfuric acid (*B.P. 342,407*, I.G.—Neumann; *Bull. Fed.*, **I,** 69).

Wool and rayon staple mixed fabrics can be dyed with the Indigosols (*B.P. 478,663*—I.C.I.). Since acid dye baths are more suitable for the animal fiber and an alkaline bath better for the vegetable fiber, padding the Indigosol color is recommended. The pad liquor contains, besides the dyestuff, a wetting agent, a solvent (Cellosolve), an acid-forming compound (diethyl tartrate), and a swelling agent (sulfocyanide). The padding is done at 60°C; the development by ageing and an aftertreatment in persulfate follow.

Table 4. Auxiliaries for the Indigosols

Name	Manufacturer	Constitution	Literature	Application
Developsol D	D. & H.	Diethyl tartrate.	*B.P. 306,800* *G.P. 479,679* *Rev. Gen. Mat. Col.*, **1930**, 72	Used in Indigosol print pastes, chlorate method, to supply acid in the ager. Replaces ammonium sulfocyanide.
Indigosol Developer D	I.G., G.D.C.			
Tinosol Developer D	Geigy			
Developsol GA	D. & H.	Monoethylglycol. $\begin{array}{l} CH_2\text{—}OH \\ \vert \\ CH_2\text{—}OC_2H_5 \end{array}$ (B.p. 125°C; Sp. Gr. 0.936)	*U.S.P. 2,044,468*	Solvent for the Indigosols.
Cellosolve	C.C.C.C.			
Indigosol Developer GA	I.G., G.D.C.			
Ethyl glycol	I.G.			
Débésolvol IND	L.Z.J.	Solvent mixture.		Efficient solvent for Indigosol colors, increasing color yield and promoting uniformity.
Fixer CDH	D. & H., Carbic	Paste containing urea.	*F.P. 680,832* (1929) *G.P. 523,262; 583,204* *Rev. Gen. Mat. Col.*, **1931**, 146; **1929**, 202	Auxiliary to improve solubility and yield of Indigosols, especially Indigosol Brown IRRD. Recommended addition: 50–80 gm per kg.
Dehapan O	D. & H., Carbic	Solvent mixture, containing urea, a high boiling alcohol, and a phenolic body.	*F.P. 769,171* *G.P. 601,860* (1933) *Rev. Gen. Mat. Col.*, **1936**, 65, 104 *Tiba*, **1935**, 58 *Mell.*, **1934**, 362	Viscous liquid, readily soluble in water, used as a solvent for difficultly soluble Indigosols.
Tinosol Solvent O	Geigy			

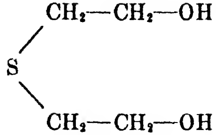
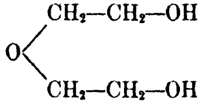
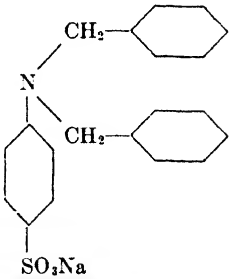
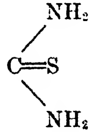
Glyecine A **Kromfax Solvent** **Dehapan GB** **Lyogen TG** **Tinosol Solvent A** **Brecolane NCI**	I.G., G.D.C. C.C.C.C. D. & H. Sandoz Geigy Kuhlmann-Francolor	Thiodiethylene glycol.  (B.p. 282°C)	*G.P. 339,690* (I.G. 1919) *B.P. 147,102; 427,058* (D. & H.) *F.P. 711,869; 713,460* *S.P. 159,928*	Solvent for Indigosols and hygroscopic agent.
Diethylene glycol **Polyglycol** **Brecolane NDG**	C.C.C.C. I.G. Kuhlmann-Francolor	Diethylene glycol.  (B.p. 250°C)	*B.P. 298,088* (D. & H.) *Rev. Gen. Mat. Col.*, **1931**, 32	Solvent and hygroscopic agent.
Carbitol	C.C.C.C.	Monoethyl ether of diethylene glycol.	*U.S.P. 1,696,874* (1928); *1,730,061* (1929); *1,732,356* (1929)	Solvent for the Indigosols.
Fibrit D **Durit O** **Eutinctol NB**	I.G., G.D.C. D. & H. Carbic Kuhlmann-Francolor	Solvent compositions based on polyglycols.	*G.P. 340,552; 391,007; 504,076* *U.S.P. 1,967,656* *B.P. 298,088; 427,058* (D. & H.) *S.P. 157,912-3*	Solvent action.
Liquid Solution Salt GV	I.C.I.		Brown liquid.	Solvent for the Soledon (Indigosol) dyestuffs.

Table 4. Auxiliaries for the Indigosols (*Continued*)

Name	Manufacturer	Constitution	Literature	Application
Unipan A	D. & H., Carbic		1938	As addition to the dye bath of Indigosols by the single-bath method, prevents precipitation of the dyestuff. Prevents precipitated dye particles from adhering to the fabric in developing, by protecting against over-oxidation.
Solution Salt SV	I.C.I.	Sodium salt of dibenzylsulfanilic acid. 	*B.P. 421,066* (I.C.I.)	For improving the yield of Soledon colors.
Dehagen II	D. & H., Carbic		1938	In dyeing Indigosols, added in small amounts (2–3 gm per l) to the developing bath to prevent over-oxidation, especially with Indigosols sensitive to over-oxidizing, as Indigosol Blue IBC and Indigosol Olive Green IB.

Dehagen FBB	D. & H.		1938	Auxiliary in padding bath of Indigosol Red IFBB by the nitrite method. Prevents nitrous gases formed from attacking the dyestuff, thus assuring maximum fastness.
Reserve X **Soledon Resist A** **Reserve T**	D. & H. I.C.I. Geigy	Yellowish powder, soluble in water, and consisting of dextrin and glue or gelatin.	*F.P. 793,279* (1935) *G.P. 625,686; 636,995*	Permits white resists under Indigosols which are otherwise difficult, for example, under Indigosol Golden Yellow IGK Blue IBC and Green IBA
Anthrasol Salt NO	I.G.	Thiourea cut 1:1 with sodium sulfate. 	*G.P. 734,399; 734,400*	Combines with excess nitric oxide Added to the acid developing bath, prevents over-oxidation Used with sensitive colors such as Indigosol Blue IBC, Red IFBB, Olive Green IB, etc.
Reservol BC	I.G.			As addition to vat color resists under Indigosols—especially under Indigosol Blue IBC—which otherwise yield dull resists with Hydrosulfite NF alone.
Indigosol Soap SP	D. & H.	Cationic product of the Sapamine type.	*Rev. Gen. Mat. Col.*, Sept., **1936** *Mell.*, **1931**, 212 *G.P. 516,669*	For improving fastness to crocking of Indigosol prints and dyeings on wool.

Chapter IV

The Insoluble Azo Dyestuffs

The technique of dyeing water-insoluble azo dyestuffs was first developed about 60 years ago, by Horace Koechlin on the one hand, and by the chemists v. Gallois and Ullrich of M.L.B. on the other. These important dyestuffs, which are generally termed "ice colors", are formed *in situ* on the fiber by an impregnation with a phenolic body, followed by development with a diazo solution.

The first experiments in the use of β-naphthol, however, should probably be credited to the German chemist, Graessler, and to the English chemists, Thomas and Holliday, who were granted *B.P. 2,757* in 1880. This described the so-called Vacancein Red, obtained by impregnation of the vegetable fiber with sodium naphtholate, followed by an aftertreatment with diazotized β-naphthylamine. Other dyestuff chemists, for instance Fehr, tried to transfer the production of ice colors into general practice, but apparently some difficulties were encountered in this Read-Holliday-Graessler process.

It was undeniably through the efforts of the dye manufacturers, Meister, Lucius & Brüning, and especially, their chemists, v. Gallois and Ullrich, that the most important representative of the group of ice colors, Para red, was so thoroughly developed, and introduced into large scale production. The interest which these dyestuffs first aroused grew to a great extent. The color shades were limited up to 1911 to red (*p*-nitraniline and *p*-nitroanisidine), bordeaux (α-naphthylamine), orange (*m*-nitraniline and *m*-nitroanisidine), and blue (dianisidine). The fastness properties of these colors could not be classed as high. But progress of immense importance was made in 1911 when Griesheim-Elektron brought out a new coupling component* in 2,3-oxynaphthoic acid anilide. This was soon followed by other products of similar constitution, which were known as the Naphthol AS series. The field of insoluble or "Ingrain" dyestuffs, which up to this time had been based solely on β-naphthol, received a tremendous impetus.

Progress was interrupted by the first World War (1914 to 1918) but with the reapplication of the dyestuff chemists to this subject, new coupling components of the Naphthol AS series, as well as new dyestuff bases were

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* The term "coupling component" is used here and subsequently to denote the dyestuff component which is not diazotized. The expression covers the group better than "naphthols" since many manufacturers have other names for the corresponding products.

continuously offered to the consumer. The range of shades, restricted up to this time to a few colors, was expanded by the addition of browns, blues, violet, and even black and green azo dyestuffs. The invention of these types had the effect of over-throwing existing procedures; new methods replaced the accepted standards, dyestuffs demanding the greatest sale were thrust aside. The new products were soon indispensable to the colorists of the whole world, because of their brilliance and their fastness, and last but not least, their relatively low price.

The azo dyestuffs were eagerly adopted in printing as well as in dyeing. But the ingenuity of the dyestuff chemists did not stop here. After the destructions of war time, a new period of creative research began, toward finding easier and speedier application methods. The first step in the trend toward simplification was the development of the Rapid Fast Colors. The fabrication of these colors was based on an old method of Badische A.S.F. of 1893 which had failed when applied to β-naphthol. Further patient and scientific research culminated in the achievement of the Rapidogen dyestuffs which were put on the market by the I.G. in 1931. They are stable mixtures of the diazoamino intermediates with sodium salts of the 2,3-oxynaphthoic acid anilides, and are developed by ageing in steam containing acetic acid vapors. Thus a single operation substitutes the two steps of impregnation of the coupling agent and developing with the diazotized base.

It could be foreseen that the Rapidogens would have a great success. Their adoption became general overnight. The reasons for their success lie in their brightness and fastness, and the large range of colors of this class, which have lately been strengthened by addition of new yellow, brown and navy shades, and furthermore, because they can be readily printed alongside dyestuffs of other classes, such as Chromes, Vats and Indigosols.

The introduction of these dyestuffs into general practice led to new methods and styles, and stimulated further research in the laboratories of the dyestuff factories. Some of these ideas, which were transformed into useful processes, will be discussed.

DYEINGS AND PRINTS BASED ON IMPREGNATION

Coupling Components (Naphthols)

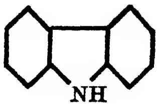
The coupling agents used for producing insoluble azo dyestuffs on the fiber can be divided into five groups.

(1) α- and β-Naphthol and their derivatives, such as aminonaphthols, naphthocetols, etc.

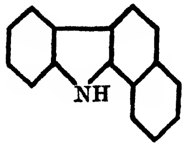
(2) Derivatives of oxynaphthoic acid, especially the anilides of 2,3-oxynaphthoic acid, which constitute the Naphthol AS series.

(3) Complex components of the "AS" series, derived from *o*-oxyanthracene carboxylic acid (Naphthol AS-GR), from carbazole or diphenylimine

(Naphthol AS-LB), and from benzocarbazole (Naphthols AS-SR and AS-SG):



Carbazole

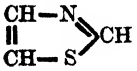


Benzocarbazole

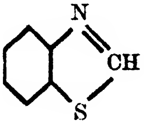
(4) Components for production of yellow azo dyestuffs.

(a) Derivatives of diphenyl bases, diacetodiacetyl compounds (Naphthol AS-G).

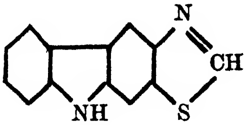
(b) Thiazole and carbazothiazole compounds (Naphthol AS-L4G).



Thiazole



Benzothiazole



Carbazothiazole

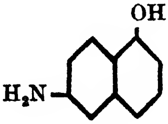
(5) Coupling components, not of naphtholic character, but capable of forming insoluble dyes with diazo compounds. The dye substances Nigrophor, Nigrogene, Vesuvine and Chrysoidine belong to this group.

α- and β-Naphthol and Their Derivatives. For more than twenty years, and until about 1912, β-naphthol was used almost exclusively as a coupling agent, but it had many disadvantages. The insoluble azo dyestuffs prepared from it lacked good all-round fastness (fastness to light, chlorine, soaping and crocking). The sodium β-naphtholate solution possessed poor stability, the prepare gave difficulty in drying and the tendency of the naphtholate to be oxidized easily had the effect of giving the fabrics a brownish shade. Dyeing with the β-naphthol "ice colors" required special precautionary measures, such as the necessity of developing immediately after impregnation, which is unnecessary when using the Naphthols AS. In spite of these drawbacks, the quantity of β-naphthol used was high, owing to its low price, and continued to remain high in England and France for manufacturing textiles for the colonies, in Eastern Europe for the Asiatic market, and for home consumption, even after the introduction of the Naphthol AS series.

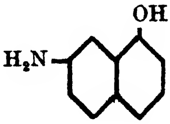
α-Naphthol was probably not used alone because the shades produced from it are dull and of poor fastness. However, it was of some use for blending with β-naphthol in order to make the shades deeper, and for imparting a brownish tint. It was used, for example, as an addition of 2 to 3 gm per liter to the usual β-naphthol solutions.

Another product for altering the shade of the β-naphthol dyeings was 2-naphthol-7-sulfonic acid (F-acid) sold by Cassella under the name Nuanciersalz. When used together with β-naphthol as prepare for *p*-nitraniline red, it served to produce a bluer red. Naphthol R (MLB) is a prepared mixture of 90 parts of β-naphthol and 10 parts of F-acid. Similar products have been marketed by Bayer and Cassella under the names Naphthol AR and β-Naphthol RC, and by Kuhlmann as Naphthol NB (*G.P. 181,721*—Cassella; compare also Rittermann and Felli, *Bull. Mulh.*, **1907**, 142).

The aminonaphthols have been used to a limited degree for production of black with *p*-nitraniline in printing. For this purpose the Naphthols BD and 3B were used.



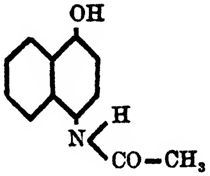
Naphthol BD



Naphthol 3B

The Dosne process (*Bull. Mulh.*, **1897**, 408; *Rev. Gen. Mat. Col.*, **1898**, 113) was based on impregnation with a mixture of β-naphthol and aminonaphthol, and aftertreating with a solution of diazotized *p*-nitraniline. A uniform puce brown was so obtained.

The naphthocetols, invented by O. Witt, are acetyl or benzoyl derivatives of 4-amino-α-naphthol (*G.P. 93,312*). They were intended as substitutes for β-naphthol but they attained no commercial importance. The method of application consisted of the usual impregnation, drying and treatment with diazo solution. The constitution of a naphthocetol is



The most important combination shades produced with β-naphthol are the following:

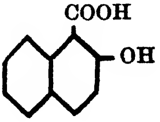
β-naphthol + *p*-nitraniline	red (Ullrich, v. Gallois, H. Koechlin, 1889)
β-naphthol + *p*-nitroanisidine	bluish red (*G.P. 98,637*, 1897)
β-naphthol + *p*-nitro-*o*-toluidine	orange (M.L.B., 1904)
β-naphthol + *m*-nitro-*p*-toluidine	red (Badische A.S.F., 1908)
β-naphthol + *o*-nitraniline or *p*-nitraniline	orange
β-naphthol + *m*-nitroanisidine	orange
β-naphthol + α-naphthylamine	bordeaux (*G.P. 81,039, 94,280*)
β-naphthol + chloranisidine	bright orange-scarlet
β-naphthol + dianisidine	violet blue (F. Storck, 1893)
Also aftertreated with copper salts for light-fastness	blue

Other diazo compounds, less generally used, are the following:

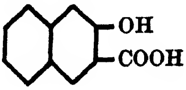
β-naphthylamine	garnet
tolidine, benzidine, or *m*-nitrobenzidine	puce brown
aminoazobenzol or toluol	garnet
o-nitro-*p*-phenetidine (Blue-Red Base of M.L.B.)	bluish pink
Azo Pink BB (of M.L.B.), a benzyl ether of aminocresylol	bright pink
diaminodiphenylamine (Azophor Black DP[*])	black

(Compare Georgievics and Haller, "Handbuch des Zeugdrucks", p. 658 ff.)

Coupling Components Derived from Oxynaphthoic Acid. Two oxynaphthoic acids were studied for the production of azo dyestuffs.



2-Oxy-1-naphthoic acid
(M.p. 158°C)



2-Oxy-3-naphthoic acid
(M.p. 216°C)

The compound 2-oxy-1-naphthoic acid has poor stability. It is hydrolyzed by boiling water into β-naphthol and CO_2. The carboxylic group is detached from the nucleus by diazo compounds. For this reason the same final products are obtained by combining this acid with diazotized bases as β-naphthol. (Battegay, *G.P. 238,841;* Bayer, *Rev. Gen. Mat. Col.*, **1914,** 293; *Bull. Mulh.*, **1914;** Schmidt, *Ber.*, **1911,** 462; *Rev. Gen. Mat. Col.*, **1913,** 70.)

The 2-oxy-3-naphthoic acid on the other hand, is a very stable compound. It is soluble in alcohol and glacial acetic acid. By boiling with bisulfite, β-naphthol is formed. This compound is manufactured by the reaction of carbon dioxide on sodium β-naphtholate at 230 to 240°C. At 130°C, the first stage, an addition compound of β-naphthol and sodium carbonate, is formed. This is transformed into 2-oxy-1-naphthoic acid, which by molecular rearrangement at 230 to 240°C yields 2-oxy-3-naphthoic acid. (Schwenk, *Chem. Ztg.*, **53,** 297; *U.S.P. 1,700,546; G.P. 485,274* and *423,034; U.S.P. 1,503,984*—National; *U.S.P. 1,450,990* and *1,648,839*—Du Pont.)

This 2,3-oxynaphthoic acid, more commonly called β-oxynaphthoic acid, was first used by Fischesser and Pokorny to produce a dianisidine blue which was fast to perspiration (*F.P. 212,063; Bull. Mulh.*, **1891,** 216 and 625). For the same purpose, M.L.B. in Höchst offered Naphthol D, which was a mixture of β-naphthol, 2,3-oxynaphthoic acid and 2-naphthol-7-sulfonic acid. It can be noted at this point that Pleschkow's research revealed that the dull red shade obtained by printing diazo-*p*-nitraniline on 2,3-oxynaphthoic acid prepare could be changed to a very bright red by treatment with barium chloride followed by steaming. Kielbasinski

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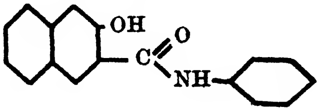
[*] According to Schultz, "Farbstofftabellen," Azophor Black DP is a mixture of tetrazodianisole with tetrazobenzidine and diazotized *m*-nitraniline (*G.P. 80,409, 83,963*).

disclosed that blue-red combinations were manufactured by printing diazotized dianisidine and *p*-nitraniline with additions of barium chloride on 2,3-oxynaphthoic acid prepare as early as 1906 by Bukowiecki, chemist at Poluchin's in Russia (*Z. f. Frb. Ind.*, **1912,** 97, 128, 185; *Rev. Gen. Mat. Col.*, **1913,** 70–73; *Frb. Ztg.*, **1912,** 241, 417; Kielbasinski, *Mell.*, **1926,** 611).

These combinations are of interest today in showing the modest beginnings of this form of dyeing and printing, and as a comparison with the much more important derivative of β-oxynaphthoic acid manufactured in 1912 by Griesheim-Elektron under the name Naphthol AS.* For other trade names of this product, see Table 5, page 350.



(M.p. 243°C)

2,3-Oxynaphthoic acid anilide was made in 1892 by Schöpff and described in *Ber.*, **#25,** 2744 (*G.P. 256,999, 261,594; Frdl.*, **1912–14,** XI, 462–6).

It was first recommended in dyeing by Badische A.S.F. for developing diazotized dyeings such as Primuline, but it was at the instigation of Griesheim-Elektron that it was first applied in dyeing and printing. The azo dyes produced with this naphthol compound have many advantages: the fastness to light and washing is considerably improved, the depth and brightness of color is enhanced, and the blue produced with dianisidine is not only deeper and brighter, but faster to acids, perspiration and light than corresponding β-naphthol couplings.

2,3-Oxynaphthoic acid anilide is a pale-grey powder, sparingly soluble

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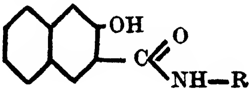
* References:

Kunert and Acker, "Naphtol AS and BS," *Frb. Ztg.*, **1916,** 49, 66, 86; Kunert, *Frb. Ztg.*, **1914,** 175, 337.
Dr. Rath, "Über Entwicklungsfarbstoffe," *Mell.*, **1922,** 367, 388.
F. Kunert, "Neue Eisfarben mittels Naphtol AS," *Rev. Gen. Mat. Col.*, **1912,** 255.
Battegay—Langjahr—Rettig, *Chimie et Industrie*, Mar., **1924.**
Cain and Thorpe, "Synthetic Dyestuffs," 7th Ed., p. 126.
Rowe and Levin, *J. Soc. Dy. & Col.*, **1921,** 404; **1924,** 218; **1930,** 82, 227; **1935,** 287; **1938,** 422.
Lomanowitsch, *Frb. Ztg.*, **1912,** 391; *Rev. Gen. Mat. Col.*, **1914,** 154.
Scholl, *Mell.*, **1935,** #16, 444, 515.
Schober, *Mell.*, **1925,** #6, 499.
Rittner and Gmelin, *Mell.*, **1927,** #8, 530.
Schwen, *Mell.*, **1928,** #9, 673.
Ziersch, *Mell.*, **1929,** #10, 56.
Lederer, *Mell.*, **1931,** #12, 112, 461.
Christ, *Mell.*, **1931,** #12 ,192; **1932,** #13, 24, 68, 426; **1933,** #14, 18; **1934,** #15, 18.
Mecheels, *Mell.*, **1931,** #12, 581.
Krostewitz, *Mell.*, **1931,** #12, 584.
Schneevoigt, *Mell.*, **1933,** #14, 36.
Rath, *J. Soc. Dy. & Col.*, **1923.** 334.

in alcohol and benzol, but readily soluble in caustic soda, giving a yellow, fluorescent solution. It is obtained by direct condensation of 2,3-oxynaphthoic acid and aniline at elevated temperatures in the presence of a catalyst such as $POCl_3$ or PCl_3. The acid is dissolved in toluol, then the aniline and catalyst are added, and the mixture warmed at 80 to 90°C for several hours. The yield of anilide is about 95% of theory. Dimethylaniline can be used in place of toluol (Rohner, *S.P. 111,922, 108,072*) or simply an excess of aniline (M.L.B., *G.P. 294,799*). Other methods depend on the reaction of the chloride, anhydride or an ester of 2,3-oxynaphthoic acid on aniline or other amine (*Rev. Gen. Mat. Col.*, **1933,** 161).

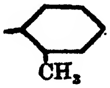
Naphthol AS is particularly interesting for the production of an improved dianisidine blue. With β-naphthol, dianisidine yields a violet shade, changed by application of copper salts to a blue, fast to light and washing, but not to acids. For this reason, the style was restricted. An improvement was made in the use of Naphthol D, but upon the advent of Naphthol AS, the fastness and brightness of the blue coupling was generally satisfactory. It will be seen how further developments in the Variamine Blues and in Fast Blue BB and RR, which appeared fifteen years later, greatly enhanced the beauty and practicability of the Naphthol AS blues.

Soon after the introduction of the anilide, other arylides of 2,3-oxynaphthoic acid were produced, increasing the range of Naphthols, and shades obtainable with them. The general formula for these arylides is

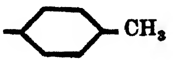


wherein R denotes the substituted aryl radical, as follows:

Anilide = *Naphthol AS*

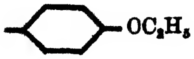


o-Toluidide = *Naphthol AS-D*

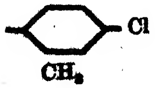


p-Toluidide = *Cibanaphthol RT*

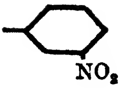
p-Anisidide = *Naphthol AS-RL*



p-Phenetidide = *Cibanaphthol RPH*

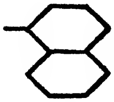


4-Chloro-o-toluidide = *Naphthol AS-TR*

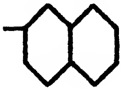


m-Nitranilide = Naphthol AS-BS

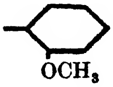
p-Nitranilide = Naphthol AS-AN



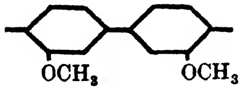
α-Naphthalide = Naphthol AS-BO



β-Naphthalide = Naphthol AS-SW

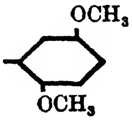


o-Anisidide = Naphthol AS-OL

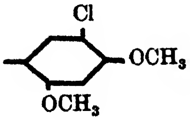


Dianisidide = Naphthol AS-BR

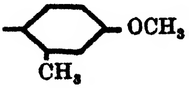
p-Chloroanilide = Naphthol AS-E



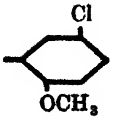
2,5-Dimethoxyanilide = Naphthol AS-BG



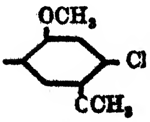
4,6-Dimethoxy-3-chloroanilide = Naphthol AS-ITR



p-Methoxy-o-toluidide = Naphthol AS-LT



5-Chloro-2-methoxyanilide = Naphthazol NEL

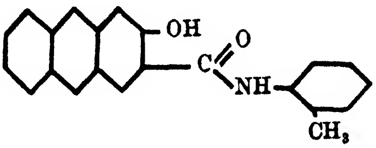


2,5-Dimethoxy-4-chloroanilide = Naphthol AS-LC

The importance of the Naphthol AS series for production of an abundant range of very bright shades was reviewed in a report by Dr. M. Bader to the Congress of the A.C.I.T. in Brussels on September 21, 1935 and again to the Swiss Section of the I.V.C.C. on Dec. 1, 1935 (*Bull. Fed.*, **I,** 451). It was brought out that these colors rival the vat colors in fastness, in many cases equalling the "I" fastness of the anthraquinoid vats.

The work of E. Sack and Niederhauser concerning the naphthols and their combinations with diazo compounds may be referred to. A report of this work was published in 1933 in the yearbook of the Textile Institute of Mulhouse. An excellent study has been published on this subject by G. Martin in *Rev. Gen. Mat. Col.*, **1934,** 169, and in the monographs of the *Rev. Chim. Ind.*, **II** (1934). An article, written by Predelli in the *Boll. d'Assn. Ital. Chem. Tess. e Coll.*, **1934,** # 7–8, 749, and a treatise concerning the Naphthols AS, published in *J. Soc. Dy. & Col.*, July, **1934,** 204, describing the constitution of these compounds and their application, should also be mentioned.

Coupling Components Derived from Anthracene, Carbazole and Benzocarbazole. The introduction of arylides of anthracene oxycarboxylic acid widened the scope of the azo dyestuffs to include green, brown and black shades (*Rev. Chem. Ind.*, **1932,** 182; Dr. Kramer, *Tiba*, **1931,** 743). For example, Naphthol AS-GR produces a green, not very bright, but fairly fast, by combining with diazotized Fast Blue Base BB. Naphthol AS-GR is (*F.P. 724,123, G.P. 549,983*—I.G.—1930):



It is therefore similar to Naphthol AS-D, except that the basic nucleus is anthracene instead of naphthalene. The effect of the change is to produce yellower couplings.

By further enlarging the molecule of Naphthol AS, for example, by forming the benzocarbazoles,[*] further intensification of the color shade results. Two of the Naphthols, AS-SR and AS-SG belong to this type. They produce dark brown and black by combination with some bases, for instance with *p*-nitroanisidine (Fast Red Base B)

Naphthol AS-SR is the arylid of benzocarbazole oxycarboxylic acid.

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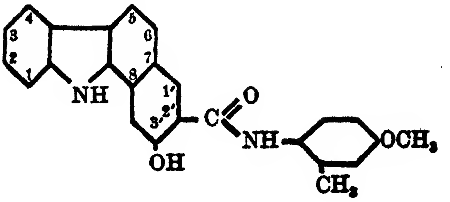
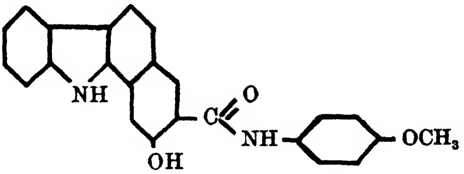
[*] Naphthols of the carbazole series: *G.P.446,221*—I.G.; *Frdl.*, # 15, 557; *G.P. 504,127*—I.G.; *Frdl.*, # 17, 984; *F.P. 699,339; B.P. 347,113; Chem. Zent.*, **1932,** # 1, 2100; *G.P. 576,966*—I.G.; *Chem. Ztg.*, **1933,** # 2, 618.



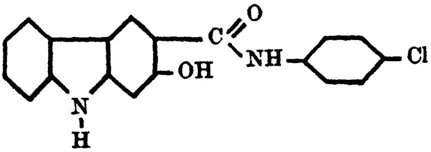
It can also be considered a pyrrol derivative, *i.e.*, a naphthophenopyrrol-3′-oxy-2′-carboxylic acid.

Naphthol AS-SG



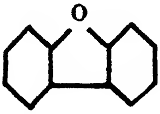
is the *p*-anisidide of benzocarbazole-3′-oxy-2′-carboxylic acid (*G.P. 539,116*—I.G.)

Naphthol AS-LB

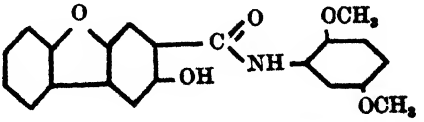


is the *p*-chloranilide of oxycarbazole carboxylic acid, giving dark brown shades (*G.P. 535,670*—I.G., 1930).

If instead of the carbazole ring, diphenylene oxide



is used as a nucleus, Naphthol AS-BT can be obtained as its derivative. It is the 2,5-dimethoxyanilide of 6-oxydiphenylene oxide-7-carboxylic acid.



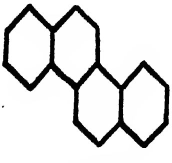
Derivatives of Naphthol AS-LB substituted in the imino group have been prepared, such as the *p*-chloranilide of methoxycarbazole carboxylic

acid, producing fast brown shades with diazotized nitranilines or chloranilines (*F.P. 734,845*—I.G.).

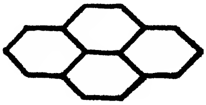
Whereas β-naphthol adheres only mechanically to the fiber when padded on, the Naphthol AS compounds are substantive, and are absorbed by the fiber. This property of the Naphthols AS is a function of their structure, and depends particularly on their large molecular size. Dr. E. Feber described in *Mell.*, **1942,** 598, the preparation and application of an interesting compound. He made β-oxynaphthoic acid anthraquinonylamide, and described its dyeing characteristics. This compound consists of a naphthol (β-oxynaphthoic acid) linked with a vat color (aminoanthraquinone). It therefore combines the properties of a normal Naphthol AS coupling component, with those of a vat color, in this case colorless. It was expected that because of its great molecular size, the compound would have a strong affinity for the fiber, and in that way promote a high degree of fastness to crocking and kier-boiling.

The application of this product differs substantially from the usual methods. Bottoming was carried out in a vat of the compound. A 5-gm piece of cotton was dyed with 0.6 gm of coupling agent, vatted with 1 to 2 cc of NaOH 30° Bé and hydrosulfite in a liquor ratio of 20:1 for 40 to 50 minutes at 50 to 60°C. The sample was wrung out, aired, soured off and rinsed. Under these conditions the absorption of the coupling compound reached 60 to 65%. The substantivity was therefore greater than Naphthol AS-SG which is considered high in this respect. It was expected that dyeings of this new component with diazotized bases, for example Fast Blue Base BB, Fast Red Base B, GL, Fast Black Base G, etc., would exhibit particularly good fastness to boiling with soap, and this was found correct. This new method has not advanced, however, beyond the experimental stage.

Arylamides of 2-oxy-3-naphthoic acid can be prepared by condensing β-oxynaphthoic acid, or its acid chloride, with aminopyrene or aminochrysene (as 3,8-diaminopyrene, 3-aminopyrene, or 2,8-diaminopyrene) in the presence of pyridine.



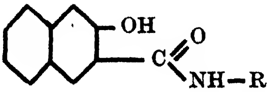
Chrysene



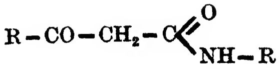
Pyrene

The condensates have a strong affinity for the cellulosic fibers. They combine with diazotized arylamines to produce red, brown, violet, navy and black dyestuffs of excellent fastness properties (*B.P. 515,381*—Ciba).

Naphthol AS Compounds for Production of Yellow Shades. For comparison, the two principal types of anilides are:

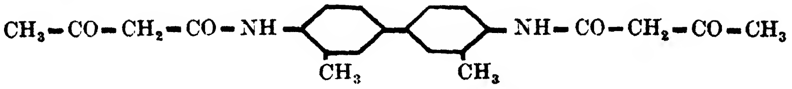


o-Oxyarylanilide

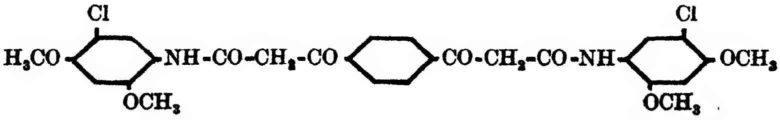


Acylacetic acid anilide

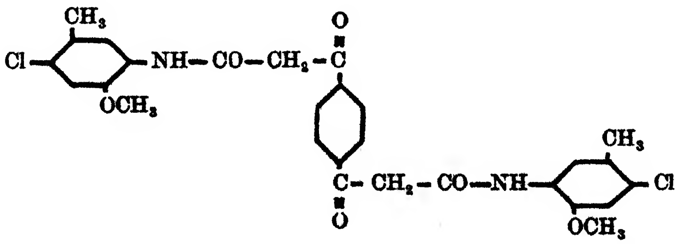
The first type has been developed to manifold extent, as noted on page 218. The second type, derived from acetoacetic acid, was first suggested by M.L.B. as an agent to develop dyeings of diazotized Primuline, to improve the fastness of the Primuline and as a component in the manufacture of yellow color lakes. While the derivatives of *o*-oxyarylanilide produce shades ranging from orange to blue, the compounds formed with acylacetic acid are restricted to yellow dyes. The particular derivatives of acylacetic acid which are important are those of diphenyl bases. The chemists Laska and Zitscher of Griesheim-Elektron discovered Naphthol AS-G (*G.P. 386,054*).



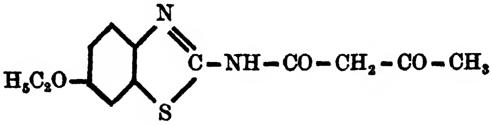
This compound is formed by warming tolidine and acetoacetic acid ester in a neutral medium. Naphthol AS-G was the only representative of the yellow group for ten years. Its main disadvantage lies in the fact that its azo dyestuffs are not dischargeable with sulfoxylate formaldehyde. In 1931 two new naphthols were added, Naphthol AS-LG and AS-L3G. Combinations of these types with diazotized bases yield very fast greenish yellow shades, but the drawback of poor dischargeability is not overcome here. The first, Naphthol AS-LG is the dimethoxychlorodianilide of terephthalyldiacetic acid (*F.P. 716,871*—I.G., 1930).



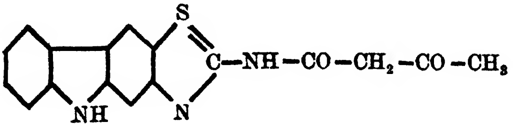
Naphthol AS-L3G corresponds to the formula:



Finally, yellows which can be discharged are made possible by the new Naphthol AS-L4G, which is 2-acetoacetyl amine-6-ethoxybenzothiazole, and corresponds to the formula (*G.P. 603,623*—1933; *600,101*—1933, I.G.):

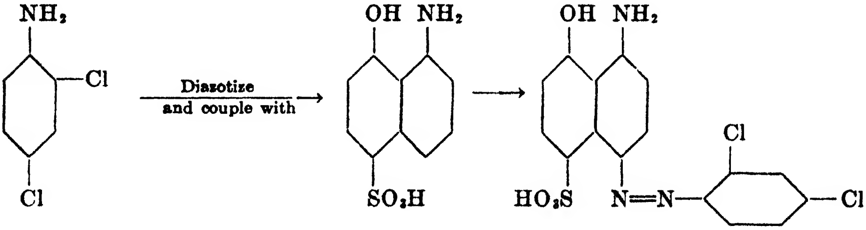


According to *G.P. 611,882*, other naphthols can be formed by substituting the amides of amidobenzothiazoles and the acetoacetic esters with other derivatives, such as benzoyl acetic acid esters, aminonaphthothiazoles and carbazothiazoles, for instance (*G.P. 612,072*—1933):



All of these derivatives form yellow dyes which can be discharged with sulfoxylate formaldehyde.

Coupling Components Other Than Naphthols. Azo dyes have been produced on the fiber from intermediates which do not belong to the classifications already detailed. Of such, the earliest is probably Nigrophor, which was discovered by Schraube in 1896 (*G.P. 116,176*) and is made by the action of diazotized 2,4-dichloroaniline on 1-amino-8-naphthol-5-sulfonic acid.



By coupling diazotized p-nitraniline or α-naphthylamine with Nigrophor, a brownish black, fast to soaping, is produced, which can be discharged with Hydrosulfite NF.

Nigrogene B (Badische A.S.F.) is a condensate of acetone and 1,8-diaminonaphthalene-4-sulfonic acid, which yields a black dye by combination with diazotized p-nitraniline (Manual 220a of Badische A.S.F., 1921, p. 291).

Instead of β-naphthol, other products have been used in the past, such as catechu and tanning agents. Bistre and pure brown shades can be dyed with them (Bedford, 1880; Kalle, 1890; Kayser). These dyes were used in Russia during the first World War (1914–18) to replace β-naphthol which was not available. A garnet shade similar to that prepared from α-naphthylamine could be obtained, for example, by preparing the fabrics with a solution of catechu and acetic acid to which some Crystal Fuchsine had been added and developing after drying with a solution of diazotized *p*-nitraniline.

In 1899, F. Binder invented a brown on the basis of Chrysoidine (*Rev. Gen. Mat. Col.*, **1904,** 199, 203; *Bull. Mulh.*, **1905,** 54). This style was a great success and is still manufactured in some countries. The procedure is as follows. The cloth is impregnated with Chrysoidine, Brown Salt R or G, Bismarck Brown, Manchester Brown, Vesuvine or Bruns pour Foulardage N or NJ (Kuhlmann) or *m*-phenylenediamine or *m*-toluylenediamine. After preparation, the cloth is developed in diazobenzol or the diazo compounds of *m*- or *p*-nitraniline. These combinations produce a bistre brown. *m*-Nitrodiazobenzol gives a coffee brown with the same coupling agents.

The material is padded on the mangle with a solution of Brown Salt G or R to which acetic acid has been added and then treated with a solution of diazotized *p*-nitraniline, skyed, rinsed and dried.

Finally the dark brown shade obtained by cross-dyeing a *p*-nitraniline red with a dilute aniline black solution should be mentioned. This style was developed by Schmid (*Rev. Gen. Mat. Col.*, **1898,** 111; *Bull. Mulh.*, **1897,** 411). By using a sodium acetate resist under the aniline black pad the Para red of the ground forms a contrasting print. This style was manufactured in Russia in large quantities.

There are more than thirty coupling components which are available today. The different types of old and new products which can be used are compiled in Table 5 on page 348.

Naphtholation. The impregnating bath generally contains caustic soda, either soap or a fatty compound, and a protective colloid (*Mell.*, **1929,** 111; Dr. Rath, Report to the 14th Congress of the I.V.C.C., Budapest; *Mell.*, **1930,** 32; **1931,** 585; Dr. Kramer, *Tiba*, **1931,** 741).

The soap or fatty compound, as sulforicinoleate, is added for a twofold purpose: to improve penetration of the fiber and also to brighten the shade. Para red, for example, turns out bluer with such addition. It has been found that the ammonium salt of sulforicinoleic acid has a better effect than the sodium salt. The fastness to crocking is improved by the emulsifying action of these soaps on the superficially formed color lakes. Haller showed that the bluer shade of Para red obtained when fatty products are added to the β-naphthol prepare is caused by mutual absorption by the fiber of dyestuff and dispersed fatty acids (Lehne, *Frb. Ztg.*, **1915,** 306).

As a rule, soaps are used which are obtained by the partial neutralization of oxy acids or ricinoleic acid. A product of this type was put on the market by Höchst under the name of Paraseife N (Para Soap N).

A special soap, based on ricinoleic acid, was developed by Dr. Wojcik, and recommended at that time by Cassella (Erban, "Theory and Practice of Yarn Dyeing with Azo Compounds," Berlin, 1906; Cassella, "Handbook," 1923, p. 170).

Sazanoff suggested the use of naphthenic acid sulfonates instead of the sulforicinoleates (*Mell.*, **1927,** 275). Besides the ordinary sulforicinoleates, special products which are particularly stable to lime salts were brought out. These are complex sulfonic acid esters, as polyoxysulfonic acid derivatives. The polysulfo products of Juillard, the Monopole soaps of Stockhausen, the Universal oils of Schmitz, etc. belong to this class. Similar products are offered by almost all the textile specialty manufacturers.

Investigation of dyeings of several naphthols was carried out by Nabar, Barve, Pastel and Desai (*Proc. Ind. Acad. Sci.*, **1939,** 10A, 344–358). They determined the concentration of Naphthols AS-G, AS, AS-TR, AS-BO and AS-SW before and after impregnation by volumetric analysis, and found that absorption decreased with increased amounts of alkali, gum tragacanth or agar-agar in the impregnating liquor. If the naphthol solution was mildly alkaline, or contained sodium chloride or sodium phosphate, increased absorption resulted, but the absorption increased to a maximum value, then decreased. The absorption decreased at increasing temperatures, especially in the case of the more substantive naphthols.

A process for dyeing a bluish *p*-nitraniline red has been described by Dr. Bochter of Landshoff and Meyer (*Appretur-Ztg.*, **1920,** #10, 60). A very small amount of a substantive dyestuff which combines with diazonitraniline, for instance 0.01% Diamine Nitrazol Violet or Parazol Violet, is added to the solution of β-naphthol. The presence of this dyestuff is claimed to aid the dispersion of the resulting azo dyestuff.

Dissolving the Naphthols. β-naphthol is dissolved with an equal weight of caustic soda 38° Bé with water at elevated temperature. To the solution a sulforicinoleate soap is added. An excess of caustic soda should be avoided, as it promotes oxidation of the naphthol, causing brown discoloration of the impregnation in a short time.

The Naphthol AS compounds can be dissolved by two methods: by heating, or by cold dissolving (*Dyer*, **1936,** 519; *Rev. Gen. Mat. Col.*, **1937,** 371).

In dissolving the naphthols by heating, the naphthol is pasted with caustic soda in the presence of a protective colloid. The naphtholate is formed and dissolved by adding hot water. To obtain a clear solution the liquid should be boiled.

To dissolve the naphthols at room temperature, caustic soda 38° Bé and denatured alcohol are added to the naphthol powder (*F.P. 679,411*).

Solution takes place immediately on adding water. ("Manual of Cotton Dyeing," I.G., 1923, p. 468–504.)

The naphthols are not easily soluble, and are sensitive to lime salts. If solutions are made with hard water, it is possible that naphtholates of the alkaline earths can precipitate out. Various agents have been proposed for preventing the precipitation of these naphtholates, and of these Eunaphthol AS (G.D.C.) and Sapidan CAN (A. Th. Böhme) can be mentioned. Also recommended is Acorit (Böhme F.C.) according to *F.P. 739,066* and *U.S.P. 2,026,817*, which is a fatty alcohol sulfate like Duponol.

Such agents as a rule are employed when preparing the liquors by the hot solution method. The ratio of Eunaphthol to naphthol should be 1:1 or 2:1. When impregnating for hot-flue drying, the addition of Monopole Brilliant Oil or Laventine HW is recommended, the latter being especially efficient in dyeing Variamine Blue.

The addition of products like Calgon, or Trilon A or B, Quadrafos, etc., which have the property of preventing lime precipitates, or of redissolving lime naphtholates, has merited advantages.

The fastness to crocking depends to a large extent on the complete solution of the naphthol. It is therefore important to select an appropriate dispersing and solubilizing auxiliary. Any agent so used must be stable to alkalis and hard water metals. Satisfactory dispersing agents may be selected from the Dekols or Nekals, which have given good results in yarn dyeing in machines as well as on the foulard for piece goods. Quantities recommended are 4 to 5 gm of Dekol per liter or 1 gm of Nekal BX per liter.

Solunaptols. The Solunaptols, made by John W. Leitch & Co. Ltd., Milnsbridge Chemical Works, Huddersfield, have been reported on by G. A. Wallwork in *J. Soc. Dy. & Col.*, **1939**, #55, 477–480. These interesting products are not simply sodium salts of the Naphthol AS series but fine powders obtained by treating soluble naphtholates with boiling water. Impregnating liquors can be prepared from Solunaptols in a simple manner. They have better penetrating properties than the usual naphthol baths, and are stable to hard water conditions. The Solunaptols contain a certain amount of free alkali, but can be used for wool as well as cotton and rayons. When impregnating acetate cellulose it has been found that best yields are obtained with naphtholate solutions with lowest excess alkali at elevated temperatures, so that these Solunaptols should prove superior to the usual naphthols on this fiber.

Naphthol solutions possess the property of fluorescing in ultraviolet light (black light). This strong fluorescent reaction is utilized for detecting printing faults during the application printing of Rapid Fast and Rapidogen dyestuffs. Most of the naphthols exhibit a greenish-yellow fluorescence, but Naphthol AS-LG shows a dull yellow, AS-L3G a bright bluish green, AS-BS an olive green, AS-GR a reddish orange, AS-L4G a reddish blue and AS-LB a blue. M. Déribéré determined the pH values at which this characteristic fluorescence is strongest. The optimum range is between pH 8.2 and 8.6, or between pH 9.5 and 10.0 (Déribéré, "Application des Naphtols particuliers comme indicateurs fluorescents," *Ann. Chim. Analytique*, Nov. **1936,** #11). Other references pertinent to this question are: D. A. Derret-Smith, "Portable Lamp for Detecting Fluorescence," *J. Text. Inst.*, May, **1937**; Mecheels, *Mell.*, **1931,** 581; Déribéré, "La Fluorescence des Naphtols," *Tiba*, **1937,** 495; *Rev. Gen. Mat. Col.*, **1937,** 388.

Stability of the Naphthol Solutions. The solutions of β-naphthol are unstable and soon become turbid on standing. Lauber and Caberti tried to remedy this defect by adding glycerin and tartar emetic (*G.P. 79,802*). This was the Naphthol LC of Bayer Co. A glycerin-tartar emetic solution is prepared by dissolving antimony oxide in caustic soda and adding glycerin.

Sieber obtained stable solutions of β-naphthol, at the same time preventing a brown discoloration of the impregnated goods by replacing the sodium naphtholate solution with the corresponding potassium naphtholate (*Mell.*, **1926,** 616, "The Use of Potassium Compounds in Printing," paper read before 3rd Congress of the I.V.C.C., Dresden, 1926). By adding potassium sulforicinoleate to the β-naphthol solution, it was possible to obtain a *p*-nitraniline red of a bluer cast. Sieber recommended the following impregnating liquor.

I. 2000 gm β-naphthol	II. 4000 gm ricinoleic acid
1200 gm potash	1200 gm potash
20 l hot water	20 l hot water

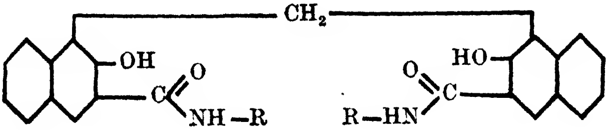
Mix I and II and bring to 100 l volume. The liquor is kept at 40°C, because it is at this temperature that clarity of the solution is maintained. The impregnated goods can be stored for weeks without visible brown discoloration.

Stability of the prepare on the goods can be improved by additions of glycerin, tartar emetic, glucose, and Rongalite C to the padding liquor, for example:

1.2 gm Rongalite C
48.0 gm tartar emetic
20–30 gm glycerin
20–50 gm gum trag.
per liter

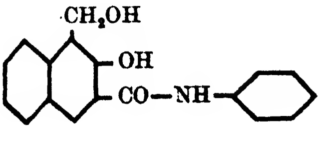
The solutions of the Naphthol AS products are generally more stable than the β-naphthol solution, but they also become turbid on standing. The decomposition starts with a negligible cloudy formation which after some time forms a flocculent precipitate. When baths are used wherein decomposition has begun, dyeings are obtained which exhibit low color yield and poor crocking fastness. For this reason, much work has been done to obtain clear Naphthol AS solutions which should not be sensitive to the carbon dioxide of the atmosphere.

The Naphthols AS, that is, the anilides of 2,3-oxynaphthoic acid, had not been in use long when it was discovered that formaldehyde had a remarkable stabilizing effect (*G.P. 279,314*—Griesheim, 1913). It is assumed that a complex substance is formed in which the naphthol molecules are linked with a methylene radical,



forming, for example, the anilide of methylene di-β-oxynaphthoic acid (Brass and Pummerer, *Ber.*, **1928,** #61, 993). The CH₂ group is split off at the moment of coupling, so that the insoluble azo dyes are obtained almost as easily as without the formaldehyde addition (compare Dumas, "Function of Formaldehyde in the Application of Naphthol," *Rev. Gen. Mat. Col.*, **1937,** 449; Mayer, *Z. f. angew. Chem.*, **1923,** 530; Higgins, *J. Soc. Dy. & Col.*, **1927,** 213).

Another explanation of the process was put forth by P. W. Weber in *Z. f. angew. Chem.*, **1937,** 411. He assumed that a methylol derivative is formed, that is, an addition product of formaldehyde with one molecule of the anilide.



When the coupling is completed with the diazo compound, the formaldehyde is released and the azo group takes its place on the naphthol radical. The stabilizing effect of formaldehyde against the carbon dioxide of the air is a recognized advantage, but the method cannot be used for dyeings which are to be discharged, as the whites are adversely affected.

Furthermore, formaldehyde cannot be applied with Naphthol AS-G because the coupling component loses its dye-forming property thereby.

Additions of protective colloids are made to keep the naphtholates in clear solution as long as possible. Glue solutions have been recommended, which, with Naphthol AS-BO, have the property of preventing gelatinizing. Special products have been marketed, either wetting agents or protective colloids, or with properties of both. They are mostly highly sulfonated compounds, sulfated fatty alcohols or phenol-formaldehyde condensates combined with a fatty radical. Such agents, stable to hard water conditions, are Eunaphthol K and ED, Acorit, Intrasol and Prestabit Oil MA, Tibalene NED, Naphtosolvine and others. These products promote the stability of the naphthol solution (see Table 7, page 405). The use of sodium oleyl taurine (Igepon T) is recommended in padding heavy cotton cloth.

Solutions of gum arabic have a stabilizing effect which is superior to that of starch or tragacanth gums (*Mell.*, **1930,** 943; *Tiba*, **1931,** 779). The I.C.I., in *B.P. 362,548*, recommends mixing the naphthols in a dry state with gum arabic, then pasting this mixture with sodium sulforicinoleate, and then dissolving the entire composition in caustic soda. On the other hand, it should be remembered that gum promotes the decomposition of nitrosamine compounds.

According to the following patents (*F.P. 777,860; G.P. 620,322*, I.G.; *U.S.P. 2,030,859; B.P. 444,071*, Gen. Aniline Works), Turkey red oil, trisodium phosphate and cellulose sulfite waste liquor are added to the padding liquor in about the following proportions:

300 parts	Turkey red oil 50%
100 parts	monoethylether of glycol
6 parts	caustic soda 38° Bé
300 parts	cellulose sulfite waste
20 parts	trisodium phosphate
60 parts	sodium butyl naphthalene sulfonate
214 parts	water
1000 parts	

The padding bath is prepared with 15 parts of the above mixture, 10 parts of naphthol and 15 parts of caustic soda 38° Bé per 1000 parts of liquor.

G.P. 524,181 (I.G.) claims that solution of the naphthols is facilitated by the presence of substances having phenolic or enolic characteristics, as an example of which hydrolyzed starch (alkali starch) is mentioned.

To increase stability of the naphthol solutions, *G.P. 560,580* (I.G., 1931) recommends adding heterocyclic water-soluble compounds containing at least three nitrogen atoms. The triazines belong to this class, for instance 1,3-dimethyl-5-oxyhexahydrotriazine, formed by condensing acetaldehyde-ammonia (two parts) with urea (one part). Hexamethylenetetramine can also be used for this purpose.

U.S.P. 2,026,817, *F.P. 739,066* and *Aus. P. 135,670* of Böhme-Fettchemie indicate that the sulfonates of unsaturated fatty alcohols as well as the unsaturated sulfo fatty acids containing a free OH group, aid in dissolving the naphthols. These compounds are obtained by sulfonating the unsaturated fatty alcohols at 0°C, whereby the sulfo group is linked to the double bond and not to the CH_2OH group. Probably Acorit, manufactured by Böhme-Fettchemie and P.C.M.R. in Mulhouse, is covered by this patent.

The sulfonates of wool grease (lanolin, produced according to *G.P. 531,296*) are recommended as aids in dissolving naphthols (*G.P. 535,845*, I.G.—Thauss—Mauthe—Günther). These products are water-soluble, have an acid reaction, and are not precipitated by mineral acids. They are excellent dispersing agents in an alkaline medium and can be applied for dissolving the naphthols.

B.P. 443,638 (I.G.) states that the coupling component can be dispersed in the impregnating liquor in the presence of an organic base, instead of dissolving it in alkalis. This base must be built on a high-molecular aliphatic chain, for example, triethyldodecyl ammonium hydroxide. A strong wetting effect is attained. In similar vein, *G.P. 636,328* (I.G.—Dietrich, 1934) advises high-molecular substituted quaternary bases as additions to the impregnating liquor as well as to the diazo solution. An example is trimethyllauryl ammonium hydroxide. These compounds are stable to acids and to alkaline earths and they are sufficiently basic to maintain the diazotized compound in solution.

The naphtholate solutions readily undergo hydrolysis and since the free naphthol couples only very slowly there is danger of obtaining gradually weaker shades after running some time. To avoid hydrolysis it is essential to dry quickly at elevated temperatures by running the goods through the hot flue immediately after padding (*Mell.*, Mar., **1929**; **1930,** 32; **1931,** 585).

The impregnation is at once sensitive to light, air and acid fumes. The goods will fade quickly and the coupled shades will be weaker and duller (*Mell.*, **1930,** 943; *Tiba*, **1931,** 779). This sensitivity can be reduced by the addition of the sodium salt of nitrobenzene sulfonic acid (Ludigol) or of sodium chromate (*G.P. 614,254*—I.G.). Goods padded with naphtholates to which formaldehyde has been added are less sensitive to the influence of the atmosphere.

The sensitivity of the naphthol-prepared goods has been studied by Moryganow and Rostovtsev (*Report of Inst. for Chem. Tech.*, Iwanowo-Wosnessensk, Russia, **1939,** #2, 96). The sensitivity of the naphthols was determined by exposing the impregnated goods in a moist atmosphere. The sensitivity was found to be comparatively as follows:

Naphthol AS < AS-RL < AS-BS < AS-G

It was further found that the influence of light or pyridine fumes has no relation to the influence of the atmosphere. The addition of formaldehyde has a salutary effect on the sensitivity to the air. The authors explain the action of the air as a reaction with the CO_2 of the air: it combines with the free alkali, promoting hydrolysis of the naphtholate. The free naphthol formed is changed by rearrangement to a tautomeric form, *i.e.*, a ketone derivative, which cannot couple with the diazo compound.

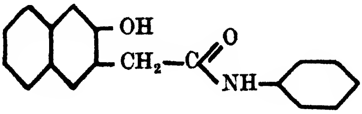
Substantivity of the Naphthols. As distinguished from β-naphthol which has no affinity to the fiber at all, the Naphthol AS compounds have a definite affinity which varies according to their constitution (Scheel; see also *Rev. Gen. Mat. Col.*, **1929,** #33, 270–272).

In padding, the fixation of the naphthol depends on the amount of liquor which is picked up by the fabric, and not on an absorption reaction. The padding bath is not exhausted, so that the depth of shade depends entirely on the concentration of the liquor and the amount picked up by the fabric.

In dye baths, however, the substantivity can be measured (P. Mougeot, *Teintex*, **1943,** 89; Zuber, *Teintex*, **1943**, 91).

The Naphthols AS and AS-D are the least substantive while dye baths containing the most substantive Naphthols, the AS-SG, AS-SR and AS-GR brands, are almost completely exhausted. Other Naphthols may be rated in comparative figures as follows: Naphthol AS, 10%; Naphthol AS-TR, 25%; Naphthol AS-BO, 25%; Naphthol AS-SW, 40%; Naphthol AS-BR, 50%. This substantivity has the effect of conferring the character of a true dyeing process on the padding operation, to such an extent that the padded fabrics can be developed with the diazo solution without intermediate drying.

Krzikalla and Eistert attempted to find a relationship between constitution of the different Naphthol AS compounds and substantivity. They showed that the substantivity decreased considerably by the insertion of a methylene group between the naphthalene and amido radicals, for instance



This compound was termed a "Homonaphthol". It is not any more substantive than ordinary β-naphthol. The same is true for sulfanilides (*Rev. Gen. Mat. Col.*, **1935,** 255).

The substantivity of the naphthols decreases as the temperature increases, and increases at lower temperatures. Naphthol AS-BR is an exception. Its substantivity increases slightly at elevated temperatures. Generally the impregnation is carried out at 30°C, but in dyeing in machines a temperature of 40 to 45°C gives better results, with 45°C the maximum. Higher temperatures cause precipitation of the naphthol solutions which contain formaldehyde. If formaldehyde is omitted, padding can be carried out as high as 90°C, whereby a better penetration can be gained. At the same time, however, the substantivity is decreased. The difference between the concentration of the starting liquor and the feed liquor can be held in this way to a negligible minimum.

Moryganow and Rostovtsev (*Report of Inst. for Chem. Tech.*, Iwanowo-Wosnessensk, Russia, **1939,** 102), studied the influence of various reagents such as caustic alkalis, formaldehyde, alcohols, protective colloids, etc., on the substantivity of the naphthols. It was shown that variations in amounts of alkali, from 4 to 14 molecules per molecule of naphthol, had almost no influence on the substantivity. Sulforicinoleates, and increasing amounts of common salt, have the property of increasing the substantivity, while on the contrary, formaldehyde, gelatin and alcohols decrease it. Finally, the article repeats the recognized fact that the affinity of the naphthols decreases with increased temperatures.

An article by Creslow in the *Dyer*, **1939,** #81, 111 ff, discusses warp dyeing with insoluble azo dyestuffs. Here the problem is to bring about good penetration of the fibers, and at the same time exhaust the bath economically, and as thoroughly as possible, even when using naphthols of different substantivity rates. For these reasons the impregnation is carried out at the boil, as the penetration is highest at that point, and although the substantivity is greatly reduced, the difference between the various brands is more or less equalized, and under these conditions absorption is almost uniform. It is essential that the volume of the impregnating liquor remain constant, and that the goods are extracted as evenly as possible.

Application of Naphthols on Animal Fibers. The application of naphthols on animal fibers is made difficult by the sensitivity of the fibers to alkaline solutions and by the poor fastness to crocking of the dyed material.

*Natural Silk.** Naphthol AS dyeings are indicated where superior fastness is required, particularly for sewing and embroidery threads and for washable articles of clothing. The dyeing procedure is practically the same as in dyeing cotton or rayon. The main operations are impregnation with the alkali naphtholate, developing in the diazo solution, rinsing, soaping and rinsing well.

The naphthol is dissolved by the cold method, using alcohol. A wetting agent and a protective colloid, for example, cellulose sulfite (Protectol) are added. The quantity of alkali is added in a ratio 1:1 or 1:1½ of the weight of naphthol. The silk is protected from the deteriorating action of the alkali by the presence of the Protectol. Moreover, this agent promotes the level-dyeing property of the naphthol.

It should be mentioned that the substantivities of the naphthols to natural silk are different than to the vegetable fibers. Certain azo dyes, for instance the Naphthol AS-G-Fast Red Base RBE combination, are much faster to light on silk than on cotton.

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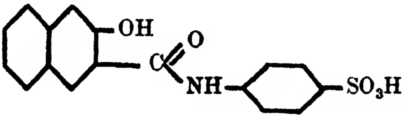
* H. Goerlich, *Mell.*, **1935,** 333–5.

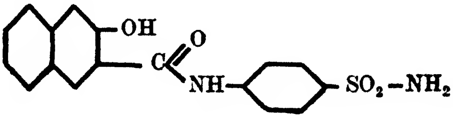
The action of the alkali in attacking the fiber may be at least partly prevented by adding protective agents such as soap, glue or cellulose sulfite liquor (*B.P. 310,758*—Ciba).

Azo dyes of the Naphthol AS series can be applied to silk according to the method of *G.P. 655,633* (I.G., Günther-Alt). The silk is first padded in a solution of an acid amide which is substantive to the silk fiber, for instance the acid salt of a high-molecular substituted aminooxynaphthalene sulfonic acid, and thereafter developed in the diazo solution as usual. A similar process is suggested in *U.S.P. 2,115,136*—I.C.I.: aminosulfanilides of hydroxynaphthoic acid are applied. Solubility is acquired by the amino-substituted sulfo group, but dispersibility in the solution is increased by adding an organic base, for instance, triethanolamine, to the padding liquor.

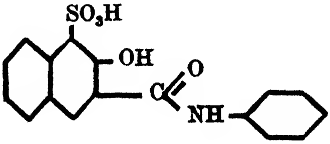
*Wool.** The application of alkaline naphthol solution can be circumvented by the introduction of a solubilizing sulfonic acid group into the constitution of the naphthol, as for example (*G.P. 478,331*—I.G.):



This compound is formed by the reaction of sulfanilic acid and β-oxynaphthoic acid. *B.P. 281,795* (I.C.I.) suggested the application of sulfonamides, produced by the reaction of sulfanilic acid amide on β-oxynaphthoic acid



Finally, the monosulfonic acid of Naphthol AS was recommended for the same purpose (*G.P. 482,944*—I.G.):



The Naphthol AS solutions partake of the nature of colloidal solutions, like those of the direct dyestuffs. It has been suggested to prepare neutral colloidal solutions containing the naphthol arylides in a suitably dispersed

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* Lederer, *Mell.*, **1931**, 112; Kirst, "Naphthol Dyeing on Wool", *Mell.*, **1937**, #18, 739; Rath, *Mell.*, **1928**, #9, 585; *J. Soc. Dy. & Col.*, **1928**, 334; Kayser, *Am. Dyes. Rep.*, **1926**, 638; Clark and Borho, *Am. Dyes. Rep.*, **1926**, 311.

state. The problem is that a decrease in the dispersion causes loss in the fastness to crocking, and that the free naphthol couples at a much slower rate than the alkali naphtholate.

The I.G. proposed an addition of methyl cellulose to the alkaline naphthol solution, followed by neutralization with acetic acid. The addition of a sulfonated lanolin is recommended in *B.P. 307,777* (I.G.) as an efficient dispersing agent. A colloidal solution prepared in this way is stable even under acid conditions.

A method of preparing the naphtholates in the form of dry powders which avoid the necessity of alkali for dissolving was advocated by I.G. in *B.P. 325,563*—1923. The naphtholate can be considered as the salt of a weak acid, so that it is subject to hydrolysis in aqueous solution, but this hydrolysis can be greatly minimized by the addition of a protective agent such as alkali starch. A clear solution is prepared in this way, which can be used on wool without further precaution.

An interesting method of dyeing wool with naphthols is disclosed in *U.S.P. 1,958,307* and *1,964,934*, *B.P. 401,938* and *G.P. 610,315* (Ciba—Landolt, 1933). Any damage to the wool fiber by the naphtholate solution can be avoided by treating the goods after impregnation with a solution which reduces the alkalinity of the impregnation. Such a solution would be made with sodium bicarbonate, magnesium sulfate, or the like, and the protective action can be still further increased by adding a protective colloid such as cellulose sulfite liquor. The woolen material is then coupled with the diazo solution without intermediate drying.

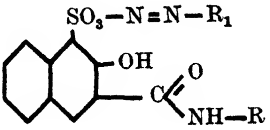
Development of the naphthol without intermediate drying is favorable, according to *F.P. 778,547* (I.G.) provided the surplus liquor is removed by a heavy duty mangle. The impregnating liquor contains the alkali naphtholate, a wetting agent and a protective colloid. Chlorinated wool material is impregnated at 30°C with a solution containing:

5 gm Naphthol AS
10 gm alcohol
2½ gm caustic soda flakes
5 cc water, *added to*
8 gm Protectol II
1 gm Igepon T
4 gm sulfooleic acid methyl anilide
10 gm caustic soda 38°Bé
per liter

After impregnation the material is well-squeezed and without intermediate drying is coupled with the diazo compound, dissolved in water containing 0.5% of 30% solution of Peregal O. Finally the material is scoured with Igepon T and ammonia at 60 to 70°C, rinsed and dried.

The absorption of naphthol solutions by animal fibers is increased by pretreating the material in a boiling solution of alkali thiocyanates (*G.P. 640,260*, I.G.—Kirst, *F.P. 779,541*). A good absorption of wool material is realized by adding common salt to the impregnating bath. The wool is first boiled off and dried, then dyed with a solution as given in the previous paragraph (*F.P. 778,547*), adding common salt gradually over a period of one hour. Thereupon the material is hydroextracted and coupled with a diazo solution containing Peregal O.

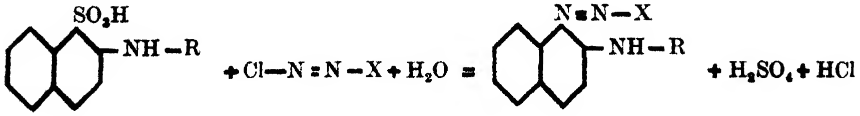
Very fast dyeings can be obtained on wool by applying aryl diazosulfonates (*F.P. 738,795* and *B.P. 385,307*—I.C.I.). These compounds have a suitable affinity for animal fibers under acid conditions. The azo dyestuff is finally produced by the action of acetic acid at 90°C. These diazosulfonates are made by sulfonating Naphthol AS. The HSO_3 group is linked to the C atom in the *alpha* position, and thereby prevents a coupling reaction. In neutral medium the following compound is formed:



R, R_1 = aryl groups

which, by treatment with alkalis, is transformed to the sodium salt of 1-aryl azosulfo-2-naphthol-3-carboxylic acid arylamide (compare *F.P. 720,109*—Ciba). By the action of sulfuric acid, the sulfonic acid group easily splits off and the azo dyestuff is formed.

The same trend of thought is followed in *F.P. 759,802* (St. Denis—A. Wahl), describing the procedure. The fiber is impregnated with a solution of an arylamino-2-naphthalene sulfonic acid, dried, and developed with a diazo compound having no solubilizing radical. The HSO_3 group located in the *alpha* position is eliminated and the insoluble azo dyestuff is formed according to the equation



The dyestuffs so formed are therefore *o*-arylaminoazo compounds (Wahl, "Uses of Tobias Acid," *Rev. Gen. Mat. Col.*, **1932,** 201).

The process is further clarified in *U.S.P. 2,139,987* (St. Denis—Dec., 1938). The goods are padded with a salt of 2-aminonaphthol-1-sulfonic acid, wherein the amino group is substituted by a hydrocarbon chain, but which contains no other water-solubilizing group. The material is then developed in a solution of a diazo compound which contains no water-solubilizing group.

The conditions most favorable for applying naphthols to wool material are indicated in *F.P. 734,189*—Ciba. The ratio of liquor to material should not be below 6:1 nor above 50:1. The naphthol should be present in an amount exceeding 5% of the weight of the wool, while the alkali should not exceed 1½ to 2½ times the weight of the naphthol. The goods are treated with this solution until the bath is exhausted, whereupon they are dyed in solutions of diazo compounds having no group which promotes water solubility. Cellulose sulfite should be added as a protective colloid to the naphtholating bath. According to *U.S.P. 1,940,551*—Ciba, relating to the same subject, arylides of 2-oxy-3-naphthoic acid derived from aromatic amines which have no solubilizing groups other than one or two amino groups, are especially preferred for producing red shades fast to crocking.

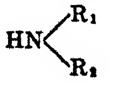
The naphtholation is improved if the wool is first given a slight chlorination, that is, with solutions containing 0.3 gram available chlorine per liter for 1½ minutes (*B.P. 457,798, G.P. 591,315*—Ciba), followed by rinsing with bisulfite. Wool so prepared has increased affinity and the fastness to crocking of the dyeings is improved.

Excessive alkali in the naphthol solutions can be replaced by alkaline salts, for instance, by phosphates, silicates, etc. (*B.P. 452,142, F.P. 797,140*—I.G.). An impregnating bath made up according to this proposal contains 0.15 gm of caustic soda and 15 gm of sodium pyrophosphate per liter, plus formaldehyde. Igepon and alcohol may optionally be added.

Since formaldehyde attacks wool in a strongly alkaline liquor, it is suggested that dyeings on wool and wool-mixed fibers be carried out without the addition of formaldehyde (*B.P. 451,264*—I.G.). Although formaldehyde serves to reduce the light sensitivity of the padded goods, and is a stabilizing agent in the preparation of Naphthol AS solutions, the advantage of working with weakly alkaline solutions is apparent.

With due regard to the necessity of working with highly alkaline solutions in the case of some of the naphthols, *G.P. 669,184* (I.G.—Kirst) recommends the use of salts of alkaline reaction, such as silicates, borates, pyrophosphates, together with formaldehyde and a wetting agent (Igepon T). It is worthwhile noting that formaldehyde which attacks wool in a caustic solution, seems to act favorably in this case.

In order to reduce the alkalinity of the impregnating solution, *G.P. 560,580* and *637,317* (1932) suggest using nitrogenous heterocyclic compounds, as triazines or hexamethylene tetramine. The caustic alkali can also be partly replaced by urea, or amines of the general structure



$$HN\begin{matrix}\diagup R_1\\ \diagdown R_2\end{matrix}$$

where R_1 is H or a low-molecular alkyl group and R_2 is another alkyl group. Examples are dicyanodiamide, ethylamine, etc. Compounds in which the alkyl group is linked to the nitrogen by a CO bridge are not suitable. The use of caustic alkalis can be almost entirely avoided by this method. *B.P. 443,638* and *G.P. 636,328* claim also that the amount of alkali can be decreased by the use of high-molecular substituted ammonium bases, as trimethyllauryl ammonium hydroxide, which also aid in dissolving the naphthols.

In order to prepare alkali-sensitive fibers, as wool and silk, with coupling components, certain products called "aza" compounds can be applied (*U.S.P. 2,117,614*, I.G.—Koeberle; *B.P. 478,696*). These aza compounds are of cyclic character, soluble in acids, but free of sulfo groups, in which one or more CH groups have been substituted by N; for example, methyl aminoazaphenanthrene. The nomenclature was introduced by the *J. Am. Chem. Soc.*, **55**, 3905. The difference between an aza compound and an amino compound, is that in an aza compound a C atom or a CH group is replaced by N, as in pyridine, while amino groups are replacements for H atoms.

H. Rath and Kubitzky report (*Z. f. ges. Tex. Ind.*, **1939**, #92, 632) on research done for the purpose of diminishing the tendering of wool by alkaline naphtholate solutions. This end may be achieved by increasing the solubility of the Naphthol AS by introducing a hydroxymethylene group in the *alpha* position. Provided that the impregnation is carried out as prescribed, the naphthols are said to be evenly absorbed by the fibers, and the coupling can be made without difficulty with the diazo solutions.

It is difficult to produce uniform dyeings on mixed fabrics of cotton and wool when following the usual methods, as the wool is generally found to dye a lighter shade. *G.P. 646,338* and *F.P. 801,886* of I.G.—Jantsch, 1936 (also, in similar vein, *B.P. 457,798*—I.G.) recommend pretreating the fabrics with oxidation agents, for instance, with a solution of hydrogen peroxide stabilized with pyrophosphate. To insure a close match on the two fibers, it is further recommended to impregnate with the naphtholate solution to which a wetting agent (Igepon T) and Protectol are added.

A method for dyeing wool-mixed fabrics continuously is described in *G.P. 641,517* (I.G., Kirst—Gutesohn). The separate steps are first, an impregnation with naphthol solution of short duration (3 minutes), squeeze and immediate coupling with the diazo solution. Finally the goods are conveyed through a slightly alkaline bath, as, for instance, an ammoniacal bath. Additions of auxiliaries to the diazo solution as well as to the naphtholating bath are essential. Igepon and Peregal are mentioned as suitable (compare *G.P. 663,523*, I.G.—Just—Kirst).

G.P. 622,976 (I.G., Christ—Berthold) further develops the idea, already mentioned above, of employing dispersions of naphthols instead of naphtholate solutions. Dispersions of this kind are made with the aid of Igepon, Nekal, etc. Not only wool and silk, but also acetate fibers, benefit from the complete absence of alkali. Another advantage lies in the increased yield of those naphthol brands whose alkali salts are difficultly soluble.

In dyeing wool with the naphthol colors, there is danger of dulling the shade since the diazo compounds have an affinity for the wool fibers in themselves, staining it yellow or brown. This side reaction in the coupling process can be cleared by an aftertreatment with a reducing agent, for instance 1 to 2% of zinc formaldehyde sulfoxylate with mineral acid and Igepon at 100°C (*G.P. 621,758*, I.G.—Kirst). On the other hand this reaction of the diazo solutions with the wool fiber can be utilized for producing certain dye shades. These dyeings can be improved in their light fastness by aftertreatment with Cr, Cu, Ni or Co salts, as copper sulfate of sodium bichromate (*B.P. 437,049* and *454,729*—Huddersfield).

Application of Naphthols on Acetate Cellulose. It is possible to apply the insoluble azo dyestuffs on acetate rayon. As early as 1907, Knoll (*G.P. 198,008*) found that the diazotizable amines and phenols are absorbed from aqueous solution, or from dispersions, by cellulose acetate, forming "solid solutions". These dyeings are suitable for producing dyestuffs on the fiber.

It was Clavel, however, who found in 1922* that it is possible to dye the diazotizable base and coupling component in the same bath, and to complete the coupling subsequently by treating the goods in a fresh bath with nitrous acid solution. The dyeing is carried out at 65°C, with both naphthol and base dispersed in a finely divided state. After the dyeing, nitrite and acid are added to the bath, thus bringing about diazotization and coupling at the same time.

This method of adding acid and nitrite to the dye bath was suggested by Burger, Ledward and Harrison in 1922 (*B.P. 193,646*). The fastness to rubbing, however, is improved by carrying out the developing operation in a separate bath, as Clavel described it.

An interesting dyeing method has been described by Röhling in *Mell.*, **1937**, 644 and **1939**, 63. The particulars are as follows: naphthol and base are dissolved together in ethylene glycol, caustic soda and soft water at 100°C. The mixture is poured into the dye bath which contains caustic soda, Nekal BX, glue, sodium nitrite and Glauber's salt. Dyeing is carried out at 65°C for one hour, whereupon 5 cc of formic acid are added per liter. Diazotization and coupling are complete in about a quarter of an hour. The goods are then rinsed, soaped and rinsed. The quantity of alkali is kept at a minimum to prevent saponification of the cellulose acetate.

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* *Addition Patent 25,936* to *F.P. 528,230.*

With proper supervision, the dyeing of naphthols on cellulose acetate offers no difficulties. The amount of alkali necessary for solution of the naphthol is hardly enough to cause saponification of the fiber. Dyeings of light and dark colors are level and shades are easily reproducible. The fastness to light, soaping and cross-dyeing is, with few exceptions, excellent. Satisfactory results are obtained on yarns as well as on piece goods.

The extraordinary affinity of the naphthols and bases to cellulose acetate, and their excellent yield in color value, make them especially suitable for dyeing this fiber. This affinity for cellulose acetate is much greater than for cotton, so much so, in fact, that in dyeing mixed fabrics of cotton and acetate the cotton is left nearly white. Of interest here is the fact that the bases are practically quantitatively exhausted from the bath by the cellulose acetate, while the base has no affinity for cotton.

The Rhodiaceta Company developed a process which is simpler and affords greater color yield than Röhling's method. The procedure is as follows: 1 gm of naphthol and a corresponding weight of diazotizable base are pasted up with 1 to 2 gm of furfuryl alcohol (or glycol or denatured alcohol). The necessary amount of caustic soda 36° Bé and 1 gm of soft water are added. The mixture is heated on the steam bath to 80 to 85°C and strained into the dye bath. The dye bath, prepared for a liquor-goods ratio of 30:1 contains

0.15–0.5 cc NaOH 36°Bé
0.3 gm wetting agent (Nekal BX)
2–5 gm gelatin, *dissolved in water*

per liter. The boiled-off goods is introduced at 65°C and dyeing carried out for a quarter of an hour. Glauber's salt (10 gm per liter) is added, dyeing is continued for a second quarter of an hour; the bath is heated to 80°C and the goods are dyed one hour at this temperature. The goods are rinsed in cold water for 5 minutes, then treated in a fresh bath containing 2 gm of sodium nitrite and 5 cc of formic acid 80%, per liter at 55 to 60°C for 15 minutes. The diazotization of the base and coupling with the naphthol proceeds at the same time. After development the goods are rinsed well, scoured for a half an hour at 80°C with 5 gm of soap and 1 gm of sodium hydroxide per liter, rinsed and dried.

An investigation of the operations of the naphthol dyeing process on cellulose acetate was made by A. Baron.* He challenged the generally accepted rule that an excess of naphthol should be applied. He found, however, that the bases which do not stain the acetate could be added to the bath in excess of theoretical amounts, without any detrimental effect on the fastness to milling of the colors, but when brightness of shade is desired, an excess of base should be avoided. Those bases which dye the acetate fiber themselves, produce shades which are poor to milling. When

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* A. Baron: *Teintex*, Mar., 1945; Joly, *Teintex*, Apr., 1944; J. P. Sisley; *Teintex*, 1941, 190.

using combined naphthols, the amount of base necessary is calculated as the sum of the quantities required for each naphthol. By adding 10 gm of calcined Glauber's salt per liter to the impregnating bath, the substantivity of the naphthol is increased 10 to 15%, and in this case the amount of the base must be correspondingly adjusted.

Black shades on cellulose acetate, generally produced by dyeing, diazotizing and coupling with β-oxynaphthoic acid can also be obtained in a single bath which contains both dyestuff and naphthol.*

A new process is suggested in *F.P. 851,482* (I.G.). Acetate rayon is impregnated with an aqueous suspension of an arylide of an aliphatic or aromatic carboxylic acid, containing a diazotizable amino group and at the same time, capable of coupling to a diazo compound. The impregnated fiber is treated with acid and nitrite. By adding an alkaline substance, the compound couples with itself in an intermolecular reaction. *F.P. 850,502* recommends aminonaphthols for this type of intermolecular reaction.

G.P. 609,475 (Aceta) avoids the alkaline naphtholate solutions by the use of acylated derivatives of oxynaphthoic acid, instead of the acid itself, and gives as an example the product of the reaction of acetic anhydride with 2-oxynaphthalene-3-carboxyaminobenzene. This naphthol can easily be hydrolyzed, and is therefore capable of coupling with diazo compounds.

According to *U.S.P. 2,008,691* (Celanese Corp.), the cellulose acetate material may be impregnated with a dispersion of a naphthol, aged or steamed and then conveyed in a continuous range through diazo solution, rinse water and soap bath. It is also possible, according to *B.P. 394,317* and *421,122* (Celanese Corp.), to apply an emulsion of the coupling component and base dispersed in a solution of a sulforicinoleate, and then to diazotize, rinse and soap. It is claimed that better penetration and increased fastness to crocking results.

The use of nitrogenous bases to circumvent the necessity for caustic alkali is recommended in *F.P. 795,471* (I.G.). These basic compounds combine with the coupling component to give more or less stable salts. Acetate rayon can be dyed with such compounds without undergoing saponification. The solutions can be further stabilized by adding heterocyclic substances (*G.P. 560,580*). An example for an impregnating bath is as follows:

2 gm naphthol
2 cc denatured alcohol
0.8 gm caustic soda 34° Bé
412 gm water
2 gm Igepon T
2 gm dicyanodiamide
per liter

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* G. Lister, *J. Soc. Dy. & Col.*, **1943**, #59, 889.

(Compare Metzger, "Le Naphtol AS dans la teinture de la rayonne à l'acétate", *Mell.*, Fr. ed., **1937,** 156.)

Naphthol AS dyeings can also be obtained on acetate rayon, according to *U.S.P. 2,048,796* of Celanese Corp., by impregnating with naphthol, base and glucose, and then diazotizing in a nitrite-acetic acid bath (*Bull. Fed.*, **III,** 116).

An entirely new process for dyeing cellulose acetate with insoluble azo dyestuffs is described in *U.S.P. 2,132,456* (I.C.I.). In this process, instead of first dyeing the fiber with the base, then diazotizing and coupling with a naphthol, the fiber is dyed with a compound which contains the triazole group $-N=N-N=$. Such compounds are prepared by the reaction of secondary amines, as diethanolamine with a diazotized base, for instance with diazotized 5-chloro-2-toluidine. The fiber is first dyed with the triazole compound, and then aftertreated in an acid bath with the developer (coupling component), for example, with hydroxynaphthoic acid.

The Diazotizable Bases

The number of bases available for producing insoluble azo dyestuffs with β-naphthol was at first very small, but since the invention of the Naphthol AS series, has increased tremendously. These new bases have made it possible not only to improve the quality of reds and oranges, but also to expand the range of colors of these azo dyestuffs to include brown, blue, violet and black shades.

The earlier bases known before the first World War will be discussed first, and then the types which were added over the last thirty years.

The first azo dyestuffs formed on the fiber were the reds produced with *p*-nitraniline, amidoazobenzene, *o*-aminoazotoluene and *p*-nitro-*o*-anisidine, α-naphthylamine bordeaux and the oranges made with *o*- and *m*-nitranilines or nitrotoluidine.

p-Nitraniline red was made with *p*-nitraniline on β-naphthol (Holliday & Sons, 1880; *B.P. 2,757*, 1880; H. Koechlin, 1888; Ullrich and v. Gallois, 1889). *p*-Nitraniline S (Bayer) is the sulfate of *p*-nitraniline in a 50% paste with sodium β-naphthalene sulfonate. *p*-Nitraniline N (M.L.B.) is *p*-nitraniline with nitrite added. Equivalent names for *p*-nitraniline are Fast Red 2G Base (G.D.C.) and Fast Red N2J Base (Kuhlmann.)

The diazonium salt of *p*-nitraniline has been marketed under various trade names, as Diazo Red (F.P.C.T.M.), Nitranil C and CF (Cassella), Azophor Red PN (M.L.B.), Benzonitrol (Bayer), Azogen Red (Kalle), Parazol (Bayer), and Paranil A (Bayer). The last named was stabilized with sodium β-naphthalene sulfonate. Present designations are Fast Red 2G Salt (G.D.C.) and Fast Red N2J Salt (Kuhlmann).

The shade of the red produced by *p*-nitraniline with β-naphthol has a yellowish cast. Different methods for altering the shade to a more bluish red have already been mentioned on page 215, and consist of application of Naphthol R or AR, or by blending β-naphthol with Nuanciersalz, Cassella, which is F-acid or 2-naphthol-7-sulfonic acid, or by the addition of potassium or sodium sulforicinoleate to the naphthol solution.

Diazotized *p*-nitraniline combines with Chrysoidine to yield dark brown shades (Chrysoidine Bistre, invented by F. Binder, *Bull. Mulh.*, **1905,** 54) and with Nigrophor to produce a brownish black. Finally, it can be used for developing direct dyestuffs which contain free amino or hydroxy groups (Para, Paradiazol, Paradiamine Colors).

α-Naphthylamine bordeaux is produced from α-naphthylamine and β-naphthol (*G.P. 81,039* and *94,280*). In order to facilitate the preparation of the diazo compound, α-naphthylamine was offered in a dispersible form, as Garnet Salt (F.P.C.T.M.) and α-Naphthylamine S in powder and paste (M.L.B.). A diazotized product, stabilized by the addition of naphthalene sulfonic acid was marketed under the names Naphthol Garnet 50% paste and Puce Naphthol (F.P.C.T.M.).

p-Nitroanisidine red, produced by coupling diazotized *p*-nitroanisidine with β-naphthol (*G.P. 98,637*, 1897) is remarkable because of its good fastness to chlorine. *p*-Nitroanisidine was sold under the names Tuscaline Red Base (Badische A.S.F.), Rose Naphthol (F.P.C.T.M.), Nitroanisidine (A.G.F.A.), etc. Present designations are Fast Red B Base (G.D.C.), Fast Red NB Base (Kuhlmann). The diazotized product was sold as Azo Pink NA (M.L.B.), and equivalent names are Fast Red B Salt, Fast Red NB Salt. It is frequently used with Naphthol AS or AS-RL to produce raspberry shades, fast to light and chlorine.

Amidoazobenzol combines with β-naphthol to produce a dull bluish red of good fastness to soaping. It is seldom used. Diazotization can be carried out at 15°C.

β-Naphthylamine and β-naphthol gives a dull bluish red of poor light-fastness. It was used in the resist style with tin salts, and in application printing for red violet shades on a prepare of β-naphthol with which small amounts of α-naphthol had been mixed.

o-Aminoazotoluene (Fast Garnet Base of M.L.B.) yields a garnet of good wash-fastness with β-naphthol.

o-Nitro-p-phenetidine pink (Blue-Red O of M.L.B.) found but little use. A bluish red of fairly good fastness is obtained with β-naphthol. Diazotization can be carried out without ice.

Azo Pink BB (M.L.B.) was used for the production of bright pink shades. The fastness properties were not good. The base is the benzyl ether of 3-amino-4-cresol. The azo dyestuff is resistant to the reducing action of glucose, so that Azo Pink BB was used for red discharge on indigo

(Method of Prochoroff, Scheunert and Wosnessensky, *Bull. Mulh.*, **1920**, 266).

o-Anisidine, which was manufactured in the form of its stable azo derivative by M.L.B. (Azophor Pink A) had little practical value.

Chloroanisidine (Chloranisidine Salt M of M.L.B., Chloranisidine P of Badische A.S.F.) gives a bright scarlet shade with β-naphthol. Present designations are Fast Red RC Base (G.D.C.) and Fast Red NRS Base (Kuhlmann).

Orange shades on β-naphthol are obtained with the diazo compounds of *m*-nitraniline (Azophor Orange MN of M.L.B.) *o*-nitraniline (Azo Orange LO of M.L.B.) *m*-nitroanisidine (Tuscaline Orange of Badische A.S.F., Azo Orange NA of M.L.B.) and of the nitrotoluidines (*p*-nitrotoluidine of M.L.B., 1909 and *m*-nitrotoluidine of Badische A.S.F., 1908). The methyl ester of anthranilic acid (Azo Orange Yellow G) gives a reddish orange, fast to light and soaping.

Brown shades are obtained by coupling β-naphthol with the diazo compounds of benzidine, of *m*-nitrobenzidine and of tolidine. They are fast to soaping. The tolidine brown has more of a violet cast, and is faster to light than the benzidine brown. Prints of *m*-nitrobenzidine can be improved in clarity and light-fastness by an aftertreatment with a boiling solution of copper sulfate.

Dianisidine produces a blue with β-naphthol. Although not fast to acids, it was often used for the blue-red style of printing. It has already been remarked in the first section of this chapter that the fastness properties of this dianisidine blue are unsatisfactory. In 1893 F. Storck observed that the dyestuff gave a dark blue with copper salts, similar to indigo in shade. But this blue, although improved in light-fastness, was still susceptible to the action of acids, perspiration and dry heat. A stabilized diazo compound of dianisidine, obtained by evaporating the tetrazo compound in the presence of aluminum or zinc sulfate, was sold under the name of Azophor Blue D.

Black could be dyed by using Azophor Black S, a mixture of Azophor Blue D with Azophor Orange MN (M.L.B.). Azophor Black DP* is a stabilized diazo compound of diaminodiphenylamine, and was recommended to produce black on β-naphthol prepare (*G.P. 80,409*).

With the development of the Naphthol AS series, new arylamine bases were invented and offered for sale, the detailed description of which will be found in Table 6 on page 364. Following those arylamines which contained NO_2 and NH_2 groups, appeared compounds, which besides the

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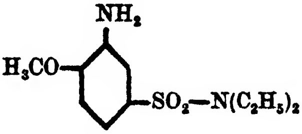
* According to Schultz, "Farbstofftabellen", Azophor Black DP is a mixture of tetrazodianisole with tetrazobenzidine and diazotized *m*-nitraniline (*G.P. 80,409, 83,963*).

NO_2 and NH_2, contained methoxy, ethoxy or halogen groups. The introduction of these groups was made to secure improved fastness to light and chlorine. The advantage of the methoxy group had been shown by previous experience in the case of *p*-nitroanisidine, and this knowledge served as the basis of the development of numerous new products, such as Variamine Blue B Base, Fast Blue BB Base and more recently, Fast Red ITR Base:



However, the connection between the constitution of the azo dyestuffs and their fastness to light, chlorine and boiling alkalis is not easily discernible, as pointed out by Sack (1933 Yearbook, Chemical College of Mulhausen). Although it is true that the fastness to light is quite generally improved by the introduction of methoxy, ethoxy, benzoylamino, sulfamino or halogen groups into the molecule, the influence of these groups varies depending on whether they are linked to the amino base or to the carbanilide remainder of the coupling components. Apparently the substitution in the carbanilide group has a stronger influence on the properties. Sack quotes the following examples (the trade names are those of Kuhlmann-Francolor).

	Fastness Rating
m-nitraniline (Fast Orange Base NR) + *m*-nitranilide of 2,3-oxynaphthoic acid (Naphtazol NB)	3
m-nitraniline + 5-chloro-*o*-toluidide of 2,3-oxynaphthoic acid (Naphtazol NTR)	4–5
m-nitraniline + *p*-chloro-*o*-aniside of 2,3-oxynaphthoic acid (Naphtazol NEL)	7

But on the other hand:

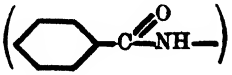
5-chloro-*o*-toluidine (Fast Red Base NTR) + Naphtazol NB	3
p-chloro-*o*-anisidine (Fast Red Base NRS) + Naphtazol NB	4

Thus it is clear that the introduction of Cl, OCH_3, and OC_2H_5 radicals increases the fastness to light if the substitution is made in the carbanilide group of the coupling component, whereas their substitution in the amino base has little effect.

In general the position of a group in the *meta* position has the effect of shifting the shade more to the red than if the position is *ortho*, while in the *para* position the shift is stronger, as for instance

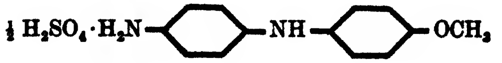
o-nitraniline	orange
m-nitraniline	red-orange
p-nitraniline	red
m-nitro-*o*-anisidine	scarlet
p-nitro-*o*-anisidine	red
m-nitro-*p*-anisidine	bordeaux

Enlargement of the molecule has the effect of deepening the shade, and shifting it to a bluer cast. For example, bordeaux and garnet shades prepared from benzidine and aminoazotoluene change to violet when a methoxylated toluidine is used having a substituted group of high molecular weight, as:



Probably the most important contributions to the series of bases were the Variamine Blue B, Fast Blue BB and Fast Blue RR Bases. These achievements, brought about in the laboratories of the I.G., and under the direct supervision of Zänker, gave the textile industry deep, fast and bright blues to replace the troublesome dianisidine. The importance of these bases and the diversity of styles obtainable with them are well known throughout the world. Besides the poor light fastness of dianisidine blue, the base gave a great deal of trouble in dyeing. Dianisidine, being a diamine, forms a tetrazo compound on diazotization, which can couple on either one or both of the azo groups with the naphthol according to the degree of acidity or alkalinity of the developing bath, thus explaining the irregular results which sometimes occur in its application. The search for monoamino bases led to the discovery of the Variamine Blue and Fast Blue BB and RR Bases.

Variamine Blue B Base[*] is the sulfate of 4-methoxy-4-aminodiphenylamine:



The blue shades obtained with this base meet the highest standards for light-fastness (5–7). The best results are obtained with Naphthol AS and AS-D (Rowe, *Rev. Gen. Mat. Col.*, **1930**, 382; *Chem. Zent.*, **1930**, 2190).

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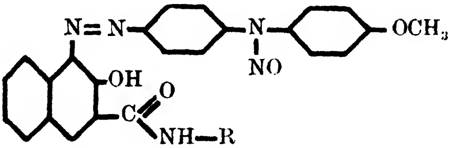
[*] *G.P. 508,585*; *Frdl.*, #17, 967; *D.F.Z.*, **1929**, #65, 498, 552, 834, 951; **1930**, #66, 313; Dr. Neuwirth, *Mell.*, **1930**, 33; Dr. Christ, *Mell.*, **1930**, 447; Rath, *Mell.*, **1929**, #10, 535; Rowe, *J. Soc. Dy. & Col.*, **1930**, #46, 227; Krostewitz, *Mell.*, **1931**, #12, 584; *Mell.*, **1929**, #10, 814; **1930**, #11, 144.

Certain difficulties are experienced in diazotizing Variamine Blue B Base. With the minimum amount of hydrochloric acid and 2 molecules of sodium nitrite, a nitrosodiazo compound is formed at 12°C. If one molecule of nitrite is employed, a violet solution is obtained which gradually precipitates a brown sludge. This is redissolved when the second molecule of nitrite is added, and a clear yellow solution results. The amount of nitrite necessary therefore is considerably higher than the stoichiometric relation indicates. The nitroso (NO) group can be split off in a subsequent alkaline soap bath, or by a special reducing agent, such as sodium sulfide or sodium sulfite (Variamine Blue Developer A), giving the bright blue azo dyestuff.



Nitroso compound

The development of the original Variamine Blue B Base dyeings therefore differed from the usual method of producing azo reds because of the necessity for reduction aftertreatment. It is possible to avoid the formation of the nitroso compound and to obtain the pure azo coupling directly, but the diazo compound prepared in this way has the disadvantage of coupling at a very slow rate, so that uneven dyeings result. The uneven dyeings are caused by solution of the naphthol during the procedure of coupling. Variamine Blue Salt B* 50% is the pure diazo compound of the base, stabilized by magnesium salts. This product has proved satisfactory for printing and dyeing.

Variamine Blue Salt B is dissolved in water and some acetic acid. The prepared goods are coupled in the same way as with the diazotized base, and the dyeing developed at 50 to 60° C with or without soda ash addition.

The diazo solutions of Variamine Blue B are sensitive to acids and alkalis. If the coupling operation is carried out in neutral solution, the diazo solution is quickly destroyed by the alkali carried by the naphthol-prepared fabric, and if the developing bath carries only enough acid to neutralize this alkali, the blue obtained will be weak. The sulfates of zinc or magnesium are apparently the best agents to add to the developing bath to neutralize the excess alkali (*G.P. 698,772*) Acetic acid or aluminum sulfate, used for neutralization of other diazo solutions are not suitable with Variamine Blue B (*B.P. 429,025.*) Zinc salts are sufficiently acid, forming neutral zinc hydroxide with alkalis, whereas magnesium salts yielding

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* According to Rowe, *J. Soc. Dy. & Col.*, **1930**, 227, Variamine Blue Salt B is the magnesium salt of the nitroso-free diazo component of 4-ethoxy-4-aminodiphenylamine.

magnesium hydroxide, are somewhat less efficient, since the magnesium hydroxide is a stronger base than zinc hydroxide.

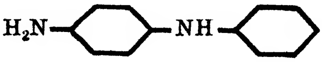
On the other hand, *F.P. 792,434* and *G.P. 627,324* of I.G. recommend another method for dyeing tightly woven or greige goods with Variamine Blue Salt B, wherein the usual agents, zinc or magnesium sulfates, are replaced by ammonium sulfate (10 gm per l). After developing with the diazo bath, the goods are steamed, or conveyed between hot plates to improve the penetration.

In order to avoid the intermediate formation of the nitroso compound, *G.P. 534,639* (I.G.-Jellineck) recommends passing the naphtholated goods through a diazo solution solution containing acetic acid. The coupling does not take place in this phase, but in the following bath of warm solution of soda ash. The reaction proceeds quickly and evenly in this bath, and the typical shade of Variamine Blue B results (Dr. Christ, *Mell.*, **1930,** 447).

Good results are also obtained by the addition of salts of organic bases, like pyridine, ethanolamine, or salts of quaternary ammonium bases to the developing bath (*G.P. 662,935*-I.G.). The fabrics, impregnated with naphthol solution, are dried, and developed in a bath containing Variamine Blue Salt B, Peregal O as a dispersing agent and piperidine-, or triethanolamine hydrochloride.

The use of acetic acid in the developing bath, with subsequent treatment in a warm bath of soda ash, can be extended to the dyeing of Fast Blue BB and RR Bases and Variamine Blue RT Base (Variamine Blue FG is not included). In fact, all of the various orange and red bases and Black Salts G and KN can be coupled by this means, but the method is not suitable for the resist style under Variamine Blues.

Variamine Blue RT Base is 4-aminodiphenylamine:

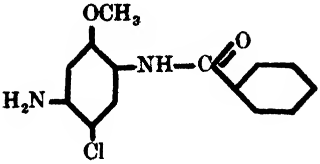


The corresponding Variamine Blue Salt RT 50% is the magnesium salt of the nitroso-free diazo component.

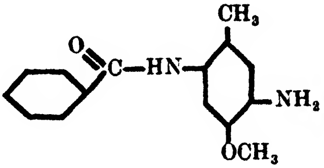
Fast Brown V Base is a recent addition to the series of diazotizable products, and is of importance for printing as well as dyeing for discharge. It is *o*-chloro-*p*-nitraniline azo-*p*-aminocresol methyl ether. Azo dyestuffs with this base and Naphthols AS, AS-RL and AS-OL are dischargeable dark browns of excellent light-fastness. Combination with β-naphthol gives a violet brown, similar in shade to the Chrysoidine Bistre, but exhibiting superior fastness properties. Fast Brown V Base is diazotized in a manner which is somewhat different from the usual procedure. The base is first pasted with acetic acid, then hydrochloric acid and nitrite are added and finally urea to neutralize the solution. The diazo compound is rather unstable, being decomposed by light or on contact with iron, but the stability is improved by the presence of hydrochloric acid. Coupling is completed by passing the goods through a soda ash bath (10 gm per l at 70°C), whereby the shade is deepened without changing the dischargeability.

The introduction of the aminobenzoyl group in different amino bases has served to produce many new products which yield brown, blue, violet and currant red dyeings.

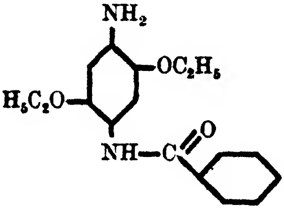
Fast Corinth LB Base is an example of this type. It is 1-methoxy-2-benzoylamino-4-chloro-5-aminobenzene, corresponding to the formula:



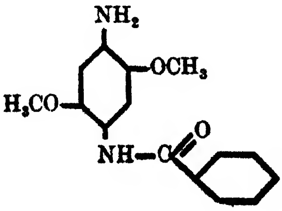
Fast Violet B Base of the I.G. (Fast Violet NB Base of Kuhlmann) is 6-benzyolamino-4-methoxy-*m*-toluidine:



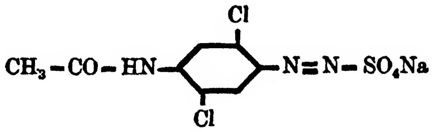
Fast Blue BB Base is 1-amino-4-benzoylamino-2,5-diethoxybenzene:



Fast Blue RR Base differs from the Blue BB in that the two ethoxy groups are replaced by methoxy groups. It is, therefore, 1-amino-4-benzoylamino-2,5-dimethoxybenzene:

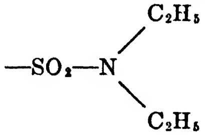


According to *G.P. 560,798*, garnet shades of outstanding fastness properties can be obtained by coupling naphthols with diazosulfates of the following constitution



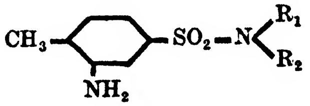
2,5-Dichloro-4-acetylamino-1-diazobenzene sulfate

By introducing a substituted sulfonamino group, as for instance



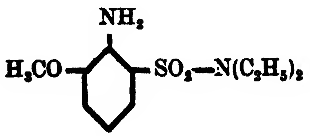
$$-SO_2-N(C_2H_5)_2$$

into certain bases increased all-round fastness results, particularly fastness to chlorine and boiling soap. *F.P. 761,607* (I.G.) mentions bases of the following general formula:

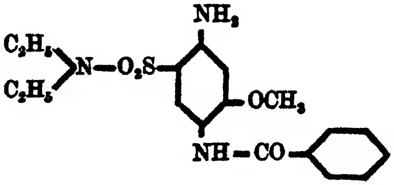


wherein R_1 and R_2 represent alkyl, aralkyl, etc. radicals. These compounds are prepared by the reaction of 2-nitrotoluene-4-sulfonic acid chloride with amino bases, followed by reduction.

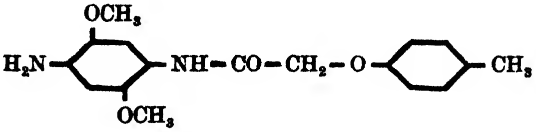
Fast Red ITR Base (I.G.) equivalent to Fast Red NSTR Base (Kuhlmann) is diethyl sulfonamino-*o*-anisidine:



Fast Rubine NS Base (Kuhlmann) is 1-amino-3-methoxy-4-benzoylamino-6-diethylsulfonamidobenzene:

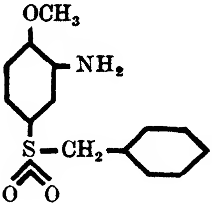


Violet Base Ciba III (Devol Violet A—Sandoz—and Violet Base Irga III—Geigy) exhibits a substituted acetylamino group. It is 1-amino-2,5-dimethoxy-4-tolyl acetylaminobenzene:

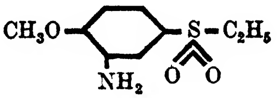


Several sulfone derivatives which produce red and scarlet shades with the naphthols of excellent fastness to light and boiling soap have been prepared. As examples,

Fast Scarlet LG Base, or 2-aminobenzene-1-methoxy-4-benzylsulfone:

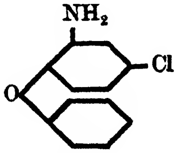


Fast Red GTR Base or 2-aminobenzol-1-methoxy-4-ethylsulfone:

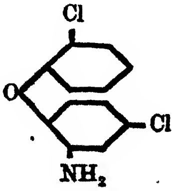


Many derivatives of diphenyloxide have practical value.

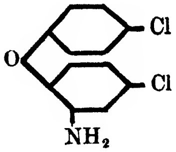
Scarlet Base Ciba R, or *Fast Red FG Base* (I.G.) is 4-chloro-2-aminodiphenyloxide (*G.P. 479,713* and *F.P. 568,839,* Ciba); also called Brown Base Ciba I:



Scarlet Base Ciba IV, Devol Scarlet D, or Scarlet Base Irga IV (2-amino-4,2′-dichlorodiphenyloxide):

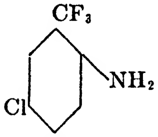


Scarlet Base Ciba V, identified with Brown Base Ciba II and Fast Red FR Base (I.G.) is 4,4′-dichloro-2-aminodiphenyloxide (*G.P. 572,663* and *F.P. 725,326*, Ciba):

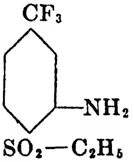


The introduction of fluorine, especially in the form of the trifluoromethyl group, CF_3, has been found to give excellent light-fastness. The group is contained in several diazotizable bases of the I.G. For example:

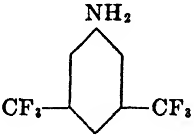
Fast Scarlet Base VD (G.P. 551,882):



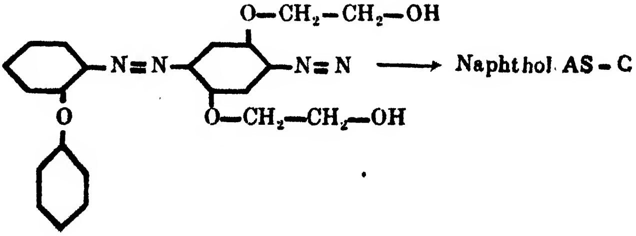
Fast Golden Orange Base GR (G.P. 588,781):



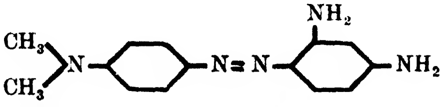
Fast Golden Orange Base GGD:



Scarlet shades of outstanding brilliance can be dyed on Naphthol AS-G prepare by coupling with the diazonium compound of diphenyloxide-2-azo-2,5-hydroxyethoxyaniline (*G.P. 513,323*, I.G.—Saunders). The dyeings have excellent fastness to light. The schematic formula of these dyestuffs is:



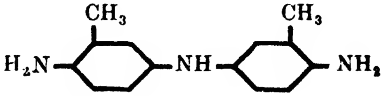
The first azo *blacks* were mixtures of stabilized tetrazotized dianisidine blended with diazo-*m*-nitraniline, such as Azophor Black S (M.L.B.). Black shades were also produced with azobenzenes, such as Azotol (Cassella), an unsymmetrical alkyl derivative of di-*p*-aminobenzene,



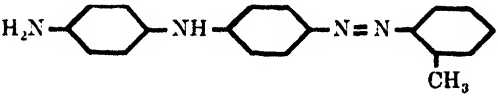
p-Dimethylamino-o′, p′-diaminoazobenzene

The most important azo blacks, however, are produced with diphenylamine derivatives, for example, with diaminodiphenylamine. Some of the principal black components are:

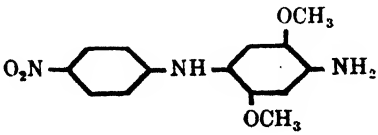
Fast Black B Base (I.G.), or *p-p′*-diaminoditolylamine:



Fast Black Salt G (Fast Black Salt NJ-Kuhlmann), or *p*-aminodiphenylamino-*p′*-azotoluol:

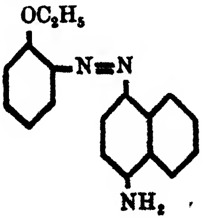


Fast Black Salt K (I.G.), or *p*-nitro-*p′*-amino-2,5-dimethoxydiphenylamine:



Finally, there are azo black dyes derived from ethoxylated aminobenzenes diazotized and coupled with α-naphthylamine. Such compounds yield deep black shades with different naphthols; for example:

Fast Black LB Base (1-ethoxybenzene azo-α-naphthylamine, or phenetol-2-azo-α-naphthylamine):



Despite the great number of shades which can be obtained by coupling the numerous bases with the different naphthols (more than 2000 combinations is a conservative estimate), it is sometimes necessary to mix two or more bases or naphthols for certain shades. One base may be coupled with two naphthols, or one naphthol may be coupled with a mixture of two or three bases. The latter possibility offers the more practical advantages. In blending different naphthols, their different substantivities must be taken into consideration. The substantivity gradually increases with the dilution of the bath, thus making it advisable to work with liquors of maximum concentration.

On the other hand, not all bases can be mixed with one another: Fast Corinth Base V precipitates Fast Red Bases TR and B. An interesting study of these problems has been made by Blackshaw (*J. Soc. Dy. & Col.*, **1937,** 373).

Diazotization. The diazo and tetrazo compounds generated by the action of free nitrous acid on the salt (sulfate or hydrochloride) of amines or diamines are very unstable. The safest temperature for diazotization, and for stability of the solution is at 0 to 5°C, so that the use of ice is indicated. In this connection v. Gallois found that diazotization can be performed without ice by working with dilute solutions or by adding an excess of mineral acid to the more concentrated solutions. Cassella described a procedure for carrying out the diazotization without ice by adding salts which lower the temperature by dissolving, such as Glauber's salt.

Para red and naphthylamine bordeaux can be dyed without ice by either of the following two methods.

(1) Two thickened solutions are prepared, one containing nitrite, the other the salt of the base and acid. The solutions are mixed before use. The thickening acts as a stabilizer, and the coupling takes place smoothly.

(2) The base is diazotized in the presence of sodium phosphate (in the case of *p*-nitraniline, a bluer red is obtained). Part of the mineral acid can be substituted with oxalic acid, while the addition of some gum tragacanth has proved advantageous.

Some of the amine bases can be diazotized at higher temperatures (15 to 20°C), among which are aminoazobenzene, aminoazotoluol, nitrophenetidine, etc.

An excess of acid and nitrite works favorably in most cases: the mineral acids slow down and even prevent the formation of decomposition products (diazoamino compounds, phenols, etc.). However, while these acid diazo solutions are more or less stable, they cannot be used for coupling. Before use, they must be neutralized with sodium acetate. In this condition they decompose easily, but their stability may be increased by the addition of Paradurol (sodium naphthalene di- or trisulfonate-1,3,6). Posdejeff asserts that the diazo solutions can also be stabilized by substituting part of the sodium acetate with alumina (*Mell.*, **1928,** 755).

Stabilization of the Diazo Solution. Before the invention of stable diazonium salts, which can be stored and readily transformed into diazo solution simply by dissolving in water, a great deal of work was done on the stabilization of the diazo solutions of the amine bases.

Ullmann observed that diazo solutions are improved in stability by the addition of organic acid, except acetic acid, as for example, oxalic, citric, tartaric, or inorganic acids such as phosphoric, boric and chromic acids (*Chem. Ztg.*, **1899,** #129).

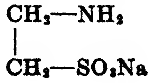
Dr. L. Lichtenstein stated in a paper concerning the azo developing agents, that from the physicist's point of view the neutralization with sodium acetate has the effect of maintaining the hydrogen-ion concentration at a constant level (*Z. f. Elek. & Phys. Chem.*, **1908,** #14, 586–591).

W. Sieber, in a study of stable printing pastes and of the nature of the diazo compounds, found that some mineral acids can replace acetic acid, as for example boric or tungstic acid, without damage to the fiber (*Mell.*, **1927,** 609). Sieber employed neutral diazo solutions without sodium acetate and naphthol solutions prepared from potassium hydroxide and with added potassium ricinoleate (*Mell.*, **1926,** 616).

An early method of stabilization was developed by Becker in 1893 (*G.P. 81,039, 86,367, 88,949, 92,237; Frdl.*, **1894–97,** IV, 679). It is based on the use of mono- or polysulfonic acids of naphthalene, particularly β-naphthalene sulfonic acid and naphthalene-1,5-disulfonic or 1,3,6-naphthalene trisulfonic acid. The trisulfonate was offered by Bayer to the trade under the name Paradurol, as a stabilizing agent for every kind of diazonium salt solution (*G.P. 263,431; Frdl.*, **1912–14,** XI, 370). An analogous product, Parasanol, was manufactured by M.L.B. Present trade names are Diastersol N (Kuhlmann), Stabilisol (S.P.C.M.C.), Diazophile (St. Denis), and Paradurol (G.D.C.).

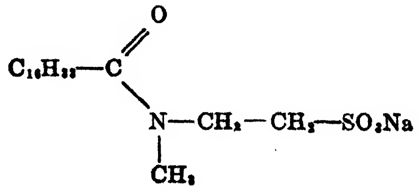
In more recent times di- or polysulfo compounds of benzene, and diphenyl or halogen derivatives thereof have been suggested for the same purpose (*F.P. 697,425*—1931 and *717,193*—1932, —I.G.). It is shown that anisol-*p*-sulfonic acid acts as a stabilizer, especially in diazo solutions of 5-chloro-*o*-toluidine and 5-chloro-*m*-toluidine.

A method of stabilization of diazo solutions using dispersing or emulsifying agents is described in *B.P. 413,257, G.P. 593,790*—1931 and *Aus.P. 135,053* (I.G.). Sulfite cellulose liquor and the reaction products of



$$\begin{array}{l} CH_2{-}NH_2 \\ | \\ CH_2{-}SO_3Na \end{array}$$

Taurine



Igepon T

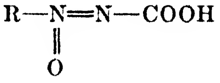
aliphatic acids with amino sulfonic acids are especially indicated. As examples, the products of the reaction of oleyl chloride with the sodium salt of taurine, or isethionic acid, corresponding to the products Igepon T or A (*B.P. 343,899*) are mentioned.

By the addition of one of these compounds, the fastness to crocking of the dyeings is improved, because no intermediates are formed by the decomposition of the diazo solutions. On the basis of this study, the product Diazopon A was manufactured. It is recommended to be added at the rate of 2 to 5 gm per liter. It is a non-ionic compound of high molecular constitution, belonging to the Peregal type. Because of its highly protective colloidal property, it has a favorable influence on the particle size of the pigment azo dyestuff formed. These dye-lake particles are very finely dispersed by Diazopon A in the diazo solution as well as on the fiber, so that any excess can be readily removed by a soaping, thus considerably increasing the fastness to crocking. Used as a pasting agent for the bases and salts, Diazopon promotes the diazotization.

High-molecular substituted quaternary ammonium compounds, such as trimethyllaurylammoniumhydroxide are recommended for addition to the diazo solution in *G.P. 636,328* (I.G.).

Another stabilizing agent has been prepared (*S.P. 167,488*—I.G., 1933) by the following reaction. Technical ethanolamine is condensed with sperm oil, and the salt is treated with 2½ times its weight of ethylene oxide in the presence of small quantities of caustic alkali. The substance is a water-soluble waxy paste, with good emulsifying, leveling and dispersing properties, and is recommended as a stabilizer for diazo solutions. For sperm oil, wool fat can also be used (*S.P. 171,585*).

In later patents, derivatives of azooxycarboxylic acids have been proposed for the same purpose (*F.P. 806,895*, *B.P. 477,689*—Strasser)

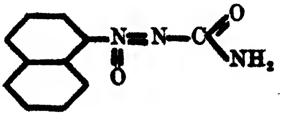


$$R-\underset{\underset{O}{\|}}{N}=N-COOH$$

R = aromatic radical, as
phenyl, diphenyl,
naphthyl, etc.

The acids are unstable, but their esters or amides are perfectly stable. The following derivatives are specifically recommended:

Benzoazooxycarboxylamide



Naphthyl azooxycarboxylamide

By treatment with alkalis, the amino group is hydrolyzed or the ester split off. The dyeing operation therefore follows this procedure:

(1) The material is padded with the naphtholate solution.

(2) The material is dyed with diazo solution containing one of the azooxycarboxylic acid derivatives at 30°C.

(3) Aftertreatment in an alkaline bath. In this solution the azooxycarboxylic acid is transformed into the corresponding diazo compound and coupling proceeds.

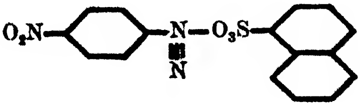
The process described in *G.P. 662,935* and *B.P. 489,972* (I.G.) aims to stabilize the diazo solutions by the addition of amines or quaternary ammonium compounds, such as piperidine hydrochloride or triethanolamine sulfate. *U.S.P. 2,124,899* and *F.P. 817,431* (I.G.) are similar in context. Water-soluble amines, themselves incapable of undergoing a coupling reaction, are active stabilizers of diazo solutions against the surplus alkali carried into the diazo solution by the impregnated fabric. The best effect of these auxiliaries can be observed in their action with diazo solutions most sensitive to alkalis, such as Variamine Blue B (methoxy-*p*-aminodiphenylamine). The material is naphtholated by a process described in the French patent, dried, and coupled with diazotized Variamine Blue Base solution containing Peregal O and triethanolamine sulfate.

Manufacture of Stable Diazonium Salts. A great deal of the research work which was carried out on insoluble azo dyestuffs, dealt with the problem of producing diazonium salts in dry, stable form, ready for use.* Some of the steps taken in this direction will be discussed, dividing the chronological development of the subject into two categories:

(1) Preparation of diazo compounds with suitable acids.

(2) Preparation of diazo compounds which consist of double salts, and employing alum, chlorozincate, chlorostannate and other inorganic salts for their formation.

Some of the earliest recorded experiments of the first category were made by P. Becker (1893). By the reaction of α-naphthalene sulfonic acid on diazonium chlorides or sulfates, stable but sparingly soluble compounds can be obtained in the dry state (*G.P. 81,093, 86,367*—Becker; *G.P. 88,949* and *G.P. 92,237*—F.P.C.T.M.; *G.P. 92,169* and *93,306*—Bayer). Diazo Red (Rouge Diazo of F.P.C.T.M.) is an example of this early method. It corresponds to the α-naphthalene sulfonate of *p*-nitrodiphenyl diazonium:



It had little practical success because of its poor solubility.

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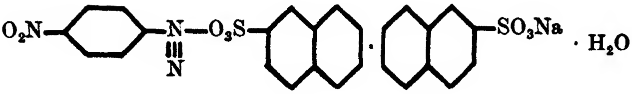
* Compare Ullmann, Vol. III, p. 665; Grandmougin, *Rev. Gen. Mat. Col.*, 1907, 232.

"Rose Naphthol" and "Bleu Naphthol" were also produced; they are the naphthalene sulfonates of *p*-nitro-*o*-anisidine and of dianisidine respectively.

To improve the solubility of these products, O. N. Witt proposed replacing the α-naphthalene sulfonic acid with its isomeric *beta* compound (*G.P. 264,268; Frdl.*, **1912–14,** XI, 370). The *beta* derivative forms a double salt which is readily soluble in water, and which consists of one molecule of the diazonium salt, one molecule of β-naphthalene sulfonate and one molecule of water. It is equivalent to Paranil A (Bayer):



This stabilizing method is still used for certain diazo compounds.

Naphthalene polysulfonic acids are recommended for the same purpose in *B.P. 94,280.* Some diazonium salts are being manufactured today with naphthalene disulfonic acid as stabilizer. Naphthalene trisulfonate, sold under the name of Paradurol, is recommended, as already mentioned, as stabilizing auxiliary for diazo solutions (*G.P. 263,431; Frdl.*, **1912–14,** XI, 376). More recently the di-, tri-, and polysulfonates of benzene, diphenyl, or halogen-substituted compounds thereof, are proposed for the same purpose in *F.P. 697,425*—1931 and *717,193*—1932 (*Chem. Zent.*, **1931,** I, 1638; **1932,** II, 1715).

Furthermore, the diazonium salts stabilized with thiosulfates (*G.P. 80,652; Frdl.*, **1894–97,** IV, 676), ferro- and ferricyanides (*G.P. 532,402;. Chem. Zent.*, **1932,** II, 775) and especially the fluoroborates, belong to this first group. The double compounds on the base of fluoroborates are sufficiently soluble and very stable (Bart's process, *G.P. 281,055* and *478,031; Frdl.*, **1931,** XVI, 900; **1914–16,** XII, 311). Use of this last-named diazo compound yields very bright dyeings of better fastness than with the usual diazo solutions. Better solubility of the fluoroborate diazonium salts can be obtained by mixing them with alum, aluminum chloride, sodium chloride, or anhydrous sodium sulfate (*U.S.P. 1,862,241*; I.G.—Schnitzspahn). A double decomposition takes place, and complex diazonium salts having better solubility than the simple diazofluoroborates result.

In the second category, the alum double salts described by v. Gallois in 1894 are the earliest examples. They follow the following general formula:

$$Al_2(SO_4)_3 \cdot M_2SO_4 \cdot 24H_2O$$

where M is the diazonium radical. The acidic, concentrated solutions of the diazonium salts are mixed with anhydrous aluminum- or zinc-sulfate and evaporated to dryness under reduced pressure (*G.P. 94,495*). This process is the basis for the production of the Azophor dyestuffs of Höchst, *i.e.*, Azophor Orange NN (*m*-nitraniline), Azophor Red PN (*p*-nitraniline), Azophor Pink A (*o*-anisidine), Azophor Blue (dianisidine). The diazo salts are stable enough to be concentrated *in vacuo,* in the presence of excess mineral acid. Aluminum or zinc sulfates are added to prevent explosive decomposition (*G.P. 85,387*—M.L.B., 1896). The excessive acidity of these types presented some difficulty in their application.

Nitrazol C (Cassella) is produced in an analogous manner. The strongly acid solution of the sulfate of *p*-nitrodiazobenzene is concentrated in the presence of anhydrous sodium sulfate. The salt takes up the excess of water and forms a bisulfate with the surplus sulfuric acid (*G.P. 97,933;* compare also *G.P. 281,098*—Cassella; Ullmann, Vol. **III,** p. 664; *Frdl.,* **1897-1900,** V, 482).

Double salts of the diazo compounds, especially the chlorozincates, were described in *G.P. 89,437* (F.P.C.T.M.) in 1894. The patent mentions diazo components of α- and β-naphthylamine and of tolidine, and the products particularly covered by this patent were sold under the names Rouge Naphthol pâte, Grenat pâte and Puce Naphthol pâte (*Frdl.,* **1894-7,** IV, 675). The method was later restricted to the stabilization of diazo compounds of aminoazo bases, or diaminoazo bases. It led to the general patents *G.P. 454,849* of 1923 and *G.P. 491,318* of 1931. The latter also includes double salts of cadmium compounds (*Frdl.,* **1925-7,** XV, 569 and **1931,** XVI, 1064). A practical solution of the manufacturing problem was found by Griesheim-Elektron, who isolated the zinc double salts by salting out from aqueous solution.

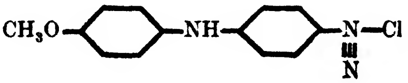
Wacker and Schmitt (Mulhouse) prepared a double salt of diazo-*p*-nitraniline and tin tetrachloride. This unstable chlorostannate was known as Rouge Explosif.

A process for preparing stabilized diazonium compounds is described in *G.P. 587,509.* Diazonium salts are treated with potassium sulfite at low temperatures, dried, and mixed with potassium bromate or potassium sulfite. Acidified solutions of this product in cold water are very stable.

G.P. 572,268 (Ciba, 1930) discloses a method for obtaining stable diazo compounds by separation of the product of the reaction of diazotized bases with halogenated benzene sulfonic acid. For example, 1-chlorobenzene-2,4-diazo sodium sulfonate is added to a solution of diazo-*m*-nitraniline. The double salt crystallizing from solution is very stable. According to *G.P. 572,269,* sulfonic acids and metal salts can also be used together. In this way double salts are obtained, of which naphthalene-1,5-sulfonic acid with magnesium chloride is an example.

Three methods are in general use today for the manufacture of diazo salts: the chlorozincate method (for *o*-chloroaniline, dichloroaniline, *o*-chloro-*p*-toluidine, dianisidine), the sodium naphthalene disulfonate method (for *m*-chloroaniline, *m*-nitraniline and *p*-nitro-*o*-anisidine), and the fluoroboric acid method. The dyestuff manufacturers have prepared nearly all of the available bases in a stabilized diazo salt form. The trade names are Fast Salts (G.D.C., A.A.P., N.A.C.), Sels solides (Kuhlmann), Azogen Fast Salts (S.P.C.M.C.), Diazo Fast Salts (Rohner), Devol Salts (Sandoz), Ciba Salts (Ciba), Irga Salts (Geigy), Naphthosol Fast Salts (Calco), etc. The practical advantages of these products is obvious: their application eliminates all the difficulties of diazotization and neutralization, and precludes the necessity of adding special stabilizing agents.

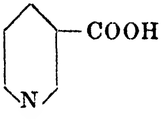
The hydrochlorides of the diazonium compounds of *p*-aminodiphenylamine, and of its derivatives, especially 4-methoxy-4′-aminodiphenylamine are sufficiently stable and at the same time insoluble enough in salt solutions that they may be salted out and obtained directly in a dry state (Variamine Blue Salt B).



Other stabilizing agents have been proposed for the preparation of diazonium salts, some of which have found practical application in the manufacture of the Rapidogen type dyestuffs. Some of them may be mentioned here as applicable to the formation of stable diazonium salts and solutions.

Sulfamic acid, NH_2HSO_3, and its salts are recommended for stabilizing diazo solutions, as 100 parts of the double salt of 4-chloro-2-diazobenzene and zinc chloride are mixed with 11 parts of sulfamic acid (*U.S.P. 2,314,196* —1943, Allied Chem. & Dye.—Clark).

Maleic or crotonic acids are recommended in *U.S.P. 2,319,265*, 1943 (Du Pont—Rossander); picolinic or furoic acids in *U.S.P. 2,346,790*— 1944 (Du Pont—Rossander). The formula of picolinic acid is:



Benzoic acid or dinitrobenzoic acid is recommended in *U.S.P. 2,355,618*, while the same compounds together with naphthalene sulfonic acids are mentioned in *U.S.P. 2,357,226* (Du Pont—Rossander).

Pyridine β-sulfonic acid, added to the press cake containing the diazonium salt and zinc chloride or aluminum sulfate is described in *U.S.P. 2,402,106* —1946 (Gen. Aniline, Glahn-Walsh).

The various bases and salts with their formulas and applications are listed in Table 6 on page 364.

Dyeing and Printing Methods

Impregnation of the yarn or fabric with a naphtholate solution to which sodium sulforicinoleate and dispersing agents have been added is still the most common procedure. Subsequently the fiber is dyed with the diazo solution, often on a two- or three-roll mangle.

The following examples may serve as a basis for dyeing procedure with the insoluble azo dyestuffs.

p-Nitraniline Red

Pad Liquor

18 gm β-naphthol
17 gm caustic soda 38° Bé
30 gm sodium sulforicinoleate
100 gm gum trag. 6%
per liter

The β-naphthol is pasted with the sodium sulforicinoleate (sulfonated castor oil) and caustic soda, 100 cc boiling water is added and a homogenous paste is obtained, whereupon 500 cc of boiling water is added and the naphtholate solution so formed is brought to one liter.

A cold dissolving procedure is favored. The naphthol is wet out with denatured alcohol and the caustic soda added. Solution is effected with soft water at room temperature.

The fabric is padded with this solution at 30 to 40°C, at about 100% pick-up, and dried in the hot flue.

Developing Bath

18 gm *p*-nitraniline
44 gm hydrochloric acid 20° Bé
80 gm hot water
Cool with
200 gm ice water to 5°C

Add slowly a cold solution of 10 gm of sodium nitrite in 35 gm of water. After ½ hour the bath is neutralized with 30 gm of sodium acetate in 100 gm of cold water. At last 13 gm of acetic acid is added, and the whole diluted to 1 liter.

Developing is carried out on the padding mangle, after which the cloth is treated in a hot soda-ash solution (0.3%), rinsed, soaped, rinsed and can-dried.

Naphthol AS Colors

Pad Liquor

14 gm Naphthol AS-D
20 gm sulfonated castor oil
18 gm caustic soda 38° Bé
Paste with
100 gm boiling water
Add
500 gm hot water
1 liter

The material is padded on the mangle with above liquor at 70 to 80°C, and dried in the hot flue. Padding at high temperature is advisable to reduce the effect of substantivity of the naphthol. It is also recommended to dilute the first trough liquor by 10% with water, feeding the full concentration from then on.

Developing Bath

14.5 gm Fast Red KB Base, *pasted with*
160.0 gm hot water
Add
14.5 gm hydrochloric acid 20° Bé

The solution is filtered and poured into ice water to cool to 10 to 12°C. A solution of 5.75 gm of sodium nitrite in 30.0 gm of water is added while stirring. After ½ hour, 11 gm. of sodium acetate in 45 gm of water is added (or 40 gm of Calgon 1:2 solution).

Finally 10 gm of acetic acid 50% or 10 gm of aluminum sulfate is added and the whole brought to 1 liter.

The use of Calgon for sodium acetate substantially increases the stability of the bath.

The development is carried out on the pad, the goods are skyed one minute and aftertreated in a hot soda-ash solution (0.3%) in the open width, rinsed, soaped and dried.

Development with Fast Color Salts

Pad Liquor	Developing Bath
15 gm Naphthol AS	70 gm Fast Scarlet Salt VD
18 gm NaOH 38° Bé	10 gm acetic acid 50%
20 gm sulfonated castor oil	
per liter	per liter

Preparation and development are carried out as in the foregoing illustration.

Dark blue dyeings of good fastness to light and washing can be obtained on cotton and rayon fabrics with Naphthol AS and Variamine Blue Salt B.

Depth of shade can be increased by adding Variamine Blue Salt RT to the developing bath, or Naphthol AS-G to the impregnating bath. Attractive dark blue shades can also be obtained with Naphthol AS and Fast Dark Blue Salt R (*Mell.*, **1940,** 29). This combination is of interest because the deep blue obtained is dischargeable, and the dyeings possess good fastness to boiling.

Pad Liquor	Developing Bath
12 gm Naphthol AS	40 gm Fast Dark Blue Salt R
20 gm sulfonated castor oil	210 gm water 30°C
15 gm NaOH 38° Bé	28 cc acetic acid 50%
per liter	350 cc soft water
	per liter

The impregnation takes place at 80°C and the goods are dried in the hot flue. The developing bath is kept at 30°C because the salt has best solubility at this temperature. After padding with the Fast Salt solution, the goods are skyed 40 seconds to secure complete coupling reaction, then treated in a hot 1% soda ash solution at 50°C, washed, soaped and rinsed. In manufacturing dark navy cotton or rayon fabrics for uniforms, desired depth is obtained by application of impregnating baths of 13 to 15 gm of Naphthol AS per liter, and developing with 90 to 105 gm of Fast Dark Blue Salt R with the addition of 4 gm of Diazopon A and 40 cc of acetic acid 50% per liter.

A new dyeing process has been described in *G.P. 534,639*, *598,772* and *B.P. 429,025* (compare Dr. Christ, *Mell.*, June, **1930,** 447; Dr. Kramer, *Tiba*, July, **1931,** 741; Dr. Rath, paper read at the 14th conference of the Internatl. Assn. of Chemists and Colorists in Budapest, 1929; *Mell.*, **1929,** French edition; and Dr. Neuwirth, *Mell.*, **1930,** 33).

It consists of adding acetic acid to the diazo solution; after padding with the diazo solution, the material is led through a soda-ash solution at 30 to 40°C. The coupling starts at once. This method has advantages, especially when working with Fast Blue BB and RR Bases, Variamine Blue B Base, Fast Violet B Base and Fast Corinth Salts V or LB. The influence of the alkali carried along by the naphtholated material on these slowly coupling bases is eliminated. Furthermore, the diazo compounds are more stable in acetic acid solutions. The results are in general more uniform and the dyeing improved as far as penetration, depth of color and fastness is concerned.

Certainly, by this method the speed of dyeing is retarded, but on the other hand, the diazo solution is not completely utilized, and the results therefore not always satisfactory. Despite the poor stability of the diazo solutions it seems possible to carry out the coupling process completely and quickly at elevated temperatures before decomposition of the bath sets in. An increase of 20 to 25% in the depth of shade can be assumed under these conditions.

G.P. 608,847, *F.P. 743,329*, *B.P. 404,304* and *U.S.P. 2,046,425* of I.G. and *B.P. 389,853* of Bleacher's Assoc. (see *Wengraf's Ber.*, Feb., **1935,** April, **1936,** 11; *Tiba*, May, **1933,** 349) suggest that after saturation with the diazo solution, the fabrics be conveyed over hot cans or through a steam chamber, in order to improve the yield. The steam chamber, heated to 100°C is connected in tandem with the padder. Another suggestion is to pass the material between hot plates for 18 to 20 seconds. In any case a strong drying effect must be avoided, as the material must leave the apparatus in a slightly moist condition. This method has worked well in dyeing Variamine Blue B and Fast Blue BB and RR Bases.

An original method developed in the Alsatian plant of Scheurer-Lauth deserves mention. It consists of coupling with a solution of Variamine Blue Salt B heated to 30 to 35°C. The yield surpassed that obtained where the hot plates, cans and the like were employed. The same depth of color is reached with 24 gm of Variamine Blue Salt B as against 30 gm by the foregoing method, thus effecting a 20% saving. The procedure is described as follows: The naphtholated and dried material is padded with Variamine Blue Salt B solution at 30 to 35°C. A copper coil placed in the trough of the padder heats the solution, and the coil is covered with sand to hold and regulate the heat. The padded material is then skyed 20 to 30 seconds, washed in soda-ash solution, and rinsed.

B.P. 410,669 (Ciba) claims that the addition of 2 to 5% of pyridine to the diazo solution has a favorable effect. The combination of diazo components with those coupling components which have two coupling groups capable of coupling reaction, does not always yield a homogeneous dyeing, because the speed of coupling is different for each of the groups. This difficulty is eliminated by the pyridine addition.

The fastness of naphthol dyeings is improved, according to *B.P. 450,981* (I.C.I.) by an aftertreatment with mono- or diglycerides of higher fatty acids (compare *B.P. 450,868* and *F.P. 801,131*).

The I.G. calls attention (*G.P. 696,362*—1937) to the fact that buffer substances used in the developing baths of ice colors might have the drawback of forming insoluble metal soaps with the textile oils, which can stain the fabrics. This drawback can be avoided if the coupling is carried out in the presence of water-soluble chromium compounds, for instance, chromium sulfate, -fluoride or -acetate. These chrome salts may also be added to the dry diazonium compounds (Fast Color Salts).

B.P. 502,144 (I.G.) gives a method for increasing the fastness of the Naphthol AS dyestuffs produced on the fiber. A metal salt, for instance a chromium or aluminum compound is added to the diazo component. The material is subsequently steamed, so that complex metallic dyestuffs can be assumed to form upon the vegetable fiber substrate. Cotton is impregnated, in one example, with Naphthol AS, and combined with diazotized methoxyaminodiphenylamine to which chromium acetate has been added. Finally the material is passed through the ager. It is interesting to note that in resist styles the dyed goods are treated with metal salts only after the dye is developed and the resist fixed.

F.P. 842,215 (I.G.) relates to an almost identical procedure. Chromium, nickel, cobalt or aluminum salts are added to the coupling bath. It is claimed that insoluble azo dyestuffs having a metal complex linked to the molecule are generated. Although the real constitution of these compounds is not explained, the metal organic linkage is evidently very strong because the metal is not split off by repeated boiling. The metals are applied in the form of their tartaric, oxalic or acetic acid salts.

Certain dispersing agents, for instance, oleyl alcohol sulfates, are added to the diazo solution in order to increase the fastness to rubbing of the dyeings (*G.P. 663,415*—I.G.—Gund, Christ, Drapal). Additions of this kind to the naphtholate liquors do not have the effect of improving the crocking-fastness. The patent claims that the dyestuff lake, formed in the solution and not fixed upon the fiber, is held in a colloidally dispersed state and can be removed in the subsequent soaping process (see also *Mell.*, **1943**, 99, 366).

In order to increase the fastness to crocking of the insoluble azo dyestuffs, *G.P. 721,217* (1937) recommends an aftertreatment with condensates of ethylene oxide with aliphatic or aliphatic-aromatic alcohols or with phenols. These products are used in conjunction with pyrophosphates or metaphosphates and amino acid salts as detergents and scouring agents. Very small amounts of oxygen developing agents (persulfates or perborates) are said to aid substantially these detergents in improving fastness to crocking.

The fastness to crocking of Naphthol AS dyeings can be improved by aftertreating the dyed fabrics in a soap solution containing fatty alcohol sulfates, soap or emulsifying agents (for instance Emulphor) and organic or inorganic substances which prevent the formation of hard water soaps (*F.P. 837,182*—I.G.). Agents of this kind are phosphates, Trilon, Calgon, etc. It is also an advantage to add oxygen-yielding compounds, such as perborates. This method is said to give particularly good results regarding crocking-fastness when working in dyeing machines *B.P. 514,059*—I.G. proposes a similar method.

Scouring agents mentioned in these processes are soaps of saturated or unsaturated fatty acids, fatty alcohol sulfates (Gardinols), fatty acid condensates of the Igepon type, condensates of the Peregal type, etc.

U.S.P. 2,105,326 (Pharma) suggests using the protein detergents as protective agents against the premature formation of the dyestuff lake in mixtures of stabilized diazo compounds and coupling components.

Kuhlmann (Paris) describes in the more recently published *G.P. 739,977* and *746,571* (1944) a process for increasing the fastness to light of certain insoluble azo dyestuffs by transforming them during or after the coupling process into complex copper compounds. As an example the patent recommends an aftertreatment in a bath of 5 gm of copper sulfate and 0.5 gm of acetic acid per liter.

Application Printing of Salts and Bases. The usual printing procedure is to naphtholate the material, dry, and apply thickened diazo solutions in printing. The reverse method of printing the thickened naphtholate solution, drying, and dyeing with diazo solution is seldom followed, because of limitations of color and difficulty of maintaining pure white grounds.

The diazo printing pastes are generally thickened with starch tragacanth or locust bean gum (see also A. Gotthardt "Preparation of Ice Colors for Application Printing", *Mell.*, **1924**, 248). Sometimes stabilizing agents such as Paradurol or Parasanol are added. The diazo solutions are neutralized with sodium acetate just before printing. The temperature of the print pastes should not exceed 10 to 15°C, so they must be constantly cooled. Winternitz proposed the use of a printing trough containing a hollow copper or iron roller which could be packed with shredded ice and salt (sealed report of Soc. Ind. de Mulh., 1908; *Rev. A.C.I.T.*, **1926**, 117).

However, when using Fast Color Salts, printing pastes can be allowed to reach room temperature. The salts are simply dissolved in tap water and suitably thickened. It is necessary to add acetic acid in applying Fast Black Salts K and G, Fast Blue Salts BB and RR and Variamine Blue Salt B (see Loeser, "Printing Variamine Blue", *Z. f. ges. Tex. Ind.*, **1936**, 511, 533).

The material is prepared as usual with the naphtholate solution. A padder is used for the impregnation, having a trough with as low a capacity as possible (20 to 40 l). The temperature is maintained at about 80°C during padding to minimize the effect of the naphthol's substantivity. The material is then dried in the hot flue, or on a festoon drier. The naphthols, especially Naphthols AS-RL and AS-LB, are very sensitive to light, so the material must be stored in the dark.

Diazotized bases, as well as Fast Color Salts, can be used for printing on the naphthol prepare. The bases are diazotized in the same manner as for preparation of dye baths: nitrite, dissolved in water, is added to the hydrochloric acid solution of the base. If the base is sparingly soluble in dilute acid, the base can be pasted with nitrite solution and charged into the dilute acid, or the hydrochloric acid salt of the base is first pasted with water, and the nitrite slowly added. After diazotization, the mineral acid content is neutralized with sodium acetate (I.G., "Naphtol AS auf dem Gebiete der Druckerei", 1930).

The Fast Color Salts offer advantages over the bases. They are readily soluble in water, and are stable at room temperatures.

The material is prepared, for example, with:

20 gm Naphthol AS-D
20 cc Turkey red oil
30 cc caustic soda 38° Bé
per l

It is then dried, and printed with the following print paste:

13 gm Fast Scarlet G Base
20 gm hydrochloric acid 20° Bé
100 cc boiling water

Add 200 cc of ice water, and 6.5 gm of sodium nitrite dissolved in 20 cc of water. After ½ hour, add 15 gm of sodium acetate dissolved in 50 cc of water, then 12 cc of acetic acid 50%. Thicken with 500 gm of starch-trag. paste (I.G. Printing Manual).

Vat colors may be printed alongside the Fast Color Salts. In this case the material is aged five minutes and the vat colors fixed in subsequent rinsing. Indigosols alongside the Fast Color Salts may be printed according to the steam or nitrite methods, and it is also possible to apply chrome mordant and basic colors on naphthol-prepared material.

Application Printing of Naphthols. A method frequently used in Russia consisted in printing thickened naphtholate solutions on white ground followed by coupling in a diazo solution. By the selection of different naphthols, a multi-colored effect is possible. The method is interesting for ease of application and because of saving of chemicals.

The thickened naphtholates are printed, the material is then dried, and dyed out in a solution of Fast Color Salt or diazotized base. For example:

Print Pastes

20 gm Naphthol AS
50 gm Monopole Brilliant oil
50 gm denatured alcohol
25 gm caustic soda 38° Bé
Paste up, heat, and add
355 gm hot water
500 gm starch-trag. thickening
1000 gm

38 gm wheat starch
48 gm water
Paste up and add
125 gm gum trag. 6%
8 gm caustic soda 38° Bé
55 gm β-naphthol
24 gm caustic soda flakes
500 gm gum trag.
2 gm Safranine (sightener) in
200 cc water
1000 gm

Print on white cloth, dry, and dye in a solution of diazotized α-naphthylamine, rinse, sour off in 2½° Bé sulfuric acid, and soap on the reel in rope form. The whites are sometimes slightly tinted, in which case the material is padded with 5 gm of Hydrosulfite NF per liter, dried, aged and washed.

Two-Tone Print. The material is first padded with the following ingredients:

4 gm β-naphthol
4 gm caustic soda 38° Bé
20 gm sulfonated castor oil
per liter

dried, and printed with a concentrated naphthol paste consisting of:

625 gm gum trag. 6%
60 gm sulfonated castor oil
300 gm naphthol solution →
15 gm turpentine
1000

40 gm β-naphthol
80 gm caustic soda 22° Bé
180 gm water
300 gm

The printed and dried goods are led through a solution of *p*-nitro diazobenzene rinsed and soaped. The fabric shows a dark red pattern on a light red ground. The goods may be further cross-printed with a Hydrosulfite NF white discharge paste containing anthraquinone, and with an aniline black or Diphenyl Black cover print, aged, rinsed and soaped. Black, white and dark red are thus obtained on a light red background. This style was produced in large quantities in Russia. It can, of course, be produced with Naphthol AS dyestuffs as well.

Naphthol-Nitrite Pad Method (Gürtler). A variant on the naphthol application process, the so-called naphthol-nitrite process, was developed by Dr. Gürtler (*G.P. 446,541, 451,049, 459,902, 459,975.*) The principle of this method is the addition of sodium nitrite to the naphthol pad liquor, while the print paste contains the base suitably dissolved with hydrochloric acid, and also an organic acid. The diazotization takes place on the fiber and the coupling reaction proceeds at the same time. This method can be used only with those bases the hydrochlorides of which are readily soluble in water. It is therefore not suitable for *p*-nitraniline. Similarly, for small patterns, the naphthol-nitrite may be printed and the dried prints dyed with the base-salt and organic acid (naphthol-nitrite printing method).

Impregnation

20 gm Naphthol AS-OL
10 cc denatured alcohol
30 gm Monopole Brilliant oil
20 cc NaOH 38° Bé
500 cc boiling water
Add
25 gm sodium nitrite
1.5 gm Nekal BX
to 1 l.

Print Paste

15 gm Fast Orange GC Base
135 cc water
75 gm tartaric acid solution 1:1
75 gm lactic acid 50%
700 gm starch-trag. paste
1000

Indigosols lend themselves admirably for printing alongside the Fast Color Salts. The nitrite method is generally used, but it is also possible to apply them by the ammonium oxalate or ammonium sulfocyanide methods, with sodium chlorate. When using the nitrite method alongside Variamine Blue B print, care must be taken not to permit nitrous fumes to attack the undeveloped Variamine Blue, as it quickly loses its blue cast, turning violet. The safest operational procedure is to age the prints of Variamine Blue Salt B and Indigosol-nitrite colors in order to develop completely the Variamine Blue before the sulfuric acid bath. This short ageing (4 minutes) is also favorable for the Indigosol print. The material is then passed through 2% sulfuric acid at 65°C. In this way bright, rich shades are obtained.

G.P. 596,186 (I.G.—Aubauer) discloses a method for printing vat dyestuffs with Fast Color Salts on naphtholated goods, using the properties of Colloresin. After naphtholating and drying, the material is printed with a diazotized base to which a compound having moderately oxidizing properties has been added (as nitrobenzene sodium sulfonate) and vat dyestuffs, incorporated into a printing paste with Colloresin, containing, however, no sulfoxylate formaldehyde or alkali. The printed and dried material is then padded with alkaline hydrosulfite solution, and aged in a specially constructed Colloresin ager.

The Rhodiaceta Company of Lyon developed the following formula for printing naphthol dyes on acetate rayon:

30 gm naphthol
10 gm Fast Base
100 gm tetrahydrofurfuryl alcohol (Hystabol D)
10 gm caustic soda 30° Bé
220 gm water
Heat to boiling; add
600 gm gum thickening
30 gm sodium nitrite
1000

The printed goods are aged 20 minutes at 100°C, then developed in a solution of 50 cc of formic acid and 10 gm of sodium nitrite per liter at 60°C, rinsed, neutralized and soaped. Good results are obtained with:

Cibanaphthol RK and Scarlet Base Ciba V
Cibanaphthol RK and Red Base Ciba III
Cibanaphthol RK and Red Base Ciba V, etc.

Aftertreatment of Dyeings and Prints. Dyeings and prints of the insoluble azo dyestuffs are aftertreated in boiling soap and soda-ash solutions. Both soap and soda are indispensable, because the soda is necessary as solvent for removing the naphthol residues while the soap treatment is particularly important for rendering the dyeings fast to rubbing.

Naphthols AS-BR, AS-SW, AS-GR, AS-SG, AS-SR, AS-BS, AS-LG and AS-L3G cannot be completely stripped from the fiber, because of their high substantivity. They are therefore unsuitable for discharge prints, and for naphtholating in application printing. They are well adapted, however, for printing of the naphtholates and passage through diazo solution.

Small quantities of high-molecular fatty alcohol sulfates, when added to the scouring liquor (for example, 2% soap and 0.5% sodium dodecyl sulfate and 5% soda ash), can improve the purity of shade and the fastness to crocking of the naphthol dyestuffs, according to *G.P. 610,710*—1930 of Böhme F.C., and *G.P. 621,038* (see *Wengraf's Ber.*, Feb., **1935,** and *Rev. Gen. Mat. Col.*, **1935,** 398). According to *B.P. 450,868* and *450,981* of I.C.I. (*D.F.Z.*, **1937,** 23) compounds formed by condensing glycerine with higher fatty acids in the presence of alkalis can be added for the same purpose. These patents do not refer to triglycerides, or in other words, normal fats, but to water-soluble esters, having free OH groups only. They are manufactured with excess glycerin. The reaction product of 120 parts of oleic acid, 400 parts of glycerin, and 1 part of sodium hydroxide at 280°C, is given as an example. The same principle is also found in *G.P. 634,952* of Böhme F.C., wherein it is explained that when one to two molecules of fatty acid are reacted with excess glycerin or other carbohydrate, one or more OH groups remain unsubstituted. In this manner true soaps (saponified fats) are not formed, but rather products which are water-soluble, stable to hard water and excellent foaming agents. The patent names as example, palmityl acid esters of lactose or saccharose.

In general, an increased fastness to crocking is obtained by adding auxiliaries of high detergent and dispersing power to the soaping bath, such as sulfated fatty alcohols (Duponols, Cyclanones), or synthetic products (Igepals, Ultravons).

The use of complex phosphates as addition to the soap bath to increase fastness to crocking is recommended in *G.P. 679,679* (Benckiser Co. and Volz, 1939). Calgon and Quadrafos also come into question.

Intrasol (Stockhausen) acts in a different manner. This aliphatic sulfonic acid has no wetting or foaming properties, but is more active than soap in removing superficially adhering particles of dyestuff from the fiber. In working with hard water Intrasol prevents precipitation of lime compounds. Even if used without soap it guarantees an excellent fastness to crocking.

Another product which has been especially developed for the purpose of increasing crocking fastness is Solidogen AS (I.G.). This product is recommended for aftertreatment of Naphthol AS dyeings which must satisfy the strictest requirements for fastness to marking-off, as in towels, bathrobes and the like. The Solidogen AS is applied in a 0.1 to 0.3% solution at 60 to 90°C for half an hour (Drapal, *Mell.*, **1940**, 235).

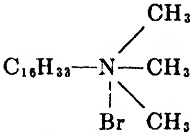
Stripping of Azo Dyes. Dyeings produced with the insoluble azo dyestuffs are difficult to strip. A partial decomposition can be effected by the action of sulfoxylate formaldehyde, to which caustic soda, and sometimes anthraquinone has been added.

For stripping Naphthol AS dyeings, I.G. recommends the following bath:

1 cc Igepal C or Peregal O
3–4 cc caustic soda 40° Bé
3–4 gm hydrosulfite conc. pdr.
0.5–1 gm anthraquinone 30% paste
per liter

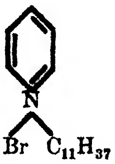
The treatment is carried out at temperatures near the boil.

In *F.P. 748,510, 771,349, G.P. 605,913, B.P. 400,239*, the I.C.I. claims that an almost complete decomposition of these dyeings can be obtained using hydrosulfite to which amines or amine salts, and particularly high-molecular (over ten C atoms) substituted ammonium salts have been added, for example cetyl trimethyl ammonium bromide



(see Rowe, *J. Soc. Dy. & Col.*, **1936**, 205). These patents cover the products Decamine A and Lissolamine A of I.C.I. which have proved to be excellent dispersing agents (compare also *G.P. 632,066, 632,728; B.P. 444,169; U.S.P. 2,052,612; F.P. 791,217*).

Pyridinium compounds can likewise be applied, for instance, octadecyl pyridinium bromide



or β-diethylaminoethylol cetylamide in the form of its acetate or hydrochloride (*F.P. 752,728*—1936). Later, *G.P. 652,347* disclosed that small additional quantities of anthraquinone, or of oxy, amino, alkyl or halogen derivatives of anthraquinone, increase the stripping effect.

G.P. 701,845—1936, and *F.P. 820,153* (Ciba) recommend the use of sulfonic acids of long-chain substituted amines (for example, laurylbenzylmethylamine) or of substituted benzimidazoles (for example, methylheptadecyl benzimidazole) as assistants with hydrosulfite in stripping naphthol dyeings. The addition of small amounts of anthraquinone aids the action. Further details are given in *F.P. 820,353* (Ciba). The benzimidazoles are prepared by the reaction of *o*-phenylene diamine with fatty acids. The stripping bath, containing 5 gm of caustic soda, 3 gm of hydrosulfite and 2 gm of Ultravon, is applied at 90°C. Ultravon is the trade name of the benzimidazoles (Graenacher, *Bull. Fed.*, **III**, 268 and ff.)

Resists under Azo Dyestuffs. This style was very popular between 1890 and 1905. It was quite generally abandoned after the invention of sulfoxylate formaldehyde, because the discharge style on dyed azo colors was much simpler. The resist method, however, attained new importance in textile printing when the bases were introduced which have slow-coupling diazo derivatives, for example, Variamine Blue B Base. With this innovation, new processes of practical importance were developed. Resists are obtained by printing substances which destroy, precipitate or change the diazo compounds or which destroy the coupling ability of the naphthol.

Acids or strongly acid salts counteract the coupling process of the diazo compounds. Thus by printing citric or tartaric acid, sodium persulfate or nitrite plus an acid salt on naphtholated goods, white resists are easily produced. Ammonium chloride gives partial resists if printed immediately before development in the diazo bath. Further, Öhler and Kallab recommended hydrazine and hydroxylamine as resisting agents (*G.P. 147,632, F.P. 327,554*). Sulfonated phenylhydrazine is said to give particularly good results, and has been marketed under the name Reserve H. Phenylhydrazine sulfonic acid is insoluble in water, and must be transformed to its ammonium salt (*Frb. Ztg.*, **1903,** 226). This process can be applied to the azo dyestuffs derived from the arylides of oxynaphthoic acid, according to *F.P. 766,957* (I.G.). A fabric impregnated with oxynaphthoic acid anilide is printed with a paste containing 100 gm of phenylhydrazine sulfonic acid, 246 gm of water, 50 gm of ammonia 23%, 4 gm of ammonium thiocyanate and 600 gm of thickener. The printed goods are dried, and dyed with a diazo solution.

Gandourine described a resist method (*G.P. 108,504; Fischer's Ber.*, **1900,** 476) based on transformation of *p*-nitrodiazobenzene to the isodiazo compound by the action of alkalis, whereby it loses its coupling ability.

Other substances, for instance, glue, paraffin or wax to which organic acid is added have been recommended as resisting agents. These are printed before impregnation of the naphthol, in order to avoid staining of the whites by the naphthol (Oswald, *Bull. Mulh.*, **1899, 272**).

Ciba published a process comprising the application of xanthogenates as resists under prints or dyeings of insoluble azo dyes (R. Haller, *F.P.*

739,810—1932; *B.P. 387,922; G.P. 577,702; Tiba*, **1933,** 347; *Rev. Gen. Mat. Col.*, **1934,** 111; *J. f. prakt. Chemie*, #**41,** 183).

The general formula of the xanthogenates is

$$\underset{\overset{\|}{S}}{R—O—C—SH} \qquad (R = Alkyl)$$

They are obtained by the reaction of carbon bisulfide with alkali alcoholates. A printing paste containing 125 gm of sodium xanthogenate per kg is printed on naphtholated goods and the material is then passed through a diazo solution or cross-printed with the diazo solution. In Ciba's *B.P. 526,689*—1940, a naphtholated fabric is printed with a paste containing

500 gm	thickener
400 gm	water
50 gm	potassium xanthogenate
50 gm	magnesium chloride
1000 gm	

This patent is similar to *G.P. 702,280*—1938 and *F.P. 851,747*—1940. In these patents it is pointed out that the resisting effect of the alkali xanthogenate is increased by the addition of alkaline earth salts, so that the resist is obtained in clear white print by washing in cold water only. This resist works well under *p*-nitraniline red dyeings. To obtain colored resists, Indigosol dyes, sodium nitrite, magnesium sulfite and potassium xanthogenate are combined and printed on naphtholated fabrics; after drying and passing through a diazo solution the goods are dyed, and conveyed through hot dilute sulfuric acid (20 gm H_2SO_4 66° Bé per l) to develop the Indigosols, and thoroughly rinsed.

Another resist method has been disclosed in *B.P. 405,005* (Hardcastle-Schwabe-Parker). In this method a paste containing aluminum formate and a salt of manganese is printed on the goods before naphtholating. *B.P. 386,365* and *421,406* (Schwabe-Parker) aim to produce tone-in-tone effects by application of a print which forms a semipermeable membrane, thus preventing complete penetration of the naphthol dyestuff. A dispersion of a naphthol in a Colloresin thickening is printed on white goods, and a naphtholate solution is padded over the pattern. A semipermeable diaphragm is produced on the printed areas. Finally the goods are dyed out in a diazo solution. A similar method is recommended in *U.S.P. 2,031,546* (Schwabe-Parker). The resist consisting of aluminum acetate, a paste of raw starch and a hydrolyzing and peptizing agent (ammonium thiocyanate) is printed on white cloth. Such printed material can be stored without deterioration. In this process the principle of semipermeable diaphragms, first observed by Zeidler and A. Haller, is applied again. The use of native starch (raw or unprocessed) has been noted in the early *Aus. P. 126,753.* Further ramifications of the Schwabe-Parker method are found in *G.P. 629,895*. Resists of this type are especially suitable under the most substantive naphthols, also under dyestuffs which require special developing operations, such as aniline black, Rapidogens and Rapid Fast colors (*Rev. Gen. Mat. Col.*, **1937,** 237; *G.P. 638,755, 642,581; Rev. Gen. Mat. Col.*, **1938,** 103, 225).

The most important resist methods are based on the application of tin salt (Koechlin Frères, F. Binder), of sulfites (Tigerstedt), of tannic acid (Langer, Romann, J. Koechlin, Rolffs), of persulfates (M.L.B.), of acid salts—especially of aluminum sulfate or of salts developing acids in ageing (ammonium oxalate). Of these methods, the aluminum sulfate is used only for resists under Variamine Blue B.

*Tin Crystals Resist**

This method gives resists under *p*-nitraniline red. It is based on the observation that *p*-nitrodiazobenzene undergoes transformation to phenylhydrazine by the action of tin crystals (*Ber.*, **1883,** 3976). A disadvantage lies in the possible tendering of cellulose fibers by hydrolysis of tin crystals. Moreover, the white resists have a yellowish cast which darkens in storage. The print paste contains besides tin crystals, organic acids which assist the effect of the tin crystals, and purely mechanical agents such as china clay, glue, wax or paraffin.

White Resists with Stannous Chloride

400	500	300	250	stannous chloride
400	—	550	250	gum thickener
100	—	50	—	citric acid
—	150	—	50	tartaric acid 1/1
100	—	—	—	glucose
—	350	—	350	gum thickener or glue 1:2 water
—	—	100	100	china clay
		1000 gm		

Colored resists are obtained by applying pigments fixed with albumen, or with basic or vat dyestuffs. The basic colors are printed with tannic acid, as for example,

60 gm	Methylene Blue NNX
75 gm	acetin
235 gm	starch-trag. thickening
100 gm	citric acid
180 gm	tannic acid 1:1
50 gm	tartaric acid
300 gm	tin crystals (stannous chloride)
1000 gm	

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* Koechlin, *Bull. Mulh.*, **1900,** 44; *Rev. Gen. Mat. Col.*, **1900,** 36; F. Binder, *Bull. Mulh.*, **1900,** 92; *Rev. Gen. Mat. Col.*, **1900,** 171.

This resist is printed on naphtholated goods, and aged. The prints are developed with the diazo solution, conveyed through a 3% sulfuric acid bath, and washed well.

Salts of titanium yield good resist effects; for example, a paste of $Ti_2(SO_4)_3$ plus NH_4CNS plus starch thickening gives results superior to tin salts (Nanson, *Text. Col.*, **1928**; *A.C.I.T.*, **1928**, p. 105). Colored resists are made with basic colors or with pigments.

Sulfite Resists

Tigerstedt* in Serpoukoff, Russia, was the first to recommend sulfites as resists under azo dyeings. M. Richard,** without any knowledge of the discovery, also studied the style, and produced dark blue resists under *p*-nitraniline red with sulfites. The characteristic property of sulfite which causes the resist is the formation of a sulfonate of the diazo compound, which has no coupling ability. Tigerstedt printed a white resist composed of bisulfite, caustic soda and glycerin on cotton prepared with naphthol and antimony salts.

White Resist with Sulfite

145 gm	potassium carbonate
120 gm	water
490 gm	sodium bisulfite 38° Bé
60 gm	wheat starch
90 gm	British gum
95 gm	gum thickening
1000 gm	

Potassium sulfite is preferred to other sulfites because of its good solubility. The printed goods are aged and subsequently dyed out in the diazo solution, preferably on the padder. Colored resists are produced by adding pigments, direct dyes, chrome colors or basic colors. The naphtholating liquor contains tartar emetic for the basic colors, or according to Bourcart, potassium ferrocyanide, in order to form the ferrocyanide lake (*Bull. Mulh.*, **1912**, 595).

The sulfite resist was used principally under *p*-nitraniline red, and some special Naphthol AS dyeings, but is not suitable under α-naphthylamine bordeaux. The whites are generally better than those produced with stannous chloride, and no tendering of the fibers occurs.

Tannic Acid Resist†

Tannic acid forms insoluble compounds with the diazo solutions which are incapable of coupling with the naphthol. This method made it possible

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* *Rev. Gen. Mat. Col.*, **1901**, 75; *Bull. Mulh.*, **1901**, 153, 269.

** *Bull. Mulh.*, **1901**, 97, 161; *Rev. Gen. Mat. Col.*, **1901**, 101, 143.

† Dr. Langer, report under seal, depos. at the Soc. Ind. de Rouen, 1894; *Bull. Mulh.*, **1899**, 76; *Rev. Gen. Mat. Col.*, **1900**, 22; *Bull. Rouen*, **1898**, 145; Romann, *Bull.*

to print colored resists with basic colors, and it therefore enjoyed a great success. It could be used to imitate the blue-red Schlieper-Baum style (indigo discharges on Turkey red). The following steps comprised the procedure:

(1) Print of tannin and basic color on naphtholated goods.
(2) Ageing.
(3) Padding with diazo solution.
(4) Passage through tartar emetic.
(5) Washing, soaping, rinsing.

Since β-naphthol was sensitive to the passage through the ager, M. Battegay proposed the use of β-oxy-1-naphthoic acid instead (*Rev. Gen. Mat. Col.*, **1914,** 283; *Bull. Mulh.*, **1914;** *G.P. 238,841*—Bayer Co.).

White Resist

400 gm	tannin
250 gm	water
200 gm	gum thickening
50 gm	glycerin
100 gm	liquid soap
1000 gm	

Dyestuffs which can be printed with chrome mordant and tannic acid also come into question for manufacture of the blue-red style. Such colors are the Gallo and Modern dyestuffs, for example, Gallo Violet DF, Gallo Navy Blue 2CB, Modern Violet, etc.

Blue Resist with Gallo Violet DF

30 gm	Gallo Violet DF
150 gm	water
30 gm	glycerin
250 gm	acetic acid—starch-trag. thickening
200 gm	British gum 1:1
200 gm	gum trag. 6%
60 gm	chromium acetate 20° Bé
80 gm	tannin-acetic acid 1:1
1000 gm	

This paste is printed on naphtholated goods (15 gm of β-naphthol per l), dried, and aged 2–3 minutes in the rapid ager. The goods are then padded in a solution of diazotized *p*-nitraniline, rinsed in hot water, and then treated with 2 gm of sodium bichromate and 0.5 gm of soda ash per liter at 30°C. Finally the prints are rinsed, soaped and rinsed.

Mulh., **1897,** 152; J. Koechlin, *Bull. Mulh.*, **1899,** 74; *Rev. Gen. Mat. Col.*, **1900,** 22. Despite the priority of Langer's and Romann's work, the company Rolffs obtained *G.P. 113,328* and *116,694* (*Bull. Mulh.*, **1900,** 94). Law suits and other trouble resulted from this situation.

Persulfate Resist

This method is described in *G.P. 83,964*—M.L.B. (*Fischer's Ber.*, **1895,** 981), and is based on the oxidizing action of sodium or ammonium persulfate, which destroys the excess naphthol. A mixture of tetrazotized dianisidine and persulfate was printed on naphtholated goods. The persulfate has no effect on the azo solution nor on the blue shade generated by the print. The method was used for manufacturing a blue-red pattern. Tetrazotized dianisidine with potassium persulfate and cupric chloride were printed on naphtholated goods, then the goods were aged. Here the surplus naphthol was destroyed by the persulfate, so that in the subsequent passage through *p*-nitrodiazobenzene solution, red was produced only on the unprinted areas. *p*-Nitraniline red, which is sensitive to the copper of the rollers, was prevented from the discoloration by the addition of ammonium oxalate to the diazo solution. The red shade produced by *p*-nitro-*o*-anisidine is not influenced by copper ions, and is therefore preferred in this process.

The print paste is made up as follows:

Blue	
495 gm	thickening
396 gm	tetrazo solution
59 gm	potassium persulfate
50 gm	copper chloride 40° Bé
1000 gm	

Tetrazo Solution	
40 gm	dianisidine salt
250 gm	water
25 gm	HCl 22° Bé
620 gm	water
65 gm	nitrite 30% solution
1000 gm	

Aluminum Sulfate Resist

The blue-red style was further improved by the invention of the Naphthol AS series. The process was first proposed by Griesheim-Elektron and was carried out by printing dianisidine blue resist on Naphthol AS impregnation, and developing in diazotized *p*-nitraniline (Tschudi process). The reverse is also an important article. A thickened solution of diazo *p*-nitraniline (or Fast Red, or Fast Orange Base) with 120 gm of aluminum sulfate per kg of print paste is printed on naphtholated goods. The printed fabric is padded with tetrazotized dianisidine solution without ageing.

Later, the style was still further improved by the invention of Variamine Blue B and Fast Blue BB and RR. Combinations of these blues with Fast Red 3GL or TR Bases have been printed in nearly every cotton print shop.

Variamine Blue Resist Styles

The blue-red print style attained its highest degree of beauty and perfection in the development of the Variamine Blue resist. This method can be readily carried out using the property of Variamine Blue to couple slowly with the naphthol component.

The sensitivity of Variamine Blue diazo derivatives against acids has been felt to be an inconvenience in the dyeing process. However, this sensitivity has made it possible to create a well-known style, which by its outstanding beauty and brilliance has maintained its importance in the trade. The application of a printing paste containing 100 to 120 gm of aluminum sulfate per kg on naphtholated fabric has the effect of completely preventing any coupling reaction of Variamine Blue diazo solution on the printed areas; at the same time a coupling reaction of orange or red salts is no way impaired. Thus it is simple to print white resists alongside red or orange effects, producing sharp and attractive contrasts with the navy blue ground.

When printing on rayon, for which the naphthols have a greater affinity, it is necessary to augment the chemical action of aluminum sulfate with other agents.

In place of aluminum sulfate, potash alum can also be used, but because of its poor solubility (10 parts per 100 of water at room temperatures) there is always danger of crystallization. This drawback can be avoided by adding lactic acid which forms complex compounds with the alum, whereby the solubility is considerably increased. The following white resist, for example, gave good results at the firm of Scheurer-Lauth, Alsace:

700 gm	starch-trag. thickening
180 gm	water
80 gm	potash alum
40 gm	lactic acid 50%
1000 gm	

Heated to 80°C under constant agitation until dissolved

Lactic acid alone can be used as resist under Variamine Blue.

It sometimes happens that when aluminum sulfate resists are laid up for any length of time before developing, the prints mark off onto unprinted areas, particularly when the aluminum sulfate has been intensified with additions of lactic or glycollic acids. Such mark-offs can cause large losses, but where the condition is recognized before development, it may be corrected by padding with dilute caustic soda, and drying in. This operation may be advantageously carried out on the print machine with a stipple blotch roller.

The addition of tartaric acid or other acid-reacting compound has been recommended in *G.P. 531,474* to enhance the resist paste of aluminum sulfate, particularly when printing fine patterns.* Resist prints with such additions require no ageing; the fabrics are simply dried well after printing and padded on the mangle with full dip in Variamine Blue Salt solution.

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* *Mell.*, June 1933, 250.

It has been shown (*B.P. 389,853*, Bleacher's Assn., *B.P. 404,304*, *F.P. 743,329*, *G.P. 608,847*), that the color yield of the Variamine Blue is increased by passing the padded goods between hot plates for 10 to 20 seconds. This fact has already been reported in discussing the dyeing procedures, but the method has apparently greater significance in the production of resist prints. Finally, the prints are soured in a hydrochloric acid bath (20 gm HCl per l) at 90°, or treated with bisulfite, then rinsed and soaped. The material must not carry traces of the diazo solution into the soaping bath, otherwise the whites will be stained with blue (Dr. Rath, *Mell.*, **1929,** # 3, French edition).

Colored resists under Variamine Blue are produced with chrome mordant, vat and Indigosol colors, and also basic colors, although these are of little importance. The most suitable are the Indigosols, for which the processes may be divided into two groups: (1) Those requiring ageing; (2) those not requiring ageing.

In general, acids, or substances which develop acid (ammonium oxalate) or acid salts (aluminum sulfate) are added to the Indigosols as resist agents.

Steam Methods. Sodium chlorate is used in the steaming or ageing methods. (*G.P. 551,508*, *551,525* and *555,304*, D. & H.)

(1) The naphtholated fabrics are printed with a paste containing Indigosol color, ammonium oxalate, sodium chlorate and ammonium vanadate, dried, aged and developed in a solution of Variamine Blue Salt B. The yield in printing is sometimes insufficient, as the prints are not stable enough. Moreover, the resist effect is not always complete (compare Krostewitz, *Mell.*, **1931,** 585, wherein some interesting details are given).

Print Paste

30	gm Indigosol Green IBA
50	gm Débésolvol IND
155	gm hot water
460	gm starch-trag. thickening
5	gm ammonia 25%
50	gm ammonium oxalate
100	gm hot water
12.5	gm sodium chlorate
37.5	gm hot water
100	gm ammonium vanadate 1%
1000	gm

(2) This modification of the sodium chlorate method has been used in several European plants. Aluminum sulfate is used as resist agent, and no other acid salt is necessary. Vanadate is also deleted. Freshly prepared pastes give good results, but unfortunately they cannot be kept for any length of time. The printed material is dried and aged, then passed immediately through a solution of Variamine Blue Salt B.

Print Paste

30 gm	Indigosol Golden Yellow IGK
30 gm	Fixer CDH
30 gm	Glyecine A
239 gm	hot water
450 gm	starch-trag. thickening
200 gm	aluminum sulfate 1:1
20 gm	sodium chlorate
1 gm	soda ash
1000 gm	

Methods without Steam. In the *lead chromate method,* which is still frequently used, the naphtholated fabrics are printed with a paste containing Indigosol dyestuff, potassium sulfite, ammonium thiocyanate and lead chromate.

Print Paste
(*D. & H.*)

80 gm	Indigosol Golden Yellow IGK
70 gm	Dehapan O
255 gm	hot water
400 gm	neutral starch-trag. thickening
65 gm	$NaHSO_3$ 38° Bé or K_2SO_3 45° Bé
10 gm	ammonium thiocyanate
120 gm	lead chromate 60% paste
1000 gm	

It is interesting to note that the paste contains a reducing agent, necessary for resisting the diazo solution (sulfite) and the oxidizing agent necessary for developing the Indigosol. The effect of these substances which act in opposite ways can only be explained by considering that the compounds react one after the other, first the sulfite, as a resist, then the chromate as an oxidant.

The yield can be improved by replacing the potassium sulfite and ammonium thiocyanate with zinc sulfate. The following formula has been suggested:

40 gm	Indigosol Golden Yellow IGK
50 gm	Glyecine A
300 gm	hot water
470 gm	starch-trag. thickening
70 gm	lead chromate 60% paste
70 gm	zinc sulfate
1000 gm	

The printed and dried goods are padded in Variamine Blue Salt solution without intermediate ageing. After skying for 30 seconds, the fabrics are conveyed through a solution of 20 cc HCl 19° Bé per liter for 30 seconds, rinsed and soaped. This method gives colored resists of outstanding purity and brightness.

The copper sulfate method depends on the oxidation of the Indigosol after the blue development (*B.P. 372,190*—D. & H.) A paste is printed containing Indigosol dyestuff plus zinc sulfate or sodium bichromate. The printed and dried goods are developed in Variamine Blue Salt B, skyed and led through a 70°C bath of copper sulfate and sulfuric acid for 2 seconds. The copper sulfate may be replaced by peroxide.

Print Paste

40 gm	Indigosol Golden Yellow IGK
60 gm	Glyecine A
250 gm	hot water
600 gm	starch-trag. thickening
50 gm	zinc sulfate
1000 gm	

The aluminum chlorate process may be carried out in either of two ways: (1) The naphthol liquor contains vanadate, the print paste sodium chlorate and aluminum sulfate. (2) The naphthol liquor contains sodium chlorate, the print paste contains aluminum sulfate and vanadate.

(1) It is necessary to add the ammonium vanadate to the hot naphtholate solution, and to pad the goods at elevated temperatures. According to D. & H., preparation of the solution in this way does not impair the stability of the naphthol. The print paste contains aluminum sulfate and sodium or aluminum chlorate. After drying, the goods are laid up for 24 hours, then padded with Variamine Blue Salt B (35 gm per l).

Naphthol Prepare

17.5 gm	Naphthol AS
20 gm	caustic soda 34° Bé
16 gm	Monopole Brilliant oil
846.5 gm	boiling water
100 gm	ammonium vanadate 1%
1000 gm	

Print Paste

30 gm	Indigosol Printing Blue IGG
60 gm	Glyecine A
250 gm	water
500 gm	starch-trag. thickening
40 gm	aluminum sulfate 1%
120 gm	aluminum chlorate 25° Bé
1000 gm	

The addition of vanadate to the naphthol solution does not reduce the stability of the impregnated goods.

(2) This method is the more recent, and can be handled more easily. The addition of chlorate to the naphthol does not impair the stability of the padding liquor, nor affect the tensile strength of the material. The resist pastes do not contain the very active aluminum chlorate, but this salt is formed only on the print itself. The procedure therefore consists

in padding with the naphtholate solution and sodium chlorate, in printing the Indigosol with aluminum sulfate and vanadate, drying and laying up, then padding with Variamine Blue Salt B. The color yield can be considerably improved by ageing instead of laying up. The results are excellent, especially regarding purity of the resist and stability of the print pastes and naphthol solutions.

Naphthol Preparation

17.5 gm	Naphthol AS
20 gm	caustic soda 34° Be
16 gm	Monopole Brilliant oil
886.5 gm	boiling water
	Cool; add
10 gm	sodium chlorate, *dissolved in*
50 gm	water
1000 gm	

Print Paste

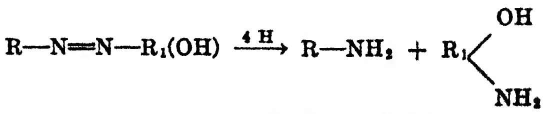
25 gm	Indigosol Scarlet IB
50 gm	Débésolvol IND
115 gm	hot water
585 gm	starch-trag. thickening
200 gm	aluminum sulfate 1:1
25 gm	ammonium vanadate 1%
1000 gm	

The strong coupling action of the other Fast Color Salts cannot be sufficiently affected by aluminum sulfate to make resist prints in this way. It has been observed that Peregal OK forms a white precipitate with Naphthol AS which does not couple with the Fast Salts, and white resists can be produced employing this reaction. The following paste is printed on goods naphtholated with Naphthol AS-BG:

500 gm	starch-trag. thickening
120 gm	hydrosulfite
120 gm	Peregal OK
200 gm	zinc oxide 1:1
60 gm	water
1000 gm	

After dyeing, coupling is performed in the usual way on the mangle with Fast Blue Salt BB. Indigosol pastes containing Peregal OK can be used for colored resists (Lanczer, Enschede Holland, *Mell.*, **1941**, #22, 2).

Discharge Prints. Discharge styles can be produced on dyeings of the insoluble azo dyes by applying reducing agents. The chromophore group —N=N— is destroyed and the dyestuffs are split into amines or aminonaphthols which are mostly colorless and can be removed from the fiber.



$$R{-}N{=}N{-}R_1(OH) \xrightarrow{4\,H} R{-}NH_2 + R_1\left\langle\begin{matrix}OH\\ NH_2\end{matrix}\right.$$

R and R_1 = aralkyl groups

The early discharge formulas employed stannous chloride and zinc dust. The invention of sulfoxylate formaldehyde revived and improved these earlier discharge formulas and the sulfite and tannin resist processes.

The azo dyestuffs possess considerable resistance to oxidation, and the dyeings are not dischargeable by oxidizing agents. Nevertheless oxidation discharges were attempted, but did not have any practical success. Pokorny (*Bull. Mulh.*, **1921,** 311; **1922,** 331) suggested the application of a sodium chlorate-ferrocyanide discharge to which Leucotrope was added, while Pollak described a discharge paste of chlorate and ferrocyanide with an aftertreatment of glycerin and caustic.

Apparently H. Schmid was the first to develop reduction discharge on dyeings made with β-naphthol (Report. dep. under seal Soc. Ind. de Mulh., 1896; *Frb. Ztg.*, **1898,** 150, 373; *Bull. Mulh.*, **1897,** 141; *G.P. 95,827*, *F.P. 255,997*; *Rev. Gen. Mat. Col.*, **1897,** 44). *p*-Nitraniline red is printed with a stannous chloride-sodium citrate paste containing acetin. The method was adopted by M.L.B., who offered a series of dischargeable dyes called "Aetze PN". In *G.P. 94,174*, Wolff suggested $SnCl_2 + NH_4CNS$; Cassella advised $SnCl_2$ + acetic acid + ammonium acetate.

H. Züblin and A. Zingg of Schlaepfer, Wenner and Co., in Italy[*] showed that glucose in alkaline solutions or with glycerin and acetin would reduce the azo dyes, and developed a discharge process. The *p*-nitraniline red dyeings were padded in a hot glucose solution of 12 to 14° Bé, then printed with a paste containing indigo and an alkali. The printed goods were aged 40 seconds in the special ager adapted for the Schlieper process, immediately acidulated at low temperatures and washed in the open width.

E. Knecht recommended in the *J. Soc. Dy. & Col.*, **1902,** 359, the use of titanous chloride or sulfocyanide (*B.P. 9,847*, May, 1901).

The first hydrosulfite discharges were made with pastes containing zinc powder and bisulfite. This method has the drawbacks of poor stability of the printing pastes and also of sticking in the engravings of the print roller. G. Pelizza and L. Zuber (*Rev. Gen. Mat. Col.*, **1900,** 137; **1904,** 130; *Bull. Mulh.*, **1900,** 49) considerably improved the method by replacing the bisulfite with bisulfite-formaldehyde, or bisulfite-acetone. The same recommendation was also made by M.L.B., Höchst.

Aluminum powder was tried as a substitute for zinc. As early as 1891, Weiss recommended mixtures of aluminum and magnesium with potassium sulfite as discharge on wool. H. Alt (*Bull. Mulh.*, **1902,** 22, 39) applied this process for discharging Para red, and Kalle Co. was granted *G.P. 123,138* for the process. A. Scheurer, however, claimed priority for the

[*] *F.P. 267,205*, *B.P. 13,088*, 1897; *G.P. 98,796*, *Frb. Ztg.*, **1898,** 110; see also Starek, *Bull. Mulh.*, Proc. Soc. Ind. de Mulh., 1910; Lauber, "Handbuch des Zeugdrucks," 1898, p. 56; and *Mell.*, **1923,** 536.

invention since the Scheurer-Lauth Company had been using aluminum to discharge direct dyeings since 1895 (*Bull. Mulh.*, **1901,** 187). But all these methods failed to give satisfactory results on azo dyeings.

The use of hydrosulfites in discharge printing pastes can be found first in patents of the Badische A.S.F., namely *G.P. 133,478*, 1900; *G.P. 135,725*; *F.P. 297,370*; *Rev. Gen. Mat. Col.*, **1905,** 60. See also *G.P. 184,381* and *188,837*, 1907, of Ciba. Badische A.S.F. proposed in *G.P. 133,478* the application of zinc-sodium hydrosulfite and in *G.P. 135,725* an addition of bisulfite, whereby some improvement was claimed.

The calcium hydrosulfite, Redo, invented by L. Descamps in Lille (*F.P. 320,227*, 1902; Grossmann, *G.P. 112,774*, *113,940*, *113,949*, 1908; *Rev. Gen. Mat. Col.*, **1903,** 35, 37 and 85) was not successful because of its slow rate of reaction and its poor solubility.

Credit for important progress is due Badische A.S.F. for their preparation of the salts of hydrosulfurous acid by salt precipitation. The sodium hydrosulfite obtained by this method, proved to be an efficient reducing agent, and advantageously replaced stannous chloride and zinc bisulfite discharges (*G.P. 112,483*, *125,303*, *144,632* relating to the preparation of solid hydrosulfites by common salt precipitation; see also *G.P. 133,040*, *138,093*, *138,315* and *160,529*).

Use of the hydrosulfite together with glycerin and sodium hydroxide in print paste is described by Badische A.S.F. in *G.P. 186,442*. In *G.P. 186,443* the sodium hydroxide is replaced by a salt solution (*G. P. 191, 495, 192, 431*).

Hydrosulfite powder ground with glycerin and sodium hydroxide forms a grayish paste which was marketed as Eradit B or Rongalite B, and was used as a discharge agent for Para red and naphthylamine bordeaux.

The printing plant of E. Zündel in Moscow (Charles Schwartz-Thesmar, sealed communication Oct., 1902; *Bull. Mulh.*, **1904,** 36, 43) used zinc hydrosulfite as a discharging agent. The method was patented (*F.P. 311,938*–1901) by M.L.B.-Höchst. The salt is very stable but sparingly soluble. The discharge paste is prepared by pasting zinc hydrosulfite with glycerin, and adding stannous hydroxide, sodium acetate and common salt. During ageing sodium hydrosulfite is formed by the action of the sodium salts on the zinc hydrosulfite.

White Discharge (*Zündel, 1901*)

120 gm	stannous hydroxide paste
420 gm	zinc hydrosulfite paste
280 gm	gum Senegal paste
100 gm	sodium acetate
80 gm	common salt powder
1000 gm	

The zinc hydrosulfite was made up as follows:

Dissolve	20 kg zinc powder 10 l water 28 kg sulfuric acid 52° Bé
Cool with	60 l water 60 kg ice

This mix is poured into 200 kg of bisulfite 38° Bé and 120 kg of ice. Agitate, settle, decant. To the clear solution 10% common salt is added, whereby zinc hydrosulfite is precipitated. By decantation and extraction the paste is brought to 55 kg. To make the zinc hydrosulfite paste of the formula, 27 kg of water are added.

Despite the improvement of this discharge formula the problem was not completely solved. Results were not consistent and the print paste had but moderate stability.

At this time the discovery of the stable salts of formaldehyde sulfoxylic acid was made. This discovery can be said to be one of the most important of the last forty years in the field of applied chemistry. It is further proof that great inventions do not originate from a single and unrelated idea. Rather, the gradual development of research work approaches a definite goal in logical steps.

The first steps in the preparation of formaldehyde sulfoxylate were undertaken in an attempt to improve the poor stability of hydrosulfite. Addition of formaldehyde was made by M.L.B. Bisulfite was replaced by the aldehyde compound by Pelizza and Zuber. The next logical steps were the investigation of the course of these reactions, with all attendant details. Different chemists arrived at the desired result at almost the same time.

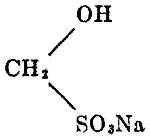
To recapitulate the steps, C. Kurz of Darnetal first observed the stabilizing action of formaldehyde to a paste containing hydrosulfite powder, and the improvement to the discharge effect on Para red (Report sealed with the Soc. Ind. de Mulh., Dec. 1, 1902; *Bull. Mulh.*, **1904,** 46).

The analogous observation, that formaldehyde stabilized zinc formaldehyde sulfoxylate print pastes was made by E. Zündel in Moscow.

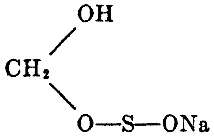
A new, well-defined compound was then isolated, having the unexpected properties of strong reductive action at elevated temperatures, while having no action at low temperatures. This research work must be credited to the chemists Schwartz, Baumann and Thesmar who deposited the first report concerning the subject with the Soc. Ind. de Mulh., Dec. 15, 1902 (*Bull. Mulh.*, **1904,** 48; *Rev. Gen. Mat. Col.*, **1904,** 196; Schmid, *Rev. Gen. Mat. Col.*, **1904,** 202).

C. Kurz's invention was assigned to L. Descamps in Lille. This company was granted *F.P. 337,530*—1903 and *B.P. 19,446*—1903 (*Rev. Gen. Mat. Col.*, **1904,** 153; **1905,** 102). Royalties of the patent rights were transferred to the Manufacture Lyonnaise des Matieres Colorantes in Lyon (Cassella) who offered sodium formaldehyde sulfoxylate for sale under the trade name Hyraldit A*.

M.L.B. (Höchst) bought the Zündel process and obtained *G.P. 165,280* (Feb., 1903). Their product was known as Hydrosulfite NF. More details of the history of this invention can be found on page 34. The first two products named above, i.e. Hyraldite A and Hydrosulfite NF, consisted of equimolecular parts of sodium oxymethane sulfonic acid, or, sodium formaldehyde bisulfite:



having no appreciable reducing action, and comprising 56% of the mixture, and sodium formaldehyde sulfoxylate or sodium oxymethane sulfinic acid



having strong reducing action and comprising 44% of the mix. The mixture can be considered as hydrosulfite-formaldehyde, $Na_2S_2O_4 \cdot 2CH_2O \cdot H_2O$.

The second component was first prepared in pure form by fractional crystallization by Badische A.S.F. It was given the name Eradit C (1905) and later on Rongalite C. At the present time this very efficient reducing agent is marketed under many names (see page 36). The content of these products is 96 to 100% sodium formaldehyde sulfoxylate, $NaHSO_2 \cdot CH_2O \cdot 2H_2O$.

The textile printing industry seized the opportunity of exploiting the strong reductive action of this new product. It was found that the majority of the azo dyestuffs are dischargeable with sulfoxylates alone.

p-Nitraniline red is quantitatively split by the action of Rongalite C into aminonaphthol and *p*-phenylenediamine according to the following equation:

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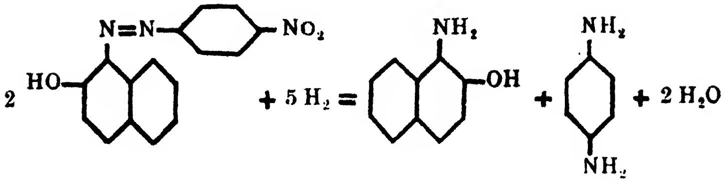
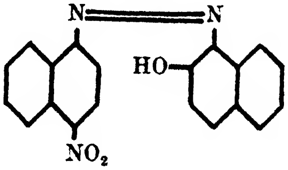
* References regarding the invention of sodium formaldehyde sulfoxylate: J. Garçon, *Rev. Gen. Mat. Col.*, 1903, issue 74; H. Schmid, *Rev. Gen. Mat. Col.*, 1905, 256; *Chem. Ztg.*, 1904, 1905; J. Lefevre *Rev. Gen. Mat. Col.*, 1905, 102; Descamps, "Les Rodos", *Rev. Gen. Mat. Col.*, 1905, 286; compare also "L'industrie des Hydrosulfites", *Tiba*, Sept. and Oct. 1924.



The cleavage products are readily removed by washing: 200 gm Rongalite C. conc. per kg are sufficient for discharging a full shade of Para red.

Most of the azo dyes known at the time of the invention of Rongalite C conc. were found to be dischargeable, but α-naphthylamine bordeaux was an exception. This problem was eventually solved also (*Leipziger Text. Ztg.*, **1906,** 324; "Das Aetzen von Bordeaux" *Frb. Ztg.*, **1906,** 473).

At first, substitute bordeaux were sought which would have better dischargeability. A garnet shade was produced by coupling β-naphthol with diazotized aminoazotoluene, which has better dischargeability but inferior fastness to light and soaping. A garnet made from nitro-α-napththylamine is also easily discharged by sodium formaldehyde sulfoxylate.



This fact led observers to continue experimentation for the discharge of α-naphthylamine bordeaux. Charles Sunder assumed (*Bull. Mulh.*, **1906,** 364) that Para red might be more easily discharged than bordeaux because the NO_2 radical imparts an acid character to the dyestuff. This explanation is not quite exact, although it is true that formaldehyde sulfoxylate has a somewhat better effect in a slightly acid medium. It has even been suggested to prepare dyed fabrics with ammonium chloride or with *m*-nitrobenzene sulfonic acid before printing. But more recent research proved that difficultly dischargeable azo dyeings could be white discharged with the aid of certain substances which act as catalytic hydrogen carriers.

The first discharge on naphthylamine bordeaux consisted in transforming sodium hydrosulfite into a stable product by adding sodium hydroxide. The method was recommended by Badische A.S.F., and the products Eradit B or Rongalite B manufactured for the purpose (*G.P. 133,478, 135,725, F.P. 297,370*). Likewise Zündel (Baumann, Frossard, *Bull. Mulh.*, **1905,** 117, 374, 421; *Rev. Gen. Mat. Col.*, **1905,** 243) and Wilhelm, a chemist with Konschin in Serpoukhoff (*Bull. Mulh.*, **1906,** 75) recommended a hydrosulfite and alkali discharge for the same purpose.

Alkaline Discharge for Bordeaux

220 gm	glycerin
300 gm	gum thickening
200 gm	caustic soda 38° Bé
280 gm	sodium hydrosulfite
1000 gm	

Historical Development of Discharge Processes

In the following paragraphs the historical development of the processes which led to the discovery of the catalytic action of anthraquinone, and eventually to the present formula for discharging the naphthol dyeings will be traced.

Effect of Iron Salts. Baumann and Thesmar, addition of ferrous nitrite in alkaline medium (*Bull. Mulh.*, **1905,** 374; *Rev. Gen. Mat. Col.*, **1906,** 69) or in acid medium (Thesmar and Hug, *Bull. Mulh.*, **1905,** 425; *Rev. Gen. Mat. Col.*, **1906,** 105, 137) to the discharge paste containing sulfoxylate formaldehyde. The latter method was patented by Badische A.S.F. (*G.P. 167,530, 172,675–6*). Substitution of iron salts by the oxide or by the metal itself (*Fischer's Ber.*, **1906,** 426; Koechlin, *Bull. Rouen*, 1907).

Catalytic Action of Various Dyestuffs. Setopalin (Geigy); Nitroalizarine, Rhodamine 6G, proposed by Wilhelm (sealed reports of Aug. 2, 1905 and January 6, 1908; *Bull. Mulh.*, **1906,** 75, 83, 84; *Rev. Gen. Mat. Col.*, **1906,** 193, 362; J. Mueller, *Rev. Gen. Mat. Col.*, **1907,** 199, 403.

Setopalin, Kurz (sealed report of June 25, 1905, *A.C.I.T.*, **1927,** 417).

Patent Blue V: Höchst, *G.P. 188,700, Fischer's Ber.*, **1907,** 456.

Induline Scarlet: Badische A.S.F., *F.P. 355,117*, *G.P. 184,381*; *Rev. Gen. Mat. Col.*, **1907,** 61.

Induline Scarlet has catalytic effect on the discharge even though it is added in very small amounts. Badische A.S.F. offered a product, under the name *Rongalite special* which was a physical mixture of

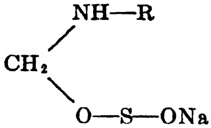
10 kg	Rongalite C
26 gm	Induline Scarlet
4 gm	Methylene Blue
10 gm	Leucotrope O

The dyes which act catalytically can be added to the diazo bath as well (0.6 to 0.8 gm per liter), whereby bordeaux shades are obtained which can be discharged by the regular white discharge pastes.

Acid Reaction in the Ager. Addition of salts of aromatic bases (*o*-anisidine) or of esters (ethyl tartrate) to develop an acid reaction during the ageing process: Baumann, Thesmar and Hug, *Bull. Mulh.*, **1906,** 216, 219; *Rev. Gen. Mat. Col.*, **1906,** 329, 330.

Xylidine, Aniline. A. Scheunert and J. Frossard (Prochoroff Co. in

Moscow) recommend addition of xylidine or aniline to the discharge paste. Alkali salts of aniline (or xylidine) methylene-ω-sulfinic acid are probably formed by the action of aniline or xylidine with sulfoxylate formaldehyde, corresponding to the formula



$$CH_2\begin{cases} NH{-}R \\ O{-}S{-}ONa \end{cases}$$

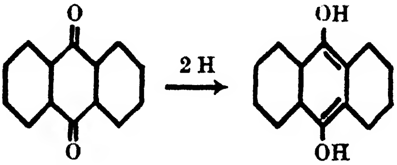
The products are active reducing agents. It may be noted that the application of these products has been proposed for discharge printing of acetate rayon (*F.P. 805,937, U.S.P. 1,912,008*—D. Powers.—U. S. Finishing Company).

Solidogen, a condensate of formaldehyde with a mixture of *o*- and *p*-toluidine was proposed by M. L. B., Höchst, for preparation of the bordeaux dyeings before printing. The product appeared as the aqueous solution of the hydrochloride. (*Z. f. Frb. Ind.*, **1902,** 12; *G.P. 180,727*—1906). Höchst also manufactured the product Rodogen MLB, which, according to Bohn, was an oxalate of anhydroformanilide (*Z. f. Frb. Ind.*, **1906,** 257), or (according to other references) was produced by condensation of formaldehyde and xylidine.

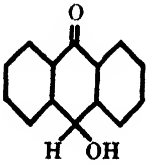
Superheated Steam. Simon—Weckerlin (L. Lefevre, *Rev. Gen. Mat. Col.*, **1906,** 65; Baumann and Thesmar, *Rev. Gen. Mat. Col.*, **1906,** 137). This process, with its attendant high quantities of formaldehyde sulfoxylate, is based on an incorrect assumption. Formaldehyde sulfoxylate has very little reducing action at temperatures exceeding 105°C and the use of this agent in amounts as high as 500 gm per kg of paste is not indicated, where 100 to 150 gm give satisfactory results.

The eventual solution of the problem of discharging the azo dyestuffs was found by Slatonstoffski and Ch. Sunder (sealed report of March 26, 1906, *Bull. Mulh.*, **1906,** 365; **1907,** 382; *G.P. 186,050*—1906) with the addition of anthraquinone to the print paste, although they could not explain the catalytic action of the product. The anthraquinone must be added in a finely dispersed state to the paste. This condition may be attained by dissolving anthraquinone in 96% sulfuric acid, and precipitating with water, or by reducing anthraquinone in alkaline solution and reprecipitating by passing a current of air through the solution. In the latter method, anthraquinone dissolves as a red-colored solution of hydroquinone, and is precipitated by the oxygen of the air.

Anthraquinone is sold as a 15% or 30% paste. The chemical action of this substance in discharge processes has been studied by Planowsky (*Z. f. Frb. Ind.*, **1907,** 109; *Rev. Gen. Mat. Col.*, **1907,** 215). He assumed that oxanthrone is formed by reduction. This was disproved by K. Meyer (*Ann.* **1911,** 43; **1902,** 113, 420) who showed that hydroanthraquinone is formed by reduction of anthraquinone in neutral or alkaline solutions while oxanthrone is produced only in acid media:



Hydroanthraquinone



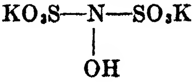
Oxanthrone

It is thus the reduction of anthraquinone and the oxidation of hydroanthraquinone which constitute the chemical reactions of the catalyst in the discharge process.

Battegay, Lipp and Wagner (*Bull. Mulh.*, **1921,** 233) assumed that replacement of anthraquinone with one of its soluble derivatives, for instance, α- or β- anthraquinone monosulfonic acid, might give a better catalytic effect, but this work apparently had no practical consequences (M. Battegay "Etude sur l'anthraquinone", *Rev. Gen. des. Sciences,* **1922,** 502). Sunder and Bader likewise experimented with derivatives of anthraquinone (*Bull. Mulh.*, **1921,** 187). They found that the sulfonated derivatives are not better catalysts than anthraquinone itself, despite their solubility in water. References on this subject: Thesis of Philippe Brandt, Strassbourg, 1922; communication of M. Battegay, *Bull. Mulh.*, Proceedings of March 7, 1923; M. Battegay and Philippe Brandt, "L'Anthraquinone comme catalysateur dans le rongeant sur grenat d'α-naphthylamine", *Bull. Mulh.*, July, **1923,** Battegay and Hueber, *Bull. Soc. Chim.*, **1923,** 1904.

Zinc sulfoxylate formaldehyde combined with quaternary ammonium compounds (for instance, dimethylphenylbenzyl ammonium salts) can also be used to discharge insoluble azo dyeings according to *F.P. 713,972*, *G.P. 548,203* (I.G.—Fischesser).

An interesting use of insoluble formaldehyde sulfoxylates is given in *G.P. 563,764* (I.G.—Siefert). Addition of salts which give acid reaction on steaming aids the result. Salts useful for the purpose are ammonium sulfate and nitrate, and potassium hydroxylamine disulfonate.



$$\underset{\displaystyle OH}{KO_3S\text{—}\overset{}{N}\text{—}SO_3K}$$

The pastes are exceptionally stable, being therefore suitable for block and screen printing. This concludes the references on the development of the white discharge formula.

Printing Formulas for Discharges

White Discharge on Naphthylamine Bordeaux

175–200 gm	sodium formaldehyde sulfoxylate
200–250 gm	water
560–480 gm	starch-trag. or gum thickening
50 gm	anthraquinone 30% paste
15–20 gm	caustic soda 38° Bé
1000 gm	

The discharge of Naphthol AS dyeings requires a strongly alkaline paste, as for example the addition of 30 to 50 gm of potash per kg. In cases wherein difficultly soluble decomposition products are encountered, sodium hydroxide is preferred. Exceptions in this connection are the brown azo dyestuffs produced with Naphthol AS-BT, which are white-discharged only with a strictly neutral printing paste, the addition of such a mildly alkaline compound as zinc oxide yielding yellowish discharges (*Mell.*, **1937**, 728). However, titanium oxide may be added, or better, zinc sulfate.

Discharges on Naphthol AS-BT Dyeings

200 gm	sodium formaldehyde sulfoxylate
80 gm	water
400 gm	starch-trag. thickening
200 gm	titanium oxide
60 gm	Solution Salt 1:1
20 gm	anthraquinone 30% paste
40 gm	zinc sulfate
1000 gm	

Discharge on Naphthol AS Dyeings

150–175 gm	sodium formaldehyde sulfoxylate
175–200 gm	water
400–330 gm	starch-trag. thickening
150–170 gm	zinc white 1:1 paste
50 gm	anthraquinone 30% paste
25 gm	caustic soda 38° Bé
50 gm	potash
1000 gm	

Some of the more difficultly dischargeable dyeings can be improved by the addition of 40 to 60 gm of Leucotrope W per kg of print paste.

Development of the prints takes place as follows:

(1) The material is aged for six minutes at 101°C. It is not advisable to let the goods lay up either before or after the ageing operation.

(2) The prints are soaped in the open width or in rope form in a bath of 4 gm of soap and 1½ gm soda ash per l at the boil.

(3) Rinsing and drying.

Dyeings of β-naphthol are relatively easy to discharge cleanly. However, the Naphthol AS series components are substantive and are completely detached only with great difficulty. In order to obtain a clear white it is necessary to remove every trace of naphthol from the goods before they are dried.

Some of the naphthols cannot be discharged at all, for example, the dyeings of Naphthols AS-G, AS-BR, AS-LG and AS-L3G.

For colored discharges, basic colors fixed with tannin, chrome and sulfur dyes and, above all, vat colors, are employed.

The Zündel Co. in Moscow used basic colors for discharge using sulfoxylate formaldehyde as early as 1903 (*Bull. Mulh.*, **1905,** 111, 119). The only trouble encountered in the process lay in finding a proper solvent for the tannin lakes, which had to be in neutral solution. Romann of Koechlin Frères (Mulhouse) suggested impregnating the dyed Para red material with tannic acid before printing (*Rev. Gen. Mat. Col.*, **1905**, 241; *Bull, Mulh.* **1905,** 110). Phenol was proposed as a solvent by Gassmann, *G.P. 99,750*–1897, and Baumann and Thesmar (*Bull. Mulh.*, **1905,** 111; *Rev. Gen. Mat. Col.*, **1905,** 241). However, the basic colors are somewhat dulled by phenol. Jeanmaire proposed aniline, and this solvent was successful in a practical way. Print pastes could be kept some time with aniline as solvent for the tannin lakes. (*Bull. Mulh.*, **1905,** 121; *Rev. Gen. Mat. Col.*, **1905,** 224; *F.P. 344,681, G.P. 165,219, Rev. Gen. Mat. Col.*, **1905,** 60.)

Resorcin has proved an excellent solvent for basic dyestuffs in general, and for their tannic acid lakes. (Diserens, *Rev. Gen. Mat. Col.*, **1919,** 117, Schneevoigt, "Use of Resorcin in Textile Printing," *Mell.*, **1925,** 106). A printing formula from plant practice is the following:

30 gm	basic dyestuff
120 gm	resorcin 1:1 water
30 gm	glycerin or alcohol
420 gm	gum thickening
200 gm	Hydrosulfite NF
80 gm	aniline
120 gm	tannin 1:1 alcohol
1000 gm	

Diserens claims further that when resorcin and zinc salts are used the tartar emetic aftertreatment can be dispensed with (page 111). The following print formula is recommended:

40 gm	basic dyestuff
120 gm	resorcin 1:1 water
30 gm	alcohol
320 gm	Senegal gum thickening
200 gm	Rongalite C
80 gm	aniline
160 gm	tannin 1:1 alcohol
50 gm	zinc acetate 10° Bé, or zinc glycollate
1000 gm	

A similar method was suggested later by Bayer in *G.P. 312,584*—1919.

In recent times diethylene glycol and its ethers (Carbitol, Fibrit, Hystabol D, etc.), as well as thiodiethylene glycol (Glyecine A) have been proposed as solvents. Another special solvent, Debetanlac A or C (L. Z. J.) is recommended for use with basic color-tannin lake and metal salts.

Justin Müller used zinc ferrocyanide to fix basic colors on the fiber (*Bull. Mulh.*, **1907,** 428; *Rev. Gen. Mat. Col.*, **1908,** 148; *Bull. Mulh.*, **1920,** 636). The fabrics are prepared with potassium ferrocyanide, then printed with paste containing, beside basic color, Rongalite C and zinc sulfate.

Substitutes for tannic acid are the products Katanol O and ON. The material is preferably prepared before printing with a solution of Katanol (Fischer, *Mell.*, **1924,** 119; L. Gaillard, "Katanol im Zeugdruck," *Mell.*, **1924,** 608).

No difficulties are experienced in using vat colors as color discharges on naphthol dyeings. For this reason there are few published references to the style. The prints are aged and washed well.

An interesting variation was developed by Rebert and Lantz (*Bull. Mulh.*, **1924,** 638) The goods are prepared with β-naphthol. A paste containing alkaline sulfoxylate formaldehyde is cross-printed with diazo solution in which a vat dyestuff is dispersed, whereupon the goods are aged and soaped.

Chrysoidine Bistre

Chrysoidine Brown or Bistre is produced by coupling Chrysoidine with *p*-nitrodiazobenzene (Nitrazol CF, Parazol FB, etc.). The material is first prepared with Chrysoidine (Chrysoidine R ex, Chrysoidine AG, Bayer, Manchester Brown GG, Brun pour foulardage NJ, Kuhlmann) then coupled with the diazo compound (F. Binder, *Bull. Mulh.*, **1905,** 54; *Rev. Gen. Mat. Col.*, **1904,** 199, 203).

The style was manufactured in Russia on a large scale, having an importance next to Indigo and Para red. It still has a market in the manufacture of "Satin-Cuir" along with naphthylamine bordeaux and *p*-nitraniline red.

In general, two passages are given through the diazo solution, for which the three-roll mangle with two dips is preferred.

Padding Solution

20 gm	Chrysoidine AG
75 gm	acetic acid 6° Bé
805 gm	water
100 gm	gum tragacanth
1000 gm	

The padded fabrics are dried, rolled up, developed in *p*-nitrodiazobenzene, washed and rinsed.

The same discharge pastes are employed in discharging Chrysoidine Bistre as for the naphthol dyeings. Any trace of uncoupled Chrysoidine must be soaped off before printing. It is advisable to sky 10 to 15 seconds after coupling with the diazo solution and to soap the dyeing well in order to obtain good white discharges.

It has been found that preparation of the dyeings with ammonium chloride or sulfate, or sodium nitrobenzene sulfonate before printing aids the discharge. Sunder (*Bull. Mulh.*, **1921**) suggested the addition of 20 gm of ammonium citrate per kg of printing paste.

Binder describes (*Bull. Mulh.*, **1905**, 54) a half discharge, for tone-in-tone effect, used at Zündel Co. A strongly alkaline Rongalite C paste is printed on Chrysoidine Bistre.

700 gm	Rongalite C paste 25%
300 gm	caustic soda 38° Bé
1000 gm	

Other diazo compounds than *p*-nitrodiazobenzene can be employed with Chrysoidine; for example, *m*-nitrodiazobenzene gives a Havana brown, *o*-nitrodiazotoluene a tobacco brown.

A two-tone style which received much attention was carried out by printing *p*-nitrodiazobenzene on a fabric prepared with Chrysoidine, then coupling the rest of the fabric in a bath of *m*-nitrodiazobenzene. The two-tone brown might then be discharge-printed with white.

p-Nitraniline Bistre is prepared by aftertreating *p*-nitraniline red with copper salts. Another method consisted of padding white cloth with sodium naphtholate solution containing copper tartrate, and then developing in the diazo solution. *p*-Nitraniline Bistre can either be printed with a stannous chloride resist or white discharged with Hydrosulfite NF. Conversion styles have been described on page 225. A further development of this style has been explained by Rebert (*Bull. Mulh.*, **1924**, 643). *p*-Nitraniline red is changed to dark brown by padding with a solution of a chrome blue which can be discharged by either sulfoxylate formaldehyde or by chlorate ferrocyanide, and which, moreover, is fixed by ageing in the rapid ager. Thus a fabric is dyed Para red, and padded with solution of Chromal Blue G, Geigy. The resulting bistre brown is discharged white with Hydrosulfite NF plus sodium citrate and red by chlorate and ferrocyanide. See C. Favre, *Bull.Mulh.*, **1908,** 139; *Rev. Gen. Mat. Col.*, **1906,** 312; Baumann and Thesmar, *Bull. Mulh.*, **1904,** 53 (reserves with pigments).

SPECIAL DYESTUFFS INCORPORATING BOTH NAPHTHOL AND BASE*

In the usual method of producing insoluble azo dyestuffs, the well-known two-bath process is employed, in which the fiber is prepared with the naphthol solution, and after dyeing, is coupled with the diazo compound.

This method is used in dyeing, and for the resist and discharge styles in printing. For application printing, simplification has long been the goal of experimenters. Even from the first appearance of β-naphthol, ways have been sought to combine the naphthol with the diazo compound into the same printing paste.

The first experiments, made by Badische A.S.F. with compositions of mixed sodium β-naphtholate and the nitrosamine of *p*-nitraniline, did not meet with success. The idea was, however, not dropped, but applied by Griesheim-Elektron in 1913 to the sodium salts of arylides of 2,3-oxynaphthoic acid. Their efforts led to an interesting solution of the problem, which can be expressed as follows:

The print paste should contain the Naphthol AS coupling component together with a compound which is capable of producing the diazo compound at a given time after printing, thus permitting the development in one operation.

The first results obtained in this field—the Rapid Fast colors of Griesheim-Elektron (1915)—were successful enough to stimulate further investigation and research. The final result of this development work is a new class of colors, the Rapidogens, which appeared in 1930. Colorists found these dyestuffs simple to handle, and readily adaptable for printing alongside vats, Indigosols, aniline black, chrome and basic dyestuffs. The many possibilities which these dyestuffs opened up were eagerly investigated.

The research which will be reported here is based on three principal ideas:

(A) To render the diazo compound inactive, in order that it might be incorporated in the printing paste with the Naphthol AS, and subsequently reactivate it on the fiber to form the azo coupling.

The following groups belong here.†

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* A. Wolf, *Teintex*, **1942,** 247.

† See *Wengraf's Ber.* Oct. **1936,** 19; Report on a general survey by Desai, Metha and Thosar in *J. Soc. Dy. & Col.*, Aug., **1938,** 371.

(1) The Rapid Fast dyestuffs of I.G., the Cibagens of Ciba, the Tinogens of Geigy, the Momentogens of Sandoz, the Naphthazol Direct dyestuffs of Kuhlmann: they are mixtures of naphtholates with antidiazotates.

(2) The Rapidogens of I.G. (Naphthazogens of Saint-Denis): very stable mixtures of AS-coupling components with diazoamino compounds of certain bases.

(3) The Rapidazols: mixtures of naphtholates and diazosulfonates.

(4) The Photo Rapid dyestuffs of Saint-Denis: likewise mixtures of antidiazosulfonates, derived from amines, with arylides of 2-3-oxy-naphthoic acid.

(5) Furthermore various combinations contained in references of recent years, of little practical importance.

(B) To employ soluble compounds which are capable of forming not the diazo compound, but the amine, and to add nitrite to the print paste, which will, on subsequent treatment of the prints in acid, diazotize the amine.

The method may very well have been suggested by Dr. Bader's work on the nitraminates. Variations of the same idea may be found as the basic principle in different patents of Ciba, I.G., I.C.I. and Kuhlmann.

(C) The third fundamental principle has been developed in recent times, and consists of rendering the final azo dyestuff soluble by chemical substitution of the hydrogen of the OH group by a radical. This complex dyestuff is printed, and by an appropriate aftertreatment the original insoluble dyestuff is obtained.

This process has been brought out by Ciba. The dyestuff classes corresponding to the idea are the Neocotones of Ciba, Neogenoles of Sandoz and the Tinogens of Geigy. Provided that these dyes satisfy practical requirements for solubility, they should be strong competitors for the Rapidogens, which in spite of all their advantages offer difficulties in printing, by reason of their tendency to attack the doctor blades, and in their necessity for acid steaming.

Because of the interest which these dyestuffs possess, their novelty and their many diversified uses, a detailed report of their development will not be amiss. This report will follow the three fundamental principles enunciated above, and the references to the research and patents arranged accordingly.

Principle A

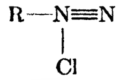
To transform the diazo compound into a stable and inactive substance, in order to be able to incorporate it into the printing paste with the Naphthol AS component, and to regenerate the reactive diazo compound on the fiber when the coupling reaction takes place. Such compositions therefore combine naphthols with stabilized, water-soluble indifferent diazo complexes, which can be transformed into active diazo compounds, capable of combining with the naphthol with which they are printed.

Rapid Fast Colors*

The Rapid Fast dyestuffs are mixtures of naphtholates and antidiazotates.

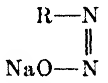
The antidiazotates or isodiazotates, which formerly were known as nitrosamines, were discovered by Schraube and Schmidt (*Ber.*, **1894,** #27, 518), and Bamberger (*Ber.*, **1894,** #27, 679). They are prepared by the action of alkalis on diazonium salts.

There are various explanations for the reaction which takes place when diazonium salts are treated with an alkali. According to the earliest interpretation, offered by Peter Griess, the diazo compounds are derived from a divalent radical $C_6H_4N_2$ linked to an acid radical, for instance $C_6H_4N_2 \cdot HCl$. Later Kékulé showed that the two nitrogen atoms are not linked with double bonds to the nucleus and that the diazo compound has the formula R—N═N—X. Blomstrand considered that the diazonium salt was analogous to a quaternary ammonium salt, with a trivalent nitrogen atom attached to a pentavalent nitrogen atom. At present this formula is very much in favor:



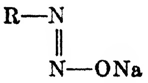
$$\begin{array}{l} R\text{—}N\equiv N \\ \quad\;\; | \\ \quad\;\; Cl \end{array}$$

According to Hantzsch (*Ber.*, **1894,** #27, 1727, 3530; **1897,** #30, 75, 90) caustic alkalis produce stereoisomers which can be represented by the following formulas:



$$\begin{array}{r} R\text{—}N \\ \| \\ NaO\text{—}N \end{array}$$

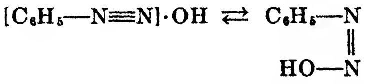
Syndiazotate (coupling)



$$\begin{array}{l} R\text{—}N \\ \;\;\;\;\| \\ \;\;\;\;N\text{—}ONa \end{array}$$

Antidiazotate (non-coupling)

The corresponding diazonium hydrate cannot be isolated. It must be assumed that the alkaline solution loses basicity in time, and the compound acquires an acidic character, according to the equation



$$[C_6H_5\text{—}N\equiv N]\cdot OH \rightleftarrows \begin{array}{r} C_6H_5\text{—}N \\ \| \\ HO\text{—}N \end{array}$$

Syndiazo acid

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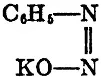
[*] References regarding Rapid Fast dyestuffs: G. Martin, *Rev. Gen. Mat. Col.*, **1934,** 172; Kienzle, Thesis, Paris, 1934; E. Sack, Lecture addressed to the College for Chemistry in Mulhouse, Yearbook, 1933; Ullmann, Vol. III, p. 676; Rowe and Stafford, *J. Soc. Dy. & Col.* **1924,** 218 and 228; *Tiba,* **1929,** 929; Lubs, *Am. Dyes. Rep.*, **1927,** 101; *G.P. 291,076* (Griesheim) and *F.P. 471,123, 511,296, 583,661, 671,164,* (I.G.) and *F.P. 639,498,* (I.C.I.). Trade names used for products of this group are: Cibagen dyestuffs (Ciba), Momentogen dyestuffs (Sandoz), Tinogen dyestuffs (Geigy), Rapid Fast dyestuffs (I.G. formerly Griesheim-Elektron, and G.D.C.), Naphthazol-direct dyes (Kuhlmann-Francolor), Pontagen and Du Pont Naphthanil colors (Du Pont), Naphthosols (Calco).

This second form is very unstable. By treatment with potassium hydroxide, a coupling potassium syndiazotate is obtained:

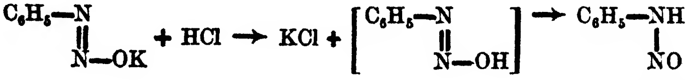


$$\begin{array}{c} C_6H_5\text{—}N \\ \| \\ KO\text{—}N \end{array}$$

By heating to 130°C, the isomeric and more stable modification is produced

$$\begin{array}{ll} C_6H_5\text{—}N & \\ \qquad\quad\ \| & \\ \qquad\quad N\text{—}OK & \end{array}$$

which, however, is not capable of coupling. This antidiazotate should theoretically yield an antidiazo acid. The acid however, is very unstable, and is readily transformed into the nitrosamine, according to the equation



$$\begin{array}{l} C_6H_5\text{—}N \\ \quad\ \| \\ \quad N\text{—}OK \end{array} + HCl \rightarrow KCl + \left[\begin{array}{l} C_6H_5\text{—}N \\ \quad\ \| \\ \quad N\text{—}OH \end{array}\right] \rightarrow \begin{array}{l} C_6H_5\text{—}NH \\ \qquad\quad | \\ \qquad\quad NO \end{array}$$

Nitrosamine

The antidiazotates have the advantage of stability over the diazonium salts. They can be prepared in solid form or in concentrated pastes. (*G.P. 78,874; Frdl.*, **1894-97,** IV, 658, 671.) They are easily transformed into the corresponding diazonium salts by the action of acids. Their stability to alkalis allows their mixture with the naphtholate solutions. In 1893, Badische A.S.F. offered Nitrosamine Red 20% based on this principle. It is a composition of *p*-nitraniline antidiazotate and of sodium β-naphtholate (*G.P. 80,263, 81,791, 83,010, 87,874, 81,206, 81,134, 81,202, 81,203, 84,389, 84,609*; *Nitrosamine Salt:* see Erdmann, *Chem. Ind.*, **1894,** 17, 291; P. Friedländer, *Chem. Ztg.*, **1894,** 18, 1186; *G.P. 83,010,* Badische A.S.F.: describing an antidiazotate of *o*-anisidine plus β-naphthylamine.)

The method seemed to offer great possibilities, but difficulties were met in practice. The antidiazotates are not permanently indifferent to β-naphthol and after some time the coupling reaction gradually sets in. Furthermore, the β-naphtholate, as already noted, alters quickly on exposure to the air. For these reasons the mixtures with sodium β-naphtholate were not successful.

The development of Azo Red on the fiber was brought about by the action of carbon dioxide or acetic acid (Badische A.S.F., *G.P. 81,791;* Schweitzer and Ebersol, *Frb. Ztg.*, **1909,** 163; Chayloff, *Bull. Mulh.*, **1908,** 65; *Frb. Ztg.*, **1909,** 64, 240; Felmayer, *G.P. 199,143, 204,707, 204,799; Z. f. Frb. Ind.*, **1909,** 630).

Some antidiazotates are, however, almost completely indifferent; for example, that of *p*-nitro-*o*-anisidine, which was sold by Badische as Nitrosamine BX or Naphthol Pink (*F.P. 271,908*).

Instead of β-naphthol the Calico Printers Assn. recommended 2-naphthol-1-sulfonic acid (Fourneaux, *G.P. 204,702*) while Heilmann and Co. suggested 2-oxy-1-naphthoic acid (*G.P. 238,841*) as coupling component.

G.P. 83,010 (Badische A.S.F.) covers the manufacture of antidiazotate of dianisidine together with β-naphthylamine. A large excess of caustic alkali is necessary in transforming the tetrazo derivative of dianisidine into the antidiazotate. In order to facilitate this reaction the *G.P. 292,118* of Griesheim suggested use of the aryl sulfonates of the tetrazo derivative, for instance, the sodium salt of naphthalene 1,5 di-sulfonic acid.

The antidiazotate of *p*-nitro-*o*-anisidine has been used together with sodium β-naphtholate to produce red discharges on indigo. The method, widely used in practice, was originated by W. Pluzanski, Dziewonski and Kopec, who also found that a good red could be obtained with the antidiazotate of *p*-nitraniline provided that sodium acetate and sodium aluminate are added to the printing paste (*Z. f. Frb. Ind.*, **1900,** 282; *Frb. Ztg.*, **1910,** 117; *Bull. Mulh.*, **1909,** 169–173; also *A.C.I.T.*, **1927,** 150).

Many Russian and Central European print shops had good results in producing red discharges on indigo. The procedure is as follows:

The indigo-dyed fabrics are prepared with a boric acid solution or with aluminum acetate and printed with a discharge paste containing the antidiazotate of *p*-nitro-*o* anisidine, β-naphtholate and chromate of sodium. The printed goods are aged for 2 to 3 minutes, and discharged in a bath of sulfuric and oxalic acids. The indigo is oxidized and destroyed on the printed areas and at the same time β-naphthol is coupled with the re-formed diazonium salt.

The difficulties which arose in combining antidiazotates with β-naphthol could be overcome by replacing the naphthol by the arylides of 2,3-oxynaphthoic acid. The alkali salts of these naphthols are more resistant to the atmospheric oxygen, and further, proved to be unreactive to the antidiazotates. The principle expressed above was therefore taken up by Griesheim-Elektron in 1914 and the results met with wide adoption in the trade. A wide color range was made from different mixtures, which were given the collective name of Rapid Fast dyestuffs (*G.P. 291,076*; *Frdl.*, **1914–1916,** XII, 370). The line was further extended during later years. About thirty dyestuffs—combinations of this type—were regularly sold in powder or paste form (Rapid Fast colors of G.D.C. and I.G.; Naphthazol Direct colors of Kuhlmann; *G.P. 408,505; Frdl.*, **1921–25,** XIV, 1043.)

The choice of appropriate amines is important for preparing the antidiazotates. The stability of the compounds depends in large measure on the basicity of the amines used, the higher the basicity the poorer the stability and passivity. Thus the strong bases, nitraniline and its chloroderivatives, do not form stable antidiazotates, and so the Rapid Fast colors are all derived from antidiazotes of amines of very weakly basic character.

The following gives the constitution of some of the Rapid Fast colors:*

Rapid Fast Yellow G = 2,5-dichloroaniline + Naphthol AS-G
Rapid Fast Orange RG = *o*-nitraniline + Naphthol AS
Rapid Fast Red B = *p*-nitro-*o*-anisidine + Naphthol AS
Rapid Fast Red BB = *p*-nitro-*o*-anisidine + Naphthol AS-BS
Rapid Fast Red GG = *p*-nitraniline + Naphthol AS
Rapid Fast Red 3GL = *o*-nitro-*p*-chloroaniline + Naphthol AS
Rapid Fast Red GZH = 2,4-dichloroaniline + Naphthol AS
Rapid Fast Red GL = *m*-nitro-*p*-toluidine + Naphthol AS
Rapid Fast Blue B = dianisidine + Naphthol AS
Rapid Fast Bordeaux IB = 5-nitro-2-amido-1-anisol + Naphthol AS-BO

The H brands are very stable and therefore particularly interesting for printing purposes. At present the following brands are on the market:

Rapid Fast Scarlet ILH (Cibagen Scarlet 2GA, Momentogen Scarlet G, Tinogen Scarlet 2G) = 2,5-dichloroaniline + Naphthol AS-OL
Rapid Fast Red RH (Cibagen Red BA, Momentogen Red B, Tinogen Red 2B) = 1-methoxy-2-amino-4-chlorobenzene + Naphthol AS-OL
Rapid Fast Scarlet RH = 4-chloro-*o*-toludine + Naphthol AS-PH
Rapid Fast Yellow GGH = 1-methoxy-2-amino-4-chlorobenzene + Naphthol AS-G
Rapid Fast Brown IBH = 1-methoxy-2-amino-4-chlorobenzene + Naphthol AS-LB
Rapid Fast Yellow IGH powder: A very pure yellow which can be developed in neutral steam atmosphere; can be printed beside vat dyestuffs since it is indifferent to formaldehyde vapors.
Rapid Fast Yellow GH powder (Cibagen Yellow RA, Tinogen Yellow RA, Momentogen Yellow GR)
Rapid Fast Yellow I 3GH powder: Lemon Yellow; can be developed by rapid ageing in neutral steam; applicable alongside vat dyestuffs, since it is indifferent to formaldehyde vapors.
Rapid Fast Orange IRH powder
Rapid Fast Orange IGH powder
Rapid Fast Orange GH powder
Rapid Fast Orange RH powder (Cibagen Orange 3RA, Momentogen Orange R, Tinogen orange 3R)
Rapid Fast Red FGH powder
Rapid Fast Red IRH powder
Rapid Fast Red I L B paste
Rapid Fast Bordeaux RH powder
Rapid Fast Brown GGH powder
Rapid Fast Brown IRH powder (Cibagen Brown RA, Momentogen Brown R, Tinogen Brown R)
Rapid Fast Olive Brown I G H

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* Rowe and Stafford, *J. Soc. Dy. & Col.*, **1924**, 228; J. Rowe and Levin, *J. Soc. Dy. & Col.*, **1924**, 218; Report of Office of Technical Service, Dept. of Commerce, Washington.

The Rapid Fast colors are printed from alkaline print paste on unprepared cloth. Sodium chromate is usually added to the print paste to increase their stability during ageing. The development takes place by exposing the prints to the air,* or by ageing in saturated, acid-free steam, followed by passage through a bath containing acetic and formic acids at 70°C, or by ageing in acid steam.

The Rapid Fast colors become dull alongside prussiate aniline black, but are not influenced if the aniline black is printed by the copper sulfide or vanadium method (Hängeschwarz).

According to *U.S.P. 2,047,543*, the I.G. suggests developing the Rapid Fast colors in a steam chamber with carbon dioxide. The normal content of CO_2 in the atmosphere is insufficient, but with 3 to 10% CO_2 in the steam supply a full development is attained. The method is of theoretical interest. The process could be useful in ageing vat colors alongside the Rapid Fast colors.

Another method of producing stable mixtures is described in *U.S.P. 2,048,745* (N.A.C.-Kern). The aqueous solution of the nitrosamine is crystallized together with an organic sulfonate, for instance, sodium salt of dichlorobenzene sulfonic acid. The latter compound has no coupling property of its own. The mixture is applied in printing or dyeing.

Pyridine or similar bases are said to increase the penetration and fastness to crocking when added to the printing pastes, while the shades obtained are fuller (*G.P. 572,693*—Böhme F.C.—Perndanner—Hackl).

Ciba's *F.P. 861,900* also comprises a method for applying antidiazotates together with coupling components of the Naphthol AS series in order to obtain full, bright brown prints. The printing paste contains nitrosamine, Naphthol AS, sodium hydroxide and Turkey red oil. The prints are developed in a 10% formic acid solution, then washed with 5% sodium carbonate solution, rinsed, soaped and rinsed.

The Rapid Fast colors can be printed alongside Indigosols, vat colors and with those chrome dyestuffs which require only short ageing for fixation. Rittner and Gmelin printed mixed pastes of Rapid Fast colors and Indigosols (*Mell.*, **1927**, 530). This print paste contains the normal ingredients for Rapid Fast colors (dyestuff, neutral chromate and Turkey red oil) and in addition the Indigosol dyestuff and sodium nitrite. The printed fabrics after drying are aged two minutes in neutral steam, then passed through a hot solution of 50 gm of formic acid and 100 gm of sodium chloride per liter to develop the Indigosol, and washed.

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* In this event the rearrangement of the diazo compound and the formation of the dyestuff is brought about by the carbon dioxide of the atmosphere. See *F.P. 782,655*-Ciba, 1935, wherein the prints are first treated with acid, then with a neutralizing compound, as Na_2CO_3.

The Rapidogens*

The Rapidogens are very stable mixtures of the arylanilides of 2,3-oxynaphthoic acid plus diazoamino compounds of the appropriate bases. These mixtures do not undergo a coupling reaction in alkaline media but with acid reagents the diazoamino compounds are split, permitting coupling of the diazo compound with the naphthol.

Development of these mixtures was made by the chemists of the I.G. By employing diazoamino compounds they made use of chemical reactions which were known for many years. In 1869, Peter Griess studied these compounds, and Schraube, Fritsch and Green undertook to use them for application printing of insoluble azo dyestuffs (*Ber.*, **1896,** #29, 287).

The first reference regarding the use of diazoamino compounds for textile printing was given by Wimmer (*Ber.*, **#20,** 1577; *G.P. 40,890*). He suggested printing mixtures of diaozamino compounds, phenols, alcohol and thickening, drying and then ageing the prints to produce the azo dyestuff on the fiber. Obviously the I.G. chemists followed this train of thought in preparing the Rapidogens colors.

The diazoamino compounds have the following schematic formula

$$R{-}N{=}N{-}NH{-}R'$$

Their simplest representative is diazoaminobenzol.

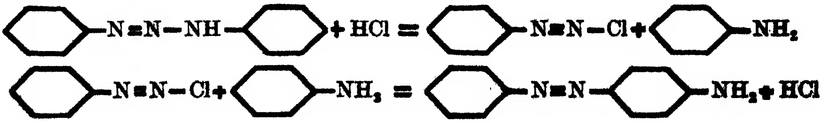
The diazoamino compounds are formed by the reaction of the diazo derivative of a strong base with an amine of weak basicity. By treatment with an acid the diazo compound is re-formed

$$R{-}N{=}N{-}Ar$$

It is to be noted that Griess did not realize that the reaction is reversible, but Frieswell and Green considered the possibility which O. Wallbach confirmed in 1886.

Diazoamino compounds bearing an exchangeable H atom in *para* position to the NH group tend to undergo an intermolecular rearrangement whereby the isomeric aminoazo compound is formed, according to the formula

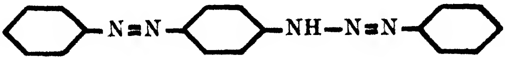
The rearrangement takes place in the presence of small amounts of aniline salt or of free acids, as follows:



*** Trade names: Diagens (Du Pont); Rapidogens (G.D.C. and I.G.); Pharmasols (Pharma Chem. Co. and Carbic Color); Naphthazogenes (Francolor). *G.P. 500,437, 510,441, 530,396; Frdl.,* 17, 1058, 1060.**

It can be seen that only very small amounts of aniline salt or hydrochloric acid are necessary, as these substances are continuously being regenerated.

A by-product of the above reactions is benzene diazoamino azobenzene

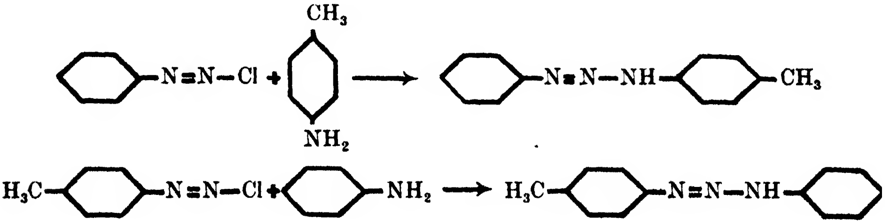


formed by the reaction of aminoazobenzene with diazobenzene.

Furthermore, diazoamino compounds are capable of rearrangement, as in the following formula

$$R—N{=}N—NH—R_1 \longrightarrow R—NH—N{=}N—R_1$$

This singular reaction was observed by Griess as early as 1874 (*Ber.*, **1882,** # 15, p. 2160). He actually obtained the same diazoamino compound by reacting diazobenzene with *p*-toluidine as by the reaction of diazo-*p*-toluidine with aniline.



It can therefore be assumed that the H atom wanders from one N atom to the second N atom. This reaction gave stimulus to much research work, and resulted in the following references; Noelting and Binder (1887); Meldola and Stretfield (1886); Goldschmidt (1888) and Dimroth (1905); compare Earl, *Chem. & Ind.*, **55,** 192 (1936).

Binder and Noelting proved that it did not matter which amine was diazotized, *i.e.*, aniline or toluidine, the same compound was formed (*Ber.*, **1887,** # 20, 3004)

thereby proving the migration of the azo group in the formation of diazoamino compounds.

Schraube and Fritsch noted in 1896 that four diazoamino combinations are theoretically possible, according to the conditions of the reaction, when diazo-*p*-toluene is combined with sulfanilic acid. Thus, the two unsymmetrical combinations are:

$$R—N{=}N—NH—R_1$$
$$R_1—N{=}N—NH—R$$

and the two symmetrical combinations are:

$$\mathrm{R{-}N{=}N{-}NH{-}R}$$
$$\mathrm{R_1{-}N{=}N{-}NH{-}R_1}$$

In preparing the diazoamino compounds for Rapidogens it is important to select the proper stabilizing (secondary) base. The conditions can be explained as follows:

The diazoamino compounds must contain the unsymmetrical derivatives only, and the diazo group must be linked directly to the amine which combines with the naphthol and not with the secondary base. That is, the proper combination is

$$\mathrm{R{-}N{=}N{-}NH{-}R_1}$$

in which R is the radical of the coupling base and R_1 is the radical of the secondary base.

The other possible combinations,

$$\mathrm{R{-}N{=}N{-}NH{-}R}$$
$$\mathrm{R_1{-}N{=}N{-}NH{-}R_1}$$
$$\mathrm{R_1{-}N{=}N{-}NH{-}R}$$

must be excluded. The diazonium salt regenerated by the action of the acid must consequently correspond to the formula

$$\mathrm{R{-}N = N{-}Cl}$$

and not to the formula

$$\mathrm{R_1{-}N{=}N{-}Cl}$$

Other conditions inherent to the production of the diazoamino compound require sufficient stability of the complex in water and in alkalis, but with the capacity to regenerate quantitatively the diazo compound by short passage through dilute acid, and under such conditions that the fibers are not injured.

Goldschmidt and Bruno Bardach showed in forming diazoamino compounds that the imino group (NH) tends to combine with the nucleus which is most strongly substituted by electro-negative groups, such as NO_2 or halogen regardless of which molecule is diazotized. Consequently, in making diazoamino compounds for coupling with naphthols, the diazotized amine should be strongly basic, while the stabilizing amine should be weakly basic.

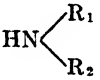
In order to avoid the danger of producing compounds in which the NH group might migrate in the undesired direction, it has been found advisable to use stabilizing amines which cannot be diazotized. Examples are aromatic or aliphatic secondary amines, or bases such as cyanamide. These stabilizing bases may be variously substituted. Solubility is assured by employing compounds containing water-solubilizing groups such as sulfo-or carboxylic radicals, sulfonamides, etc. The electro-negative character of these substituted groups has, at the same time, the effect of reducing the basicity of the amine, a desired condition in leading the hydrolysis of the diazoamino compound in the right direction.

$$Ar{-}N{=}N{-}NH{-}Ar_1 \longrightarrow Ar{-}N{=}N{-}Cl + Ar_1{-}NH_2$$

The stability and coupling capacity of a diazoamino compound are entirely dependent on the choice of the stabilizing base. According to the selection of the stabilizing base, the same diazotizable base forms different diazoamino compounds which are more or less readily split and thus yield dyestuffs more or less speedily.

The Stabilizing Amines. These compounds can be divided into three groups: (1) Aliphatic or aromatic secondary amines, (2) primary aromatic amines, and (3) other basic compounds which contain a trivalent nitrogen atom.

Aliphatic or Aromatic Secondary Amines. Included in this group are amines with the general formula:

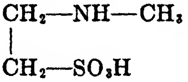


$$HN\begin{matrix}\diagup R_1\\ \diagdown R_2\end{matrix}$$

in which R_1 and R_2 are alkyl, aralkyl or aryl groups with a solubilizing radical. For example, sarcosine,

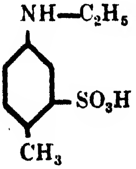
$$CH_3{-}NH{-}CH_2{-}COOH$$

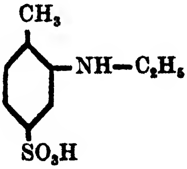
or methyl taurine,



$$\begin{array}{l}CH_2{-}NH{-}CH_3\\ |\\ CH_2{-}SO_3H\end{array}$$

Furthermore, secondary amines which are capable of diazotization have been proposed.* Examples are secondary amines derived from benzene such as sulfonated monoethyl-*p*-toluidine or 2-ethylamino-1-methyl benzene-4-sulfonic acid:





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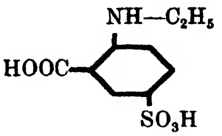
* *G.P. 500,437, 502,334, 510,441, 530,396, 532,562; Chem. Zent.*, **1932**, II, 773; *Frdl.*, **1932**, XVII, 1060–1065; *F.P. 674,195, 674,637, 674,638; B.P. 320,324; G.P. 500,437; Frdl.*, **1932**, XVII, 1058; *F.P. 769,838*, I.G.; *Russ. P. 50,823, 51,249, 52,351* (see Weisberg, *Rev. Gen. Mat. Col.*, **1936**, 370).

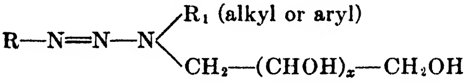
and 2-ethylamino-5-sulfobenzoic acid:



U.S.P. 1,968,879, *B.P. 429,618*, and *F.P. 764,755* (Du Pont, 1934) describe combinations of diazotized amines with secondary stabilizing amines derived from sugars, such as tetroses, pentoses or hexoses of the general formula,

$$R{-}NH{-}CH_2{-}(CHOH)x{-}CH_2OH$$

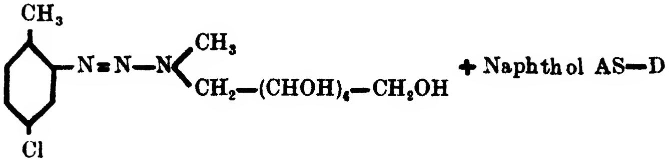
that is, glucamine or methyl glucamine. The diazoamino compounds correspond to the schematic formula



$$R{-}N{=}N{-}N\begin{cases}R_1 \text{ (alkyl or aryl)} \\ CH_2{-}(CHOH)_x{-}CH_2OH\end{cases}$$

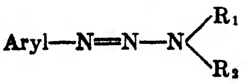
Water-soluble substances are produced from which the coupling diazo compound is readily generated. The product is incorporated in the printing paste with an alkali and the sodium salt of an arylide of 2,3-oxynaphthoic acid. The prints can be developed in a bath of acetic and formic acids at 90°C.

U.S.P. 2,035,518 (Du Pont) mentions as example of an amine similar to the above the diazoamino compound of 4-chloro-2-amino toluene plus methyl glucamine



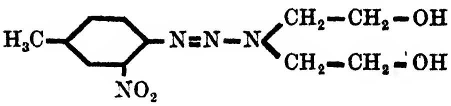
This patent also suggests the addition of salt (NaCl or Na_2SO_4) to the acid developing bath, as, 1 part acetic acid plus 0.5 part formic acid plus 2.8 parts NaCl per 30 parts of water.

U.S.P. 2,078,388 (Du Pont) recommends diazo compounds in the form of their diazoamino derivatives of the general formula



$$Aryl{-}N{=}N{-}N\begin{cases}R_1 \\ R_2\end{cases}$$

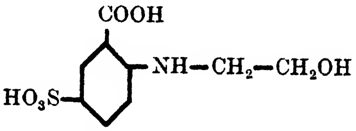
These compounds are obtained by reacting diazo compounds with oxyalkyl amines, for example by the reaction of diazo-*m*-nitro-*p*-toluidine with diethanolamine:



Coupling with the naphthol is brought about with warm hydrochloric acid bath, followed by passage through sodium acetate solution. The acid is introduced on the goods by means of a pad roller. This splits the diazoamino compound, and the free diazo derivative combines with the naphthol when the goods enters the alkaline solution.

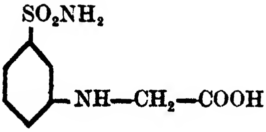
U.S.P. 2,138,572 (Du Pont, 1936) belongs to the same category. The fabrics are printed with a paste containing an azo compound, a diazoamino compound, urea and triethanolamine. The dyestuff is developed in acetic acid steam.

Kuhlmann describes (*F.P. 860,132*) another group of stabilizing agents for diazo compounds: the condensates of 2-chloro-5-sulfobenzoic acid with primary oxyalkylamines or cycloalkylamines, for example 2-ethoxyamino-5-sulfobenzoic acid



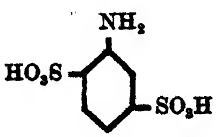
For the same purpose Du Pont recommends (*B.P. 481,019*) aliphatic secondary amines containing a furfuryl or tetrahydrofurfuryl group, such as furfuryl amino acetic acid.

In *F.P. 807,893*, Kuhlmann proposes secondary phenylamines containing a sulfonamido group and one or more carboxylic acid groups. Example:

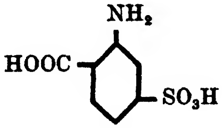


Aromatic Primary Amines. The following patents cover these compounds: *F.P. 674,638, 677,579, G.P. 513,209, 531,008, 534,640, 535,670, 550,711, 552,283.*

Phenylamines come into question here, especially those substituted in the benzene nucleus with solubilizing groups, for example, 1-aminobenzene-3-6-disulfonic acid:

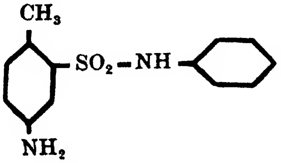


and sulfanthranilic acid (1-amino-3-sulfo-6-benzoic acid):

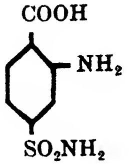


Naphthylamine sulfonic acids are recommended as stabilizing amines in *G.P. 532,401* (I.G.), for example α-naphthylamine-2,4-disulfonic acid or β-naphthylamine-4,6,8-trisulfonic acid.

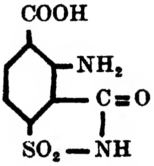
In *G.P. 535,076*, *G.P. 671,788* of the I.G.; *F.P. 800,876*, *F.P. 807,893*; *B.P. 459,342* of Kuhlmann, a number of stabilizing amines are enumerated, containing one or more sulfamido groups,* a sulfamido and a carboxyl group, or a sulfamido and one or more carboxyl groups, which may or may not be linked to a sulfamido group as a carboxylsulfimido radical. Examples given are 1-methyl-4-aminobenzene-2-sulfanilide,



1-carboxy-2-amido-4-sulfamidobenzene,



and 1-carboxy-2-amido-3,4-carboxysulfimidobenzene:



In the last three patents Kuhlmann specifies a method for applying diazoamino compounds, obtained by combining diazo compounds with primary amines containing one or more unlinked carboxy groups, besides a sulfamido group, for example 1-amino-2-carboxybenzene-4-sulfamide. The forma-

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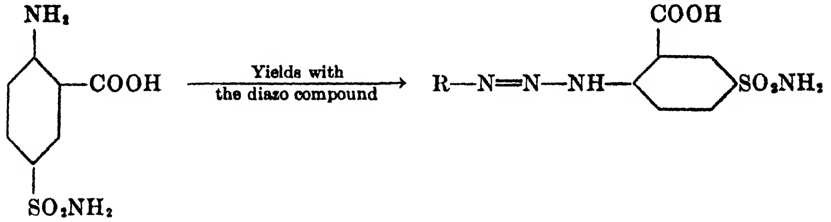
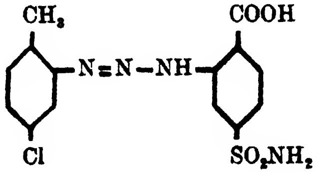
* See footnote page 13.

tion of a diazoamino compound by reaction of this compound with a diazo compound is illustrated by the equation:



This last product is mixed with the sodium salt of an arylide of 2,3-oxynaphthoic acid, thickened and printed. The azo dyestuff is developed by ageing the printed goods in acid steam. This process differs from the Rapidogen type of the I.G. only in the special stabilizing amines. The I.G. patents comprise quite generally chemicals containing solubilizing radicals such as HSO_3 and COOH, besides the amino group (as sulfanthranilic acid) so that the Kuhlmann patents are very similar.

According to *G.P. 671,788* (I.G.) diazoamino compounds produced by the action of primary or secondary amines on diazo compounds can be used as stable products for printing. The amines should contain one sulfamido and one free carboxy group, for example, the diazoamino compound formed by the reaction of 4-chloro-*o*-toluidine with 2-aminobenzene-4-sulfamido-1-carboxylic acid:



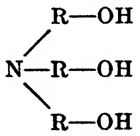
It forms insoluble azo dyestuffs in combination with a coupling component on the fiber by an aftertreatment with acid steam.

Primary aromatic amines bearing electro-negative radicals such as NO_2, HSO_3, COOH , have the least tendency toward inter-molecular migration. (See Goldschmidt and Molinari, *Ber.*, **21**, 2578; Dimroth, *Ber.*, **40**, 2394; Hantzsch and F. Perkin, *Ber.*, **30**, 1394.)

Other Basic Derivatives Containing a Trivalent Nitrogen Atom. The use of mixtures of alkaline solutions of naphthols and combinations of diazo compounds with protein degradation products is suggested in *B.P. 458,808* of I.C.I. The development is carried out as usual in acid ageing. The proteins are degraded to amino acids. Further details can be found in *U.S.P. 2,111,692* of the same company, evidently corresponding to the

British patent. Glue is hydrolyzed with sulfuric acid, neutralized with lime, then converted to the sodium salts by soda and treatment. The diazotized base is combined with the solution of these proteins, standardized to a certain concentration. When this reaction is complete, the coupling component can be mixed in.

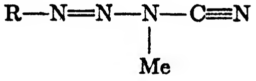
According to *B.P. 463,515* (Heaton) stabilized diazo compounds are obtained by the reaction of a tertiary alkylolamine with the diazonium salt of an arylamine, for example, triethanolamine:



Development is carried out by acid steam.

Stabilizing with cyanamide or its derivatives: I.G.—Taube, *F.P. 777,401, G.P. 614,198, 615,846, 624,765, 625,585, B.P. 433,222, U.S.P. 2,054,397.*

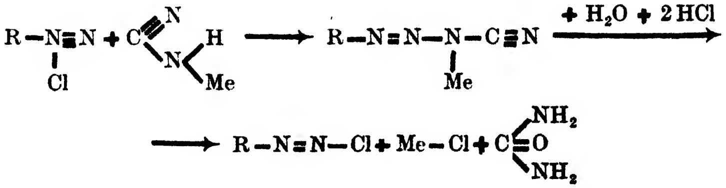
Cyanamide forms stable diazoamino compounds with diazonium compounds, of the following general formula



$$\underset{}{R-N{=}N-}\underset{\displaystyle Me}{\underset{|}{N}}-C{\equiv}N$$

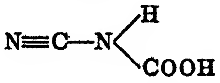
Me = alkali metal

The reaction proceeds according to the schematic equation

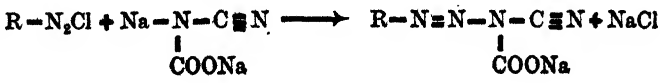


For example, *p*-nitro-*o*-anisidine is diazotized and combined with sodium cyanamide. The compound obtained crystallizes from solution and can be completely separated by salting out. The compounds are readily decomposed by acids, regenerating the diazo compound and urea.

Cyanamide can be replaced by cyanamide carboxylic acid



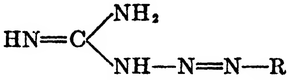
according to *G.P. 625,585.* The reaction follows the equation:



$$R-N_2Cl + Na-\underset{\displaystyle COONa}{\underset{|}{N}}-C{\equiv}N \longrightarrow R-N{=}N-\underset{\displaystyle COONa}{\underset{|}{N}}-C{\equiv}N + NaCl$$

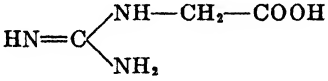
A mixture of this compound and the sodium salt of an arylide of 2,3-oxynaphthoic acid is printed and developed in acid steam.

In line with the above, an interesting thesis has been published by P. Kienzle (Paris, 1934) on the subject of diazo guanidines, first described by Walther and Grieshammer in 1915 (*J. prakt. Chem.*, #**92,** 209).



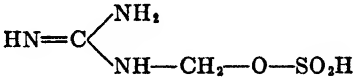
$$HN{=}C\Big\langle\begin{matrix}NH_2\\ NH{-}N{=}N{-}R\end{matrix}$$

These compounds are stable and have the property of regenerating the diazo compound to which they are linked, and in addition have water solubility. The solubility in water is imparted to the guanidines by the introduction of HSO_3, arylcarboxyl or arylsulfonic acid groups, such as glycocyanamine,



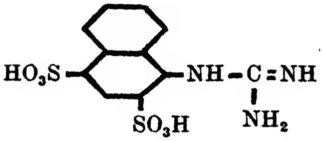
$$HN{=}C\Big\langle\begin{matrix}NH{-}CH_2{-}COOH\\ NH_2\end{matrix}$$

guanidine methylene sulfinic acid,



$$HN{=}C\Big\langle\begin{matrix}NH_2\\ NH{-}CH_2{-}O{-}SO_2H\end{matrix}$$

or guanidine-1-naphthalene -2,4-disulfonic acid:



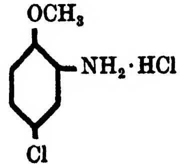
These guanidine derivatives are water-soluble, either as the acid or in the form of their alkali salts. They couple readily with diazonium salts, forming diazoguanidines, outstanding for their good stability and solubility. They can be mixed with naphthols without danger of premature coupling. Kienzle states that the mixtures are stable only in the dry state, not in solution. This property is evident in combinations with sodium β-naphtholate wherein the coupling reaction proceeds in an alkaline medium.

Piperidine compounds are employed in *U.S.P. 2,099,091* and *2,099,104*, *F.P. 758,889* (1933) and *B.P. 422,195* (Du Pont). Hydroxylamine compounds of the general formula,

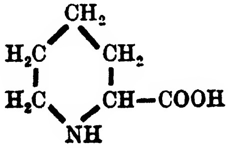
$$H_2N{-}Aryl{-}OH$$

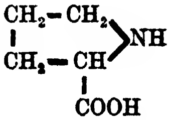
are diazotized and coupled with piperidine-α-carboxylic acid, whereby stabilized mixtures can be obtained which can be developed in acids.

Similarly *U.S.P. 2,112,764* (Du Pont) described the manufacture of a diazoamino compound, 4-chloro-2-aminoanisol, corresponding to Fast Red RC Base:

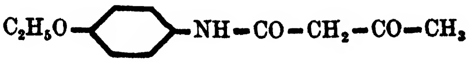


is diazotized and compounded with piperidine-α-carboxylic acid or "proline" (pyrrolidine-α-carboxylic acid):



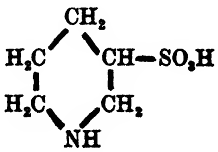


This product is printed in admixture with the alkaline solution of a coupling component, for example, an acetoacetyl-4-ethoxyanilide:

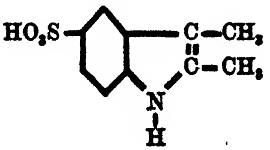


and developed as usual in acid steam.

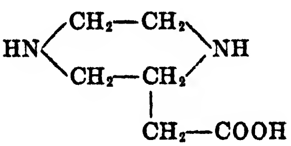
According to *B.P. 407,840* (I.G.) derivatives of piperidine or pyrrhol containing solubilizing substituents can be used for the same purpose, as, for example, piperidine-3-sulfonic acid,



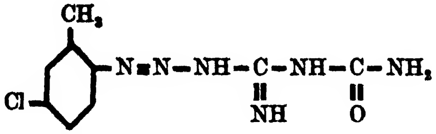
and 2,3-dimethyl indole-5-sulfonic acid:



B.P. 423,507 and *F.P. 775,097* (I.C.I.) recommend piperazine acetic acid

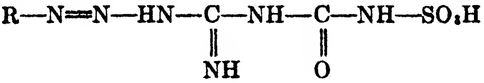


A new method for preparing stabilized diazo dye bases is proposed in *U.S.P. 2,154,405*, *B. P. 515,980* and *F.P. 840,322* (Calco). It has been observed that by the reaction of salts of diazo bases with guanyl urea sulfate, insoluble yellowish compounds are obtained. For instance, the diazochloride of 5-chloro-2-aminotoluol is linked with guanyl urea sulfate, forming:



This complex compound, ground together with an appropriate dispersing agent and a coupling component yields a paste which is stable in storage. This paste can be dispersed with the aid of an alkali and Cellosolve in a starch-tragacanth thickener for printing, and the prints developed in acid steam like the Rapidogens. The acid reaction, however, must be more intense in this case. Animal fibers are prepared with sulfuric acid or bisulfate, vegetable fibers with salts evolving acid (such as ammonium salts) before printing. The sodium salt of disulfodinaphthyl methane (Tamol or Setamol WS), prepared by reacting formaldehyde with naphthalene disulfonic acid, is especially recommended as a dispersing agent for the diazo product.

F.P. 840,322 and *840,445* (Calco) recommend in particular guanyl urea-N-sulfonic acid and N-nitroguanyl urea as stabilizing agents. The following types of diazo compounds are mentioned:

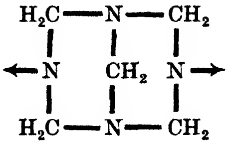


$$R{-}N{=}N{-}HN{-}\underset{\underset{NH}{\|}}{C}{-}NH{-}\underset{\underset{O}{\|}}{C}{-}NH{-}SO_3H$$

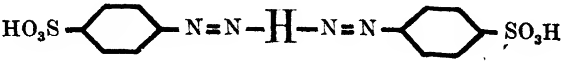
$$R{-}N{=}N{-}NH{-}\underset{\underset{NH}{\|}}{C}{-}NH{-}\underset{\underset{O}{\|}}{C}{-}NH{-}NO_2$$

The printing paste contains the stabilized diazo compound, Naphthol, monoethyl glycolether and thickening agent, and the prints are developed in acid ageing (*Can.P. 388,639*, Am. Cyanamid Co.).

Another process (*U.S.P. 2,155,942*—N.A.C.) of producing diazoamino compounds is carried out by linking the diazotized base to hexamethylenetetramine*:

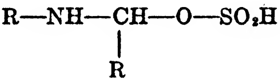


The nitrogen atoms marked with arrows can combine with the diazo radicals, so that a compound of the following constitution ensues:



where H represents hexamethylenetetramine. As in preceding cases, the dyestuff base should bear solubilizing groups. The corresponding alkali salts can be easily mixed with the coupling component in the printing paste. The prints are developed in an acid bath at 90°C.

Derivatives of methylamino formaldehyde bisulfite



$$R{-}NH{-}\underset{\displaystyle R}{\underset{|}{CH}}{-}O{-}SO_2H$$

for instance, monomethylamino formaldehyde sodium bisulfite ($CH_3{-}NH{-}CH_2{-}O{-}SO_2Na$) can be used as stabilizing agents according to *B.P. 309,610* (I.G.), *F.P. 673,052* and *G.P. 502,334* (I.G.).

A somewhat different process is described in *B.P. 374,479*—I.C.I., using the reaction product of formaldehyde bisulfite on an aromatic amine, as:

$$\text{Aryl}{-}NH{-}CH_2{-}SO_3H$$

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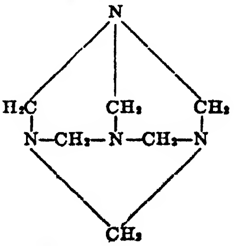
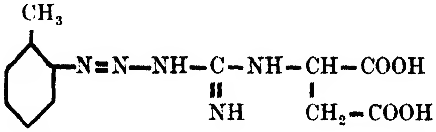
* The formula as given in the patent is not the recognized formula for hexamethylenetetramine, but rather the following with six methylene groups (Diserens):

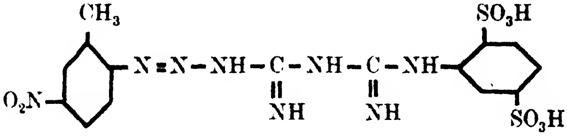


Compare *Wengraf's Ber.*, Jun., 1939, 17.

The printing paste comprises the solubilized amine with sodium salt of 2,3-oxynaphthoic acid arylide and sodium nitrite, and the development takes place in acid ageing.

Amidines of carbamic acid are used as stabilizers according to *F.P. 840,666* (May Chem. Co.). They are better known as guanido and biguanido acids. Examples of the corresponding diazoamino compounds are

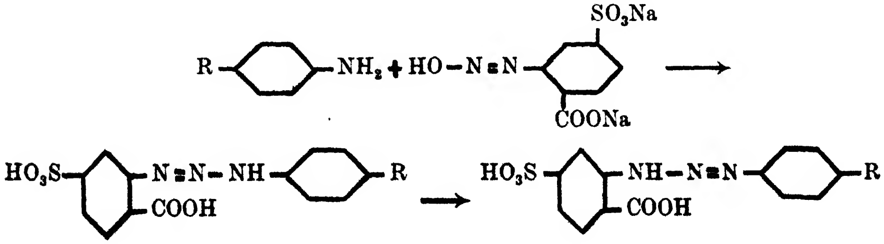




B.P. 427,803 (I.G.) mentions other compounds, containing besides a cyclic nitrogen, solubilizing groups; for instance, tetramethyltetrahydroquinoline sulfonic acid or hexahydrocarbazole sulfonic acid, etc.

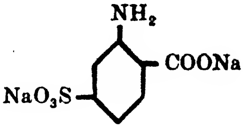
A similar process has been patented by *G.P. 696,270* (I.G.). Alkaline mixtures of 2-oxynaphthalene-3-carboxylic acid arylides, bearing a sulfogroup in position 1, plus diazoamino compounds or nitrosamines, substituted by strongly negative groups, are printed and the color developed by acid ageing.

B.P. 433,878 and *F.P. 769,838* describe the preparation of diazoamino compounds by a radically different process. The diazo compound of the stabilizing amine (sulfanthranilic acid) is linked with a primary amine which is blocked in the *para* position. The diazoamino compound undergoes a rearrangement and is split by acid according to the equation:



By this reaction the diazo derivative of the amine which has no solubilizing group results, and combines with the naphthólate to form an insoluble azo dyestuff.

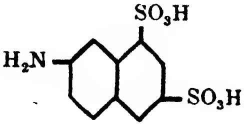
Thus the problem was satisfactorily and abundantly solved for the industrial manufacture of diazoamino compounds by introducing stabilizing amines which contain, besides the NH_2 group a solubilizing group such as COOH or HSO_3. The most commonly used amine is sulfanthranilic acid:



G.P. 513,209, Frdl., **1932,** XVII, 1062; *G.P. 531,009, Chem. Zentr.*, **1932,** II, 774.

The first Rapidogen Red and Scarlet dyestuffs were prepared with this agent. Sarcosine was used for newer Rapidogens such as the Red GS and Scarlet RS.

Other patents mention 3-amino-5 sulfobenzene carboxylic acid, naphthalene-1-amino-2,5-disulfonic acid, and amino-G-acid (*F.P. 769,838, B.P. 433,878*):



The Diazotizable Bases. It has been noted that only those diazotizable amines which have a strongly basic character can be expected to give satisfactory results in the manufacture of the Rapidogen type dyestuffs. This is just the opposite to the antidiazotates used in manufacturing the Rapid Fast type of dyestuff, which are based on amines having low basicity.

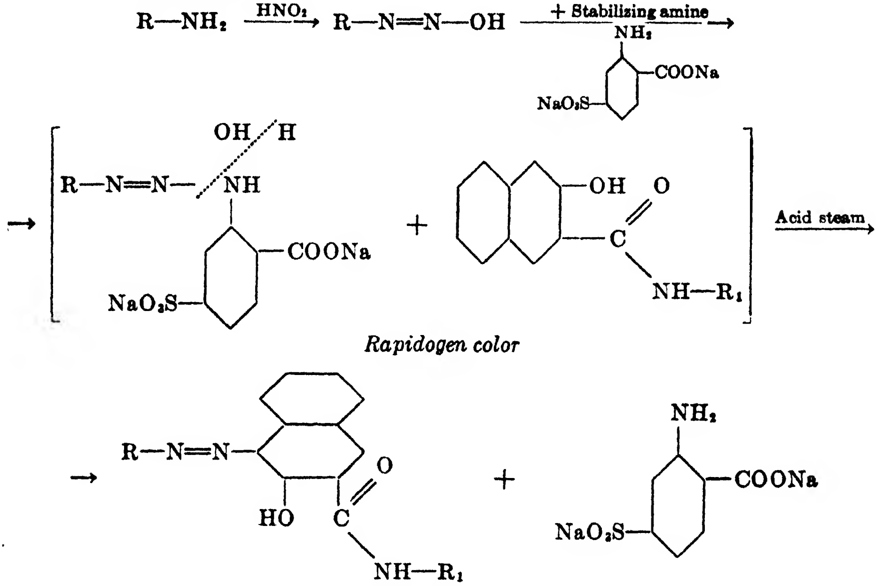
The different bases which are suitable for preparing Rapidogens and Rapid Fast colors may be classified according to the scheme below. The amines in the upper rectangle are suitable for Rapidogens, those in the lower for Rapid Fast type colors (from a paper by E. Sack, Yearbook of the Mulhouse Chem. Soc., 1933).

dianisidine
tolidine
benzidine
6-nitro-*p*-cresidine
4-chloro-*o*-toluidine
p-chloro-*o*-anisidine
5-chloro-*o*-toluidine

5-nitro-*o*-toluidine
dichloro-aniline

m-nitro-*p*-toluidine
m-nitraniline
p-nitraniline
o-nitraniline
p-chloro-*o*-nitraniline

The formation of the Rapidogen dyestuff on the fiber can be represented by the following equations:



Rapidogen color

wherein R and R_1 are aromatic radicals.

The dyestuffs of this series have been enthusiastically adopted by colorists all over the world. Many print shops have developed printing and dyeing formulas and many beautiful and original styles have been created with their help. They lend themselves for printing alongside chrome, basic, vat and Indigosol dyestuffs as well as aniline black. They are important as colored resists under aniline black and Indigosol paddings (see Bernardy, *Mell.*, Jan. **1932**, 17; *F.P. 769,838*, I.G.—1934; *G.P. 560,602; Mell.*, **1935**, #3, 209; *Tiba*, **1935**, 583).

At present there are more than forty Rapidogen colors on the market. The most important are enumerated here:*

Rapidogen Corinth IB	Azo Corinth Salt LB 4-sulfo-2-methylamidobenzoic acid Naphthol AS-LT
Rapidogen Golden Yellow IFG	Azo Red Salt RC sarcosine benzoylacetic-4′-benzoylamino-2′,5′-dimethoxy-anilide
Rapidogen Green B	Azo Blue Salt BB sarcosine Naphthol AS-GR

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* Report of the Office of Technical Services, Dept. of Commerce, Washington, D. C.

Rapidogen Red I 2 G	Azo Red Salt GR 5-sulfo-2-methylamido benzoic acid Naphthol AS-LC
Rapidogen Red ITR	Azo Red Salt ITR 5-sulfo-2-methylamidobenzoic acid Naphthol AS-ITR
Rapidogen Red R	Azo Red Salt RC sarcosine Naphthol AS-OL
Rapidogen Red Violet RR	Azo Red Violet Salt R 5-sulfo-2-methylamidobenzoic acid Naphthol AS-BO
Rapidogen Scarlet IL	Azo Scarlet Salt GG 5-sulfo-2-methylamidobenzoic acid Naphthol AS-OL
Rapidogen Scarlet R	Azo Red Salt KB 4-sulfo-2-methylamidobenzoic acid Naphthol AS-PH
Rapidogen Scarlet RS conc.	Azo Red Salt KBS sarcosine Naphthol AS-PH
Rapidogen Violet B	Azo Violet Salt B sarcosine Naphthol AS
Rapidogen Yellow G	Azo Red Salt KB 4-sulfo-2-amidobenzoic acid Naphthol AS-G
Rapidogen Yellow GS conc.	Azo Red Salt KBS sarcosine Naphthol AS-G
Rapidogen Yellow I 4 G	Azo Red Salt TR methyl taurine Acetoacetic 4′-chloro-2′,5′-dimethoxyanilide
Rapidogen Yellow I 3 G	Azo Red Salt KB sarcosine Naphthol AS-L4G
Rapidogen Olive Brown IG	Azo Orange Salt GC 4-sulpho-2-amidobenzoic acid Naphthol AS-LB

Rapidogen Orange G	Azo Orange Salt GC 4-sulpho-2-amidobenzoic acid Naphthol AS-D
Rapidogen Orange I2R	Azo Orange Salt RD 5-sulfo-2-ethylamidobenzoic acid Napthol AS-OL
Rapidogen Orange R	Azo Scarlet Salt GG 5-sulfo-2-ethylamidobenzoic acid Naphthol AS-PH
Rapidogen Red G	Azo Red Salt KB 4-sulfo-2-amidobenzoic acid Naphthol AS-D
Rapidogen Red GS conc.	Azo Red Salt KBS sarcosine Naphthol AS-D
Rapidogen Brown IB	Azo Red Salt RC sarcosine Naphthol AS-LB
Rapidogen Brown IBR	Azo Red Salt PTS sarcosine Naphthol AS-LB
Rapidogen Brown I 2 RN	Azo Red Salt RL 5-sulfo-2-ethylamidobenzoic acid Naphthol AS-LB
Rapidogen Brown IR	Azo Scarlet Salt GG 5-sulfo-2-ethylamidobenzoic acid Naphthol AS-BG
Rapidogen Black IT	Azo Red Salt B 5-sulfo-2-methylamidobenzoic acid Tetralol carbonic-2-naphthylamide Naphthol AS-SR
Rapidogen Black Brown ITR	Azo Red Salt ITR 5-sulfo-2-ethylamidobenzoic acid Naphthol AS-BT
Rapidogen Black Brown T	Azo Red Salt RC sarcosine Naphthol AS-BT

Rapidogen Blue B	Azo Blue Salt BB sarcosine Naphthol AS
Rapidogen Blue R	Azo Blue Salt RR methyl taurine Naphthol AS
Rapidogen Bordeaux IB	Azo Red Salt B 5-sulfo-2-methylamidobenzoic acid Naphthol AS-BO
Rapidogen Bordeaux BN	Azo Red Salt RL 5-sulfo-2-ethylamidobenzoic acid Naphthol AS-D
Rapidogen Navy Blue B	Azo Blue Salt MG methyl taurine Naphthol AS
Rapidogen Navy Blue R	Azo Blue Salt BB sarcosine Azo Blue Salt RR methyl taurine Naphthol AS

The Rapidogen dyestuffs with the letter "I" in the designation possess excellent light-fastness.

Rapidogen Yellow Brands I3G and I4G (lemon yellow) and Rapidogen Golden Yellow IFG are sensitive to formaldehyde fumes and therefore not recommended for printing alongside vat dyestuffs. Furthermore, Rapidogen Orange IGN, Rapidogen Golden Orange IGG, Rapidogen Bordeaux RN (which is more readily soluble than the R brand but less stable), the Rapidogen Reds ITR and IGG, Rapidogen Scarlet IL, Rapidogen Brown IBR, Rapidogen Black Brown T, Rapidogen Navy Blue R (giving a very dark and inexpensive navy shade), Rapidogen Red Violet RR, Rapidogen Bordeaux IB, Rapidogen Black IT (brownish black, of poor stability) are recent additions.

Most of the Rapidogen brands can be blended with one another. The following combinations have proved particularly useful in practice:

Pink shades: Rapidogen Red IGG + Rapidogen Scarlet IL
Highly stable red shades: Rapidogen Red ITR + Rapidogen Orange IRR
Bordeaux—garnet shades: Rapidogen Red ITR + Rapidogen Red Violet 2 R
Brown shades: Rapidogen Brown IB + Rapidogen Black Brown T
Catechu brown: Rapidogen Brown IB + Rapidogen Orange IRR

Printing. Preparation of the printing pastes is in general quite simple; few precautions are necessary. The Rapidogen color is first pasted up with sodium ricinoleate or sulforicinoleate or Monopole Brilliant oil, then a solution of caustic soda is added. Pasting directly with concentrated alkali is to be avoided. Solvents like glycol or its derivatives, or dispersing agents such as Peregal O or urea further facilitate the dispersion of the color and prevent any attack on the doctor blade or engraved roller. For thickeners, starch tragacanth gum or RPG gum are suggested.

It is further advisable to add 30 to 40 gm of neutral sodium chromate per kg of print paste to light shade prints (less than 25 gm Rapidogen color per kg) for stability. This is particularly important where the Rapidogens are printed alongside vat colors, for here the prints must be aged twice. According to *U.S.P. 2,008,966* (Röhm & Haas), the addition of salts of alkylamines has the effect of improving stability of the print pastes. Such products as diethylamine hydrochloride, butylamine oxalate, etc., have the effect of preventing premature formation of the dyestuff before the ageing operation.

The Rapidogens can be printed alongside aniline black and developed in the acid ager. Their brightness is not impaired by the aniline fumes.

Development of the Rapidogens can be carried out in various ways:

(*1*) *In an acid bath:* The goods are printed and dried, then conveyed through a solution of acetic and formic acids at 80°C. However, by this method, there is danger of staining the whites by bleeding of the prints, and the color yield is poor, so that this development has met with little success. The addition of large amounts of salt to the acid bath to prevent bleeding has been recommended (*U.S.P. 2,035,518*, Du Pont).

Indigosol prints can be developed at the same time as the Rapidogens, by the addition of mineral acids to the acetic-formic acid bath. Sulfuric acid and sodium sulfate are added to the organic acids and development carried out in 20 seconds at 75 to 80°C (*G.P. 696,268*—D. & H., 1938).

(*2*) *In acid steam:* The process consists of ageing the prints in steam to which acetic acid and formic acid vapors have been added. The acids are injected into the steam inlet so that they are vaporized before reaching the ager. This method is the most widely employed today. The greatest disadvantage is in the rapid deterioration of the ageing equipment, while a lesser drawback is the necessity for two ageings when the Rapidogens are printed alongside vat colors.

A special ager for acid steaming is described in *B.P. 435,523*. The chamber is constructed of wood, with plastic rollers. Bearings and cogwheels are located outside of the chamber. The acid is charged into the ager either by a separate spray nozzle or by injector into the steam intake pipe. The ratio of acetic to formic acid is three to one, and about 250 to 350 gm of acid are blown in per 100 yards of goods, depending on the coverage of the pattern.

(*3*) *On the dry cans:* The printed and dried material is padded with an acetic acid solution at room temperature, and immediately dried on lapped cans, or passed through a small ager (*G.P. 534,640, 562,623; Rev. Gen. Mat. Col.*, **1933**, 261).

(*4*) *In neutral steam:* New methods have been proposed for development of the Rapidogens in neutral ageing. The trend has been toward a simple process which could be applied for animal fibers as well as for vegetable fibers, and for Rapidogens alongside the important vat colors.

The patents *G.P. 639,238*, *F.P. 798,425*, *B.P. 436,371* (I.G. Tietze-Siefert) suggest treating the goods before printing with salts which split off acid, and then ageing in neutral ager. The back of the goods is slashed with a solution of chlorides of zinc, magnesium, aluminum or ammonium. A modification of this method is proposed in *B.P. 436,371*. The printed goods are sprayed with a solution of the ammonium salt of an organic acid, which can evolve the acid necessary for developing the Rapidogen in subsequent neutral ageing.

In *G.P. 639,288*, *F.P. 785,334*, *798,425*, *B.P. 466,846* (I.G.) and *Aus.P. 126,754* (Lauterbach), it is recommended to impregnate the fabrics with organic compounds which evolve acids during ageing, such as diethyl tartrate or ammonium salt of toluene sulfonic acid. The goods are then printed, dried and aged as usual in the neutral ager. By this method it is claimed that Indigosols and Rapidogens can be developed in one ageing operation. The high cost of the impregnation is however a real drawback to this process (see Torinus, *Mell.*, Jan., **1936**, 70; *Mell.*, French ed. Mar. **1937**,). Diethyl tartrate is known under the trade names Indigosol Developer D and Developsol D.

These patents indicate a safe method for application printing of Rapidogens on silk or wool, as the danger of strongly alkaline prints is avoided by the impregnation. Another product recommended for the same purpose is Laventine RA (I.G.). This product likewise possesses the property of splitting off acids during ageing, and is intended as an auxiliary in the printing of Rapidogens on natural silk. The silk is first impregnated in a lukewarm bath of 5 gm of soda ash per liter, rinsed in cold water and dried. It is then padded in a solution of 35 gm of Laventine RA per l and dried again. The Rapidogens are printed according to the following formula:

50 gm	Rapidogen dyestuff
25 gm	caustic soda 38° Bé
30 gm	Monopole Brilliant oil
395 gm	water
500 gm	starch-trag. thickening
1000 gm	

The prints are developed in a half hour's steaming, thoroughly rinsed and soaped. It has been reported from Lyons that this method has proved successful for printing pure silk. It is also possible to obtain good resists under aniline black on vegetable fibers by adding diethyl tartrate to the aniline black padding solution.

A more practical solution to this problem might be found in the following method, which offers the possibility of developing the Rapidogens without necessity of preparation of the goods, and avoiding the dangerous injection of acid into the ager. The method is proposed in *B.P. 452,482*, *454,869*, *F.P. 786,012* and *G.P. 640,935* (I.G.) and comprises adding compounds which evolve organic acids directly to the printing paste. Compounds suggested are sodium bromoacetate, succinic acid ethyl ester, methyl oxalates, dithioglycollic acid ethyl ester, diethyl tartrate, esters of inorganic acids as phosphates or borates, acetoxyethane sodium sulfonate, etc. While the method is theoretically reasonable, in practice the results are not uniformly satisfactory as far as color yield and stability of the pastes is concerned. The addition of readily saponifiable esters to a strongly alkaline print paste is the apparent cause of non-uniformity (*Rev. Gen. Mat. Col.*, **1938,** 224; *G.P. 640,935.*)

According to *B.P. 454,869* (Du Pont) substances evolving acid are also recommended as addition to the print paste, and specifically, the following: sodium chloroacetate, triethanolamine acetate, -formate or -sulfate. The print paste contains the naphthol, diazoamino compound, wetting agent, alkali and thickener, besides the water-soluble substance which splits off acid in the ager.

U.S.P. 2,088,506 (Du Pont) in a very similar manner suggests using agents which split off acids in the print paste. Examples given are salts of chloroaliphatic acids such as sodium monochloroacetate, esters of polyvalent alcohols, amides of organic acids, etc.

A modification of this idea is contained in *G.P. 740,010*—1943, and *F.P. 866,654* (D. & H.). The Rapid Fast color or Rapidogen is printed from a cellulose lacquer containing a substance which yields an acid at high temperatures, for example ammonium oxalate or diethyl tartrate. The prints are simply dried at high temperatures on cans, the dyestuff developing by the acid which is split off in the heat. To avoid stiff prints a plasticizer is added to the lacquer. Washing is omitted as unnecessary. Example:

40 gm Rapidogen dyestuff	
200 gm Solvent A	10 gm diethylene glycol diethyl ether 10 gm ethylene glycol 4 gm water
600 gm nitrocellulose lacquer	15 gm low viscosity nitrocellulose solution 20 gm butanol 10 gm butyl acetate 25 gm ethyl lactate 30 gm ethanol
8 gm ammonium oxalate *dissolved in*	
152 gm Solvent A	
1000 gm	

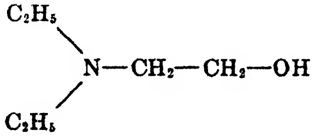
Prints on cotton are dried on cans at 120 to 130°C.

In order to utilize combinations of naphthols with diazoamino compounds which cannot be otherwise mixed together, *U. S. P. 2,263,616* (DuPont-Dahlen) recommends the use of wetting agents such as condensates of formaldehyde and napthalene β-sulfonic acid. The wetting agent is ground with the naphthol and the diazoamino compound added. The mixture is soluble in dilute alkalis.

According to *F.P. 859,710* of St. Denis, it is claimed that the alkali used as solvent for the naphthol may be dispensed with by dispersing the coupling component in the printing paste. In this instance the printing paste consists of (1) the arylamide of oxycarboxylic acid, free of solubilizing groups such as COOH or HSO_3, in which the carbamido group as well as the group which couples with the diazo compound are in the immediate vicinity of the hydroxy group, and (2) a diazoamino derivative, likewise free from solubilizing groups in the reactive part of the compound, both (1) and (2) being pasted up with some thioethylene glycol and suitably thickened. The goods are printed, dried, aged 15 minutes in neutral steam, rinsed and soaped at the boil for $\frac{1}{2}$ hour. The process is principally intended for printing of animal fibers, but the resulting prints are neither as full nor bright as those produced by the normal procedure.

A process of applying the substance which splits off acid to the back of the goods from a thickened paste is the subject of *G.P. 651,044* and *651,045* (I.G.). This method is intended to prevent the carry-over of parts of the developing components from one bath to another, and thus avoids bleeding of the prints.

A method which has been proposed for development of the Rapidogens in neutral ageing, and one which has met with considerable success in the practice, has been described in *G.P. 696,269*, *697,185*, *704,542; F.P. 824,620*, *846,748* (1938) and *B.P. 480,169* (I.G.). The principle involved here consists of replacing the alkali necessary to dissolve the naphthol component by an organic base which is volatile in steam. The printing paste thus loses basicity during the ageing operation and the naphthol combines with the diazo compound set free in the process. Suitable organic bases for this purpose are tertiary alkyl alkanolamines such as diethylethanolamine:



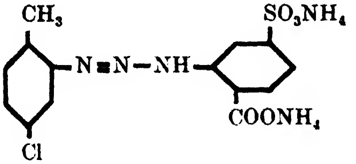
which was offered in 1939 to the trade under the name of Rapidogen Developer N (see also *F.P. 877,306; Teintex*, **1944**, 137).

The Rapidogen Developer method may be used with many of the

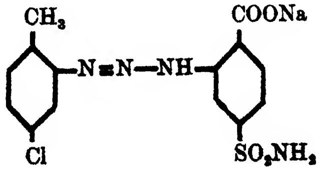
Rapidogen colors, permitting their development in neutral steam. Any alkalinity of the print paste must be avoided.

The action of the Rapidogen Developer lies in its solubilizing effect on the naphthol and the diazoamino compound, and also by the alkalinity of the developer which permits a salt formation with the hydroxyl groups of the naphthol. The printing pastes have as good a stability as those prepared with caustic alkalis. Since the developer volatilizes during the ageing process, the diazoamino compounds can split and the coupling reaction with the naphthol can proceed. The method is therefore suitable for those diazoamino compounds which split at a pH value near the neutral point, since no acid is applied during ageing. The diazoamino compounds suitable for this process are those which have been prepared not in the form of their sodium salts, but as salts of volatile bases such as ammonia or pyridine. It may be assumed that in the hydrolysis of these compounds during ageing, the acid groups of the stabilizing amine help to lower the pH, thus promoting the complete hydrolysis of the diazoamino compound.

The production of salts of diazoamino derivatives of volatile bases (ammonia or pyridine) is described in *U.S.P. 2,125,087* and *F.P. 824,620* (I.G.). For example, 4-chloro-2-toluidine is diazotized and mixed with 4-sulfo-2-aminobenzoic acid and ammonium carbonate giving a product of the formula:



This ammonium salt is printed in admixture with the naphthol and a solvent such as diethylamine. During ageing, the ammonia is volatilized and the coupling reaction takes place. In this connection the products described in *G.P. 671,788* (see page 308) are pertinent. Diazoamino compounds are described which are obtained by the reaction of primary or secondary amines which have a sulfamido group and one free carboxyl group, for instance the compound prepared from 4-chloro-*o*-toluidine and 2-aminobenzo-4-sulfamido-1-carboxylic acid:



An improvement on the above process is suggested in *F.P. 871,865*, whereby print pastes prepared according to the Rapidogen Developer method may also contain as added agents certain products which can evolve acid during ageing without impairing the stability of the print pastes. Organic solvents, in particular, Glyecine RN, should be used for dissolving the Rapidogens, but in this connection it may be noted that on an industrial scale it was found that this expensive reagent could be replaced with 10 gm of ethyl alcohol and 30 gm of urea per kg.

Similarly, *U. S. P. 2,257,190* (Gen. Aniline-Riedmair, 1941) discloses the use of volatile bases together with salts of these amines in preparations consisting of naphthol and diazoamino compound. Examples of amines given are diethyloxyethylamine, dimethylaminobutane or propylaminoethanol. A salt of one of these amines is also used, for instance the formic, tartaric or thiocyanic acid salt, or an ester which can readily be hydrolyzed, as tartaric acid diethylester.

Because of the delicacy of the reactions when using Rapidogen Developer N, it is necessary to employ only strictly neutral thickening agents. When printing Rapidogens by this method alongside vat colors it is recommended to add 15 gm of Ludigol and 15 gm of ammonium thiocyanate per kg of print paste. As an example:

60 gm	Rapidogen Red G extra conc.
80 gm	Rapidogen Developer N
10 gm	alcohol
30 gm	urea
80 gm	cold water
600 gm	neutral starch-trag. paste
30 gm	Ludigol 1:1 water
30 gm	ammonium thiocyanate
80 gm	cold water
1000 gm	

The development takes place in neutral ageing, after which the prints are soaped and rinsed as usual.

This method, using Rapidogen Developer N, solves the problem for printing of Rapidogens by neutral ageing development. In general, the results are satisfactory, and the field has grown into a very important one, particularly with screen printers.

As a developer for Rapidogens which are to be printed in a pattern with vat colors, the I.G. offered Rapidogen Developer NN which contains Rapidogen Developer N plus calcium lactate and Ludigol.

Rapidogen Developer RNA of General Dyestuff Corp. is diethylethanolamine and is therefore identical with Rapidogen Developer N. The mixture with calcium lactate and Ludigol was found to be unstable in storage. For this reason the Rapidogen Developer RNA is sold as a base to be used when no vat colors are printed alongside the Rapidogens. Calcium lactate and Ludigol are sold as a 50–50 white mixed powder under the name Rapidogen Developer Assistant. When vat colors are printed in the pattern a mixture of 90 parts of Developer RNA and 10 parts of Developer Assistant is recommended.

Another developer which has been found satisfactory, called Rapidogen Developer Base RPN, is 2-amino-2-methyl propanol.

Rapidogens suitable for developing with the Developers are as follows:

Rapidogen Golden Orange IGG
Rapidogen Orange IRR
Rapidogen Orange FFR
Rapidogen Scarlet FFG
Rapidogen Scarlet FFR
Rapidogen Scarlet IL
Rapidogen Red FFG
Rapidogen Red FFR
Rapidogen Black MG
Rapidogen Black FFM
Rapidogen Red FFBB
Rapidogen Red IGG (*for pinks only*)
Rapidogen Red ITR (*for pinks only*)
Rapidogen Bordeaux RN
Rapidogen Red Violet RRA
Rapidogen Corinth IB
Rapidogen Violet B
Rapidogen Blue BN
Rapidogen Navy Blue FFR

Rapid Fast Yellow GGH develops neutral when printed with caustic.

Rapidogen Brown FFIB can be printed either with caustic or Developer RPN when vat-ageing.

All Rapid Fast colors are dissolved with caustic soda and then can be developed neutral. However, when they are to be used together with Rapidogens, either in combinations or alongside, which are to be neutral developed, they likewise must be dissolved with Developer Base RPN in place of caustic soda.

Some of the Rapidogens do not respond with Developers. These are: Rapidogen Red GS, IGG, Black IT, Brown IB, Green B, Yellow IGG and I4G, Golden Yellow IFG.

It is also inadvisable to use the developer method alongside aniline black, as the vapors of the volatile base interfere with the full development of the black. Diphenyl Black Base, however, can be printed along with Rapidogens by the developer method, using the following formula:

30 gm acetic acid 8° Bé
55 gm sodium chlorate
660 gm starch-trag. thickener
63 gm Diphenyl Black Base I, *dissolved in*
90 gm acetic acid 8° Bé, *and*
62 gm lactic acid 50%
10 gm aniline
10 gm aniline hydrochloride
50 gm aluminum chloride 30° Bé
10 gm ammonium vanadate 1/1000
20 gm water

1000 gm

In printing the Rapidogens, difficulties are sometimes encountered in corrosion of the doctor blade and scratching of the rollers. This is caused by incomplete solution of the dyestuff, but in spite of additions of glycol, urea, alcohols, the dyestuffs are not entirely free from this drawback. The Pharmasols (Pharma and Carbic) are free from this defect, as they are sold in solution form. They differ from the Rapidogens in the method of stabilizing, but otherwise are printed and developed in the same way. According to *U.S.P. 2,105,326* (Pharma-Markush-Miller) the presence of amino acids in a solution of stabilized diazo compounds prevents the formation of insoluble chemical substances. Examples of amino acids which are specially recommended are cystine, glycine, etc.; and it is claimed that diazoamino compounds to which these agents are added do not form gummy or crystalline precipitates.

Ciba (*F.P. 849,848*—1938) claims that marking off or bleeding in the wash can be prevented by a treatment of the aged prints in water at 75°C before soaping.

The Rapidogens are often used as colored resists under aniline black; also under Indigosols (see Chapter III). Conversion styles can be worked out using the different chemical behaviors of vats, Indigosols, and Rapidogens.

In *B.P. 422,488*, it is suggested to print the Rapidogens with substances which act as resists under aniline black and Indigosols, such as zinc oxide, magnesium oxide or sodium thiosulfate. The prints, after drying, are cross-printed with Indigosols and aniline black to which ammonium glycollate is added. On ageing, the Indigosols are resisted by the Rapidogens, but the latter on the other hand are developed by the glycollic acid and ammonium thiocyanate.

Another similar style can be produced by applying the neutral steam developing method for Rapidogens according to the Developer NN method. Vat dyestuffs are combined here with Rapidogen dyes for instance:

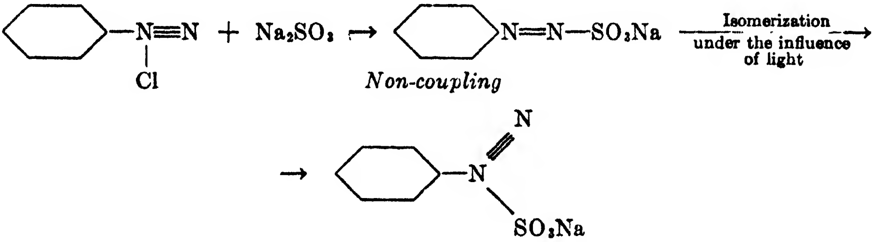
80 gm	Rapidogen Scarlet I L
50 gm	Glyecine A
50 gm	urea
120 gm	Rapidogen Developer NN
200 gm	water
400 gm	Colloresin V combined with gum-thickener
100 gm	Indanthrene Brilliant Blue 3G paste conc.
1000 gm	

This paste is printed, dried and cross-printed with a second paste containing Hydrosulfite NF and potash. Thereupon the fabrics are aged. The Rapidogen dyestuff is destroyed on the overlapping areas by the discharge effects of the hydrosulfite while at the same time the vat dyestuff contained in the paste is fixed.*

Rapidazol Dyestuffs**

The preparation of this group of dyestuffs is based on the transformation of diazo compounds into diazosulfonates or hydrazine sulfonates which cannot couple with naphthols.

The diazo sulfonates were studied by E. Fischer in 1877 (*Ann.*, **1878,** 190, 73). They are prepared by the reaction of diazonium salts in neutral or slightly alkaline solution with sodium sulfite according to the equation



Couples with naphthols

While the transformation of diazoamino compounds or isodiazotates into reactive coupling diazo compounds can be accomplished with dilute acids, this is not the case with diazosulfonates. It was noticed that in some cases the influence of light was sufficient to change diazosulfonates into active diazo compounds; in other cases, which is more practical, the change takes place by elevation of the temperature. Such is the case with the diazosulfonates of monoacetyl- or monobenzoyl-*p*-phenylene diamine and *p*-aminodiphenylamine (*F.P. 727,665*; *Chem. Zent.*, **1932,** II, 2542; *B.P. 377,207; Chem. Zent.*, **1933,** I, 317; and *G.P. 588,212; Chem. Zent.*, **1934,** I, 1899; *G.P. 560,797* and *560,798*, 1930).

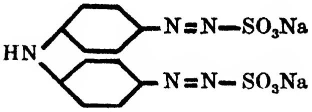
The addition of sulfur to the printing paste is recommended in *B.P. 377,207, 379,279* and *379,280* (I.G.), whereby the speed of the reaction which forms the dyestuff is raised and the uniformity of results is improved.

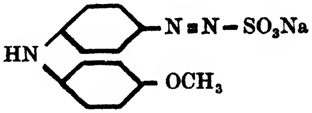
Rapidazol Blue IB is the diazosulfonate of Variamine Blue B Base plus Naphthol AS. Rapidazol Black B corresponds to Rapidazol Blue IB with Naphthol AS-G added.

* See: F. Nestelberger, *Mell.*, **1941**, 35 and *Teintex*, **1941,** 106; also H. Gurtler, *Mell.*, **1940,** 126, 127, discussing the resist effects obtained with vat dyestuffs under Rapidogen dyeings, developed according to the "Rapidogen Developer Method".

** References regarding Rapidazol dyes: *G.P. 560,797, 560,798, 563,061, 578,648, 588,212; B.P. 377,207, 377,279, 379,280, 398,846, 421,971; F.P. 727,665* and *1st add. 42,476; F.P. 735,365* and *1st add. 41,731, 2nd add. 43,623.*

The patents of the I.G. name the following compounds in the manufacture of Rapidazols; mixtures of the sodium salts of diphenylamine-4-diazo, or 4,4'-bisdiazosulfonic acid, plus alkaline solutions of Napthhol AS:

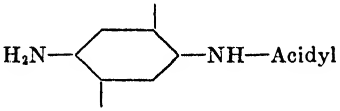




The print paste containing Rapidazol Blue IB, suitably dissolved, is printed and aged for four minutes in saturated steam. The dyestuff is speedily developed. The range of shades of this group has not been enlarged however, because difficulties have been encountered in transferring the reaction to other bases, so that the principle has been abandoned at present.

According to *G.P. 563,061* of the I.G., hydrazine sulfonic acid can be obtained by reduction of diazosulfonate. These compounds can be applied in a similar way.

Hydrazine sulfonic acids of aromatic bases, corresponding to the schematic formula:

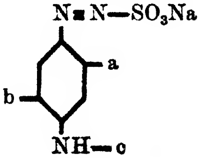


are mixed with a Naphthol AS coupling component and bichromate and developed by steam.

Photo Rapid Dyestuffs of St. Denis—Francolor*

The same principle is employed in preparing these dyestuffs as the Rapidazols of I.G. The Photo Rapid dyestuffs are mixtures of arylides of 2,3-oxynaphthoic acid, caustic soda and antidiazosulfonates derived from amines. These amines do not contain solubilizing groups such as HSO_3 or COOH, but a hydroxyl group in the *ortho* position to the diazo radical. The components are light-reactive and combine under the influence of light.

The best results are said to be obtained with diazosulfonates of the following schematic constitution:



(a = OH; b = halogen, alkyl; c = acetyl, acyl, benzoyl)

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* References regarding Photo Rapid dyestuffs: *F.P. 760,784* and *add. P. 45,829; B.P. 440,144; U.S.P. 2,078,861; F.P. 795,558* (St. Denis, Lantz); *G.P. 643,973; F.P. 766,668* (I.G.).

Examples here are the sodium salt of 2-methyl-5-chlorodiazobenzene sulfonic acid, also of 2-aminoethoxybenzene, 4-nitro-2-aminotoluene, *m*-xylidine, 5-chloro-2-aminomethoxybenzene, etc.

The mixture of the antidiazosulfonate and the alkali naphtholate is printed, dried at low temperature and thereupon exposed to sunlight or strong electric light, as the arc or mercury lamp. The Soc. des. Mat. Col. de Saint Denis, who promoted this method of developing, expected a favorable reaction from the trade, but the idea has had little success.

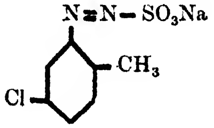
Azo Dyestuffs Developed by Oxidizing Agents

Prints of diazosulfonates in admixture with naphthols can be developed by steam containing an oxidizing agent, such as chlorine (*U.S.P. 2,078,861; F.P. 795,558; G.P. 679,768; B.P. 457,718*—St. Denis). As developing agents, substances producing chlorine or bromine are recommended. Bromine was suggested by the I.C.I. some years ago for this purpose, in a process wherein potassium bromate and potassium bromide were added to the mixture of diazosulfonates and naphtholate, followed by acid ageing. The acid liberates bromine which acts as an oxidizing agent (method of Schmitt—*B.P. 377,978* and *414,681*—I.C.I.).

$$R{-}N{=}N{-}SO_3Na \xrightarrow{+O} R{-}N{=}N{-}SO_4Na$$

Non-coupling compound *Coupling compound*

In *F.P. 795,558* St. Denis-Lantz describes the application of mixtures of salts of aryl-antidiazosulfonates (or arylhydrazine sulfonates) with coupling components. These mixtures form azo dyestuffs by the action of an oxidizing agent, such as by developing the prints in a steam atmosphere containing chlorine gas. *G.P. 679,768* (St. Denis) suggests the use of antidiazosulfonates or hydrazine sulfonates, prepared from aromatic amines with electro-negative radicals (but no COOH or HSO_3 groups). The following example is mentioned: Cotton fabrics are printed with a paste containing sodium-2-methyl-5-chlorobenzene-1-antidiazosulfonate:

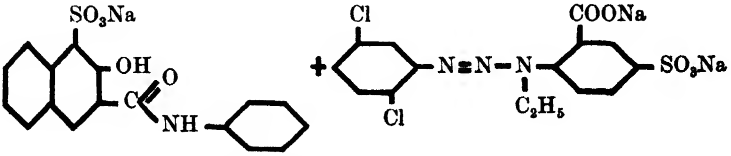


plus the sodium salt of Naphthol AS-D, caustic soda, glycerin and starch-tragacanth thickening. The dyestuff can be developed by oxidizing agents in gaseous or liquid state. Chlorine, bromine, nitrous acid, lead peroxide, hypochlorites or bromates in acid media are particularly recommended.

It is quite possible that the development of Photo Rapid dyestuffs by the action of light might take place by a similar chemical reaction. Oxygen carried along by the fibers could be activated by the light rays, thereby transforming the diazosulfonates into diazosulfates. The sulfates thus formed are able to couple with the naphtholate, forming the dyestuff.

Mixtures of Naphthols Derived from 2,3-Oxynaphthoic-1-Sulfonic Acid with Nitrosamines or Diazoamino Compounds

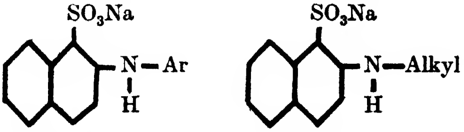
These printing mixtures are characterized as being derived from 2,3-oxynaphthoic-1-sulfonic acid, instead of 2,3-oxynaphthoic acid as in the case of the Rapidogens and Rapid Fast colors. The sulfonic acid group is thus located on the position where coupling normally occurs. By the action of acid the sulfonic acid group is split off and coupling takes place in the usual manner. The advantage of this preparation lies in the better solubility of the naphthol and the necessity for less alkali in the print paste. Examples are given in *F.P. 838,925* and *G.P. 696,270* of the I.G.



Derivatives of 2 Aminonaphthalene-1-Sulfonic Acid (Tobias' Acid)

F.P. 795,802, 811,711; G.P. 694,311; B.P. 479,708 (St. Denis-A. Wahl-M. Paillard, 1937).

These components couple with diazo compounds by treatment with mineral acids, whereby the sulfo group is split off. N-aryl and N-alkyl derivatives are employed:



The goods are impregnated or printed with a solution of 2-alkyl or 2-cycloalkylaminonaphthalene-1-sulfonic acid salt, then treated with an appropriate diazo compound which contains no solubilizing group. The diazo group replaces the sulfo group under these conditions, with formation of sulfuric acid. The alkylaminonaphthalene sulfonic acids are prepared by the reaction of primary aliphatic amines with 2-oxynaphthalene-1-sulfonic acid in the presence of sulfur dioxide.

The coupling process can be carried out in neutral or mineral acid solution, so that the process is especially adaptable to wool or natural silk.

Principle B

Use of soluble compounds which are capable of regenerating an amine.

The print paste contains these compounds together with naphtholate and sodium nitrite. On subsequent acid treatment the amine is regenerated and diazotized, and immediately couples with the naphthol.

Several methods are based on the idea:

(1) The method, invented by M. Bader, 1932: mixtures of nitraminates or isomers thereof, *i.e.*, aryl-N-nitrosohydroxylamines plus naphthols.

(2) The method of Ciba-Basle: mixtures of dispersed bases with naphthols.

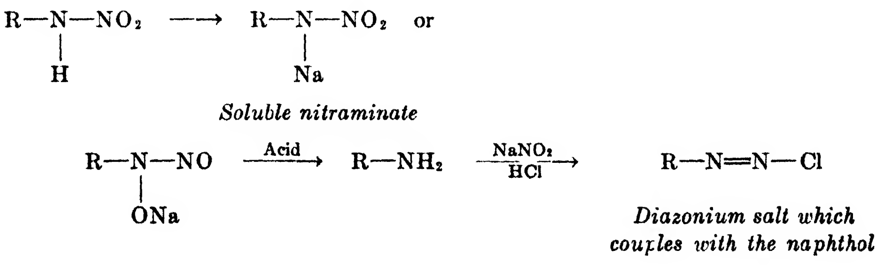
(3) Process of Kuhlmann-Francolor and I.G.: mixtures of condensates of aldehydes containing solubilizing groups with bases ("Schiff bases") plus naphthols.

(4) Process according to Tursky: amines able to couple by intramolecular reaction with themselves.

The methods of Bader (1) and Ciba (2) have been further developed by the Swiss dyestuff manufacturers (Ciba, Sandoz, Geigy) and introduced into practice under the names Cibagen dyestuffs of Ciba, Momentogens of Sandoz and Tinogens of Geigy. In October, 1938, Cibagen Bordeaux 3. GOD (Momentogen Bordeaux B, Tinogen Bordeaux 3G) appeared. It is based on a nitraminate. Apparently other analogous products followed, for instance Momentogen Blues B and R and Momentogen Violets R and 2B. It should be noted, however, that many of the Cibagens are not of the nitraminate type, but correspond rather to the Rapid Fast colors.

Mixtures of Naphthols with Nitraminates of Bases or with Their Isomers—the Arylnitrosohydroxylamines.*

The basic idea of this method has been described in M. Bader's patents* on the use of nitramines, and their alkali salts, the nitraminates, which are soluble in water. On acidification the amine is regenerated. The azo dyestuff is formed according to the following schematic equation:



$$R—\underset{H}{N}—NO_2 \longrightarrow R—\underset{Na}{N}—NO_2 \quad \text{or}$$

$$R—\underset{ONa}{N}—NO \xrightarrow{\text{Acid}} R—NH_2 \xrightarrow[\text{HCl}]{\text{NaNO}_2} R—N{=}N—Cl$$

The printing paste contains the nitraminate of the base together with sodium nitrite and the sodium naphtholate. On treatment with a dilute

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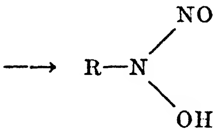
* References: *F.P. 761,811, 1st add. 43,788, 2nd add. 45,054, 3rd add. 45,630; S. P. 172,341; G.P. 642,716* (M. Bader); *B.P. 430,167, 430,222, 430,236, 437,824* (M. Bader); *F. P. 801,994; G.P. 651,044* and *-45* (I.G.).

solution of hydrochloric acid the amine is regenerated and diazotized by the nitrous acid formed, and the coupling reaction is carried out in sodium acetate solution.

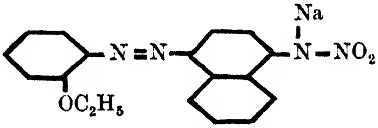
In place of the nitraminates, their isomers, the arylnitrosohydroxylamines can be used



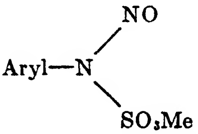
$$\longrightarrow R\text{—}N\begin{matrix}\diagup NO\\ \diagdown OH\end{matrix}$$

The alkali salts of these compounds are soluble. They are likewise transformed by nitrous acid treatments into diazo derivatives, capable of coupling with naphthols.

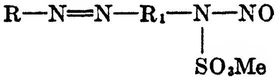
In *F.P. 788,349* and *B.P. 441,178*, Ciba applies this method to nitraminates of the preformed insoluble azo dyestuffs themselves, for example:



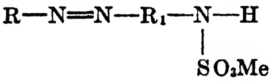
U.S.P. 1,857,230, F.P. 611,500, G.P. 433,276 and *449,018* (I.G.-Zitscher-Muris) suggest, instead, the use of soluble sulfonitrosamine salts or sulfamine salts of insoluble azodyestuffs, for instance:



$$\text{Aryl}\text{—}N\begin{matrix}\diagup NO\\ \diagdown SO_3Me\end{matrix}$$



$$R\text{—}N{=}N\text{—}R_1\text{—}\underset{\displaystyle SO_3Me}{\underset{|}{N}}\text{—}NO$$



$$R\text{—}N{=}N\text{—}R_1\text{—}\underset{\displaystyle SO_3Me}{\underset{|}{N}}\text{—}H$$

where Me represents alkali metal. They are developed as above.

When printing the sulfamines, sodium nitrite must be added to the print paste. However, in applying the sulfonitrosamines, the nitrite can be omitted as nitrous acid for the diazotizing is generated by the hydrolysis of the nitroso product.

The following patents of Ciba relate to the application of nitraminates: *B.P. 449,267; G.P. 638,878; F.P. 783,655* and *Aus.P. 147,774.*

This method is carried out in the following way. The nitraminate, naphtholate, nitrite and sodium acetate are combined in a printing paste. While the Rapidogens are developed in one operation of acid ageing, the development of the azo dyestuffs proceeds in this case in two separate steps. The printed goods are treated with a cold dilute solution of hydrochloric acid and sodium chloride. The coupling process does not take place however until the acid is neutralized in a bath of sodium carbonate or acetate. The presence of formaldehyde is favorable for the dyestuff development.

According to *G.P 644,070* and *S.P. 179,416* (Ciba) formaldehyde is recommended as a preservative for the naphthol, but in the present case the print paste of naphtholate and nitrosaminate is less stable with free formaldehyde. Therefore the naphthol is first condensed with formaldehyde before adding the nitrosaminate. Condensates of this type, *i.e.*, of formaldehyde and arylides of 2,3-oxynaphthoic acid are prepared according to *Ber.*, **61,** # 1, 998. The arylide of 2,3-oxynaphthoic acid is mixed with formaldehyde at room temperature, whereby an addition product is formed.

B.P. 468,189 (Ciba) notes that the shade of the azo dyestuff is dulled by vapors of nitrous acid, and it is suggested that formaldehyde be added to the acid bath to eliminate this drawback. The acid and formaldehyde mixture is applied by means of a pad roller, and the acid subsequently neutralized with soda ash. It is advised to sky the goods before neutralizing to allow time for diazotization.

Modifications and improvements of this method are found in *U.S.P. 2,112,864*, *F.P. 823,195*, *G.P. 663,496*, *661,225* (Ciba), and relate specifically to application of the Cibagens and analogous dyestuffs. Since the acid must be destroyed in order to bring about the coupling process, *G.P. 663,496* suggests rinsing the pieces, or hanging them in an atmosphere containing ammonia, instead of a sodium acetate treatment. The printing paste is prepared as follows:

70 gm Cibagen Bordeaux 3 GOD
240 gm water
50 gm sodium hydroxide 30° Bé
10 gm formaldehyde
40 gm ethylene glycol or Cibagen Solvent
590 gm starch-trag. thickening

1000 gm

Blue and Red Cibagen colors are dissolved with a mixture of ethyl alcohol and ethylene glycol. The printed fabrics are dried at 70°C, padded on the mangle with a thickened formic acid, or a composition of

500 cc trag. paste 6%
250 cc hydrochloric acid 21° Bé
10 cc formaldehyde
240 cc water

1000 cc

The goods are skyed two minutes, rinsed ½ minute in a soda ash solution at 50°C and well rinsed. Any contact with metal parts must be avoided in the acid treatment and skying operation.

Good results are obtained with Cibagen colors printed alongside vat colors and Indigosols, but they are evidently not suited as resists under aniline black (*U.S.P. 2,112,864*, Ciba; *Teintex*, Aug., **1938**).

F.P. 840,697 (Sandoz) discloses the application of diazotizable aminoarylsulfamides containing no solubilizing groups (except amino). The general formula is:

$$NH_2—R—SO_2—NH—R_1$$

Mixtures of Dispersed Bases with Naphthols (Ciba Patents)*

Because of the difficulties encountered with the nitramine method, Ciba reverted to the bases themselves. Water-insoluble amines, having a melting point over 60°C and therefore non-volatile, are well dispersed and mixed with naphtholates, caustic soda and sodium nitrite. The printed fabrics are aged, and developed in a bath of salt and hydrochloric acid at 25°C. In other respects the application follows the pattern of *G.P. 638,878*, *B.P. 449,267* and *Aus.P. 147,774* above.

Replacement of the sodium acetate treatment by a rinsing and skying operation is recommended in *G.P. 661,225*. Finally, *F.P. 823,195* might be mentioned as disclosing a method for obtaining uniform prints on mixed fabrics such as spun rayon and wool ("Wollstra"). The printed fabrics are padded with a thickened mixture of acid and formaldehyde, then neutralized with a solution of sodium acetate or soda ash.

Addition of thiodiethylene glycol has the effect of increasing the color yield of printing pastes consisting of primary amine, naphtholate, nitrite and alkali (*F.P. 849,849*—Ciba, 1939, and *S.P. 203,928*.) For example, a Cibagen printing color can be prepared as follows:

24.9 parts 1-amino-2-methoxy-5-methyl-4-benzoylaminobenzene (corresponding to Fast Violet B Base)
24.8 parts Naphthol AS
18.9 parts sodium nitrite
0.2 parts caustic soda
1.2 parts sodium acetate

Fifty parts of this mixture are dispersed in 180 parts of thiodiethylene glycol and 40 parts of caustic soda 30%; this dispersion is mixed with 600 parts of starch-tragacanth thickening and 70 parts of water.

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* Ciba patents: *U.S.P. 2,112,864; B.P. 449,267, 450,618, 452,177, 468,189, 487,724; F.P. 783,655* and *addition 46,657, 822,227, 823,195; G.P. 638,878, 644,070, 661,225, 663,496, 683,901.*

Condensates of Bases with Aldehydes (Schiff Bases)

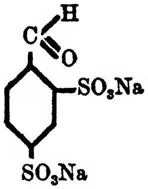
The I.G. and Kuhlmann-Francolor developed this process separately at about the same time. Aldehydimines are employed as agents for forming diazotizable amines (*G.P. 641,874*, *F.P. 803,579*—I.G.). These have the schematic formula

$$R_1{-}N{=}CH{-}R_2{-}X$$

R_1 = aliphatic, aromatic or heterocyclic group
R_2 = aromatic group
X = solubilizing group

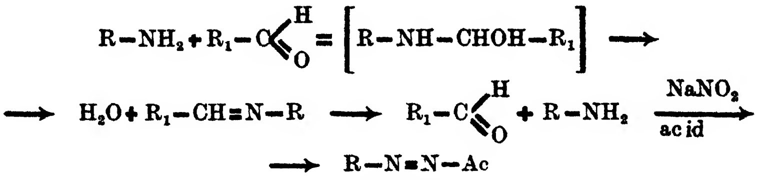
An aldehydimine is incorporated in a printing paste with the coupling component (naphthol) and sodium nitrite. The prints are developed by padding with formic acid, and drying on cans.

The process described in *U.S.P. 2,095,639*, *B.P. 459,766*, *F.P. 803,964* and addition to this patent *47,766* (Kuhlmann-Kienzle) is identical with the above, and consists of applying compounds of the Schiff-base type. These Schiff bases are formed by condensing a primary aromatic amine with an aromatic sulfonated aldehyde, such as sodium disulfonate of benzaldehyde:



An aldehyde base of this type is mixed with sodium nitrite and the sodium naphtholate, and the prints developed in acid steam, in a manner similar to the Rapidogens.

The reaction is represented by the following equation:



$$R{-}NH_2 + R_1{-}C{\scriptstyle\begin{matrix}H\\O\end{matrix}} = \left[R{-}NH{-}CHOH{-}R_1\right] \longrightarrow$$
$$\longrightarrow H_2O + R_1{-}CH{=}N{-}R \longrightarrow R_1{-}C{\scriptstyle\begin{matrix}H\\O\end{matrix}} + R{-}NH_2 \xrightarrow[\text{acid}]{NaNO_2}$$
$$\longrightarrow R{-}N{=}N{-}Ac$$

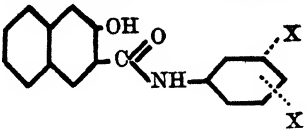
The diazo compound combines with the naphthol. Diazotization and coupling take place at the same time.

The Tursky Process, Using Diazotizable Amines Capable of Intramolecular Coupling with Themselves

Swiss P. 154,172, 156,654, 156,655, 158,239; G.P. 552,926; F.P. 689,707; B.P. 347,609 (Tursky) and *B.P. 387,360* (Ciba).

These patents describe the preparation of compounds combined from

Naphthol AS and diazotizable bases, for instance:

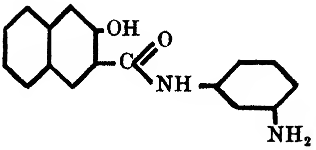


(X = NH_2, etc.)

The insoluble azo dyestuff is formed as follows: The printing paste contains, besides this complex compound, sodium nitrite plus alkali; the diazo compound is generated in an acid bath and the coupling process is carried out in an alkaline solution (see also *F.P. 738,657*—Ciba, 1932; *Chem. Zent.*, **1933**, 2320). The method is therefore characterized by thg application of amines capable of diazotization and intramolecular coupling reaction of two identical molecules with themselves. The bases correspond to the following general formulas:

$$NH_2-\text{Aryl}-NH-CO-R-OH$$
$$HO-\text{Aryl}-NH-CO-R-NH_2$$
$$NH_2-\text{Aryl}-NH-CO-R-NH_2$$

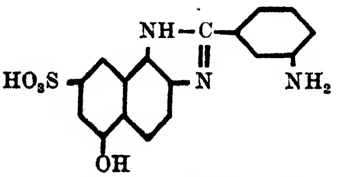
For instance:



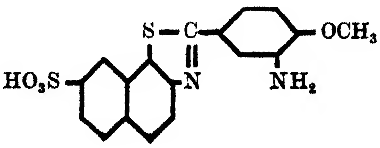
Another series of patents describes a similar method: sulfonated amines capable of diazotization and intramolecular self-coupling reaction are used. These amines are derived from 1-oxy-3-sulfonaphthalene. References are *F.P. 838,947* and first-addition *50,139; F.P. 841,521*, *843,266*, *871,658* (I.G.).

For dyeing these compounds, vegetables fibers are impregnated in an alkaline solution, diazotized and coupled in alkaline medium. For printing, the compounds are applied in the presence of nitrite, the printed goods are aged in acid steam (acetic acid) and passed thereupon through a soda-ash solution. Despite the solubility of the initial material (sulfonated products), the dyes are very fast to washing,

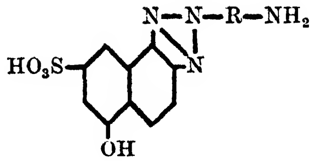
Some examples for sulfonated amines are given:



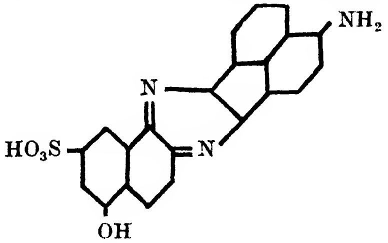
Hydroxynaphthol imidazole sulfonate



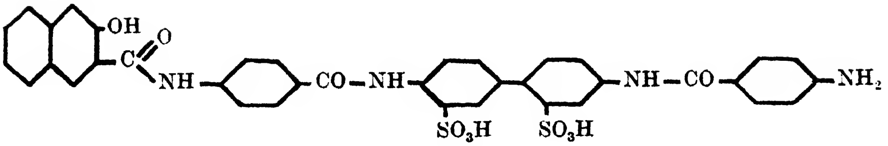
Hydroxynaphtholthiazole sulfonate



Hydroxynaphthol pseudoazimide sulfonate



Condensates of o-diaminohydroxynaphthalene sulfonic acids with aromatic o-diketones



Sulfoderivatives

Tursky was first to disclose the principle of forming the free amine within the printing paste, of diazotizing in an acid medium and thereupon coupling it immediately in an alkaline bath. Another analogous example for this method might be found in the practice of dyeing Variamine Blue B: a diazo solution is employed to which acetic acid is added and the coupling reaction is carried out in subsequent soda-ash bath. The acid carried along with the cloth is neutralized by the alkaline solution, whereby the necessary conditions for coupling are brought about.

Principle C

Use of azo dyestuffs which have been rendered water-soluble by the introduction of certain groups in the dyestuff complex, and the regeneration of the original insoluble azo dyestuff on the fiber by appropriate aftertreatment.

Neocotone Colors

A single process based on Principle C has been published. It is described in *F.P. 815,575*, *817,814*, *820,352* and *U.S.P. 2,095,600* (Ciba)*. The products corresponding to these patent specifications are sold under the names Neocotones by Ciba, Neogenoles by Sandoz and Tinogenales by Geigy.

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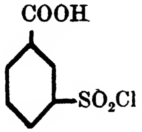
* Compare also *F.P. 830,313*, *832,779*, *833,101*, *840,459*, *850,422*, *852,400*, *852,410*, *856,423*, *856,693*, *858,333*, *862,040*, *867,110*, *B.P. 480,358*.

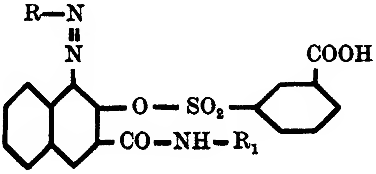
It is inferred from the above patents that the Neocotones consist of insoluble azo dyestuffs, for example, the dyestuff obtained by coupling diazotized chloraniline with the anilide of 2,3-oxynaphthoic acid, transformed into soluble compounds by reacting them with acylating agents. The acylating agents should contain, beside the acyl group, other substituents which impart solubility to the complex, such as COOH and HSO_3 groups. At least one of these groups must be present in the form of a halogenide. An example is the sulfochloride of benzoic acid:



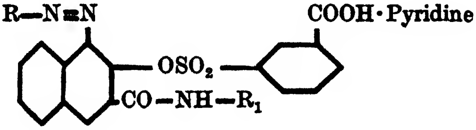
In *U.S.P. 2,170,262* (1939) other acylating agents are mentioned, for example, the chloride of 1,3,6-naphthalene trisulfonic acid.

The reaction of the acylating agent with the azo dyestuff may be interpreted in two ways.

In the first place, it can be assumed that the sulfochloride of benzoic acid reacting on an azo dyestuff which bears one free OH group, forms a water-soluble acyl compound, corresponding to the schematic formula:



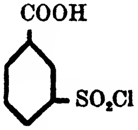
That is, carboxy compounds of sulfonic acid esters would be produced. The reaction, proceeding in pyridine solution, would form the pyridine salt



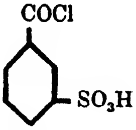
Although this conception is logically acceptable from a chemical standpoint, there are several reasons for doubting it.

Actually, the solubilizing action of a carboxyl group even in salt form, is very weak. It must be remembered that benzoic acid itself is only sparingly soluble in water, and when the molecular weight of the Neocotone complex is considered (between 400 and 600), the effect of the COOH group alone cannot logically be deemed sufficient to solubilize it. Further, the pyridine salts of high-molecular carboxylic acids of this type cannot be stable, but should dissociate readily in solution. Finally the sulfonic acid esters must be less easily hydrolyzed in alkaline media than the carboxylic acid esters.

These considerations induce another explanation of the real constitution of these complex compounds. Assume first that benzoic acid sulfochloride does not act in the pyridine solution as such, *i.e.*, as:

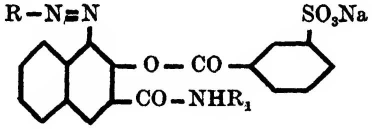


but as benzoyl chloride sulfonic acid:



This isomeric form of the chloride of benzene sulfonic acid might be set up within the molecule by the strongly chlorinating action of the SO_2Cl reacting on the COOH group and producing thereby the isomer, *i.e.*, the sulfobenzoic acid chloride which can be considered as the acylating agent proper. Pyridine probably acts here as a catalyst and as a binding agent for hydrochloric acid generated in the reaction.

It thus follows that in coupling with the free OH group of the azo dyestuff, that carboxylic acid esters are formed and the Neocotones can be considered as mono- or disulfonates of these esters



The solubility of the Neocotone molecule is accomplished by the presence of one or two HSO_3 groups, which have strong solubilizing properties. This conception also explains the ready hydrolyis of the Neocotones in alkaline solution, since carboxylic acid esters are easily hydrolyzed. Finally, the application of barium salts becomes understandable. If sulfonates are assumed, the marking-off in the developing phase is avoided because of the insolubility of barium salts of the sulfonates. There is no risk in removing any part of the Neocotone in the developing bath, as hydrolysis takes place only on the fiber.

The printing paste is prepared in the following way:

50 gm Neocotone Blue B, *pasted with*
150 gm Neocotone Solvent II, *and dissolved in*

200 gm hot water
Pour solution into:
600 gm starch-trag. thickening
——
1000 gm

The printed goods are dried at low temperatures, aged, then developed for five minutes at 20°C in a bath of

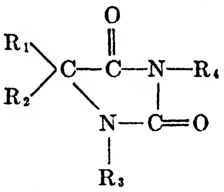
10–20 cc barium chloride
30–50 cc caustic soda 38° Bé
50 gm salt
——
per liter

rinsed, soured with 5 cc of HCl per liter at 80 C, and washed well.

Other alkalis recommended for the development are 10% NaOH plus NH_4OH or 6% NaOH and $K_3Fe(CN)_6$.

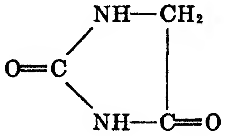
Better solution of the Neocotone color is obtained by adding urea to the print paste. *S.P. 204,218, B.P. 512,664, F.P. 850,422* and *867,110* (Ciba, 1939) recommend other auxiliaries such as unsymmetrically substituted urea derivatives, as diethyl urea, also alkali phosphates, ethers of thiodiethylene glycol, monoethyl urea, 3-ethylthioglycollic acid, etc.

To improve yields of these colors, Ciba suggests in *F.P. 856,693* (1940) the addition of hydantoin derivatives of the general formula



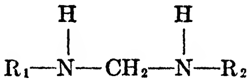
R_1 and R_2 = H or alkyl
R_3 and R_4 = H, low-molecular acyl, or alkyl

Hydantoin is the ureide of glycollic acid:



The hydantoin, or a derivative thereof, is added to the print paste, or can be mixed with the dyestuff. These products are used with hydrotropic substances such as urea, thiourea, alkylthioglycollic acid amides, thiodiethylene glycol, etc.

Other auxiliaries which improve the yield of Neocotone prints are methylene derivatives of the general formula:



$$R_1-\overset{\overset{H}{|}}{N}-CH_2-\overset{\overset{H}{|}}{N}-R_2$$

R_1 = formyl radical
R_2 = aryl group of 1 to 4 C atoms

such as methylene formamide and methylene formacetamide. These methylene derivatives have the effect of swelling the fibers (*F.P. 858,333*—Ciba). The dyestuffs penetrate deeper and the prints are fuller and brighter.

The following dyestuffs of this series are available at present:

Neocotone Yellow G
Neocotone Orange GR
Neocotone Scarlet G, and #27
Neocotone Red R and #29
Neocotone Bordeaux RB
Neocotone Blue B

When printing the Neocotones alongside vat colors it is necessary to add 3% Albatex BD or Ludigol (*m*-nitrobenzene sodium sulfonate) to counteract the reducing action of sodium formaldehyde sulfoxylate in the vat pastes. After ageing, the prints are developed by padding in the open width in a solution containing

50 cc NaOH 36° Bé
20 gm barium chloride
200 gm sodium chloride

per liter, laid up for 10 to 15 minutes, rinsed in cold water and acidulated. Where vat colors have been printed alongside the Neocotones, a weaker alkalinity is advised, because of danger of mark-off.

In the developing phase, the water-soluble acyl derivatives are hydrolyzed and partly removed from the fiber. The addition of strongly dissociated salts such as sodium chloride, calcium chloride, etc., retards any ionization of the Neocotone dyestuff. Since the Neocotones are completely coupled azo dyestuff derivatives, they may be mixed with pigment dyestuffs, or used as such in any manner desired. The print pastes prepared with them have unlimited stability.

In practical use, the Neocotones have proven to have a definite advantage over the Rapidogens, in that the acid-ageing development, which always causes rapid deterioration of equipment, is not necessary. However, the strongly alkaline development is felt to be a drawback when handling filament or spun rayon fabrics. They lend themselves well for printing alongside vat colors, since only one ageing is required for both classes of colors, and resists under aniline black can be obtained with greater reliability than with the Rapidogens (Ch. Graenacher and F. Reichert, "Neocotones, a New Class of Dyestuff Derivatives," *Mell.*, **1939,** #4).

A modification of the formula has been proposed by the addition of sodium phosphate to the print paste, and by development in a solution of barium hydroxide and salt.

The Neocotones can be printed in combination with the Indigosols, according to *F.P. 862,040*—Ciba. Indigosol O4B is prepared for printing according to the chlorate-sulfocyanide method and mixed with a regular print paste of Neocotone Red R. The goods are printed, dried and aged 7 minutes in the rapid ager, then treated in a developing bath of caustic soda, barium chloride and salt, and also some Ludigol. Finally the goods are rinsed, acidulated and soaped. A full reddish violet of good fastness is obtained.

The Indigosols can be printed only by the steam method with Neocotones, not by the nitrite method. When combined with Rapidogens, developed with Rapidogen Developer N, however, the Indigosols may be printed by the nitrite method.

As long as a simpler and more convenient method for developing the Neocotones has not been brought out, the Rapidogen processes will be preferred to the strongly alkaline development bath.

F.P. 818,918 and *B.P. 492,166* (Ciba) describe a method for using these new complex compounds for colored discharges in combining them with potassium ferricyanide according to the old indigo discharging method of Mercer. A paste containing the Neocotone dyestuff and potassium ferricyanide is printed on dyed Indigo or Ciba Blue 2B, then treated with caustic soda of 13° Bé at 50°C.

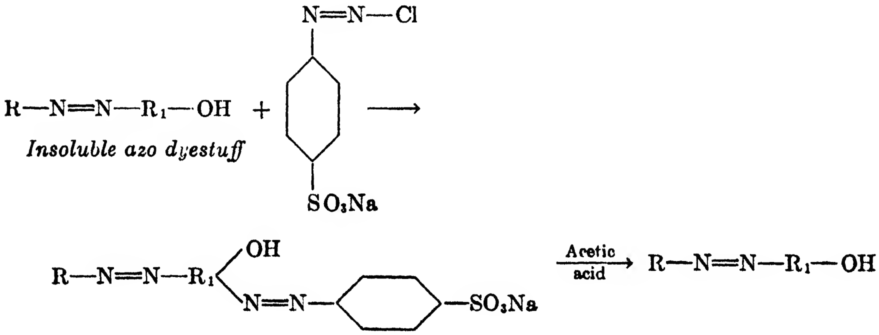
An interesting application of Neocotones as resist prints under aniline black is described in *F.P. 842,560*—Ciba. The fabrics are impregnated as usual with aniline black prepare and dried in the hot flue. The Neocotones are printed together with zinc oxide and trisodium phosphate which are not alkaline enough to hydrolyze the dyestuff. In the subsequent ageing the black is developed, and in the following treatment with NaOH, NaCl and $BaCl_2$ the dyestuff is regenerated. A final acidification and soaping completes the process.

White discharges on pad dyeings of Neocotones are obtained by using sodium formaldehyde sulfoxylate, potassium carbonate and anthraquinone (*F.P. 842,809*—Ciba). Colored discharges are prepared with vat colors.

Resists are also possible (*F.P. 843,174*—Ciba). The fabrics are first printed with 10% Hydrosulfite NF for white resist, and regular vat colors for color resist. The fabrics are then padded with a solution of the Neocotone dyestuff containing some thiodiethylene glycol and trisodium phosphate, aged for 7 minutes and developed as usual in the NaOH, $BaCl_2$, NaCl bath.

In *U.S.P. 2,115,149* of the I.C.I., a combination of the manufacturing processes of the Rapidogens with those of the Neocotones is proposed. The method is similar to the Rapidogens in that sulfanthranilic acid is used as an amine for stabilizing the diazo compound. On the other hand the basic idea of Ciba for preparing Neocotones is employed by the esterification of the OH^- group of the naphthol with benzoic acid sulfochloride.

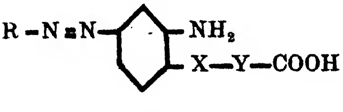
The process of the I.C.I. consists of first combining the diazo compound of an amine with a coupling component to form an insoluble dyestuff, and then dissolving the precipitate in pyridine. Thereupon the diazo compound of aniline-*p*-sulfonic acid is added. A soluble compound of the azo dyestuff results, which can be obtained in solid form by evaporating the pyridine. This complex product is printed and the azo dyestuff is split off on the fiber by ageing in acid steam. The solubilizing group, aniline-*p*-sulfonic acid or sulfanthranilic acid, separates, and the dyestuff is fixed on the fiber. A schematic explanation of this reaction follows:



It should be possible to apply this reaction to polyazo dyestuffs of every type provided that the second azo group splits in the manner described in the patent specifications. However, that does not seem to be the case in practice. It will be interesting to learn more about the chemistry of this reaction.

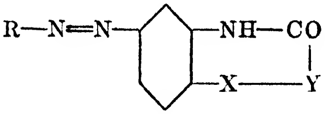
Insoluble Azo Dyes Obtained by Condensation (Lactame Formation)

A process not contained in any of the above principles is described in *B.P. 415,753* and *416,779*, also *F.P. 764,700, 768,526* and *addition 44,515.* The principal idea of the method, which has been developed by I.C.I., consists of preparing insoluble azo dyestuffs of the schematic formula:



where X and Y represent $S^=$, $O^=$, $NH^=$, $CH_2^=$, etc.

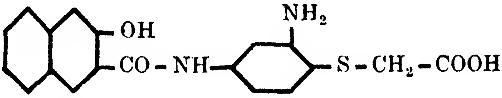
The group X-Y-COOH is capable of forming a 6-member lactame ring, by condensation with the neighboring amino group. This lactamization takes place either on the fiber or in the mass by treatment with dilute mineral acids, as



The process is principally intended for the production of insoluble azo dyestuffs on animal fibers.

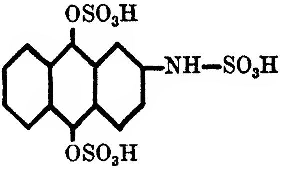
The procedure consists of dyeing 30 minutes in an aqueous solution at 90°C, and for a further 30 minutes while adding 2% acetic acid in portions. The lactame is formed by boiling with tenth-normal hydrochloric acid.

This process can be used in the application of naphthol dyestuffs, obtained by coupling a Diazo Fast Salt with an arylide of 2,3-oxynaphthoic acid capable of forming lactames. Example:



Other methods in this category are as follows:

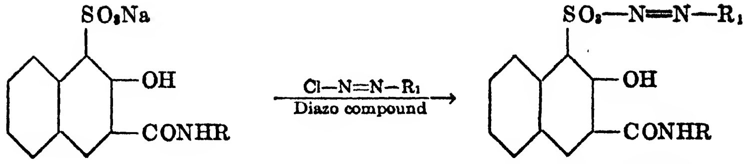
(1) *F.P. 716,951* (I.G.). As initial material, the sulfamic acid of 9,10-disulfonic acid ester of 2-amino anthraquinone:



is used. This derivative is diazotized at low temperatures with nitrite and hydrochloric acid and coupled with naphthol dissolved in caustic soda and with excess soda ash. The water-soluble azo dyestuff so produced is salted out and dyed on vegetable or animal fibers. The dyestuff is developed on the fiber by an acid oxidation whereby the sulfo group is split off, leaving the insoluble anthraquinone azo dyestuff.

(2) The process proposed in *B.P. 385,307*—1931, and *F.P. 738,795* (I.C.I.) is principally intended for the formation of insoluble azo dyestuffs on wool. It is based on the application of special aryl diazosulfonates having a certain affinity to animal fibers in acid solution.

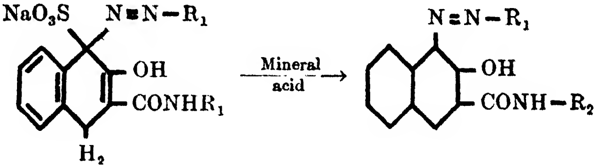
These diazosulfonates are obtained by sulfonating arylides of 2,3-oxynaphthoic acid. The HSO_3 group links to position 1, thus preventing a coupling reaction. The reaction in neutral medium corresponds to the equation:



1-Aryldiazo sulfonate of 2,3-oxynaphthoic acid arylide

R and R_1 = aryl groups

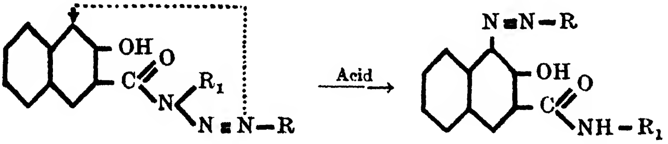
By treating this compound with alkalis, a rearrangement occurs and the sodium salt of the arylamide of 1-arylazosulfo-2-naphthoquinone-3-carboxylic acid is formed. Finally the sulfo group is split off by the action of sulfuric acid and the corresponding azo dyestuff results.



Naphthoquinone derivative addition product

A similar process has been described in *F.P. 720,109* (Ciba, 1931). Wool is treated with the naphthoquinone derivative at 90°C in an acetic acid bath. The insoluble azo dyestuff is split off by treating the dyed goods for several minutes with dilute sulfuric acid.

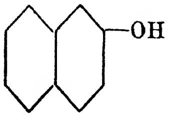
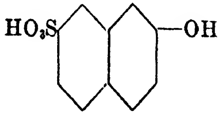
(3) In *F.P. 739,705* (Ciba, 1932) the interesting idea is broached of preparing a complex compound by the reaction of 2,3-oxynaphthoic acid chloride and a diazoamino derivative, which is dyed on the material. The insoluble azo dyestuff is thereupon formed by the action of an acid, according to the following equation:



(R, R_1 = aryl radicals)

This process has had a limited success because of the difficulties met in preparing the complex compounds and because of their poor solubilities.

Table 5. The Coupling Components

Name	Manufacturer	Constitution	Application
β-Naphthol	Kuhlmann-Francolor, I.G., Calco, I.C.I., St. Denis, etc.		For the production of *p*-nitraniline red in printing and dyeing. For developing substantive dyes on the fiber.
Sel pour Nuançage N Nuanciersalz (old name)	Kuhlmann-Francolor Cassella	2-Naphthol-7-sulfonic acid (F-salt or F-acid). 	As addition to *β*-naphtholate solutions to obtain a more bluish shade of *p*-nitraniline red.
Naphthol NB	Kuhlmann-Francolor	Mixture of *β*-naphthol with 10% Nuanciersalz.	For production of a brighter and bluer Para red.
Naphthol R	M.L.B.		
Naphthol AR	Bayer		
β-Naphthol RC	Cassella		
Färbesalz I	Badische A.S.F.		
Developer NF (old name)	Kuhlmann		
Naphthol D	M.L.B.	Mixture of: 2,3-oxynaphthoic acid, *β*-naphthol, and 2-naphthol-7-sulfonic acid.	For obtaining a faster dianisidine blue.

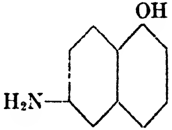
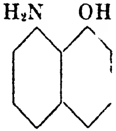
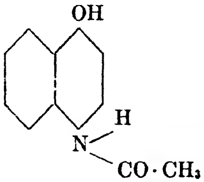
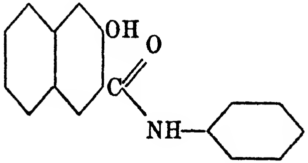
Naphthol LC		Mixture of: β-naphthol, antimony oxide, and glycerin (method of Lauber-Caberti)	Used to prevent discoloration of the prepared material. Improves stability of naphtholate solutions.
Aminonaphthol BD		6-Amino-α-naphthol (Dosne). 	For "Puce" brown with *p*-nitrodiazobenzol.
Aminonaphthol 3B		8-Amino-α-naphthol. 	Same as above.
Naphthocetol		Acetyl derivatives of 4-amino-α-naphthol. Benzoyl derivative: 	Used in the method of O. Witt. The material is impregnated with Naphthocetol instead of β-naphthol, and coupled with the diazo solution.

Table 5. The Coupling Components (*Continued*)

Name	Manufacturer	Constitution	Application
Naphthol AS	G.D.C., I.G., National	Anilide of 2,3-oxynaphthoic acid.  (M.p. 243°C) *G.P. 256,999; 261,594; 264,527; 279,314; 293,897; 268,542; 287,242*	Yellowish powder, soluble in alkalis. It has poor affinity to vegetable fibers. Used to produce orange, red, scarlet and blue shades with various bases. Yields dark blue with Variamine Blue B Base, a bluish violet with Fast Violet Salt B, and rich navy blues with Fast Blue Salts BB and RR. The red produced with Fast Red 3GL Base is one of the fastest dyes in the naphthol range.
Naphthanil AS	Du Pont		
Naphthosol ASF	Calco		
Brenthol AS	I.C.I.		
Naphthazol NA	Kuhlmann-Francolor		
Naphthazol A	St. Denis		
Naphthanilid RC	Rohner		
Anthonaphthol AS	S.P.C.M.C.		
Cibanaphthol RF	Ciba		
Celcot RF	Sandoz		
Irganaphthol RF	Geigy		

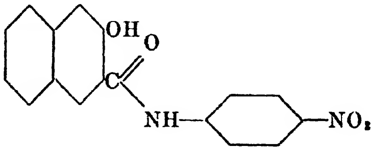
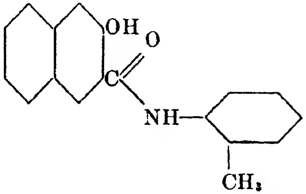
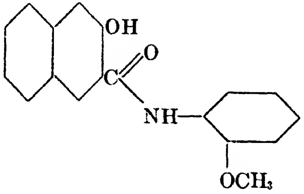
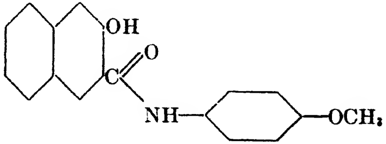
Naphthol AS-AN	G.D.C., I.G.	*p*-Nitranilide of 2,3-oxynaphthoic acid. 	
Naphthol AS-D	G.D.C., I.G., National	*o*-Toluidide of 2,3-oxynaphthoic acid. 	For production of red, scarlet, orange, blue, violet and navy shades similar to Naphthol AS combinations. The Naphthol AS-D dyeings are more easily discharged than the Naphthol AS grounds. This Naphthol has a slightly lower affinity than Naphthol AS and can be stripped by a soap and soda treatment.
Naphthanil AS-D	Du Pont	Scholl, *Mell.*, **1935**, 444, 515	
Naphthosol D	Calco		
Naphthazol ND	Kuhlmann-Francolor		
Brenthol OT	I.C.I.		
Cibanaphthol RTO	Ciba		
Celcot RTO	Sandoz		
Anthonaphthol AS-D	S.P.C.M.C.		
Naphthazol D	St. Denis		
Irganaphthol RTO	Geigy		
Naphthanilid D	Rohner		

Table 5. The Coupling Components (*Continued*)

Name	Manufacturer	Constitution	Application
Naphthol AS-OL **Brenthol FR** **Naphthazol F** **Celcot RK** **Anthonaphthol MF** **Naphthazol NF** **Cibanaphthol RK** **Irganaphthol RK**	G.D.C., I.G., National I.C.I. St. Denis Sandoz S.P.C.M.C. Kuhlmann-Francolor Ciba Geigy	*o*-Anisidide of 2,3-oxynaphthoic acid. 	Fairly indifferent to the carbon dioxide of the air. Fast to light yellow-orange with **Fast Orange GC Base.** Full greenish navy with **Variamine Blue B Base. Fast** bright scarlet **with** Fast Scarlet GGS Base and **orange** with Fast **Orange** Salt RD. Very fast red shade with Fast Red 3GL Base.
Naphthol AS-RL **Naphthanil RL** **Naphthosol RL** **Brenthol PA** **Naphthanilid RL** **Cibanaphthol RBL** **Celcot RBL** **Naphthazol RL** **Irganaphthol RBL**	G.D.C., I.G., National Du Pont Calco I.C.I. Rohner Ciba Sandoz St. Denis Geigy	*p*-Anisidide of 2,3-oxynaphthoic acid.  (M.p. 230°C)	Gives very high light-fastness, **particularly** with Fast Red RL, B and GL Bases **and** Fast Orange **RD** Base. **Deep greenish navy** with **Variamine** Blue B Base, **and** dark red with **Fast** Corinth LB **Base.**

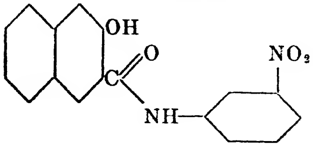
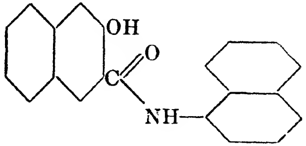
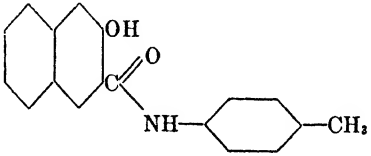
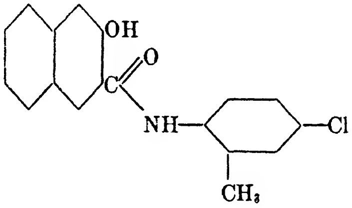
Naphthol AS-BS Naphthanil BS Naphthosol BS Naphthazol NB Irganaphthol RM Brenthol MN Celcot RM Cibanaphthol RM Naphthazol B Anthonaphthol BS Naphthanilid BS	D.C., I.G., National Du Pont Calco Kuhlmann-Francolor Geigy I.C.I. Sandoz Ciba St. Denis S.P.C.M.C. Rohner	*m*-Nitranilide of 2,3-oxynaphthoic acid.  (M.p. 246°C)	Brighter and more bluish red shades than with Naphthol AS. Used for bright dyeings with Fast Scarlet R and G Bases. A greenish blue of excellent light-fastness is obtained with Variamine Blue Salt FG.
NaphtholAS-BO Naphthosol BO Naphthanil BO Naphthanilid BO Brenthol AN Naphthazol N3B Anthonaphthol M3B Celcot RN Irganaphthol RN Cibanaphthol RN Naphthazol 3B	G.D.C., I.G. Calco Du Pont Rohner I.C.I. Kuhlmann-Francolor S.P.C.M.C. Sandoz Geigy Ciba St. Denis	α-Naphthalide of 2,3-oxynaphthoic acid.  (M.p. 223°C)	Yields bluer shades than Naphthol AS. The red with Fast Red B Base is especially fast to light.

Table 5.—The Coupling Components (*Continued*)

Name	Manufacturer	Constitution	Application
Cibanaphthol RT **Celcot RT** **Irganaphthol RT**	Ciba Sandoz Geigy	*p*-Toluidide of 2,3-oxynaphthoic acid.  	Somewhat more substantive than Naphthol AS. Used for red shades with Scarlet Bases Ciba IV and V.
Naphthol AS-TR **Brenthol CT** **Celcot RCT** **Cibanaphthol RCT** **Irganaphthol RCT** **Naphthanilid TR** **Naphthazol TR** **Naphthazol NTR** **Anthonaphthol AS-TR**	G.D.C., I.G. I.C.I. Sandoz Ciba Geigy Rohner St. Denis Kuhlmann-Francolor S.P.C.M.C.	4-Chloro-*o*-toluidide of 2,3-oxynaphthoic acid.  (M.p. 243°C)	The shade with Fast Red TR Base is very similar to that of Alizarine Red N3B, and possesses outstanding fastness to kier-boiling and chlorine.

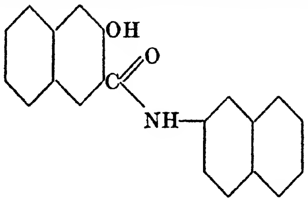
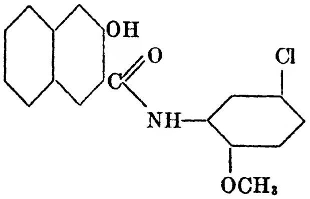
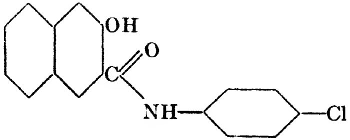
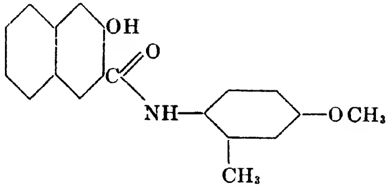
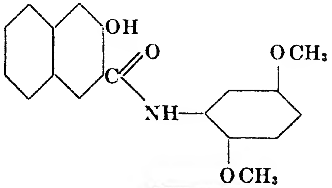
Naphthol AS-SW **Naphthanil SW** **Naphthosol SWF** **Naphthanilid SW** **Brenthol BN** **Celcot RA** **Irganaphthol RA** **Cibanaphthol RA** **Naphthazol SW** **Anthonaphthol SW** **Naphthazol NSW**	G.D.C., I.G., National Du Pont Calco Rohner I.C.I. Sandoz Geigy Ciba St. Denis S.P.C.M.C. Kuhlmann-Francolor	β-Naphthalide of 2,3-oxynaphthoic acid.  (M.p. 233°C)	Strongly substantive, particularly suitable for machine dyeing. Combines well with Fast Black LB Base and Fast Black Salt G. The black shades are very fast to chlorine. The scarlet shade obtained with Fast Red KB Base is fast to kier-boiling and to chlorine.
Naphthazol NEL **Anthonaphthol MEL** **Cibanaphthol RCA**	Kuhlmann-Francolor S.P.C.M.C. Ciba	*m*-Chloro-*o*-anisidide of 2,3-oxynaphthoic acid.  	Scarlet shades, very fast to light, are obtained with various bases.

Table 5. The Coupling Components (*Continued*)

Name	Manufacturer	Constitution	Application
Naphthol AS-E **Cibanaphthol RC** **Celcot RC** **Irganaphthol RC** **Brenthol BB**	G.D.C., I.G. Ciba Sandoz Geigy I.C.I.	*p*-Chloranilide of 2,3-oxynaphthoic acid.  OH O C NH Cl	Bluish violet of excellent light fastness with Variamine Blue Salt FG.
Naphthol AS-LT **Brenthol MA**	G.D.C., I.G. I.C.I.	*p*-Methoxy-*o*-toluidide of 2,3-oxynaphthoic acid.  OH O C NH OCH_3 CH_3	Brownish violet with Fast Corinth LB base, dull red of excellent light fastness with Fast Red 3GL Base, scarlet with Fast Red TR Base, fast-to-light orange with Fast Orange Salt LG.
Naphthol AS-DB	G.D.C., I.G.	2,5-Dimethoxyanilide of 2-oxydibenzofurane-3-carboxylic acid.	For dark brown shades.
Naphthol AS-BG **Brenthol FO** **Naphthanilid BM** **Cibanaphthol RDM**	G.D.C., I.G. I.C.I. Rohner Ciba	2,5-Dimethoxyanilide of 2,3-oxynaphthoic acid.  OH O C NH OCH_3 OCH_3	Fast brown shades, especially with Fast Scarlet GG or GGS Bases.

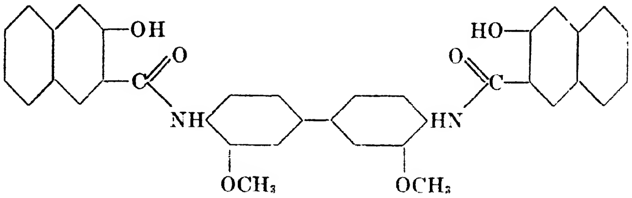
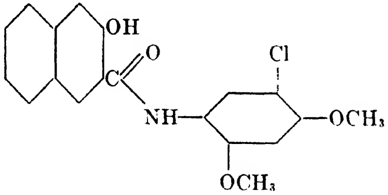
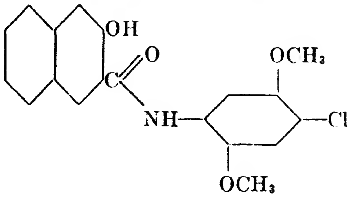
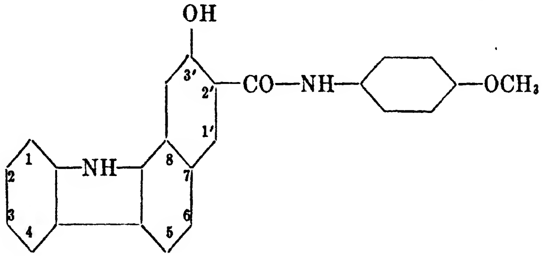
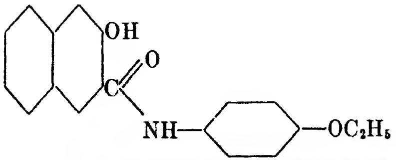
Naphthol AS-BR **Brenthol DA** **Naphthanilid M**	G.D.C., I.G. I.C.I. Rohner	Dioxydinaphthoyl dianisidide. 	Substantive and air-resistant. Cannot be discharged or removed from the fiber. With formaldehyde a compound is formed which does not undergo coupling reaction.
Naphthol AS-ITR **Naphthazol NSTR**	G.D.C., I.G. Kuhlmann-Francolor	4,6-Dimethoxy-3-chloranilide of 2,3-oxynaphthoic acid.  *F.P. 761,607; 761,623* (I.G.)	In combination with Fast Red ITR Base a bright bluish red is obtained, which has excellent light-fastness, and is the best substitute for the shade of Turkey red.
Naphthol AS-LC	I.G. (1936) G.D.C.	2,5-Dimethoxy-4-chloranilide of 2,3-oxynaphthoic acid. 	Very substantive. A red of outstanding fastness to light is produced with Fast Red FR Base.

Table 5. The Coupling Components (*Continued*)

Name	Manufacturer	Constitution	Application
Naphthol AS-SG **Brenthol GB**	I.G. (1930), G.D.C. I.C.I.	Pyrrhol derivative: *p*-anisidide of 3′-hydroxybenzocarbazole-2′-carboxylic acid.  *Mell.*, **1933**, 15 *Tiba*, **1931**, 743 *Rev. Gen. Mat. Col.*, **Nov. 1938**	Produces a black of excellent fastness with Fast Red B Base. Very high substantivity, exhausting to 80–90%.
Cibanaphthol RPH **Celcot RPH** **Irganaphthol RPH**	Ciba Sandoz Geigy	*p*-Phenetidide of 2,3-oxynaphthoic acid.  	

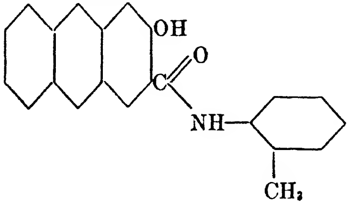
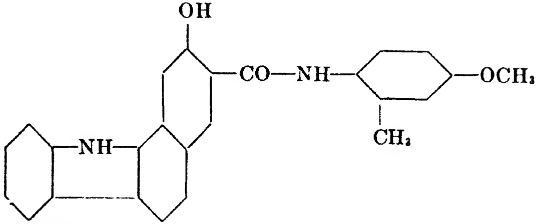
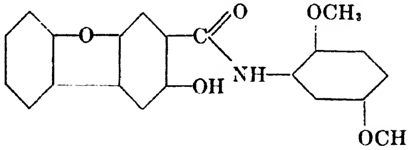
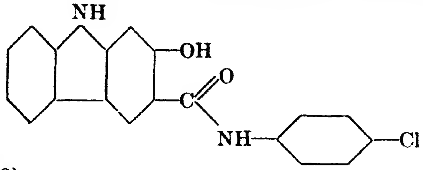
Naphthol AS-GR **Brenthol NG**	I.G. (1930), G.D.C. I.C.I.	Anthracene derivative: anilide or *o*-toluidide of 2,3-oxyanthracene carboxylic acid.  *Bull. Fed.*, **I**, 51 Kramer, *Tiba*, **1931**, 743 Christ, *Mell.*, **1932**, 25 *G.P. 549,983* (I.G. 1930) *F.P. 724,123* (1931) *Chem. Zent.*, **1932**, 622	Blue-green shades with Fast Blue RR and BB Bases and with Variamine Blue Salt B. The greens are rather dull and of a blue cast. Very substantive, the bath being 50–60% exhausted. Impregnation must be carried out at elevated temperatures. The *o*-toluidine derivative yields still bluer greens of poorer light fastness.

Table 5. The Coupling Components (*Continued*)

Name	Manufacturer	Constitution	Application
Naphthol AS-SR **Brenthol RB**	I.G. (1930), G.D.C. I.C.I.	Pyrrhol derivative: *p*-methoxy-*o*-methyl anilide of 3′-hydroxybenzocarbazole-2′-carboxylic acid.  *G.P. 539,116* (I.G., 1929)	Very fast black of reddish cast with Fast Red B Base. Substantivity similar to Naphthol AS-SG.
Naphthol AS-BT	I.G. (1935)	2′,5′-Dimethoxyanilide of 6-oxydiphenylene oxide-7-carboxylic acid. 	Very fast browns to light and washing, particularly with Fast Red TR Base and Fast Corinth LB Base.
Naphthol AS-LB **Brenthol BT**	G.D.C., I.G. (1930) I.C.I.	Carbazole derivative: *p*-chloroanilide of 2-oxycarbazole-3-carboxylic acid.  *G.P. 535,670* (I.G. 1929) *F.P. 734,845* (1932)	Fastest brown with Fast Red B Base. Very substantive. Dyeings are especially fast to crocking. Impregnation is carried out hot.

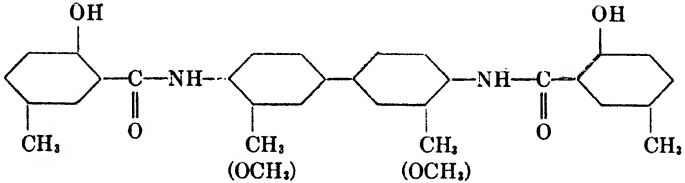
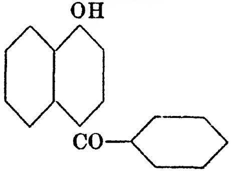
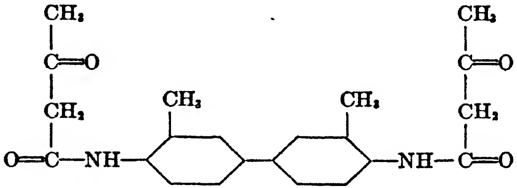
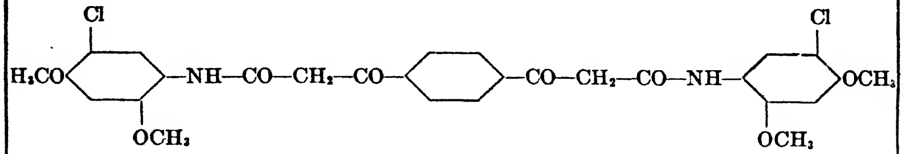
Cibanaphthol SB, ST, SD **Celcot SB, ST, SD** **Irganaphthol SB, ST, SD**	Ciba Sandoz Geigy	Produced by the reaction of *p*-cresotinic acid with benzidine–*SB*, tolidine–*ST*, dianisidine–*SD*.  *F.P. 727,003* (Ciba, 1931) *G.P. 565,340* (I.G., 1930)	In combination with Brown Salts Ciba I, II, III or IV, for browns. No longer manufactured.
Cibanaphthol RP	**Ciba**	1-Oxynaphthyl-4-phenylketone.  *G.P. 378,909; 393,701* *Frdl.*, **XIV**, 470, 1028 Lederer, *Z.f. ges. Tex. Ind.*, **1923**, 550, 560 Lederer, *Mell.*, **1931**, 461	For red with Scarlet Salt Ciba R.

Table 5. The Coupling Components (*Continued*)

Name	Manufacturer	Constitution	Application
Naphthol AS-G	I.G., G.D.C.	Diacetoacetyl derivatives of diphenyl bases. Diacetylacetotolidide.  Laska and Zitscher, *G.P. 386,054* (Griesheim, 1921) *Frdl.*, **XIV**, 1006, (1921–5)	Yellow azo dyes with all bases. Indifferent to carbon dioxide in the atmosphere, but sensitive to formaldehyde. Has a marked substantivity. Dyeings cannot be discharged with Hydrosulfite NF.
Brenthol AT	I.C.I.		
Cibanaphthol AG	Ciba		
Naphthasol NJ	Kuhlmann-Francolor		
Naphthanilid SG	Rohner		
Anthonaphthol MG	S.P.C.M.C.		
Naphthasol J	St. Denis		
Naphthol AS-LG	I.G.	By condensation of one mol. terephthalyl ethylpropanolate with two mols. 2,4-dimethoxy-5-chloraniline. Bis-dimethoxy-2,4-chloro-5-anilide of terephthalyl diacetic acid.  *F.P. 716,871* (I.G. 1930) *Mell.*, **1931**, 320 Christ, *Mell.*, **1934**, 18	Very strong substantivity, making it possible to dye on the beck. Greenish yellow shades which are not dischargeable.

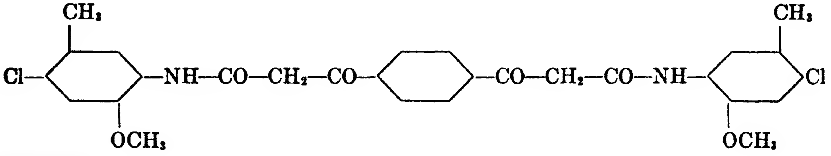
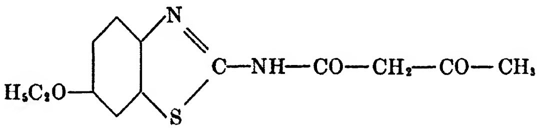
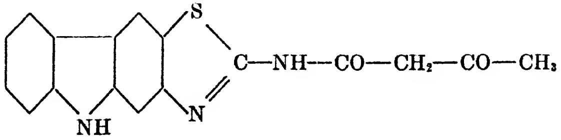
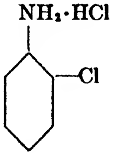
Naphthol AS-L3G	I.G.	By condensation of one mol. terephthalyl ethylpropanolate with two mols. 2-methoxy-5-methyl-4-chloraniline. Bis-methoxy-2-chloro-4-methyl-5-anilide of terephthalyldiacetic acid. 	
Naphthol AS-L4G	I.G.	2-Acetoacetylamino-6-ethoxybenzothiazole.  The aminonaphthothiazoles and the carbazothiazoles can be used in an analogous way.  *G.P. 603,623* (I.G., 1933); 612,072 (1933); 611,882 (1933).	Readily soluble, with low substantivity. Suitable for dyeing piece goods. Produces yellow dyeings which can be discharged with Hydrosulfite NF. The fastest yellows to light are obtained with Fast Yellow GC Base, Fast Red KB Base and Fast Black RD Base.

Table 6. Fast Color Salts and Bases

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Fast Yellow GC Base	G.D.C., I.G.	*o*-Chloroaniline hydrochloride. 	1 p. Naphthol AS-G combines with 1 p. Base 1 p. Naphthol AS-D. .0.95 p. Base 1 p. Naphthol AS-RL.0.75 p. Base 1 p. Naphthazol NEL. .0.7 p. Base	Canary-yellow with Naphthol AS-G, very fast to light orange for blankets and curtains with Naphthol AS-RL (Naphthazol NRL). Orange, very fast to boiling and to chlorine, with Naphthazol NEL This combination is suitable for linens and table cloths.
Fast Yellow GC Base	I.C.I.			
Base de Jaune solide NJS	Kuhlmann-Francolor			
Base pour Jaune solide GC	St. Denis			
Azogène Jaune solide GC	S.P.C.M.C.			
Echtgelbbase GC	Rohner			
Fast Yellow Salt GC	G.D.C., I.G.	Stabilized diazo compound of *o*-chloroaniline.	1 p. Naphthol AS-G. . . .5 p. Salt 1 p. Naphthol AS-RL 3.75 p. Salt 1 p. Naphthazol NEL. .3.5 p. Salt	
Fast Yellow Salt GC	A.A.P.			
Fast Yellow Salt GC	I.C.I.			
Diazo Echtgelb GC	Rohner			
Sel de Jaune solide NJS 20%	Kuhlmann-Francolor			
Sel d'Azogène Jaune solide 20%	S.P.C.M.C.			

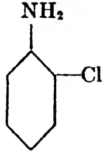
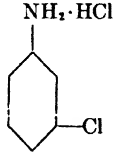
Fast Yellow G Base	G.D.C., I.G.	*o*-Chloroaniline. 		
Azogène Jaune solide G	S.P.C.M.C.			
Yellow Base Ciba I	Ciba			
Echtgelb Base G	Rohner			
Fast Orange GC Base	G.D.C., I.G., I.C.I., A.A.P.	*m*-Chloroaniline hydrochloride. 	1 p. Naphthol AS....0.90 p. Base 1 p. Naphthol AS-D..0.85 p. Base 1 p. Naphthol AS-ITR 0.65 p. Base 1 p. Naphthol AS-OL.0.80 p. Base	Orange with Naphthol AS; reddish orange with Naphthol AS-RL; brownish orange very fast to light and to boiling with Naphthol AS-ITR; yellowish orange very fast to light with Naphthols AS-OL and AS-D; very fast brown-olive with Naphthol AS-LB. Red with Naphthol AS-SW. Bordeaux with Naphthol AS-BS. Orange with Cibanaphthol RF; olive brown with Cibanaphthol RK and RTO.
Fast Orange GCN Base	G.D.C., I.G.			
Orange Base Ciba IV	Ciba			
Devol Orange C	Sandoz			
Orange Base Irga IV	Geigy			
Naphthanil Orange GC Base	Du Pont			
Echtorange-base GC	Rohner			
Base d'Orange solide GC	Kuhlmann-Francolor			
Azogène Orange solide GC	S.P.C.M.C.			

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Fast Orange G Base	G.D.C., I.G.	*m*-Chloroaniline.		As for Fast Orange GC Base.
Fast Orange G dbl.	Ph.C.			
Azogène Orange solide G	S.P.C.M.C.			
Base pour Orange solide G	St. Denis			
Echtorange-base G	Rohner			
Fast Orange Salt GC	G.D.C., I.G., A.A.P.	Stabilized diazo compound of *m*-chloroaniline.	1 p. Naphthol AS....4.5 p. Salt 1 p. Naphthol AS-D..4.25 p. Salt 1 p. Naphthol AS-ITR 3.25 p. Salt 1 p. Naphthol AS-OL..4.0 p. Salt	
Fast Orange Salt GCS	G.D.C., I.G.			
Naphthanil Diazo Orange GC	Du Pont			
Naphthosol Fast Orange Salt GC	Calco			
Diazo Echtorange GC	Rohner			
Sel d'Orange solide NJS 20%	Kuhlmann-Francolor			
Sel d'Azogène Orange solide GSN 20%, GC 20%	S.P.C.M.C.			

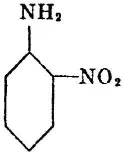
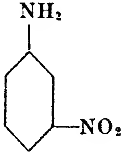
Fast Orange GR Base	G.D.C., I.G., I.C.I.	*o*-Nitraniline.  	1 p. Naphthol AS....0.65 p. Base 1 p. Naphthol AS-D..0.6 p. Base 1 p. Naphthol AS-BS..0.6 p. Base 1 p. Naphthol AS-SW.0.6 p. Base 1 p. Naphthol AS-ITR 0.5 p. Base	Orange with β-naphthol. Reddish orange with Naphthol AS and AS-BS. Brown with Naphthol AS-LB. Bluish red with Naphthol AS-D. Red, very fast to light with Naphthol AS-RL. Scarlet with Naphthol AS-ITR very fast to light, to washing and to chlorine. Reddish brown with Naphthol AS-SW.
Azogène Orange solide GR	S.P.C.M.C.			
Base pour Orange solide GR	St. Denis			
Orange Base Ciba II	Ciba			
Devol Orange B	Sandoz			
Orange Base Irga II	Geigy			
Echtorangebase GR	Rohner			
Base d'Orange solide NJR	Kuhlmann-Francolor			
Fast Orange Salt GR 20%	G.D.C., I.G.	Stabilized diazo compound of *o*-nitraniline.	1 p. Naphthol AS....3.25 p. Salt 1 p. Naphthol AS-D....3 p. Salt 1 p. Naphthol AS-SW..3 p. Salt 1 p. Naphthol AS-ITR 2.5 p. Salt	Red-orange with Cibanaphthol RF and RM. Red with Cibanaphthol RTO. Brownish red very fast to light with Cibanaphthol RBL.
Fast Orange Salt GR	I.C.I.			
Orange Salt Ciba II	Ciba			
Devol Orange Salt B 20%	Sandoz			
Orange Salt Irga II 20%	Geigy			
Diazo-Echtorange GR	Rohner			
Sel d'Orange solide NJR 20%	Kuhlmann-Francolor			

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Fast Orange R Base	G.D.C., I.G., I.C.I.	*m*-Nitraniline. 	1 p. Naphthol AS....0.65 p. Base 1 p. Naphthol AS-D...0.6 p. Base 1 p. Naphthol AS-ITR 0.5 p. Base 1 p. Naphthol AS-BS.0.6 p. Base	Orange with β-naphthol. Orange with Naphthols AS, AS-D and AS-BS. Very fast scarlet with Naphthol AS-ITR.
Orange Base Ciba I	Ciba			
Naphthanil Orange R Base	Du Pont			
Echtorange-base R	Rohner			
Base d'Orange solide NR	Kuhlmann-Francolor			
Base pour Orange solide R	St. Denis			
Azogène Orange solide R	S.P.C.M.C.			
Fast Orange Salt R	I.C.I., I.G., G.D.C.	Stabilized diazo compound of *m*-nitraniline.	1 p. Naphthol AS....3.25 p. Salt 1 p. Naphthol AS-D....3 p. Salt 1 p. Naphthol AS-ITR 2.5 p. Salt 1 p. Naphthol AS-BS..3 p. Salt	
Sel d'Orange solide NR 20%	Kuhlmann-Francolor			
Sel d'Azogène Orange solide R 20%	S.P.C.M.C.			
Diazo-Echtorange R	Rohner			
Azophor Orange MN	M.L.B.	Sulfate of the diazo compound of *m*-nitraniline, stabilized with aluminum sulfate and dried *in vacuo*.	*G.P. 85,387* *Frdl.*, **IV**, 673 (1894–1897)	

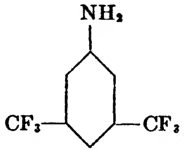
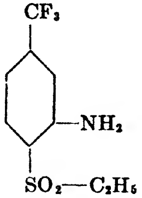
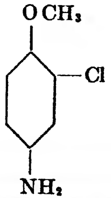
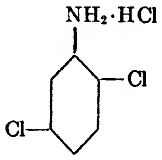
Fast Orange Salt LG 20%	G.D.C., I.G.		1 p. Naphthol AS....4.8 p. Salt 1 p. Naphthol AS-OL..4.3 p. Salt 1 p. Naphthol AS-LT. 4.1 p. Salt	Reddish orange of very good fastness on Naphthols AS-OL and AS-LT.
Fast Orange Salt RDN, RD	G.D.C., I.G.		1 p. Naphthol AS .4.25 p. Salt 1 p. Naphthol AS-RL 3.8 p. Salt	Reddish orange, of outstanding fastness on Naphthols AS and AS-RL.
Fast Golden Orange Salt GGD 20%	I.G.		*G.P. 590,255*	
Fast Golden Orange Salt GR	I.G. (1935)		*G.P. 588,781* *Teintex*, **1947**, 3	Golden orange shades of very good fastness with Naphthols AS, AS-D, AS-E and AS-TR.
Base d'Ecarlate solide N3J **Azogène Ecarlate solide 3G**	Kuhlmann-Francolor S.P.C.M.C.	*o*-Chloro-*p*-anisidine. 	1 p. Naphthol AS-G..0.9 p. Base 1 p. Naphthol AS-TR.0.7 p. Base	Pure yellow fast to boiling, to chlorine and to light with Naphthol AS-G Scarlet very fast to chlorine and to light with Naphthol AS-TR

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Sel d'Ecarlate solideN3J20%	Kuhlmann-Francolor	Stabilized diazo compound of above.		
Fast Scarlet GG Base	G.D.C., I.G., A.A.P., I.C.I.	2,5-Dichloroaniline hydrochloride.  	1 p. Naphthol AS-G ..1 p. Base 1 p. Naphthol AS. . 0.95 p. Base 1 p. Naphthol AS-BG.0.9 p. Base 1 p. Naphthol AS-RL 0.85 p. Base 1 p. Naphthol AS-BO 0.85 p. Base	Yellow shades of outstanding fastness with Naphthols AS-L3G and particularly with AS-LG. Yellow with Naphthol AS-G. Brown with Naphthol AS-BG of good fastness and scarlet with Naphthol AS-OL. Catechu-brown with Naphthol AS-BO.
Naphthanil Scarlet GG Base	Du Pont			
Scarlet Base Ciba I	Ciba			
Devol Scarlet A	Sandoz			
Scarlet Base Irga I	Geigy			
Echtscharlachbase GG	Rohner			
Base d'Ecarlate solide N2J	Kuhlmann-Francolor			
Base pour Ecarlate solide 2G	St. Denis			
Azogène Ecarlate solide GG	S.P.C.M.C.			

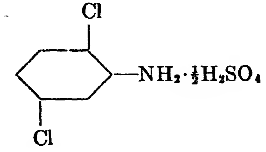
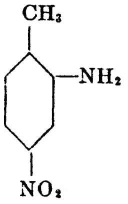
Fast Scarlet Salt 2G	G.D.C., I.C.	Stabilized diazo compound of 2,5-dichloroaniline.	1 p. Naphthol AS-G....5 p. Salt 1 p. Naphthol AS....4.75 p. Salt 1 p. Naphthol AS-RL 4.25 p. Salt 1 p. Naphthol AS-BG 4.5 p. Salt 1 p. Naphthol AS-BO 4.25 p. Salt	
Fast Scarlet Salt GG	A.A.P., I.C.I.			
Naphthanil Diazo Scarlet GG	Du Pont			
Naphthosol Fast Scarlet Salt GG	Calco			
Scarlet Salt Ciba I 20%	Ciba			
Devol Scarlet Salt A	Sandoz			
Scarlet Salt Irga I 20%	Geigy			
Diazoechtscharlach GG	Rohner			
Sel d'Ecarlate solide N2J 20%	Kuhlmann-Francolor			
Fast Scarlet GGS Base	I.G.	2,5-Dichloroaniline sulfate. 	1. p. Naphthol AS-G..1.2 p. Base 1 p. Naphthol AS....1.15 p. Base 1 p. Naphthol AS-BO 0.95 p. Base 1 p. Naphthol AS-BG .1 p. Base	Same as for Fast Scarlet 2G Base.
Echtscharlachbase GGT	Rohner			
Base d'Ecarlate solide N2JS	Kuhlmann-Francolor			
Azogène Ecarlate solide GGC	S.P.C.M.C.			

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Naphthosol Fast Scarlet G Base	Calco	*p*-Nitro-*o*-toluidine (4-nitro-2-aminotoluene).  	1 p. Naphthol AS....0.75 p. Base 1 p. Naphthol AS-D..0.7 p. Base	Very bright scarlet. with Naphthol AS Bluish red with Naphthol AS-D. Pink shades by reducing the concentration.
Fast Scarlet G Base	G.D.C., I.G., I.C.I., A.A.P.			
Naphthanil Scarlet G Base	Du Pont			
Scarlet Base Ciba II	Ciba	(1904)		
Devol Scarlet B	Sandoz			
Scarlet Base Irga II	Geigy			
Echtscharlachbase G	Rohner			
Base d'Ecarlate solide NJ	Kuhlman-Francolor			
Base pour Ecarlate solide G	St. Denis			
Azogène Ecarlate solide G	S.P.C.M.C.			
Fast Scarlet Salt G	G.D.C., I.G.	Stabilized diazo compound of *p*-nitro-*o*-toluidine.	1 p. Naphthol AS....3.75 p. Base 1 p. Naphthol AS-D..3.5 p. Base	
Sel d'Ecarlate solide NJ	Kuhlmann-Francolor			

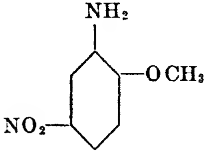
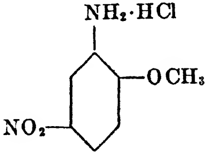
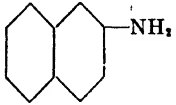
Fast Scarlet R Base	G.D.C., I.G., I.C.I.	*m*-Nitro-*o*-anisidine (5-nitro-1-amino-2-methoxybenzene).  	1 p. Naphthol AS....0.95 p. Base 1 p. Naphthol AS-D.0.85 p. Base 1 p. Naphthol AS-OL 0.85 p. Base 1 p. Naphthol AS-BS 0.85 p. Base	Bright orange shade with β-naphthol. Brilliant scarlet shade with Naphthol AS; very bright scarlet shades with Naphthols AS-D, AS-OL and AS-RL. Bright bluish red with AS-BS. Brownish yellow with AS-LB. Bordeaux with AS-BS and AS-LT.
Naphthanil Scarlet R Base	Du Pont			
Scarlet Base Ciba III	Ciba			
Devol Scarlet F	Sandoz			
Scarlet Base Irga III	Geigy			
Base d'Ecarlate solide NR	Kuhlmann-Francolor			
Base pour Ecarlate solide R	St. Denis			
Azogène Ecarlate solide R	S.P.C.M.C.			
Fast Scarlet RC Base	G.D.C., I.G., I.C.I.	*m*-Nitro-*o*-anisidine hydrochloride.  	1 p. Naphthol AS....1.15 p. Base 1 p. Naphthol AS-D.1.10 p. Base 1 p. Naphthol AS-OL..1 p. Base 1 p. Naphthol AS-BS..1 p. Base	Same as for Fast Scarlet R Base.
Naphthosol Fast Scarlet RC Base	Calco			
Base d'Ecarlate solide NRS	Kuhlmann-Francolor			
Base pour Ecarlate solide RC	St. Denis			
Azogène Ecarlate solide RS	S.P.C.M.C.			

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Fast Scarlet Salt R	A.A.P., G.D.C., I.G.	Stabilized compound of *m*-nitro-*o*-anisidine.	1 p. Naphthol AS.....4.6 p. Salt 1 p. Naphthol AS-D..4.4 p. Salt 1 p. Naphthol AS-OL...4 p. Salt 1 p. Naphthol AS-BS..4 p. Salt	
Scarlet Salt Ciba III	Ciba			
Devol Scarlet Salt F	Sandoz			
Scarlet Salt Irga III	Geigy			
Fast Scarlet Salt RC	I.C.I.			
Naphthanil Diazo Scarlet R	Du Pont			
Naphthosol Fast Scarlet Salt R	Calco			
Diazoechtscharlach R	Rohner			
Sel d'Ecarlate solide NRS 25%	Kuhlmann-Francolor			
Fast Scarlet B Base	G.D.C., I.G.	β-Naphthylamine. 		Dull red of poor fastness with β-naphthol. With Naphthol AS and AS-D red shades of insufficient fastness.
Base d'Ecarlate solide NB	Kuhlmann-Francolor			
Base pour Ecarlate solide B	St. Denis			

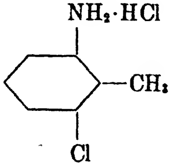
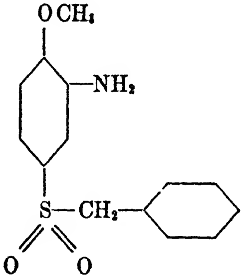
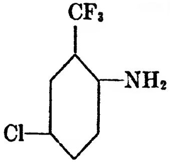
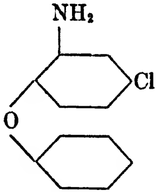
Fast Scarlet TR Base **Echtscharlach-base TR** **Base d'Ecarlate solide NTR** **Azogène Ecarlate TR**	G.D.C., I.G. Rohner Kuhlmann-Francolor S.P.C.M.C.	6-chloro-2-aminotoluene hydrochloride. 	1 p. Naphthol AS....0.9 p. Base 1 p. Naphthol AS-TR 0.85 p. Base	Bright scarlet shade with Naphthols AS and AS-D. Useful for home laundering; stable to chlorine in scarlet combinations with Naphthol AS-TR. Fast yellowish brown with Naphthol AS-LB.
Fast Scarlet LG Base and Salt	G.D.C., I.G.	Benzyl-1-methoxy-2-aminophenyl-4-sulfone. 		Beautiful, very fast scarlet with Naphthol AS-LT.

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Fast Scarlet Salt VD	G.D.C., I.G.		*G.P. 551,882* *Teintex*, **1947**, 3	Very bright bluish scarlet shades with Naphthol AS, AS-D, AS-OL. Beautiful red with Naphthol AS-E. Outstanding fastness in combinations with Naphthols AS and AS-E.
Scarlet Base Ciba R **Brown Base Ciba I** **Devol Scarlet C** **Scarlet Base Irga R** **Fast Red FG Base**	Ciba Ciba Sandoz Geigy G.D.C., I.G.	4-Chloro-2-aminodiphenyl oxide. 	*G.P. 479,713* and *F.P. 568,839* (Ciba)	Bluish red with Cibanaphthol RF (Naphthol AS). Bright scarlet with Cibanaphthol RG (Naphthol AS-E) and Cibanaphthol RA (Naphthol AS-SW).
Scarlet Salt Ciba R 20% **Devol Scarlet Salt C** **Scarlet Salt Irga R** **Fast Red Salt FG**	Ciba Sandoz Geigy G.D.C., I.G.			

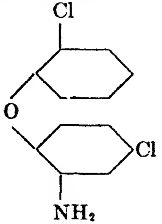
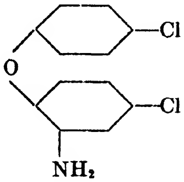
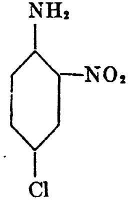
Scarlet Base Ciba IV **Devol Scarlet D** **Scarlet Base Irga IV**	Ciba Sandoz Geigy	2-amino-4,2′,2′-dichlorodiphenyl oxide. 		
Scarlet Salt Ciba IV 20% **Devol Scarlet Salt D** **Scarlet Salt Irga IV**	Ciba Sandoz Geigy			
Scarlet Base Ciba V **Brown Base Ciba II** **Devol Scarlet E** **Scarlet Base Irga V** **Fast Red FR Base**	Ciba Ciba Sandoz Geigy G.D.C., I.G.	4,4′-Dichloro-2-aminodiphenyloxide. 	*G.P. 572,663* and *F.P. 725,326* (Ciba)	Very fast and pure bluish red shades with Cibanaphthol RK (Naphthol AS-OL) and Cibanaphthols RBL and RTO (Naphthol AS-RL and AS-D)
Fast Red Salt FR 20% **Scarlet Salt Ciba V 20%** **Devol Scarlet Salt E** **Scarlet Salt Irga V 20%**	G.D.C., I.G. Ciba Sandoz Geigy			

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Fast Red 3GL Base	G.D.C., I.G., I.C.I.	*p*-Chloro-*o*-nitraniline. 	1 p. Naphthol AS....1.7 p. Base 1 p. Naphthol AS-D.1.65 p. Base 1 p. Naphthol AS-OL 1.55 p. Base 1 p. Naphthol AS-RL 1.55 p. Base	Orange with β-naphthol. Very fast shades imitating Turkey red with Naphthols AS and AS-D. Red of remarkable fastness with Naphthol AS-RL. Bordeaux with Naphthol AS-OL (of outstanding fastness). Brown with Naphthol AS-LB. Black with Naphthol AS-SR.
Red Base Ciba VI	Ciba			
Devol Red F	Sandoz			
Red Base Irga VI	Geigy			
Naphthanil Red 3G Base	Du Pont			
Echtrotbase 3GL spec.	Rohner			
Base de Rouge solide N3JL	Kuhlmann-Francolor			
Base pour Rouge solide 3GL	St. Denis			
Azogène Rouge solide 3GL	S.P.C.M.C.			
Fast Red Salt 3GL	G.D.C., I.G., I.C.I., A.A.P.	Stabilized diazo compound of *p*-chloro-*o*-nitraniline.	1 p. Naphthol AS....4.25 p. Salt 1 p. Naphthol AS-D.4.15 p. Salt 1 p. Naphthol AS-OL.3.9 p. Salt 1 p. Naphthol AS-RL.3.9 p. Salt	
Red Salt Ciba VI 40%	Ciba			
Naphthosol Fast Red Salt 3GL	Calco			
Naphthanil Diazo Red 3G	Du Pont			

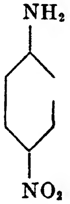
Devol Red Salt F	Sandoz			
Red Salt Irga VI	Geigy			
Diazoechtrot 3GL	Rohner			
Sel de Rouge solide N3JL	Kuhlmann-Francolor			
Fast Red GG Base	G.D.C., I.G., I.C.I., A.A.P.	*p*-Nitraniline. 	1 p. Naphthol AS.....0.7 p. Base 1 p. Naphthol AS-D.0.65 p. Base 1 p. Naphthol AS-SW.0.6 p. Base 1 p. Naphthol AS-TR.0.6 p. Base 1 p. Naphthol AS-ITR 0.5 p. Base	Yellowish red with β-naphthol. Bluish red with Naphthol R, AR or β-naphthol R. Bluish red with β-naphthol by adding Nuanciersalz (Cassella). Brown with Chrysoidine. Black with Nigrophor. Red with Naphthol AS-SW similar to the usual *p*-nitraniline red, used in machine dyeing. Red, very fast to light obtained at a reasonable price with Naphthol AS-TR. Reddish brown with Naphthol AS-ITR.
Echtrotbase GG	Rohner			
Base de Rouge solide N2J	Kuhlmann-Francolor			
Base pour Rouge solide 2G	St. Denis			
Azogène Rouge solide GG	S.P.C.M.C.			
Paranitraniline S	Bayer	1 Mol. *p*-nitraniline sulfate (50%) + 2 mols. sodium naphthalene sulfonate.	Can be easily diazotized.	
Paranitraniline N	M.L.B.	*p*-Nitraniline mixed with the amount of nitrite as required.		

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Fast Red Salt GG	G.D.C., I.G.	Stabilized diazo compound of *p*-nitraniline.	1 p. Naphthol AS.....3.5 p. Salt 1 p. Naphthol AS-D..3.5 p. Salt 1 p. Naphthol AS-SW..3 p. Salt 1 p. Naphthol AS-ITR 2.5 p. Salt	
Diazoechtrot GG	Rohner			
Sel de Rouge solide N2J 20%	Kuhlmann-Francolor			
Former Brand Names:				
Azophor Red PN	M.L.B. (1894)	*p*-Nitrodiazobenzene, stabilized with aluminum sulfate.	*G.P. 94,495; 94;496; 97,933; 85,387*	Red with β-naphthol.
Nitrazol C	Cassella	Stabilized product obtained by adding anhydrous Na_2SO_4 to a *p*-nitrodiazobenzene sulfate solution, whereby a mixture of the diazonium salt and $NaHSO_4$ is formed; very stable.	The anhydrous aluminum sulfate solution is added to the concentrated diazo solution. This mixture is concentrated *in vacuo*.	
Nitrazol CF	Cassella	Stabilized *p*-nitrodiazobenzene: double salt formed from diazonium salt and β-naphthalene sulfonate of sodium.	*G.P. 97,933* and *281,098*	
Paranil A	Bayer		*G.P. 264,268*	
Diazo Red	F.P.C.T.M.	Becker Process: Stabilization by means of α-naphthalene sulfonic acid.	*G.P. 92,237; 94,280; 92,169; 93,306; 88,949; 94,280*	
Azogene Red	Kalle	Stabilized *p*-nitrodiazobenzol.		
Benzonitrol	Bayer			
Parazol FB	Bayer			
Nitrazol CF	I.G.	Stabilized *p*-nitrodiazobenzene.		
Paranitrol N	Kuhlmann-Francolor			Used for developing certain substantive dyeings, as of the Para colors of G.D.C., Paradiazo colors of Kuhlmann - Francolor and Paradiamine colors of St. Denis.

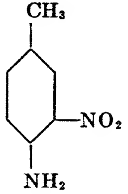
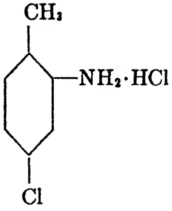
Fast Red GL Base **Red Base Ciba VII** **Devol Red G** **Red Base Irga VII** **Naphthosol Fast Red GL Base** **Naphthanil Red G Base** **Base de Rouge solide NJL** **Base p. Rouge solide G** **Azogène Rouge solide GL**	G.D.C., I.G., A.A.P., I.C.I. Ciba Sandoz Geigy Calco Du Pont Kuhlmann-Francolor St. Denis S.P.C.M.C.	*m*-Nitro-*p*-toluidine (3-nitro-4-aminotoluene). (Badische A.S.F., 1908)  	1 p. Naphthol AS....0.75 p. Base 1 p. Naphthol AS-D..0.7 p. Base 1 p. Naphthol AS-OL 0.65 p. Base 1 p. Naphthol AS-RL 0.65 p. Base 1 p. Naphthol AS-ITR 0.55 p. Base 1 p. Naphthol AS-BO.0.6 p. Base	Orange with β-naphthol. Fiery red with Naphthol AS. Very fast red shades with Naphthols AS-RL, AS-ITR and AS-BO. Black with Naphthol AS-SG. Bordeaux with Naphthol AS-D.
Devol Red Salt G **Red Salt Ciba VII 20%** **Red Salt Irga VII 20%** **Fast Red Salt GL** **Naphthosol Fast Red Salt GL** **Naphthanil Diazo Red G** **Sel de Rouge solide NJL**	Sandoz Ciba Geigy A.A.P., G.D.C., I.G. Calco Du Pont Kuhlmann-Francolor	Stabilized diazo compound of *m*-nitro-*p*-toluidine.	1 p. Naphthol AS....3.75 p. Salt 1 p. Naphthol AS-D..3.5 p. Salt 1 p. Naphthol AS-OL 3.25 p. Salt 1 p. Naphthol AS-RL 3.25 p. Salt 1 p. Naphthol AS-ITR 2.75 p. Salt 1 p. Naphthol AS-BO..3 p. Salt	

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Fast Red KB Base	A.A.P., G.D.C., I.G.	*p*-Chloro-*o*-toluidine hydrochloride. 	1 p. Naphthol AS.....1 p. Base 1 p. Naphthol AS-D..0.9 p. Base 1 p. Naphthol AS-SW 0.85 p. Base 1 p. Naphthol AS-TR 0.85 p. Base	Yellow with Naphthol AS-L3G and AS-LG. Bright red with Naphthol AS-D. Scarlet shades very fast to boiling with Naphthols AS-SW and AS-TR.
Naphthanil Red KB Base	Du Pont			
Naphthosol Fast Red KB Base	Calco			
Base de Rouge solide ND	Kuhlmann-Francolor			
Base pour Rouge solide KB	St. Denis			
Azogène solide Rouge KB	S.P.C.M.C.			
Echtrot KB Base	Rohner			
Fast Red Salt KB	G.D.C., I.G.	Stabilized diazo compound of *p*-chloro-*o*-toluidine.		
Diazoechtrot KB	Rohner			

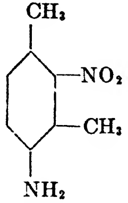
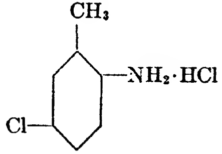
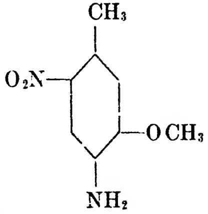
Base de Rouge solide NK **Azogène Rouge solide KX**	Kuhlmann-Francolor S.P.C.M.C.	2-Nitro-*m*-xylidine (4-amino-2-nitro-1,3-xylene). 	1 p. Naphthol NEL .0.85 p. Base 1 p. Naphthol AS-TR.0.85 p. Base	Red shades very fast to boiling and to chlorine with Naphthazol NEL and Naphthol AS-TR.
Sel de Rouge solide NK 20%	Kuhlmann-Francolor	Stabilized diazo compound of the base above.	1 p. Naphthazol NEL.4.25 p. Salt 1 p. Naphthol AS-TR.4.25 p. Salt	
Fast Red TR Base **Red Base Ciba IX** **Devol Red K** **Red Base Irga IX** **Echtrotbase TR** **Base de Rouge solide NTR** **Base pour Rouge solide TR** **Azogène Rouge solide TR**	G.D.C., I.G., I.C.I. Ciba Sandoz Geigy Rohner Kuhlmann-Francolor St. Denis S.P.C.M.C.	Hydrochloride of 5-chloro-2-aminotoluene (*m*-chloro-toluidine 1,2,5). 	1 p. Naphthol AS....1 p. Base 1 p. Naphthol AS-D..0.95 p. Base 1 p. Naphthol AS-TR.0.75 p. Base 1 p. Naphthol AS-ITR 0.75 p. Base	Red shade of outstanding fastness with Naphthol AS-LT. Red very fast to boiling and to chlorine of Turkey red shade with Naphthol AS-TR and AS-ITR. Bright red with Naphthol AS. Bordeaux with Naphthol AS-D.

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Red Salt Ciba IX	Ciba	Stabilized diazo compound of *m*-chloro-*o*-toluidine.		
Diazoechtrot TR	Rohner			
Sel de Rouge solide NTR 20%	Kuhlmann-Francolor			
Fast Red Salt TR	A.A.P.			
Base de Rouge solide NCL	Kuhlmann-Francolor	3-Methoxy-6-nitro-*p*-toluidine (or *o*-nitro-*m*-cresidine). 	1 p. Naphthol AS-BS..0.85 p. Base 1 p. Naphthol AS-BO.0.85 p. Base 1 p. Naphthazol NEL.0.75 p. Base	Bluish red, very fast to chlorine and to washing with Naphthols AS-BS, AS and AS-BO.
Azogène Rouge solide MCR	S.P.C.M.C.			
Sel de Rouge solide NCL 20%	Kuhlmann-Francolor	Stabilized diazo compound of the above base.	1 p. Naphthols AS-BS, AS-BO or Naphthazol NEL..4.25 p. Salt	

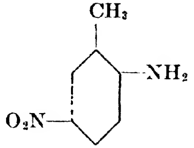
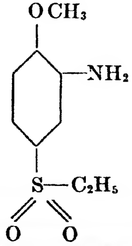
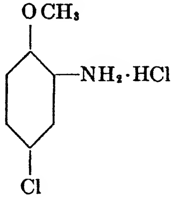
Fast Red RL Base **Red Base Ciba X** **Echtrotbase RL** **Base de Rouge solide NRL** **Azogène Rouge solide RL**	I.C.I., G.D.C., I.G. Ciba Rohner Kuhlmann-Francolor S.P.C.M.C.	*m*-nitro-*o*-toluidine (or 5-nitro-2-aminotoluene). 	1 p. Naphthol AS-G..0.75 p. Base 1 p. Naphthol AS...0.75 p. Base 1 p. Naphthol AS-OL..0.65 p. Base 1 p. Naphthol AS-RL..0.7 p. Base 1 p. Naphthol AS-ITR 0.55 p. Base	Yellow with Naphthol AS-G. Very fast brown with Naphthol AS-LB. Red with Naphthol AS. Very bright red and pink shades fast to light with Naphthol AS-OL. Garnet shades with Naphthol AS-OL and Naphthol AS-ITR.
Fast Red Salt RL 20% **Sel de Rouge solide NRL 20%** **Sel d'Azogène Rouge solide NRL 20%**	G.D.C., I.G. I.C.I. Kuhlmann-Francolor S.P.C.M.C.	Stabilized diazo compound of the above base.	1 p. Naphthol AS-G..3.75 p. Salt 1 p. Naphthol AS....3.75 p. Salt 1 p. Naphthol AS-OL..3.25 p. Salt 1 p. Naphthol AS-RL..3.5 p. Salt 1 p. Naphthol AS-ITR.2.75 p. Salt	Black with Naphthol AS-SR.
Fast Red Base GTR	G.D.C., I.G.	2-Aminobenzene-1-methoxy-4-ethylsulfone. 		Yellowish red shades of very good fastness to light with Naphthol AS-ITR.

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Fast Red Salt GTR	G.D.C., I.G.	Stabilized diazo compound of the above base.		
Fast Red RC Base	G.D.C., I.G., A.A.P.	Hydrochloride of *p*-chloro-*o*-anisidine (4-chloro-2-aminoanisole). 	1 p. Naphthol AS. . .1.05 p. Base 1 p. Naphthol AS-D. .1 p. Base 1 p. Naphtazol NEL. . .0.9 p. Base	Bright red with β-naphthol and with Naphthol AS. Red similar to Turkey red, very fast to boiling and to chlorine with Naphthazol NEL. Brown with Naphthol AS-LB.
Red Base Ciba I	Ciba			
Devol Red J	Sandoz			
Red Base Irga I	Geigy			
Naphthanil Red RC Base	Du Pont			
Echtrotbase RC	Rohner			
Base de Rouge solide NRS	Kuhlmann-Francolor			
Base pour Rouge solide RC	St. Denis			
Azogène Rouge solide RC	S.P.C.M.C.			
Fast Red RC Base	I.C.I.			
Fast Red Salt RC	A.A.P., G.D.C., I.G.	Stabilized diazo compound of *p*-chloro-*o*-anisidine.	1 p. Naphthol AS. . . .5.25 p. Salt 1 p. Naphthol AS-D. .5 p. Salt 1 p. Naphthazol NEL. .4.5 p. Salt	
Naphthanil Diazo Red RC	Du Pont			
Sel de Rouge solide NRS 20%	Kuhlmann-Francolor			

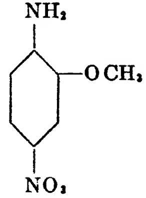
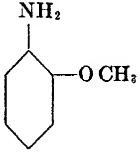
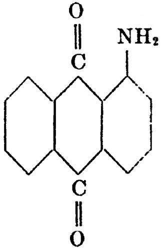
Fast Red B Base **Red Base Ciba V** **Devol Red E** **Red Base Irga V** **Naphthanil Red B Base** **Naphthosol Fast Red B Base** **Echtrotbase B** **Base de Rouge solide NB** **Base pour Rouge solide B** **Azogène Rouge solide**	I.C.I., A.A.P., G.D.C., I.G. Ciba Sandoz Geigy Du Pont Calco Rohner Kuhlmann-Francolor St. Denis S.P.C.M.C.	*p*-Nitro-*o*-anisidine. (5-nitro-2-amino anisole).  	*G.P. 98,637* (1897) *F.P. 271,908* 1 p. Naphthol AS.. .0.85 p. Base 1 p. Naphthol AS-G. .0.9 p. Base 1 p. Naphthol AS-ITR.0.65 p. Base 1 p. Naphthol AS-RL. .0.8 p. Base 1 p. Naphthol AS-BO. .0.75 p. Base	Bluish red with β-naphthol. Raspberry-red with Naphthol AS. Very fast bordeaux with AS-RL. Red of very good light-fastness with Naphthol AS-ITR. Orange yellow, cheap and fairly fast with Naphthol AS-G. Very fast reddish brown with Naphthol AS-LB. Black with AS-SG and AS-SR.
Red Salt Ciba V 20% **Devol Red Salt E** **Red Salt Irga V** **Fast Red Salt B** **Naphthanil Diazo Red B** **Naphthosol Fast Red Salt B** **Diazoechtrot B** **Sel de Rouge solide NB 20%** **Sel d'Azogène Rouge solide B 20%**	Ciba Sandoz Geigy A.A.P., G.D.C., I.G. Du Pont Calco Rohner Kuhlmann-Francolor S.P.C.M.C.	Stabilized diazo compound of *p*-nitro-*o*-anisidine.	1 p. Naphthol AS... .4.25 p. Salt 1 p. Naphthol AS-G . .4.5 p. Salt 1 p. Naphthol AS-ITR.3.25 p. Salt 1 p. Naphthol AS-RL. .4.0 p. Salt 1 p. Naphthol AS-BO.3.75 p. Salt	

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Fast Red BB Base	I.G.	*o*-Anisidine. 	Of little practical importance.	Bordeaux with β-naphthol.
Red Base Ciba IV	Ciba			
Base de Rouge solide N2B	Kuhlmann-Francolor			
Base pour Rouge solide 2B	St. Denis			
Azogène Rouge solide 2B	S.P.C.M.C.			
Fast Red Salt AL	G.D.C., I.G.	Stabilized diazo compound of α-aminoanthraquinone. 	1 p. Naphthol AS-G. 5.85 p. Salt 1 p. Naphthol AS.. ..5.5 p. Salt 1 p Naphthol AS-OL..4.9 p. Salt	The combinations with Naphthols AS-G, AS and AS-OL are especially distinguished by their excellent fastness to light. Yellow-orange shade with AS-G.
Naphthanil Diazo Red AL	Du Pont			
Naphthosol Fast Red Salt AL	Calco			
Sel de Rouge solide NAL	Kuhlmann-Francolor			
Sel de Rouge-Azogène solide AL	S.P.C.M.C.			

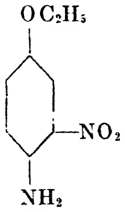
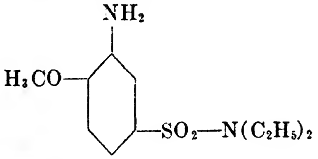
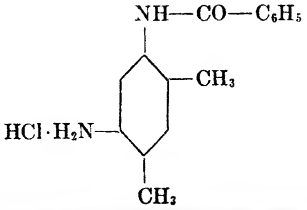
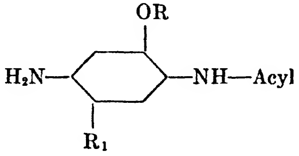
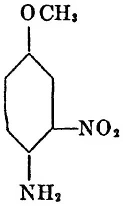
Blue-Red O	M.L.B.	*o*-Nitro-*p*-phenetidine. 	Diazotized at 15–20°C without using ice for cooling.	Fairly fast pink shade with β-naphthol. No longer used in combinations with Naphthol AS coupling components.
Fast Red ITR Base **Base de Rouge solide NSTR**	G.D.C., I.G. Kuhlmann-Francolor	Diethyl sulfonamido-*o*-anisidine (4-diethyl-sulfonamido-2-amino-1-methoxybenzene). 	*F.P. 761,607; 806,438* (1936) 1 p. Naphthol AS-ITR..0.9 p. Base $\frac{2}{3}$ p. acetic acid (calculated from the weight of the salt) has to be added in pad dyeing	Very bright red of outstanding fastness to light and to boiling with Naphthol AS-ITR.
Fast Red Salt ITR	G.D.C., I.G.	Stabilized diazo compound of the above base.		
Fast Red RBE Base	G.D.C., I.G.	1-3-Dimethyl-6-benzoylamino-4-aminobenzene hydrochloride. 	1 p. Naphthol AS... . 1 p. Base	Red of very good fastness to boiling of a shade similar to Turkey red with Naphthol AS-SW.

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Red Base Ciba VIII	Ciba	Probably  (R_1 = halogen or alkyl; R = aryl or aralkyl)	*F.P. 758,265* (1933)	Very pure bluish red, fast to light with Cibanaphthols RK and RN.
Devol Red H	Sandoz			
Red Base Irga VIII	Geigy			
Fast Bordeaux GP Base	A.A.P., G.D.C., I.G.	*m*-Nitro-*p*-anisidine. 	1 p. Naphthol AS....0.85 p. Base 1 p. Naphthol AS-D.0.8 p. Base 1 p. Naphthol AS-OL.0.8 p. Base 1 p. Naphthol AS-RL.0.8 p. Base 1 p. Naphthol AS-TR.0.75 p. Base 1 p. Naphthol AS-BO.0.75 p. Base 1 p. Naphthol AS-SW.0.75 p. Base	Bordeaux shades of very good fastness to light with Naphthols AS-OL, AS-RL, AS-TR, AS-BO, AS-SW.
Bordeaux Base Ciba IV	Ciba			
Devol Bordeaux B	Sandoz			
Bordeaux Base Irga IV	Geigy			
Naphthanil Bordeaux GP Base	Du Pont			
Base de Bordeaux solide NJ	Kuhlmann-Francolor			
Azogène Bordeaux solide G	S.P.C.M.C.			

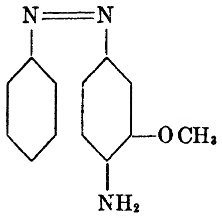
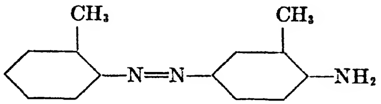
Fast Bordeaux Salt GP 20% **Naphthanil Diazo Bordeaux GP** **Naphthosol Fast Bordeaux Salt GP** **Sel de Bordeaux solide NJ 20%**	A.A.P., G.D.C., I.G. Du Pont Calco Kuhlmann-Francolor	Stabilized diazo compound of *m*-nitro-*p*-anisidine.	1 p. Naphthol AS....4.25 p. Salt 1 p. Naphthol AS-D, AS-OL, AS-RD............4 p. Salt 1 p. Naphthol AS-TR, AS-BO, AS-SW. ..3.75 p. Salt	
Bordeaux Base Ciba III Devol Bordeaux A Bordeaux Base Irga III	Ciba Sandoz Geigy	4-Amino-3-methoxyazobenzene. 		Deep bordeaux with Naphthol AS-RL, AS-BO and AS-OL.
Bordeaux Salt Ciba III 20% Devol Bordeaux Salt A Bordeaux Salt Irga III 20%	Ciba Sandoz Geigy	Stabilized diazo compound of Bordeaux Base Ciba III.		

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Fast Garnet GB Base	G.D.C., I.G.	*o*-Aminoazotoluene.  	Formed by coupling the diazo compound of *o*-toluidine with *o*-toluidine. 1 p. Naphthol AS-TR.0.9 p. Base 1 p. Naphthazol NEL.0.9 p. Base	Garnet shades very fast to light, washing and chlorine with Naphthol AS-TR and Naphthazol NEL. Orange with Naphthol AS-G. With Naphthol AS-E, azo dyestuff of excellent fastness to light.
Azo Fast Garnet M	M.L.B.			
Base de Grenat solide NJB	Kuhlmann-Francolor			
Base pour Grenat solide GB	St. Denis			
Azogène Grenat solide GB	S.P.C.M.C.			
Fast Garnet GBC Base	I.G.	*o*-Aminoazotoluol hydrochloride.	1 p. Naphthol AS....1.25 p. Base	Same as Fast Garnet GB Base.
Bordeaux Base Ciba II	Ciba			
Devol Bordeaux	Sandoz			
Bordeaux Base Irga II	Geigy			
Echtgranatbase GBC	Rohner			
Fast Garnet Salt GBC 20%	A.A.P., G.D.C., I.G.	Stabilized diazo compound of above.	1 p. Naphthol AS....6.25 p. Salt	
Naphthanil Diazo Garnet GBC	Du Pont			
Diazoechtgranat GBC	Rohner			

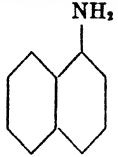
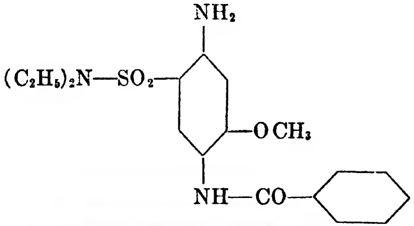
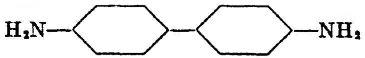
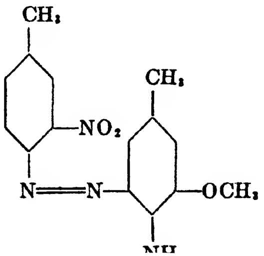
Fast Garnet B Base	G.D.C., I.G.	α-Naphthylamine. 		Bordeaux with β-naphthol. Poor fastness in coupling with Naphthol-AS components (practically out of use).
Base de Grenat solide NB	Kuhlmann-Francolor			
Base pour Grenat solide B	St. Denis			
Azogène Grenat solide B	S.P.C.M.C.			
Former names:				
Sel pour Grenat	F.P.C.T.M.	α-Naphthylamine sulfate in fine dispersion.		
Naphthylamin S pdr. or pst.	Cassella			
Grenat Naphtol en pâte 50%	F.P.C.T.M.	α-Diazonaphthalene stabilized with α-naphthylaminosulfonic acid.	Becker patents *G.P. 81,039* (1894); *G.P. 94,280*	
Acetonine NN	Kuhlmann-Francolor			
Base de Rubis solide NS	Kuhlmann-Francolor	1-Amino-3-methoxy-4-benzoylamino-6-diethyl-sulfonaminobenzen. 	1 p. Naphthol AS-ITR..1.5 p. Base	Very fast ruby shade with Naphthol AS-ITR.

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Fast Garnet GC Base	G.D.C., I.G.	*m*-Aminoazotoluene (Isomer of Fast Garnet GB Base).	1 p. Naphthol AS.....1.25 p. Base	Garnet shades with Naphthols AS, AS-D and AS-OL.
Fast Corinth B Base **Base de Corinth solide NB** **Base pour Corinthe solide B** **Azogène Corinthe solide B** **Acetonine NZ** **Benzidin**	G.D.C., I.G. Kuhlmann-Francolor St. Denis S.P.C.M.C. Kuhlmann-Francolor Rohner	Benzidine. 		Puce with β-naphthol. Shades of a poor fastness to light with naphthols, thus dropped in the more recent pamphlets of the dyestuff manufacturing companies.
Fast Corinth Salt V conc.	G.D.C., I.G.	Stabilized diazo compound of the coupling product of nitrotoluidine with metacresidine. 	1 p. Naphthol AS.. .3.75 p. Salt	Corinth shades with Naphthols AS, AS-LT and AS-RL. Dark brown with Naphthol AS-D. The shades are very fast to light but not sufficiently resistant to hot ironing.

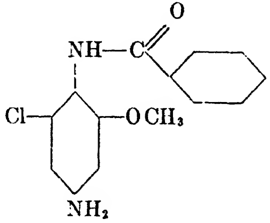
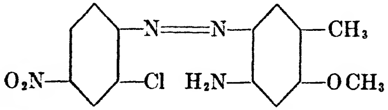
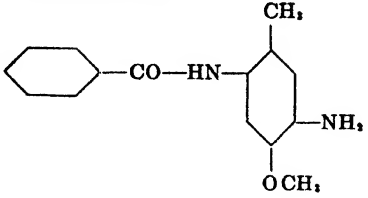
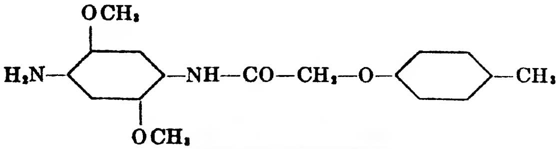
Fast Corinth LB Base	G.D.C., I.G.	2-Methoxy-1-benzoylamino-6-chloro-4-aminobenzene. 	*F.P. 793,324* 1 p. Naphthol AS.....1.3 p. Base	Corinth shade with Naphthol AS. Violet with Naphthol AS-D. Corinth with Naphthol AS-LT and AS-RL (of outstanding fastness). Garnet with Naphthol AS-LB. The shades are superior to those obtained with the brand **V** as far as fastness to light and chlorine are concerned.
Fast Corinth Salt LB	G.D.C., I.G.	Stabilized diazo compound of above.		
Fast Brown V Base	G.D.C., I.G.	*o*-Chloro-*p*-nitraniline azo-*p*-amino-*o*-cresol methyl ether. 	The diazotization process differs from the usual methods.	Deep brown shade with β-naphthol. Brown shades very fast to boiling, to chlorine and light with Naphthols AS, AS-RL, AS-OL.

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Fast Brown Salt RR	G.D.C., I.G. (1933)		1 p. Naphthol AS.. .5.85 p. Salt	Reddish brown with Naphthol AS-OL.
Fast Violet B Base **Violet Base Ciba IV** **Base de Violet solide NB**	G.D.C., I.G. Ciba Kuhlmann-Francolor	6-Benzoylamino-4-methoxy-*m*-toluidine. 	1 p. Naphthol AS....1.4 p. Base 1 p. Naphthol AS-RL.1.25 p. Base 1 p. Naphthol AS-ITR.1.2 p. Base	Blue-violet with Naphthol AS. Reddish violet with Naphthol AS-TR. Violet with Naphthol AS-D. Brown with Naphthol AS-LB. Golden orange with Naphthol AS-G (or Cibanaphthol AG).
Fast Violet Salt B **Sel de Violet solide NB 20%**	G.D.C., I.G. Kuhlmann-Francolor	Stabilized diazo compound.		
Violet Base Ciba III **Devol Violet A** **Violet Base Irga III**	Ciba Sandoz Geigy	1-Amino-4-(4′-methyl)-phenoxy-acetylamino-2,5-dimethoxybenzene. 		Very deep violet shades with Naphthols AS, AS-OL, AS-SW, AS-BS and Cibanaphthol RPH. Good fastness to washing and boiling.

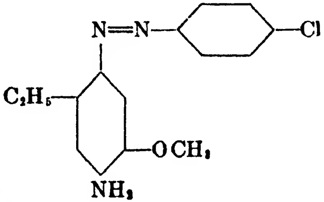
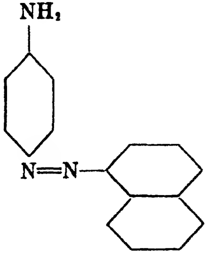
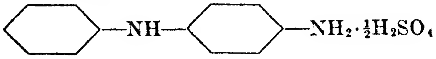
Violet Salt Ciba III Devol Violet Salt A Violet Salt Irga III 30%	Ciba Sandoz Geigy	Stabilized diazo compound of Violet Base Ciba III.		
Violet Base Ciba I	Ciba	4-Amino-3-methoxy-6-ethyl-4′-chloro-1-azobenzene. 		
Violet Base Ciba II	Ciba	1-Amino-4-phenylazonaphthalene. 		

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Variamine Blue B Base **Base de Bleu solide BL** **Base pour Bleu solide BL** **Azogène Bleu solide BL**	G.D.C., I.G. (1928) Kuhlmann-Francolor St. Denis S.P.C.M.C.	Sulfate of 4′-methoxy-4-amino-diphenylamine. 	1 p. Naphthol AS . . . 1.5 p. Base 1 p. Naphthol AS-D . . 1.4 p. Base 1 p. Naphthol AS-TR. 1.35 p. Base *G.P. 552,834; 508,585; 518,333* *Frdl.*, 17, I, 967, 974	Very fast blue shades with Naphthols AS and AS-OL. Frequently applied in piece dyeing and printing for discharges and particularly in the resist style.
Variamine Blue Salt B 50%, BA **Variamine Blue Salt B 50%** **Sel de Bleu solide NBL** **Sel pour Bleu solide B**	G.D.C. I.G. Kuhlmann-Francolor St. Denis	Stabilized diazo compound of Variamine Blue Base. Magnesium salt of the diazo compound free from nitroso groups (Rowe).	1 p. Naphthol AS . . . . . . 3 p. Salt 1 p. Naphthol AS-D . . 2.8 p. Salt 1 p. Naphthol AS-TR. 2.7 p. Salt *G.P. 515,205* *Frdl.*, 17, I, 1057	Green shade with Naphthol AS-GR. The Blue BA does not require acetic acid for developing in contradistinction to the Blue B.
Variamine Blue RT Base **Variamine Blue Salt RT** **Sel de Bleu solide NR** **Variamine Blue Salt RTA**	I.G. I.G. (1928) Kuhlmann-Francolor G.D.C., I.G.	Sulfate of 4-aminodiphenylamine. 	1 p. Naphthol AS . . . . 2.7 p. Salt 1 p. Naphthol AS-D 2.5 p. Salt 1 p. Naphthol AS-TR. . 2.3 p. Salt 1 p. Naphthol AS-RL. . 2.4 p. Salt	Same applications as for Variamine Blue Salt B. Very fast blue with Naphthol AS-RL. Green with Naphthol AS-GR. Very fast navy blue with Naphthol AS.

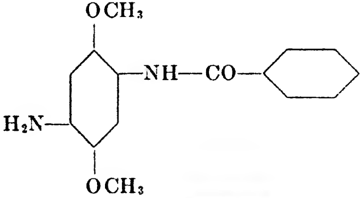
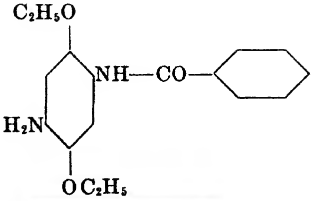
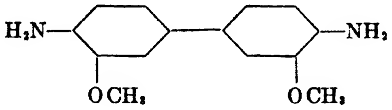
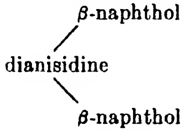
Variamine Blue Salt FB **Variamine Blue Salt FG**	I.G. I.G.		1 p. Naphthol AS	4.45 p. Salt	Very fast cornflower blue with Naphthol AS-E. Greenish blue with Naphthol AS. Green with Naphthol AS-BS.
Fast Blue RR Base **Base pour Bleu solide RR**	I.G. St. Denis	5-Amino-2-benzoylamino-1,4-dimethoxybenzene. 	1 p. Naphthol AS	1.3 p. Base	A readily dischargeable bluish violet with Naphthol AS.
Fast Blue Salt RR 40%	I.G.	Stabilized diazo compound of Fast Blue RR Base.			
Fast Blue BB Base **Blue Base Ciba IV** **Base pour Bleu solide BB** **Base de Bleu solide N2B**	G.D.C., I.G. Ciba St. Denis Kuhlmann-Francolor	5-Amino-2-benzoylamino 1,4-diethoxybenzene. 	1 p. Naphthol AS	1.45 p. Base	Navy blue with Naphthol AS. Blue with Naphthol AS-D. Both of these blue shades give poor discharges.

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Fast Blue Salt BB, BBN	G.D.C., I.G.		1 p. Naphthol AS-D 3.75 p. Salt	Green with Naphthol AS-GR. Color change in substituting naphthols derived from naphthalene by those derived from anthracene (Naphthol AS-GR).
Fast Blue B Base	A.A.P., G.D.C., I.G.	Dianisidine (Storck, 1893). 	1 p. Naphthol AS....0.6 p. Base *G.P. 83,802; 80,409; 83,963; 85,387* *U.S.P. 569,292* Dianisidine blue is the Copper salt of the compound: 	Violet-blue with β-naphthol. In the presence of copper salts gives a dark blue with β-naphthol, sensitive to perspiration and to acids. Blue, fast to perspiration with Naphthol D. Cheap blue shades, having a poor fastness to light with Naphthol AS.
Naphthanil Blue B Base	Du Pont			
Echtblaubase B	Rohner			
Base de Bleu solide NB	Kuhlmann-Francolor			
Base de Bleu solide B	St. Denis			
Azogène Bleu solide B	S.P.C.M.C.			

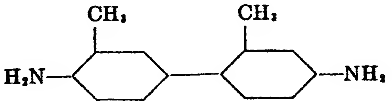
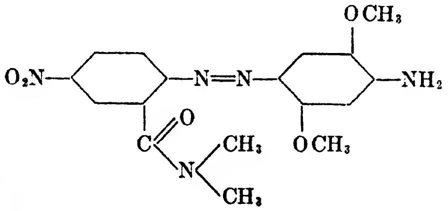
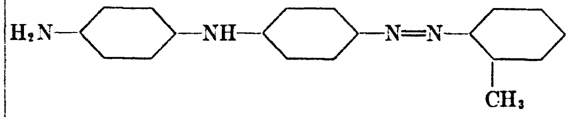
Fast Blue Salt B	A.A.P.	Stabilized tetrazo compound of dianisidine (zinc compound).	1 p. Naphthol AS......3 p. Salt	
Fast Blue Salt B, BN	G.D.C., I.G.			
Naphthosol Fast Blue Salt B	C.C.C.			
Naphthanil Diazo Blue B	Du Pont			
Diazoechtblau B	Rohner			
Sel de Bleu solide NB 20%	Kuhlmann-Francolor			
Sel d'Azogène Bleu solide B 20%	S.P.C.M.C.			
Fast Blue Salt B	Ph. C.			
Old names:				
Azophorblue D	M.L.B.	Tetrazo dianisidine stabilized with $Al_2(SO_4)_3$.	*G.P. 85,387*	
Blue Naphthol	F.P.C.T.M.	Tetrazo dianisidine stabilized with naphthalenesulfonic acids.		
Fast Dark Blue R Base (*old brand*)	I.G.	Tolidine. 		Puce with β-naphthol. Very dark navy blue with Naphthol AS; the manufacture of this dyestuff is very cheap but the fastness to light is rather poor.
Base de Bleu foncé solide NR	Kuhlmann-Francolor			
Base pour Bleu foncé solide R	St. Denis			
Azogène Bleu foncé solide R	S.P.C.M.C.			

Table 6. Fast Color Salts and Bases (*Continued*)

Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Fast Dark Blue Salt R **Sel de Bleu foncé solide NR** **Sel d'Azogène Bleu foncé solide R 31.5%**	I.G. Kuhlmann-Francolor S.P.C.M.C.	Stabilized tetrazo compound of tolidine.		
Fast Dark Blue Salt R	I.G. (1938)	Monoazo derivative. 	Main patent: *F.P. 820,249*	In combination with Naphthols AS and AS-D dark blue shades which can easily be discharged—thus, important for the discharge style.
Fast Black Salt G **Sel de Noir solide NJ** **Sel d'Azogène Noir solide G**	I.G. Kuhlmann-Francolor S.P.C.M.C.	*p*-Amino diphenylaminoazotoluene. 	*G.P. 560,602* (1929)	Black with Naphthols AS, AS-BO, AS-TR. Especially used in printing.

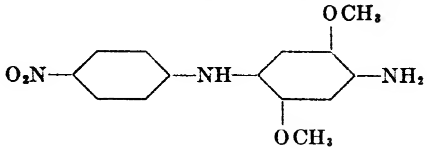
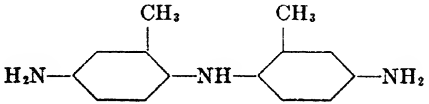
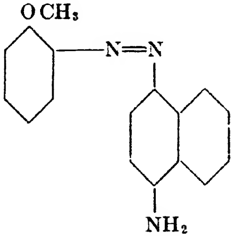
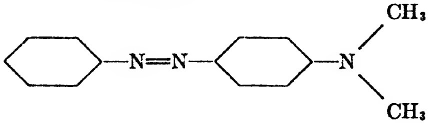
Fast Black Salt K, KN	G.D.C., I.G.	*p*-Nitro-*p'*-amino-2',5'-dimethoxydiphenylamine. 		Gives a greenish black with different naphthols.
Fast Black B Base **Fast Black Salt B**	G.D.C., I.G. I.G.	*p*-*p'*-Diaminoditolylamine. 		
Fast Black LB Base	G.D.C., I.G.	*o*-Anisidine azo-α-naphthylamine. 		
Azotol C	Cassella	*p*-Dimethylaminoazobenzene. 		Black with β-naphthol; no longer used in practice.

Table 6. Fast Color Salts and Bases (*Continued*)

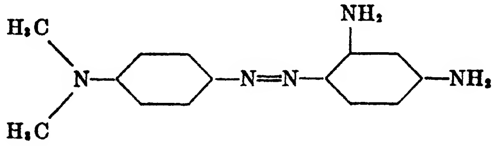
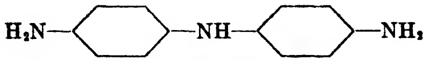
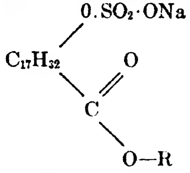
Name of Product	Manufacturer	Constitution	References and Combination Ratios	Application
Ice Black (Eisschwarz)	Kinzelberger & Co.	Asymmetric alkylderivatives of di-*p*-aminoazobenzene, for instance, *p*-dimethylamino-*o*′-*p*′-diaminoazobenzene. 	*G.P.* 94,735; 92,753; 96,361 *U.S.P.* 586,865 *Frdl.*, **4**, 697	Black with *β*-naphthol.
Azophor Black DP	M.L.B.	The base has the trade name: diaminodiphenylamine. According to Schultz: a stable mixture of tetrazodianisole with tetrazotized benzidine and diazotized nitranilines (*p*-nitraniline and mostly *m*-nitraniline). Stabilized diazo compound of diaminodiphenylamine. 		
Azophor Black S	M.L.B.	A mixture of Azophor Blue D (dianisidine) with Azophor Orange (*m*-nitraniline).	*G.P.* 83,963; 80,409	Black with *β*-naphthol.
Azophor Black O	M.L.B.	A mixture of dianisidine and benzidine plus *m*-nitraniline.		
Azophor Black ON	M.L.B.	Azophor Black O plus nitrite		

Table 7. Auxiliaries Used in Preparing Azo Dyes for Dyeing and Printing

Name	Manufacturer	Constitution	Literature	Application
Eunaphthol K, ED, AS	G.D.C., I.G.	Condensation products of sulfonaphthalene with formaldehyde.	*Mell.*, **1930**, 610 *Mell.*, **1934**, 184 Görlich, *Mell.*, **1935**, 441 Hasse, *Mell.*, **1937**, 518	Wetting agents for dissolving naphthols. AS: possesses outstanding stability to lime salts. Protective colloid, gives clear impregnating solutions and dyeings fast to crocking.
Acorit	Böhme F.C.	Fatty alcohol sulfate or sulfated oxy fatty acid.	*U.S.P. 2,026,817* *F.P. 739,066* *Aus.P. 135,670*	Solvent and emulsifying agent for dissolving naphthols; very resistant to hard water, alkalis, acids and salts. Wetting agent, improving fastness to crocking.
Tibalene NED **Naphthosolvine**	Kuhlmann-Francolor S.P.C.M.C.	Sulfonated phenol condensate.	*U.S.P. 2,006,934*	Dispersing agent; prevents formation of lime soaps. Protective colloid and leveling agent, maintaining clear naphthol solutions. Addition: 3–4 gm per l.
Sunaptol N in pst. or pdr. **Collex in pst. or pdr.**	Kuhlmann-Francolor S.P.C.M.C.	Alkylated condensate of keratin and naphthalene sulfonic acid. Casein or glue hydrolyzed with alkylnaphthalene sulfonic acid.		Penetrating agent and protective colloid for padding or developing solutions of bases and salts. The unfixed excess of dyestuff is kept in suspension, improving fastness to crocking.

Table 7. Auxiliaries Used in Preparing Azo Dyes for Dyeing and Printing (*Continued*)

Name	Manufacturer	Constitution	Literature	Application
Prestabit Oil MA	Stockhausen	Alkali salts of a sulfated fatty acid ester plus solvent.	*G.P. 591,196*	Highly concentrated pasting and wetting agent for naphthol dyeing, only to be used in soft water.
Intrasol	Stockhausen	Alkali salts of high molecular aliphatic sulfonic acids.		
Eulysin AS	G.D.C., I.G.			Binding agent for the alkali used in dyeing Variamine Blue. Gives more uniform and clearer dyes and improves the stability of the dye bath. Stable in alkaline solutions.
Avirol AH extra	Bőhme F.C.	Sulfonated castor oil ester.  Highly sulfonated oils.		Stable to magnesium and hard water salts, prevents formation of lime soaps. Used in naphthol solutions as substitute for sulfonated castor oils. Dispersing and wetting agent for Rapidogen colors. Recommended to prevent doctor streaks.
Sandozol KB, KBN	Sandoz			
Oloran B7	Oranienburg			
Prestabit Oil ZN	Stockhausen			
Flerhenol M sup. ex.	Flesch			
Tibalene NAM	Kuhlmann-Francolor			
Immersol S, SG	St. Denis			
Astrolane	S.P.C.M.C.			
Monopole Oil	J. Wolf			
Calsolene Oil HS	I.C.I.			
Tinopol Oil BH	Geigy			
Paradurol	I.G., G.D.C.	Sodium salt of naphthalene di-. and trisulfonic acid. Paradurol corresponds to sodium naphthalene 1,3,6-trisulfonic acid.	Bayer, *G.P. 263,431* *Frdl.*, XI, 370	Stabilizing agent preventing decomposition of the diazo solutions. Used in printing and dyeing processes.
Parasanol	I.G., G.D.C.			
Stabilisator SG	Sager			
Diastersol	Kuhlmann-Francolor			
Diazophile	St. Denis			
Azoguard	I.C.I.			

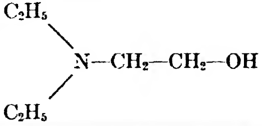
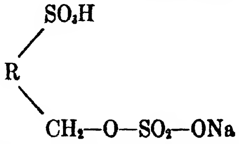
Para Soap PN	M.L.B.	Acid sodium ricinoleate. Prepared according to reference given.	*Fischer's Ber.*, **36**, 1115	The product is used for preparing naphthol solutions.
Diazopon A	I.G. (1932), G.D.C.	Derivative of oleic acid and taurine.	Basic patent: *G.P. 593,790* *Z. f. ges. Tex. Ind.*, **1932**, 337,492 Steitz, *Mell.*, **1935**, 444,515 Schwen, *Text. Mfr.*, **1936**, 153 Kirst, *Mell.*, **1937**, 739 Metzger, *Mell.*, **1937**, 644 Christ, *Mell.*, **1932**, 368	Dispersing agent improving the fastness to crocking of insoluble azo dyestuff dyeings. Increasing the stability of diazo baths, maintaining the lakes in a colloidal state and thereby promoting penetration. Addition: 2–5 gm per 1 of diazo solution.
Diazopon FFA extra conc.	I.G. (1943), G.D.C.	Substitute for Diazopon A containing no fatty acid. Ratio 1 part FFA ex. conc. = 3 parts A.		
Diazotex O conc.	Kuhlmann-Francolor			
Diastersol NDS **Dispergine CB** **Setamol WS** **Tamol** **Lomar PW**	Kuhlmann (1938) Francolor (1942) I.G. Rohm & Haas J. Wolf	Condensate of β-naphthalene sodium sulfonate with formaldehyde.	*U.S.P. 2,154,405*	For improving dispersion and retarding settling-out. Improves the clarity of the developing solutions and the fastness to crocking.
Developsol D **Developer D** **Tinosol Developer**	D. & H. I.G. Geigy	Diethyl tartrate.	*B.P. 466,846* *G.P. 639,288* *F.P. 785,334; 798,425*	In printing Rapidogen and Indigosol colors.
Rapidogen Developer N **Rapidogen Developer RNA**	I.G. G.D.C.	Diethylethanolamine.  $(C_2H_5)_2N{-}CH_2{-}CH_2{-}OH$		For developing Rapidogens in neutral steam.
Rapidogen Developer NN	I.G.	Rapidogen Developer N plus Ludigol and calcium lactate		For developing Rapidogens when printed alongside vat colors.

Table 7. Auxiliaries Used in Preparing Azo Dyes for Dyeing and Printing (*Continued*)

Name	Manufacturer	Constitution	Literature	Application
Rapidogen Developer Base RPN	G.D.C.	2-Amino-2-methylpropanol.		
Rapidogen Developer Assistant	G.D.C.	Calcium lactate and Ludigol (1:1)		
Laventine RA	G.D.C., I.G.		*F.P.* 785,334; 798,425	Used in printing Rapidogens on natural silk.
Sandozol S **Cibagen Solvent**	Sandoz Ciba	Solvent based on glycol derivatives, probably ethylene glycol.	*B.P.* 449,267 *Aus.P.* 147,774 *G.P.* 638,878	Solvent recommended as auxiliary in preparing Cibagen colors.
Neocotone Solvent **Tinogenal Solvent** **Lyoprint G** **Kromfax Solvent** **Glyecine A**	Ciba Geigy Ciba (1944) C.C.C.C. G.D.C.	Thiodiethylene glycol.		Solvent recommended as auxiliary in preparing Neocotone and Tinogenal printing pastes.
Lissolamine A	I.C.I.	Obtained from quaternary ammonium or pyridinium bases. Cetyltrimethyl ammonium bromide or octadecyl ammonium bromide. White, neutral, water-soluble paste, stable to acids, alkalis and hard water.	*F.P.* 752,728 (1933) *F.P.* 748,510 (I.C.I.)	Dispersing agent for promoting stripping with sodium hydrosulfite and alkali. Used as auxiliary agent in stripping azo dyes.

Débénaphthol A, AN	L.J.Z.	Brownish liquids.		Solvent and dispersing agent for the Rapidogen colors.
Duponol G, OS, WS	Du Pont	Sulfated derivatives of higher fatty alcohols. $R—CH_2—O—SO_2—ONa$  $R\langle{}^{SO_3H}_{CH_2—O—SO_2—ONa}$ Sulfuric acid esters of higher fatty alcohols.		In washing azo dyeings and prints. Cleansing agents, used as soap substitutes.
Gardinol KX, CA, CAX	Böhme F.C., P.C.M.R.			
Sapidan A, N, CAN	A. Th. Böhme			
Melioran F6	Oranienburg			
Sandopan A conc.	Sandoz			
Primatex NTA	Kuhlmann			
Neosapol B	St. Denis			
Duonal AM	S.P.C.M.C.			
Lissapol LS	I.C.I.			
Eriopon CA	Geigy			

Chapter V

Mordant Dyestuffs

Mordant dyestuffs* are compounds of acid reaction which have no direct affinity to vegetable or animal fibers but which can be fixed with the aid of mineral salts.

This group of dyestuffs includes the anthraquinone dyes and their most important representative, Alizarine, the oxazines (gallocyanin) and a great number of azo derivatives. Included in the azo derivatives are acid dyes which dye wool and are aftertreated with chromium salts.

The ever-growing interest in the recently developed Rapidogen and Indigosol dyestuffs which are distinguished by their all-round fastness and brightness as well as by the variety of shades they offer, has put the mordant dyestuffs more and more in the background. However, they still play an important role, and recent research by Durand and Huguenin has opened new fields of application in the field of textile printing.

TYPES OF MORDANTS

Mordants of Metal Salts

Although the natural affinity of cotton for certain colors is slight, it can be greatly increased by chemical means, that is, by employing acid or basic products which form insoluble lakes with the dyestuffs by hydrolysis. These dye lakes are complex insoluble salts in which the metal loses its cation-active properties.

Metal salts which hydrolyze readily can be used for mordants. Normal salts of strong acids, which do not hydrolyze, have no mordanting action. In general, those salts which lose acidic character by hydrolysis exhibit pronounced mordant properties. The normal salts and especially the basic salts of weak or organic acids and trivalent metals are the most commonly used mordants. In the case of acids which form only slightly

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* Trade names: Chromoxan, Diamond, Chrome Acid, Anthracene Acid, Gallo; Gallamine, Chrome, Mordant, Alizarine, Brilliant Alizarine (G.D.C. and I.G.); Alizarine, Chromazol (I.C.I.); Ultra (Brotherton); Acid Alizarine (L.B.H. and Y.D.-C.); Modern, Novochrome, Chrome, Viridine, Luxine, Chromogene, Chromorhodine (D. & H. and Carbic); Eriochrome, Erioalizarine (Geigy); Naphthochrome, Chrome Fast (Ciba); Omega Chrome (Sandoz); Colorants acides au chrome, Alizarine (Kuhlmann-Francolor); Calcochrome (Calco); Alizarine (National); Pontachrome (Du Pont).

hydrolyzed salts, and which possess the property of forming complex compounds wherein the metal loses its electropositive character, the formation of lakes is retarded and can sometimes be prevented completely. The following rule can be formulated: lakes are readily formed with normal or basic acetates; retarded with lactates; and incomplete with oxalates, citrates and tartrates.

The most important mordants which come into question in textile printing and dyeing are chromium, aluminum and iron salts. In special cases nickel, zinc and cobalt salts are used. Calcium and tin salts are used only in conjunction with aluminum mordant for Alizarine Pink or Red.

Chromium Mordants*. These mordants are derived from trivalent or hexavalent chromium, but in the latter event mordanting takes place only after reduction of the hexavalent metal to the trivalent form.. Sodium bichromate and chrome alum are the salts from which chromium mordants are prepared.

For printing, chromium acetate is most generally employed. In dyeing of spun yarns, for which mordant colors are rarely used, chromium chloride is preferred. For mordanting cottons for dyeing, chromium bisulfite is most important, while in wool dyeing, sodium bichromate with sulfuric, oxalic, or formic acid is used, or in special cases, chromium fluoride with oxalic acid.

Chromium acetate, $Cr(C_2H_3O_2)_3 \cdot 5H_2O$, is prepared in solution by dissolving freshly precipitated chromium hydroxide in the equivalent amount of acetic acid. The salt is complex. The chromium cannot be precipitated in the cold by adding caustic soda or soda ash, but it settles out by warming the solution to the boil or by steam treatment. Chromium acetate can also be obtained by double decomposition of chrome alum solution with lead or calcium acetate, or by reducing sodium bichromate in acetic acid solution with an organic substance such as glucose. The green solution of chromium acetate can be transformed to the violet modification (Ullmann, Vol. **IV**, p. 673; A. Recoura, *Comptes rendus*, **1899**, 129, 158, 208, 288).

$[Cr(OH)_2(C_2H_3O_2)](C_2H_4O_2)_2$
Chromium diacetic acid (violet)

$[Cr(OH)(C_2H_3O_2)_2](C_2H_4O_2)$
Chromium monoacetic acid (violet)

$[Cr_2O(C_2H_3O_2)_4](C_2H_4O_2)_2$
Chromium diacetic acid (green)

The violet chromium acetate of the trade, $Cr(C_2H_3O_2)_2OH$, is a basic salt obtained by adding soda ash to the green acetate. The basic salts are easily decomposed at high temperatures. The normal acetate yields

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* **Kissileff, "Mordants de chrome,"** ***Rev. Gen. Mat. Col.*****, 1936, 203.**

8.4% of its chromium content, the basic acetate 25% (Buttner, *Z. f. angew. Chem.*, 1912, **75**, 292, 370).

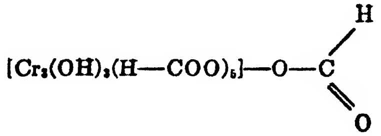
The chromium sulfoacetates are prepared by double decomposition of chrome alum with insufficient amounts of lead or calcium acetate, or by reduction of sodium bichromate in acetic acid solution in the presence of sulfuric acid. One commercial chromium sulfoacetate, $Cr_3(SO_4)(C_2H_3O_2)(OH)_6$, yields 84% of its chromium content. The normal chromium sulfoacetate, $Cr_2(C_2H_3O_2)_4SO_4$, is obtained by reducing 12 parts of $Na_2Cr_2O_7$ with 6 parts of glucose in the presence of 9 parts of H_2SO_4 66° Bé and 24 parts of acetic acid. The solution is set at 50° Bé corresponding to a Cr_2O_3 content of 15.5%.

The chromium nitroacetates $Cr_2(NO_3)_3(C_2H_3O_2)_3$; $Cr(NO_3)(C_2H_3O_2)_2$ are made by reducing sodium bichromate with glucose in the presence of acetic and nitric acids, or by the double decomposition of chrome alum with lead nitrate and lead- or calcium acetate. The basic chromium nitroacetate corresponds to the formula, $Cr_3(NO_3)_2(C_2H_3O_2)(OH)_6$.

Chromium formate and chromium thiocyanate are also used in printing, as they have the advantage of preventing premature lake formation.

Chromium thiocyanate, $Cr(CNS)_3$, is a green salt, readily soluble in water, and the green or violet solutions possess good stability. A solution of chromium thiocyanate is produced by double decomposition of chrome alum with barium or calcium thiocyanate, or by dissolving 31 parts of chromium oxide (24%) in 63 parts of water and 10 parts of sulfuric acid 66° Bé and adding 30 parts of crystallized barium thiocyanate. The filtrate is adjusted to 12° Bé.

Chromium formate, recommended by A. Scheurer for use with Alizarine Blue and Alizarine Orange, is probably a complex salt of the formula (Werner, *Ber.*, **41**, 3452):



$$[Cr_3(OH)_3(H\text{—}COO)_5]\text{—}O\text{—}C\begin{matrix}\diagup H \\ \diagdown\!\!\diagdown O\end{matrix}$$

Chromium glycollate is little used on account of its high price.

Chromium lactate has been used for many years as an efficient mordant (Böhringer, Ingelheim). It may be prepared either by dissolving chromium hydroxide in lactic acid, or by double decomposition of calcium lactate with chromium sulfate, according to the following directions: 800 parts of $Cr(OH)_3$, having a content of 22% Cr_2O_3, are dissolved in 440 parts of lactic acid 50% and the solution is adjusted to a content of 15% Cr_2O_3. Or 480 parts of $Cr_2(SO_4)_3$ 30° Bé are reacted with 220 parts of calcium lactate dissolved in 300 parts of water and the filtrate is adjusted to a concentration of 20% chromium lactate (corresponding to 4% Cr_2O_3).

This mordant has been used for printing chromium dyestuffs on silk and rayon.

Textile gum and gum arabic are coagulated by chromium acetate mordants and cause a stiff and harsh hand, so that the use of these gums which are so well adapted for printing silk and rayon, is precluded. According to *F.P. 744,137; U.S.P. 1,942,777; G.P. 583,204* (1932), the coagulation of these gums and consequently the harsh feel of the material can be avoided by adding 5% ammonium thiocyanate, 3% glycerin and 8% urea. *F.P. 770,437* (1934); *G.P. 623,648* and *631,923* (1934-D. & H.) suggest the use of chromium lactate for the same purpose. However, while chromium tartrate, -citrate and -lactate do not coagulate these gums, the prints of chromium dyestuff are much weaker with these mordants. The lake formation is impaired because in these complex salts the metal no longer has an electropositive character. The importance of using gum thickenings necessitates the search for a means of circumventing the harsh prints. It has been observed that the soft hand is obtained only after one hour's steaming, while an 8-minute ageing is insufficient. Better results can be expected if the chromium lactate is neutralized with soda ash, ammonia or amino compounds such as urea. The print pastes containing chromium lactate are, moreover, of better stability than those containing chromium acetate.

Sieber (*Mell.*, January, **1927**, 62) describes a process for fixing chromium dyestuffs in a short ageing operation of 5 to 6 minutes. The printing paste is prepared as follows: 55 parts of chromium salt (chrome alum) are dissolved in 200 parts of glycerin; 25 parts of borax is added and the mixture is heated at the boil until a homogeneous solution results. The appropriate amount of this solution is added to the printing paste.

For fixing chrome dyestuff in a short ageing passage, Borissoff (*Tiba*, **1932**, 321) suggests a mordant consisting of:

250 parts potassium bichromate
500 parts water
200 parts glycerin

adjusted to 28° Bé

The advantages of using a fatty compound with metallic mordants when dyeing chrome colors are presented in *G.P. 582,378* (Oranienburg-Lindner). However, to avoid precipitation of fatty acid by the mordant, dyeing is carried out with substituted aromatic sulfonates (*Bull. Fed.*, **I**, 518).

If a solution of bichromate with addition of Hydrosulfite NF is employed, a mordant high in $Cr(OH)_3$ is made available. After a short ageing of this preparation, $Cr_2(OH)_6 \cdot 4H_2O$ is formed on the fiber, which acts not only as a mordant but as a flameproofing agent (*G.P. 587,584*, Nankey).

Chromium chromate $Cr_2(CrO_4)_3$ is prepared by dissolving chromium hydroxide in a mixture of chromic, sulfuric and acetic acids. Mixtures of chromium chromate, chromium sulfate and acetate were offered by M.L.B. under the trade names Chrome Mordants GAI and GAII. Chromate DH of Durand and Huguenin is probably chromium chromate obtained by mixing sodium or potassium chromate with chromium chloride (*B.P. 481,854*, *G.P. 672,238*, D. & H.).

Chromium bisulfite, $Cr_2(HSO_3)_6$, is one of the most important mordants used in dyeing. It can be obtained by double decomposition of chromium sulfate and calcium bisulfite, or by the reaction of sodium bisulfite with a saturated solution of chrome alum. It is available only as a green solution which is easily decomposed at elevated temperatures. The solutions are marketed generally as 21°, 28°, or 40° Bé, corresponding to a Cr_2O_3 content of 9, 12 or 18%.

Sodium chromite (the so-called "alkaline chrome mordant" of Horace Koechlin and Henri Schmid) can be prepared either by reacting a chromium acetate solution of 20° Bé with sodium hydroxide or by precipitating chromium hydroxide from a chrome alum solution and dissolving the precipitate in caustic soda. This mordant is used in dyeing in the oxalic acid discharge process.

Chromium sulfate and chrome alum are difficult to hydrolyze and release but a small part of their chromium content to the fiber. They have little value as mordants. $Cr_2(SO_4)_3$ is able to transfer but 12.8% Cr_2O_3 to the fiber while the basic sulfate $Cr_4(SO_4)_3(OH)_6$ releases 86.4% Cr_2O_3. A. Scheurer obtained a useful mordant by the reaction of SO_2 on a solution of sodium bichromate.

Chromic chloride: $CrCl_3$, violet crystals; $CrCl_3 \cdot 6H_2O$, a green salt. Other modifications $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, a green salt; $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$, a green salt (Werner and Gubser, *Ber.*, 1901, #**34,** 1579). The chromic chloride of the trade corresponds to a basic salt, produced by dissolving $Cr(OH)_3$ in less than the stoichiometrically necessary amount of hydrochloric acid, or by dissolving chromium hydroxide in $CrCl_3$. Other basic salts are $Cr(OH)_2Cl$, $Cr(OH)Cl_2$, and $Cr_2Cl_3(OH)_3$.

Chromium nitrate has had a very limited application. It can be obtained by reducing bichromate with glucose in the presence of nitric acid, or by dissolving chromium hydroxide in nitric acid.

Chromium fluoride, $CrF_3 \cdot 4H_2O$, is a green powder readily soluble in water. It attacks copper, zinc and glass containers. It has been used principally as a mordant for wool, especially for vigoureux (slubbing) prints.

An original method for obtaining colored prints by precipitation of varicolored chromium compounds is described in *U.S.P. 2,091,539* (White). The process consists of impregnating the fabric with easily soluble chromium compounds, drying, and then transforming them by alkali treatment into colored insoluble hydroxides. The chromium compounds are obtained by hydrolysis of starch with chromic acid and subsequent reaction with chromium salts. By this reaction gluconates and saccharates of chromium of characteristic deep olive color are formed, as $Cr_2(C_6H_{11}O_7)_6$. These salts can be blended with iron salts (copperas, basic iron nitrate, pyrolignite of iron), and by using these compounds as mordants, different shades can be obtained.

It is also interesting to note that these chromium saccharates and gluconates retain a certain excess of glucose and are therefore capable of reducing vat or sulfur colors, which can be fixed by subsequent oxidation.

Aluminum Mordants*. These mordants are used particularly for printing and dyeing Alizarine Red, Alizarine Pink, Alizarine Orange and Alizarine Bordeaux. Initial materials for preparing these mordants are alum . . . $Al_2(SO_4)_3K_2SO_4 \cdot 24H_2O$ and aluminum sulfate . . . $Al_2(SO_4)_3 \cdot 18\ H_2O$, the latter containing 51.39% $Al_2(SO_4)_3$ or 15% Al_2O_3. The salts themselves are used for mordanting wool, while their basic derivatives are applied in processing cotton because they dissociate more readily and release more Al_2O_3 to the fiber. By partial neutralization, aluminum sulfate forms the following salts

$$1 \text{ molecule } Al_2(SO_4)_3 + 1 \text{ molecule } Na_2CO_3 \rightarrow Al_2(SO_4)_2(OH)_2$$
$$1 \text{ molecule } Al_2(SO_4)_3 + 2 \text{ molecules } Na_2CO_3 \rightarrow Al_2(SO_4)(OH)_4$$
$$1 \text{ molecule } Al_2(SO_4)_3 + 3 \text{ molecules } Na_2CO_3 \rightarrow 2\ Al(OH)_3$$

Actually, in the last case, a basic sulfate is formed having the formula $Al_4(SO_4)(OH)_{10}$. A basic sulfate can be produced by neutralizing aluminum sulfate with sodium carbonate and bicarbonate, having the formula $Al_4(SO_4)_3(OH)_6$. This compound is hydrolyzed on dilution with water, or by heat. It yields 58.7% Al_2O_3

$$2\ Al_2(SO_4)_3 \cdot 18\ H_2O + 6\ NaHCO_3 \rightarrow Al_4(SO_4)_3(OH)_6 + 6\ CO_2 + 18\ H_2O + 3\ Na_2SO_4$$

The compound $Al_2(SO_4)_2(OH)_2$ forms acid solutions of excellent stability to boiling, and yields 51% Al_2O_3. The compound $Al_2(SO_4)(OH)_4$ is also acid in solution, and becomes turbid quickly. The precipitate which settles out is aluminum hydroxide, and is called "Gelée d'Alumine."

It has been shown by Suida and Liechti that the more basic the aluminum sulfate, the more easily it is hydrolyzed by dilution or heating. The normal sulfate, hydrolyzed on the cotton fiber, releases only 13% Al_2O_3 while the corresponding figure for $Al_2(SO_4)_2(OH)_2$ is 51% and for $Al_4(SO_4)_3(OH)_6$ 58.7%. For this reason $Al_2(SO_4)_3$ has no practical use on cotton. $Al_2(SO_4)(OH)_4$ is not used because of its poor stability. Therefore, for

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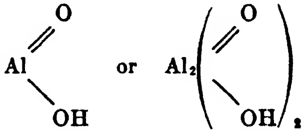
* Girard, "Sur quelques composés d'Aluminium" (The Different Aluminum Compounds), *Rev. Chim.*, **1933**, 130; Depierre, Vol. **II**, p. 156 ff.

dyeing Alizarine Red only the compounds $Al_2(SO_4)_2(OH)_2$ and $Al_4(SO_4)_3(OH)_6$ among the sulfates come into question. The basic sulfates are not used in printing cotton, while for wool printing, the normal sulfate is used with tartaric acid.

By heating solutions of $Al_2(SO_4)_2(OH)_2$ to the boil, $Al_4(SO_4)(OH)_{10}$ is obtained. Theoretically the hydroxide should be produced by complete neutralization, but it has not been found possible to precipitate it. It is assumed that it may be present in form of a suspension in the aqueous solution. By drying the gel



or $Al_2O(OH)_4$

are obtained, and by ignition the oxide Al_2O_3.

Aluminum hydroxide gel or *Gelée d'Alumine* is a basic sulfate $Al_4(SO_4)(OH)_{10} \cdot 2H_2O$ obtained by the reaction of one molecule of $Al_2(SO_4)_3 \cdot 18H_2O$ with 2½ molecules of Na_2CO_3. It is insoluble in water but soluble in dilute acids. This compound is the starting point for the preparation of the aluminum mordants by dissolving it in the appropriate acid. In this way aluminum acetate, nitrate, lactate, glycollate, formate or tartrate can be be made. These mordants, mixed with Ca and Sn compounds are used in printing Alizarine Reds and Pinks.

Aluminum acetate and aluminum nitrate are important mordants for printing Alizarine dyestuffs. In practical use they are mixed with the sulfate, and the composition varies from mill to mill.

Normal aluminum acetate, $Al(C_2H_3O_2)_3$ has not been isolated.* It is known only in water solution. The solutions decompose slowly at room temperature, rapidly at the boil, with the formation of basic salts. The normal acetate is prepared either by dissolving aluminum hydroxide in acetic acid or by the double decomposition of aluminum sulfate with acetate of lead or calcium, as

$$Al_2(SO_4)_3 + 3\ Pb(C_2H_3O_2)_2 \rightarrow 3\ PbSO_4 + 2\ Al(C_2H_3O_2)_3$$

The pure solution formed at first soon deposits the basic $Al(C_2H_3O_2)_2OH$. On the fiber, about 50% of the content of aluminum acetate is deposited as Al_2O_3. Furthermore, aluminum acetate can be prepared by the anodic oxidation of aluminum in the presence of acetic acid as electrolyte (see Wacker, *G.P. 379,512; S.P. 106,775*—1923; H. Cruse, *B.P. 213,088*).

A series of basic aluminum acetates are known, being either water-soluble or -insoluble, for instance:

$Al_2(OH)_2(C_2H_3O_2)_4 \cdot 3H_2O$: white, water-soluble mass

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* Depierre, Vol. II, p. 156.

$Al_2(OH)_4(C_2H_3O_2)_2$: insoluble in water; prepared by heating a solution of normal aluminum acetate under pressure.*

$Al_2(OH)_3(C_2H_3O_2)_3$: (E. de Haen, Chem. Fabr. List; *G.P. 190,451*)

The sulfoacetates are used in printing, and are often called "Red Mordant". Three sulfoacetates exist: the normal $Al_2(C_2H_3O_2)_4SO_4$ prepared by double decomposition according to the following equation,

$$Al_2(SO_4)_3 + 2\,Pb(C_2H_3O_2)_2 \rightarrow 2\,PbSO_4 + Al_2(C_2H_3O_2)_4(SO_4)$$

the $Al_2(C_2H_3O_2)_2(SO_4)_2$ prepared by the reaction of one molecule of $Al_2(SO_4)_3$ with one molecule of $Pb(C_2H_3O_2)_2$ and another sulfoacetate by dissolving aluminum hydroxide gel in acetic acid. This last salt is an important red mordant, possessing properties desired for printing. For dyeing, basic sulfoacetates are preferred, which are obtained by adding soda ash to normal sulfoacetates or by double decomposition of a basic sulfate with acetate of lead or calcium (Schlumberger, Crum, Suida, Liechti, Schwitzer).

The aluminum sulfoformate, corresponding to the sulfoacetate, is used for fixing Nitroalizarine. This compound, $Al_4(HCOO)_{10}SO_4$ has the advantage of preventing premature lake-formation, and of being less susceptible to hydrolysis, than the corresponding sulfoacetate (*G.P. 133,719*, M.L.B.—1902; A. Scheurer, *Bull. Mulh.*, **1911,** 153).

Aluminum formate in crystalline form, corresponding to almost chemically pure triformate, $Al(HCOO)_3 \cdot 3H_2O$ has been manufactured by Zschimmer & Schwarz in Chemnitz [Th. Hennig, "Feste ameisensaure Tonerde" (Aluminum Formate in Solid Form), *Chem. Ztg.*, **1937,** 925]. It has also been made by the Société Normande de Prod. Chim., Paris (Triformiate d'aluminium SN), and contains 23% Al_2O_3 and 63% HCOOH, and is 98 to 99% pure. The German product has 2 to 3% SO_4 as Na_2SO_4 while the French-product is free of sulfates (*G.P. 574,452, 575,597*).

Aluminum lactate, prepared by dissolving aluminum hydroxide gel in lactic acid, has the property of slowing down lake-formation. This improves the fastness to crocking.

Aluminum tartrate, $Al_2(C_4H_4O_6)_3$ (A. Scheurer, *Bull. Mulh.*, **1911,** 153) can be obtained by dissolving aluminum hydroxide gel in tartaric acid for instance, according to the formula:

1500 parts aluminum hydroxide 30% gel
2200 parts water
720 parts tartaric acid
1500 parts water

Adjusted to 15° Bé by adding water

It is used almost exclusively as a mordant in printing.

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* Wacker (*G.P. 347,606*—1920) prepared this salt by boiling 131.5 parts of $AlCl_3$ with 400 parts of glacial acetic acid for 10 hours. An almost pure product, free from chlorine, is said to result.

Another mordant used only in printing is aluminum sulfocyanide $Al_2(CNS)_6$, which yields about 33% of its Al_2O_3 content to the fiber. This mordant does not attack the steel doctor blade, thus giving brighter prints with Alizarine Pink than aluminum acetates.

Basic aluminum sulfocyanide is also known, $Al_6(CNS)_2(OH)_{16}$ (*G.P. 42,682*, Hauff). It does not attack cotton even when steamed under pressure.

Aluminum nitrate $Al_2(NO_3)_6 \cdot 5H_2O$ can be prepared by dissolving aluminum hydroxide in nitric acid. No hydrolysis takes place on warming or dilution. For printing, basic nitrates are preferred or normal or basic nitroacetates, $Al_2(NO_3)_2(C_2H_3O_2)_4$ and $Al_2(C_2H_3O_2)_2(NO_3)_2(OH)_2$ which dissociate more slowly than the corresponding acetates.

Aluminum chloride, $AlCl_3 \cdot 6H_2O$, can be prepared by dissolving aluminum hydroxide in hydrochloric acid or by the double decomposition of aluminum sulfate and calcium chloride. Generally basic chlorides are used $Al_2Cl_3(OH)_3$, Al_2Cl_5OH, $Al_2Cl_4(OH)_2$ or the chloroacetates, as $AlCl(C_2H_3O_2)_2$. This latter salt is made by decomposition of aluminum sulfate with barium chloride and lead acetate, according to the equation

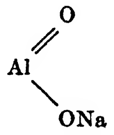
$$Al_2(SO_4)_3 + BaCl_2 + 2\ Pb(C_2H_3O_2)_2 \rightarrow 2\ AlCl(C_2H_3O_2)_2 + 2\ PbSO_4 + BaSO_4$$

The salt is resistant to dilution and to boiling, and yields only 10% of its content as Al_2O_3 to the fiber. It is used for dyeing pale shades of Alizarine Pink. A. Scheurer (*Bull. Mulh.*, **1925**, 474) observed that the influence of iron salts in printing operations in altering the shade of Alizarine Pink can be prevented by the application of aluminum chloride mordants. For this purpose he prepared the following solution:

600 parts aluminum hydroxide gel
240 parts hydrochloric acid 21° Bé
100 parts acetic acid 80%

and added 5–20 gm per kg of this mordant to the printing paste.

Aluminates:



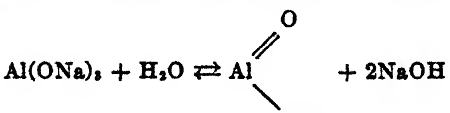
$$O{=}Al{-}ONa$$

(Erban, *Chem. Ztg.*, **1913**, 709)

Since the hydrate $Al(OH)_3$ is amphoteric, salts exist of the equivalent acid $H[Al(OH)_4]$ which is derived from

$$Al(OH)_3 \cdot OH^- = [Al(OH)_4]^-$$

Sodium aluminate is readily hydrolyzed according to the equation:



$$Al(ONa)_3 + H_2O \rightleftarrows O{=}Al{-}ONa + 2NaOH$$

This reaction proceeds on the cotton fiber, so that it can be used as a mordant. Impregnation is carried out in the cold and washing is sufficient to cause fixation. This method cannot be used for wool, however, because of the strong alkalinity of the solution.

In *B.P. 440,400,* Peter Spence & Sons employed the double salts of aluminum sulfate and phosphate which had already been described by Liechti and Suida (1888). By evaporation of a mixture of these salts in stoichiometric ratio of 0.33 molecule of P_2O_5 and one molecule of Al_2O_3, a double salt results which contains 18% Al_2O_3. It is readily soluble in cold water, and decomposes at high temperatures without the necessity of adding other ingredients. For these reasons, the double salt is useful as a mordant in printing and dyeing.

Iron Mordants*. Ferrous acetate, which can be prepared by the double decomposition of ferrous sulfate and calcium or lead acetate, or by dissolving iron in acetic acid is rarely used in practice because of its property of being easily oxidized to ferric acetate. Instead, pyrolignite of iron is preferred. It is prepared by dissolving iron filings in pyroligneous acid, a product obtained by the destructive distillation of wood. This mordant oxidizes slowly, because of its content of organic by-products, such as acetaldehyde, formic acid, propionic acid, butyric acid, phenols, cresols, pyrocatechol and pyrogallol. It forms a dark brown solution of 14° Bé, corresponding to a content of 55% Fe. This mordant is widely used in dyeing and printing logwood. In *U.S.P. 2,082,087,* White suggests the preparation of the mordant by double decomposition of ferrous sulfate with crude calcium acetate, in the presence of sulfuric acid. It is assumed that the aromatic impurities in crude calcium acetate, such as pyrocatechol and pyrogallol, are capable of preventing oxidation of the ferrous acetate, while the lower aliphatic acids present maintain the aromatic compounds in solution.

Ferrous sulfoacetate is likewise used as a mordant in dyeing and printing Alizarine Violet. It is prepared by the reaction of ferrous sulfate and lead acetate.

Ferrous sulfocyanide $Fe(CNS)_2$ is obtained by double decomposition of ferrous sulfate and barium sulfocyanide, and is known as mordant for Fast Printing Green, as it is used for printing the bisulfite compound of nitroso-β-naphthol (Fast Printing Green, Vert d'Alsace, Soliddruckgrün.)

Basic ferric sulfates, having the formulas $Fe_4(OH)_2(SO_4)_5$ and $Fe_2(OH)_2(SO_4)_2$ also known under the names of "rust mordant", "rouille" and even sometimes erroneously as "ferric nitrate" or "basic iron nitrate" are used for mordanting cotton, wool and natural silk for dyeing these materials with logwood. They are dark brown liquids of an average density of 50° Bé, obtained by reacting nitric acid on ferrous sulfate. Normal

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* Depierre, Vol. II, p. 184.

ferric sulfate, $Fe_2(SO_4)_3$ is not sufficiently reactive and therefore not used in dyeing operations.

It might finally be noted that *U.S.P. 2,085,795* (Amer. Dyewood) recommends the use of colloidal ferric hydroxide solutions, especially for dyeing acetate rayon fabrics.

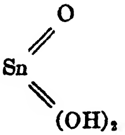
Tin Mordants. Tin mordants are used in printing Alizarine and Nitroalizarine.

The stannous salts are rarely used because of their pronounced reducing property. Lakes formed with these salts have poor stability.

Tin salt, stannous chloride ($SnCl_2 \cdot 2H_2O$), is sometimes added to Alizarine print pastes, to shade the pink toward the yellow. Alizarine Red prints or dyeings can be aftertreated with stannous chloride to brighten the shade. Stannous chloride was also used together with stannic chloride as a mordant for dyeing cochineal on wool, or catechu on silk.

Other stannous salts are the hydrate, citrate, lactate and sulfocyanide, which come into question as additions to Alizarine Red print pastes (H. Sunder, *Bull. Mulh.*, **1921,** 137).

Stannic hydroxide, $Sn(OH)_4$, and metastannic acid,



are obtained by precipitating tin tetrachloride with ammonia.

Tin oxychloride, available in 55° Bé solution is often erroneously referred to as stannic nitrate. It is prepared by slowly adding stannous chloride to nitric acid. The action is violent, and fumes of NO_2 are evolved. The product obtained is a solution of $Sn(OH)_4$ in $SnCl_4$. It is added to print pastes of Alizarine Red or Pink to brighten the shade.

Frequently stannous and stannic salts of sulfonated fatty acids are mixed with Alizarine printing pastes, in order to increase the brightness and the fastness to soap of these dyes (A. Scheurer, sealed report 1881; *Bull. Mulh.*, **1893,** 95; Wilhelm, *Bull. Mulh.*, **1908,** 78; H. Sunder, *Bull. Mulh.*, **1921,** 137).

Calcium, Nickel, Zinc, Cobalt Mordants. Nickel, zinc and cobalt mordants are used only in special cases, as in printing Alizarine Blue, for which zinc and nickel acetates are recommended, or in printing Fast Printing Green, for which cobalt acetate is recommended. Calcium acetate and calcium sulfocyanide have been noted as additions to Alizarine Red print pastes.

See Table 8, page 464, for list of all metal salt mordants.

Fatty Mordants*

The use of fatty mordants was practiced in oldest times in dyeing Turkey red. This art originated in Oriental countries, especially India, Persia and Turkey. In former times different substances containing a fat or oil were used, such as cream, cod liver oil, sesame oil and the like.

The presence of a fatty compound is indispensable for production of the genuine Turkey red. The compounds are substantially altered during the dyeing operation, proving that they take part in the formation of the dye-lake. They have the effect of improving the brilliance of the shade and the fastness to soaping of the dyeing.

For a long time insoluble oils—preferably in a rancid state (huile tournante)—were used directly, or in the form of their emulsions (D. Koechlin). Later on, in consequence of the research work done by Fremy and Runge (Depierre, Vol. **II**, p. 210; compare, *Dingler's Polytechnisches Journal*, **251**, 247 and 469) on the solubilizing action of sulfuric acid on olive oil and oleic acid, these insoluble oils were substituted by soluble oils and soaps which are more convenient to use and which in general yield better results.

Thus the insoluble fatty mordants used in former times have been replaced by sulforicinoleates—hydroxy fatty acids formed by reacting sulfuric acid on castor oil—, by ricinoleates formed by the immediate saponification of castor oil, and by chlorination products and oxidation products of oils or sulfonated derivatives thereof. This progress is due to the work of the scientists Benedict, Ulzer, Fischli, Scheurer-Kestner, W. Crum, Liechti and Suida. A detailed report regarding these studies would necessarily overstep the bounds of this book but the most important products used in dyeing and printing Alizarine dyes will be indicated here. They can be arranged in three groups:

(1) The sulforicinoleates or sulfoleates, Turkey red oils, obtained by the action of sulfuric acid on castor oil or olive oil.

(2) The soaps and oxy-soaps prepared by complete or partial saponification of castor oil.

(3) The chlorinated oils.

(*1*) *The Sulforicinoleates or Sulfoleates*** (*Red Oils*). These compounds are oxy fatty acids, formed by the reaction of sulfuric acid on castor oil, olive oil, or similar fatty acid. The sulfuric acid links on to the double

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* Depierre, Vol. II, p. 210 ff; George Hurst, "Textile Soaps and Oils," London 1904; Herbig, "Die Oele und Fette in der Textilindustrie," (Oils and Fats Used in Textile Processing) Stuttgart, 1929; Sauzay, *Tiba*, **1924**, 13; A. Beyer, "Les huiles sulfonées" (The Sulfonated Oils), *Tiba*, Nov. and Dec., **1929**, January, **1930**.

** Mueller-Jacob, *G.P. 17,264*—1881; *Dingler's Polytechn. Journal*, Vol. **229**, p. 544; Vol. **251**, p. 449, 547; Vol. **254**, p. 302; Grün and Corelli, *Z. f. angew. Chemie*, **1912**, 655; Beyer, *Tiba*, Nov., **1929**; Depierre, Vol. II, p. 220–228.

bonds of the unsaturated fatty acids, whereby the sulfuric acid ester of the corresponding hydroxy fatty acid is formed.

Olive oil was first used. Because of the difficulty encountered in its sulfonation, it was later substituted by castor oil. Recent studies contend that the sulfoleates are composed of complex mixtures of di- and triglycerides, of soaps of oleic and oxystearic acid, of the sulfoesters of these soaps, and of saturated fatty acids, as stearic and palmitic acid.

Turkey red oil* is generally the sodium or ammonium salt of sulforicinoleate. It is a mixture of triricine, of the corresponding ricinoleic acid, of dioxystearic acid, the sulfoester thereof and of di- and polyricinoleic acids (*G.P. 128,691*—M.L.B., 1902; *Fischer's Ber.*, **1902**, 515).

Schmitz and Toengs prepared oxyoleates in 1892 (*G.P. 60,579, 64,073*) by repeatedly sulfonating oleic acid or castor oil and subsequently saponifying the products. These oxyoleates, and the ricinoleic acid soaps and hydroxy fatty acid soaps which were invented by Liechti had great success in the printing and dyeing of Alizarine colors (Beyer, *Tiba*, Nov., 1929).

(*2*) *The Ricinoleates.* Liechti showed that a ricinoleic acid, neutralized 25%, gave a water-soluble soap, and recommended this acid oxy-soap for dyeing Turkey red. These acid ricinoleates of sodium or ammonium give results as good as the sulforicinoleates, and have the advantage of being free from sulfo groups. Red oils of this type are prepared by partial saponification of castor oil, or by treating freshly prepared ricinoleic acid with caustic soda or ammonia. It is important to use freshly prepared ricinoleic acid for this reaction, as an acid which has become thick by long storage does not yield a good quality soap. On the other hand, it is essential to employ only acid soaps derived from hydroxy fatty acids for the oil preparation of the material.

(*3*) *Chlorinated Oils.* Lauber suggested, in 1887, the use of chlorinated oils for oiling the goods obtained by treating olive oil or "huiles tournantes" with solutions of chloride of lime (Depierre, Vol. **II**, p. 229).

This matter was again taken up by G. Imbert, *G.P. 208,699, 214,154, 212,001, 206,305; F.P. 368,534*). He used chlorinated or oxychlorinated fatty acids as an initial material to prepare hydroxy fatty acids. The method of oxidizing oils by hypochlorites is covered by *B.P. 289,001* and *289,002* (Vidal) while E. Schmidt proposes to oxidize castor oil at 245°C with sodium persulfate (*G.P. 245,902; Chem. Ztg. Rep.*, **1912**, 97). These last mentioned products are not used in dyeing Alizarine Red, but they have detergent and emulsifying properties.

The above mordants are not mixed directly into the printing pastes, but are applied as pretreatments in concentrates of 5 to 10%.

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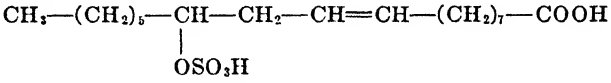
* Grün and Wetterkamp, *Z. f. Frb. Ind.*, **1909**, #8, 279; and **1908** #7, 375; *Chem. Zent.*, **1909**, I, 1749 and 67; Scheurer-Kestner and Juillard, *Bull. Mulh.*, **1891**, 53 and **1892**, 409 and 415; *Frb. Ztg.*, **1890**, 91, 337; and **1891**, 92, 275; Depierre, Vol. **II**, p. 233; Erban, *Frb. Ztg.*, **1915**, 187.

Instead of preparing the fabrics with sulfonated or saponified oils before dyeing with mordant dyestuffs, it is possible to simplify the operation, according to *B.P. 488,054, G.P. 666,464* (I.G.) by employing neutral oils, emulsified with non-ionic organic dispersing agents. These agents belong to the group of Emulphors, as, for instance, the product obtained by the reaction of ethylene oxide with high molecular hydroxy compounds. The cellulosic fabrics are padded in an emulsion of castor oil and Emulphor, impregnated with an aluminum salt mordant, and then dyed. The shades obtained in this way are fuller and brighter than by the former method. This process has the advantate of eliminating the necessity for removal of unfixed oil.

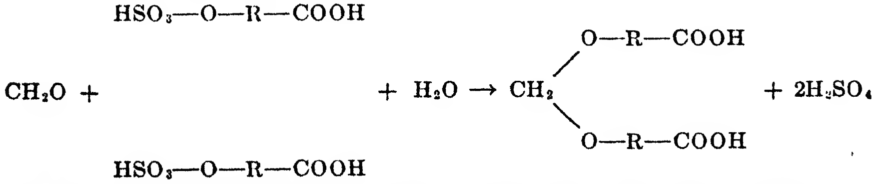
In order to simplify the process of printing mordant colors, chemists have long sought a method whereby the oil mordant could be incorporated in the printing paste without the formation of aluminum or calcium soaps. The first success in this direction came from Paul Wilhelm of the Konschin Company in Serpoukhoff (Russia). He prepared a stable emulsion of sulforicinoleic acid, which combined only very slowly with the mordant (*Bull. Mulh.*, **1909,** 69, 348). Gum tragacanth mixed with acetic and formic acids is added to freshly prepared sulforicinoleic acid. Another method, which met with instant acceptance by the practice, was invented by Tigerstädt* (M.L.B.). It depends on the use of the product Lizarol. H. Sunder (*Bull. Mulh.*, **1921**) claims that the fastness to soaping and crocking of Alizarine Red prints on oiled fabrics is superior to those obtained when using Lizarol in the print paste, but that this drawback is rectified by adding the tin salt of sulfooleic acid.

Lizarol is a condensate of ricinoleic acid and formaldehyde. Studies made by Tschilikin (*Frb. Ztg.*, **1914,** 420) indicate that castor oil undergoes saponification by concentrated sulfuric acid, without any change in the double bond of the chain:



$$CH_3—(CH_2)_5—\underset{\displaystyle OSO_3H}{\underset{|}{CH}}—CH_2—CH{=}CH—(CH_2)_7—COOH$$

The condensation takes place by the action of one molecule of formaldehyde on two molecules of this ester:



R = the unchanged radical, $CH_3—(CH_2)_5—\underset{|}{CH}—CH_2—CH{=}CH—(CH_2)_7—$

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* *G.P. 226,222 227,125* M.L.B.; *Frb. Ztg.*, **1914,** 420; *Rev. Gen. Mat. Col.*, **1909,** 343; *Frb. Ztg.*, **1911,** 12; *Rev. Gen. Mat. Col.*, Sept., **1910,** 38; **1930,** 357; *Fischer's Ber.*, **1910,** 475, 559.

Another solution to the problem lies in adding to the Alizarine Red print paste a fatty acid, combined with formaldehyde, sulfonated, then treated with persulfate at 200 °C, and finally with sodium chlorate. The resulting chlorinated oil gives a good red even on un-oiled goods.

Lizkowsky observed (*Bull. Mulh.*, Oct., **1927**) that the compound formed from aniline and ricinoleic acid is not precipitated by mordants at room temperature but only decomposed at elevated temperatures. Of this product 10 to 15% is added to the printing paste in the presence of lactic or formic acid. This "aniline soap" is prepared according to Lizkowsky's formula by saponifying castor oil with caustic. The castor oil soap is decomposed by hydrochloric acid and ricinoleic acid is formed which is then heated to the boil in the ratio of 300 parts to 95 parts of aniline until a clear oil, completely soluble in ammonia, is obtained.

See Table 9, page 477, for list of the fatty mordants.

MORDANT DYESTUFFS ON VEGETABLE FIBERS

Printing Methods for Mordant Dyestuffs

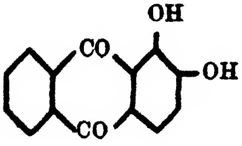
Mordant dyestuff prints have maintained a certain amount of importance to the present time, although in the last decades other types of printing colors have replaced them in many styles, especially those which do not require pretreatment of the fabric, as Rapid Fast colors, Rapidogen, Rapidazol and Neocotone dyestuffs.

Some standard styles, particularly fabrics for decorating purposes, as drapes, upholstery, etc., are currently printed with Alizarine dyestuffs, or with chrome mordant colors, such as Alizarine Blue, Anthracene Brown.

In some cases, particularly for export, cottons are printed with mordant colors alongside Rapidogens. The red, orange and navy shades are printed, for example, with Rapidogens, the green, tan and grey shades with chrome colors.

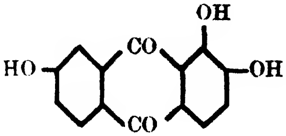
Prints with Aluminum Mordant. The following dyestuffs are used for prints with aluminum mordant:

Alizarine, dioxyanthraquinone. Bluish pink shades.

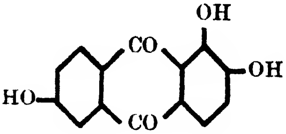


Trade names: Alizarine B2, V1, V2, IB (I.G., G.D.C.); Alizarine NB, N2B, N3B (Kuhlmann-Francolor)

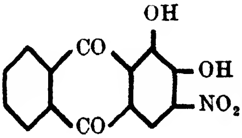
Anthrapurpurine, 1-2-7 trioxyanthraquinone (Perkins, 1872). Scarlet red.



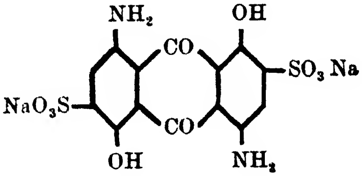
Trade names: Alizarine GD, SX (I.G., G.D.C.); Alizarine NA (Kuhlmann-Francolor)
Flavopurpurine, 1,2,6-trioxyanthraquinone. Scarlet red.



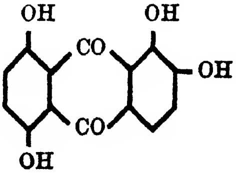
Trade names: Alizarine, GI, RG, VG, X, XG (I.G., G.D.C.); Alizarine NF (Kuhlmann-Francolor)
Nitroalizarine, 3-nitro-1,2-dioxyanthraquinone (Rosenstiehl, 1876).



Trade names: Alizarine Orange A paste (I.G., G.D.C.); Orange d'Alizarine N en pâte (Kuhlmann-Francolor)
Alizarine Sapphirol (R. E. Schmidt, 1897).

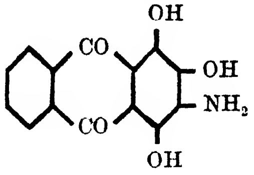


Trade names: Alizarine Sapphirol B (I.G., G.D.C.); Alizarine Light Blue B (Sandoz)
Alizarine Bordeaux, 1,2,5,8-tetraoxyanthraquinone (R. E. Schmidt, 1890).



Trade names: Alizarine Bordeaux B, Alizarine Cyanine (I.G.)

Alizarine Maroon, 3-amino-1,2,4-trioxyanthraquinone (amino purpurine).



Trade names: Alizarine Maroon W paste and powder (I.G.)

Brilliant shades can be obtained with Alizarine Red, Pink and Orange when these dyestuffs are printed in the presence of Turkey red oil. Castor oil yields brighter shades than olive oil but the quality of the white ground is impaired. When printing small patterns of low coverage, the application of a ricinoleate soap proved most favorable (Freiberger, *Frb. Ztg.*, **1912**, 85).

Good reds are not obtained with aluminum acetate and calcium acetate. The use of aluminum sulfocyanide, which hydrolyzes more slowly, is recommended.

The formation of dyestuff lakes is retarded in the presence of nonvolatile organic acids (oxalic, tartaric acid).

Two printing methods are in use: (1) printing on oil-prepared fabrics; (2) printing on nonprepared (white) fabrics with a paste containing a fatty compound (Lizarol A).

Printing on Oil-Prepared Material. For obtaining bright prints, fast to soaping, the material must be prepared with a Turkey red oil solution (5 to 7% of a 50% Turkey red oil).

It is advisable to use sodium or ammonium sulforicinoleate or sodium ricinoleate (see Table 9, page 477). The impregnated fabrics are thereupon dried in the hot flue, on the tenter frame or on dry cans lapped with cotton cloth.

Some formulas for Alizarine Red are given below:

Haller's Formula

150 gm	Alizarine paste
630 gm	acid starch-trag. thickener
60 gm	castor oil
30 gm	aluminum acetate 12° Bé
30 gm	aluminum nitrate 15° Bé
28 gm	tin thiocyanate 9° Bé
28 gm	calcium thiocyanate 24° Bé
10 gm	calcium acetate 15° Bé
34 gm	water
1000 gm	

Formula Used in a Moscow factory

474 gm starch-trag. thickener
26 gm castor oil
130 gm Alizarine GF 20%
90 gm tin citrate 20%
50 gm calcium acetate 15° Bé
90 gm aluminum sulfoacetate 15° Bé
70 gm calcium sulfoglycerate
70 gm sodium ricinoleate

1000 gm

Formula Used in an Alsatian Plant

100 gm wheat starch, *pasted with*
150 gm potassium sulfoglycerate 20° Bé, *and*
70 gm acetic acid 80%
Add
215 gm thickening, gum Shiraz, thin boiled
30 gm Alizarine B2 40%
190 gm Alizarine 5G 20%
30 gm huile tournante
The entire mass is boiled, cooled down and these ingredients added:
150 gm aluminum acetate 12° Bé
50 gm tin sulforicinoleate
15 gm calcium acetate 20° Bé

1000 gm

The lakes of Alizarine with aluminum and calcium have a bluish tinge. By adding tin mordants, the shade is changed to yellowish red.

Some formulas for Alizarine Pink are:

600 gm acetic acid starch-trag. thickener
40 gm Alizarine V new 20%
50 gm water
100 gm aluminum thiocyanate 10° Bé
40 gm calcium acetate 15° Bé
30 gm tin oxalate 15° Bé
130 gm water
10 gm chlorinated oil

1000 gm

Formula Used by Scheurer-Lauth et Cie, Thann, Alsace

100 gm Alizarine B2 40%
775 gm thickener gum Shiraz
25 gm acetic acid 80%
100 gm aluminum thiocyanate 10° Bé

1000 gm

Formula Used in the Zündel factory in Moscow

100 gm wheat starch
100 gm water
100 gm acetic acid 6° Bé
172 gm tragacanth mucilage
84 gm Alizarine for Red 20%
84 gm Alizarine for Pink 20%
65 gm castor oil
Boil; after cooling add
72 gm calcium acetate 15° Bé
150 gm aluminum nitrate 15° Bé
38 gm stannous oxalate
35 gm aluminum acetate 13° Bé

1000 gm

The most serious drawback in printing Alizarine Reds and Pinks is the dulling of the shade by iron salts, which can be present in the water used, or dissolved by the action of the acid printing pastes on the steel doctor blades. Chemists worked for a long time to eliminate the deleterious effect of iron salts. Persoz suggested the addition of tin compounds to the printing paste.

Oscar Scheurer found that the defect could be avoided by the addition of 150 to 200 gm of aluminum hydroxide gel per kg of print paste (1895). This method has proved successful and was used in the Scheurer-Lauth Plant. The formula is as follows:

Stock Color

200 gm Alizarine V1 new 20%
100 gm aluminum sulfate 10° Bé
675 gm gum thickening
25 gm acetic acid 6° Bé

1000 gm

Reduction Paste

917 gm gum thickening
100 gm china clay 1:1
150 gm aluminum hydroxide gel
25 gm acetic acid
8 gm sulfuric acid 1:10

1200 gm

Albert Scheurer observed (*Bull. Mulh.*, **1925**, report under seal, 1916) that aluminum chloride is transformed on the fiber into an oxychloride which prevents the formation of Alizarine Violet (the iron compound). Thus by adding aluminum oxychloride to an Alizarine Pink print paste, the shade change to violet is completely prevented, even when ferrous acetate is mixed with the paste.

As aluminum oxychlorides, $Al_2Cl_4(OH)_2$ or $Al_2Cl_3(OH)_3$ can be used. Aluminum oxychloride can be prepared as follows:

600 gm	aluminum hydroxide 15% gel
240 gm	hydrochloric acid 21° Bé
160 gm	acetic acid 80%
1000 gm	

Of this solution, 5 to 20 gm are added per kg of print paste, and red and pink prints can be obtained which are insensitive to iron salts.

Aluminum sulfocyanide has been suggested for the same purpose. Besides being rather expensive, it also hydrolyzes easily in steaming, liberating sulfocyanic acid which may tender the fiber.

Other suggestions to prevent contamination have been the use of brass blades instead of steel (which innovation has not met with approval by the printers), or a coating of shellac on the steel blade. A modern approach would be the coating with polyvinyl resins, or chromium plating of the blades.

Nitroalizarine has a high affinity for the metal mordants. Readily hydrolyzed salts, such as aluminum acetate, thus cannot be used as a mordant for it, as the print pastes would become unserviceable after 24 hours. Aluminum tartrate hydrolyzes slowly, and is therefore preferred, but it often tenders the fiber. The problem was solved by the use of aluminum formate together with calcium formate (A. Scheurer, *Bull. Mulh.*, **1911,** 153).

Alizarine Sapphirol (Alizarine Light Blue B) should not be printed on oiled material. The following formula has been proposed:

80 gm	Alizarine Light Blue B (Sandoz)
300 gm	hot water
100 gm	resorcinol 1:1
273 gm	gum thickening
107 gm	barium sulfocyanide
140 gm	aluminum sulfate 1:1
1000 gm	

Printing on Unoiled Material. While the preparation of the goods with fatty product is not expensive, it is nevertheless an extra operation and requires drying. For this reason ways have been sought to incorporate the fatty mordant in the printing paste. Paul Wilhelm (see page 423) developed a method whereby sulforicinoleic acid is added directly to the paste, together with a mixture of formic and lactic acids to prevent precipitation of the fatty acid by the metal mordant.

Print Formula of P. Wilhelm

150 gm starch
73 gm water
150 gm gum tragacanth
45 gm acetic acid 6° Bé
135 gm Alizarine GFX 20%
23 gm oleic acid
23 gm tin sulfoleate
115 gm aluminum nitrate 15° Bé
35 gm tin oxalate
70 gm calcium acetate 15° Bé
20 gm lactic acid 50%
55 gm formic acid 92%
90 gm sulforicinoleate composition*
16 gm sodium acetate

1000 gm

* *Sulforicinoleate composition:* 450 gm freshly precipitated sulforicinoleic acid are mixed with 100 gm acetic acid and thickened with 450 gm gum tragacanth. A white emulsion results, which is stable. The print paste needs a long steaming for complete fixation.

A solution to the problem was found in the product, Lizarol D, which gives reliable results. This was offered by Höchst (*Rev. Gen. Mat. Col.*, **1909,** 343; **1910,** 38; *G.P. 226,222, 228,125; Frb. Ztg.*, **1911,** 12).

Lizarol D is a condensate of formaldehyde and sulforicinoleic acid. It can be added to the print paste containing the dyestuff and mordant without danger of precipitation of insoluble aluminum or calcium sulforicinoleates, and without premature dye-lake formation. The I.G. offered Direct Red oil, a similar product. Bright red prints are obtained on un-oiled goods if 30 to 40 gm of the product are added per kg of print paste.

Another chemical agent was proposed in *Bull. Mulh.*, **1912,** 8, a chlorinated oil sold under the name Elisol. It is prepared by heating an oil or fatty acid with formaldehyde in the presence of persulfate to 200°C. The fatty acid sulfonate resulting is further treated with sodium chlorate. Excellent prints are obtained using this product as addition to the printing paste.

Lizkowsky describes (*Bull. Mulh.*, Oct., **1927**) a product which is intended to be added to the Alizarine print pastes. It is a reaction product of ricinoleic acid and aniline, and is used on unoiled goods (Langer, *Bull. Mulh.*, **1932,** 177; Ermakoff, *Rev. Gen. Mat. Col.*, Sept., 1930).

Steam Alizarine Red on Unoiled Material (*Haller*)

567 gm acetic acid starch tragacanth thickener
150 gm Alizarine D2NG paste 20%
135 gm aluminum thiocyanate 12° Bé
45 gm aluminum acetate 12° Bé
3 gm tartaric acid

50 gm calcium acetate 18° Bé
10 gm tin oxalate 16° Bé
40 gm Lizarol D conc.

1000 gm

Alizarine Pink (*Haller*)

600 gm acetic acid starch trag. thickener
5 gm Alizarine V new 20%
365 gm water
15 gm aluminum thiocyanate 12° Bé
3 gm calcium acetate 18° Bé
12 gm Lizarol D conc.

1000 gm

Formula Used in a Russian Plant

524 gm starch-trag. thickener
84 gm Alizarine for Red (M.L.B.) 20%
89 gm Alizarine for Pink 20%
135 gm aluminum thiocyanate 12° Bé
35 gm aluminum acetate 13.5° Bé
10 gm tin oxalate
3 gm tartaric acid
60 gm calcium acetate 15° Bé
20 gm Fuchsine S solution 10%
40 gm Lizarol D conc.

1000 gm

Reduction Gum

985 gm starch-trag.
15 gm Lizarol D conc.

1000 gm

The stability of the print paste can be increased by adding 20 to 40 gm of resorcinol per kg.

H. Sunder (*Bull. Mulh.*, **1921,** 137) found that Alizarine Red prints, produced according to the Lizarol method are inferior to the normal prints on oil-prepared fabrics as far as the brightness of the shades, the fastness to soaping and to crocking are concerned. This drawback can be eliminated by adding 15 gm of tin sulfoleate per kg of printing paste. A. Scheurer and P. Wilhelm (*Bull. Mulh.*, **1893,** 95; **1908,** 78) had already noticed this fact.

H. Sunder suggested, furthermore, using tin lactate instead of tin oxalate to avoid tendering of the fiber.

Garance (*Dyer*, **1905,** 5) proposed the use of lactates in general for printing Alizarine Red and Pink. The lactates have the effect of retarding the lake formation with the result that more uniform and complete fixation of the dyestuff is obtained. The pastes containing lactates are stable, and the prints do not mark off or bleed on washing (*Bull. Mulh.*, **1921**, 137). The red shades are bright, especially of the yellower reds.

The following formula for Alizarine Red was developed in 1918 by L. Diserens in Russia, and proved practicable.

450 gm starch-trag. thickener
40 gm Lizarol D conc.
25 gm castor oil
150 gm Alizarine Red 20%
130 gm aluminum lactate 19° Bé (4% Al_2O_3)
100 gm tin lactate 25° Bé (4.1% SnO)
25 gm aluminum acetate 13.5° Bé (5.2% Al_2O_3)
50 gm calcium thiocyanate 15° Bé (7.8% CaO)
1000 gm

Another product which is intended to replace the fatty mordants used in preparing the material is sulfoglycerate, recommended by Havraneck. It is obtained by treating glycerin with H_2SO_4, 66° Bé, and neutralizing with chalk. It has been used with advantage in printing Alizarine Reds.

Steaming and Finishing. The printed goods are first aged in the rapid ager to remove the major part of the acids, then they are steamed in the cottage steamer for one hour. Continuous steaming is advisable for large runs, and as many as five lines of goods can be run through at one time.

After steaming, the goods are washed in rope form or in the continuous washer in a bath containing 20 to 40 gm of precipitated chalk per liter at 60 to 80°C, rinsed, soaped and if necessary, slop padded with chloride of lime and dried on the cans.

The brilliance of the reds and pinks is enhanced by the addition of stannous chloride to the soap liquor. Such a soap is prepared as follows:

5 gm olein soap, *or*
2 gm Marseille soap
1 gm soda ash
1–1½ gm stannous chloride
per liter

The prints are treated ½ hour near the boil.

Print of Aluminum Mordant and Subsequent Dyeing. This style has been produced in great quantities because of its excellent fastness properties. It follows the old Turkey red style in procedure.

E. Knispel in Warnsdorf, Czechoslovakia, proposed a simplified development which has proved practicable: A thickened solution of aluminum acetate with added sightening dyestuff is printed and the cloth hung overnight in a warm room, then treated repeatedly in 400 l of water containing 100 kg of dung and 25 kg of chalk, then thoroughly rinsed. It is then dyed on the jig with 3 to 4% Alizarine V new 40% paste and 2.5% Turkey red oil. The dyeing is started at room temperature, warmed after ¾ hour to the boil and dyeing continued ½ hour, finally washing well. (Compare also "Tabular Synopsis," Bayer Co., 1927, part 2.)

Prints with Zinc Nickel and Iron Mordants. These mordants are used only for certain dyestuffs. Alizarine Blue S yields blue shades with zinc and nickel mordants which are brighter than with chromium, but which, however, are not as fast to light or washing. Fast Printing Green (Viridone FE) forms interesting prints with nickel and cobalt salts, but is generally printed with ferrous sulfocyanide. The oxyphthaleins like Eosine, the Alkali Blues and some basic dyestuffs can be fixed with chrome mordant.

Alizarine Blue S

On Zinc-Nickel Mordant	*On Nickel Mordant*
40 gm Alizarine Blue S	60 gm Alizarine Blue S
250 gm cold water	200 gm cold water
600 gm starch-trag. thickening	540 gm tragacanth gum 6%
50 gm zinc acetate 20° Bé	200 gm nickel acetate 12° Bé
50 gm nickel acetate 12° Bé	
10 gm sodium bisulfite	1000 gm
1000 gm	

Viridone FE

On Iron Mordant	*On Nickel-Cobalt Mordant*
100 gm Viridone FE	100 gm Viridone FE
100 gm water	100 gm boiling water
600 gm starch trag. thickening	440 gm starch trag. thickening
100 gm acetic acid 6° Bé	166 gm nickel acetate 12° Bé
100 gm iron acetate 20° Bé or iron thiocyanate 10° Bé	194 gm cobalt acetate 12° Bé
	1000 gm
1000 gm	

Of the dyestuffs fixed with iron mordant, Alizarine Violet was the most important.

Alizarine Violet

100 gm Alizarine V new 20%	70 gm Alizarine V new 20%
752 gm starch-trag. thickener	735 gm trag. thickening 60%
100 gm ferrous pyrolignite	70 gm acetic acid 6° Bé
23 gm calcium acetate 16° Bé	40 gm ferrous thiocyanate 11° Bé
1 gm Methyl Violet 1% solut.	25 gm barium thiocyanate 12° Bé
24 gm water	60 gm formic acid
1000 gm	1000 gm

The straight Alizarine Violet is rather dull but the shade can be brightened by adding very small amounts of Methyl Violet. Replacing the calcium salts with barium thiocyanate also helps to brighten the shade.

Cutch or catechu can be fixed by short ageing when using copper salts as oxidants. By this method, catechu can be printed alongside aniline black.

Formula

120 gm	cube catechu
150 gm	water
35 gm	acetic acid
70 gm	ammonium chloride
505 gm	starch-trag.
40 gm	copper nitrate 48° Bé
80 gm	copper acetate 15° Bé
1000 gm	

The prints are aged 4 minutes in the rapid ager, rinsed in bichromate and soda ash solution, rinsed well and soaped.

Prints with Chrome Mordants. Most of the mordant dyestuffs can be fixed with chromium acetate. Their chemical constitution varies considerably, so that it is difficult to classify them according to their origins. The following brand names are used: Chrome and Chrome Fast dyestuffs; Gallo, Chromoxan, Alizarine, Anthracene (G.D.C., I.G.); Modern, Novochrome (D. & H., Carbic).

The chrome colors are generally printed on un-prepared cloth, although the shades are much brighter on oiled material. The printed goods are often aged first for 5 minutes, then steamed 1 to 1½ hours in the cottage steamer, chalked, washed and soaped.

Printing Formulas

Alizarine Brown

40–50 gm	Alizarine Brown powder	250 gm	Alizarine Brown 20% paste
200–300 gm	water	40 gm	borax
40–50 gm	acetic acid 6° Bé	100 gm	acetic acid 6° Bé
620–450 gm	starch-trag. thickening	300 gm	starch-trag. thickening
100–150 gm	chromium acetate 18° Bé	20 gm	rapeseed oil
1000 gm		200 gm	chromium acetate 18° Bé
		1000 gm	

Modern Blue BB

42 gm	Modern Blue BB
182 gm	water
6 gm	Hydrosulfite NF 1:2
500 gm	acetic acid starch-trag. thickening
20 gm	glycerin
20 gm	formic acid
100 gm	urea: water 1:1
130 gm	chromium acetate 18° Bé
1000 gm	

A method of printing mordant colors without steaming is described in *G.P. 742,752* (D. & H.). The dyestuff is dissolved in an appropriate solvent, (such as dioxydiethylene sulfide, monoethyl glycol) and urea, and mixed with a nitrocellulose lacquer. The mixture is stirred into an aqueous solution of chromate and an agent which splits off acid at elevated temperatures, such as ammonium thiocyanate or diethyl tartrate. A homogeneous paste results which is printed and dried. The lake is formed in a finely divided form. The prints are fast to soaping and crocking.

New Methods for Fixing Chrome Colors by Short Steaming. The advent of Rapid Fast and Rapidogen dyestuffs and in general the introduction of the insoluble azo dyestuffs raised the problem of the long steaming time required of the chrome mordant colors. Colorists were anxious to extend their selection by printing the bright azo dyestuffs alongside the chromes. Since a long steaming is generally detrimental to the Rapidogen colors, short fixation methods were sought for the chrome colors.

Durand and Huguenin studied this problem and as a result of their systematic research, succeeded in developing printing methods by which the chrome dyestuffs might be fixed in shorter steaming time. At the same time, methods were found by which gum thickenings could be used with the chrome mordant colors on silk and rayon without producing a harsh hand.

The following patents of D. & H. describe the addition of urea to the print pastes as a means of shortening the time necessary for steaming. *U.S.P. 1,942,774* (1929), *B.P. 318,469*, *F.P. 680,832*, *G.P. 583,204*, *528,262*. The product "Fixierer CDH"* or Fixer CDH, largely urea, was offered by Durand and Huguenin for this purpose. It has the effect of promoting the chrome lake formation, so that the dyestuffs may be fixed in 6 to 8 minutes of ageing, instead of the usual hour's time required for good fixation in the absence of urea. However, the depth of shade resulting from this longer steaming cannot be attained in the shorter time. Comparative tests further indicate that the fastness to light and scouring is not as good as with longer steam treatment.

The addition of urea has no effect on the results in the printing of Alizarine dyes (Alizarine Red, Nitroalizarine, Anthracene Brown, etc.) but gives interesting results with Chromazurine ND, E and HB new, Gallophenine P, Ultracyanol B and most Novochrome dyes of D. & H. The use of urea for improved fixation of chrome colors was known for some time, as Wiazmitinow states in *Bull. Fed.*, **1,** 299. The Chrome Red pastes of Bayer Co. contained a certain amount of urea, and D. & H. themselves recommended adding urea to chrome dyes used as colored resists under aniline black.

Later it was observed that the action of urea is intensified by addition of certain high-boiling phenols and alcohols, such as furfuryl alcohol or

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* *Mell.*, **1933,** 412; von Niederhäusern, *Mell.*, **1934,** 362; *Rev. Gen. Mat. Col.*, **1931,** 146; **1934,** 111; **1936,** 202. See Table 10, page 479.

derivatives of glycol. In *F.P. 769,171* and *G.P. 601,860* (1933) the addition of pyrogallol is recommended, or other dioxy aromatic compounds, as in the following example:

20 gm	chrome dyestuff
200 gm	water
600 gm	starch-trag. thickening
40 gm	urea
20 gm	phenol
20 gm	furfuryl alcohol
100 gm	chrome acetate 20° Bé
1000 gm	

According to *U.S.P. 2,018,436*, *B.P. 412,391*, *F.P. 755,351*, *G.P. 623,939* (1932) of D. & H., many chrome mordant dyes such as Chromocitronine, Chromorhodine, etc. can be fixed in 6 to 12 minutes ageing by the addition of non-volatile organic acids (tartaric, oxalic acid) to the print paste. These acids should be combined with the chrome cation as chromium tartrate or chromium oxalate, or with ammonia (ammonium oxalate).* These patents refer to the product sold by D. & H. as Fixierer WDHL (Fixer WDHL) (Carbic), which is particularly recommended for printing woolen fabrics.

The use of ureides, mixed with heterocyclic bases has also been pointed out. Such a composition, which is recommended for fixing chrome mordant dyes in short steaming and with good yield, is produced by L. Z. J. and called Debechromol A.

F.P. 865,067 (I.G.) discloses that mordant dyestuffs can also be fixed in short ageing by adding carboxylic acid amides or nitriles to the print paste. Examples given are ethyl thioglycollic acid amide, and simpler compounds such as benzamide, acetamide or formamide. The product Dissolving Salt CN, offered in recent times, and which it is claimed will fix chrome mordant colors in short ageing alongside Rapidogens or Indigosols, is a mixture of 60% formamide and 40% urea.

Its use is typified in the following formula:

30 gm	dyestuff
30 gm	Glyecine A
20–80 gm	Dissolving Salt CN
340–140 gm	water
450–550 gm	starch-trag. thickening
30–70 gm	acetic acid 50%
100 gm	chromium acetate 20° Bé
1000 gm	

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* von Niederhäusern, *Mell.*, 1934, 362; *Wengraf's Ber.*, 1934, 15.

Fabrics printed with the chrome colors alone are aged 4 to 8 minutes, rinsed and soaped. Where Rapid Fast or Rapidogen dyestuffs are present the goods are acid-aged 4 to 8 minutes, and then soaped.

Another process by which the chrome color can be printed on cotton, rayon and mixed fabrics and fixed with short steaming is the Chromate DH process.

In this method the mordant is Chromate DH, which according to information given the author is ammonium chromate. The advantages of the method lie in the excellent stability of the print pastes and in the short ageing time. The possibility of printing the chrome colors alongside Rapidogen colors is particularly important. The tendency of chrome colors to form halos where they touch the Rapidogen or Rapid Fast colors is overcome when they are fixed with the mordant Chromate DH.

Chromate DH* gives especially good results with chrome mordant dyestuffs which are printed alongside vat colors. The use of chromium acetate as mordant prevents normal fixation of vat colors printed in the same pattern. This drawback can be avoided by using Chromate DH as mordant instead.

Printing Formula with Chromate DH

20 gm	dyestuff
360 gm	water
550 gm	starch-trag. (neutralized w'th ammonia)
20 gm	ammonium sulfocyanide 1:1
40 gm	Chromate DH 1:2
10 gm	ammonia
1000 gm	

The printing of silks and rayons with gum thickening without impairing the soft hand of these fabrics has long been an important problem with chrome mordant colors. The metal mordants, such as chromium acetate or formate, coagulate the natural gums, imparting a harsh touch to the printed areas. However, these gums have proved best for sharpness of detail and levelness, so that compatibility of dyestuff and gum was sought.

Durand and Huguenin proposed in *U.S.P. 1,942,774*, *F.P. 744,137* and *G.P. 583,204*—1932, to add urea, glycerin and ammonium thiocyanate to printing pastes containing chrome mordant dyestuffs, chrome acetate and gum thickener. The ready made mixture of the three ingredients mentioned here is sold by Durand and Huguenin under the trade name Dehagen S.

The softening action of Dehagen S is, however, satisfactory only on prolonged steaming. In short steaming or ageing processes, it is far from

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* *Mell.*, 1939, 585; *G.P. 672,328; B.P. 481,854* (D. & H.). **See Table 10, page 479.**

sufficient. It has been found, however, that the coagulation of the gum thickening is prevented, and the soft hand of the fabric preserved, when chrome salts of such organic acids as lactic or tartaric are used, to which urea is added.

Durand and Huguenin patents referring to this process are *B.P. 435,701*, *F.P. 770,437*—1934, *G.P. 623,648*, *623,939*, *631,923* (see also *Bull. Fed.*, **III,** 197, 312; D. & H., "Neue Wege zum Fixieren von Chromfarbstoffen", *Mell.*, **1939,** 584). These patents cover the manufacture and application of "Universal Mordant 9333", which is composed principally of chromium lactate and urea. Here also the soft hand of the prints can be obtained only by an hour's steaming, and the color yield is inferior to that obtained in normal printing methods with chromium acetate. Moreover, the fixation on cotton is poor. *G.P. 623,648* mentioned above recommends the following formula:

20 gm	chrome dyestuff
50 gm	urea
306 gm	water
600 gm	gum arabic 1:1
24 gm	chromium lactate (Cr_2O_3 content 14.5%)
1000 gm	

Later D. & H. offered improved Universal Mordants conc. and extra conc. which have some advantages over the former product. However, the colors require a longer steaming time for good fixation. With universal Mordant RC, a recent offering of D. & H., the disadvantages of the earlier mordants are claimed to have been overcome.

Some interesting experiments in this line were carried out by the author in 1934. Prints of softness comparable with those obtained with Universal Mordant 9333 were the result. It was noted that the coagulation of gum thickeners by chromium mordants was avoided by the addition of the condensation products of triethanolamine with acetic, tartaric or oxalic acid to the print paste. Silk and rayon fabrics so printed were soft after 45 minutes' steaming. Salts of pyridine bases, as pyridinium lactate, also possess the property of preventing the coagulation, while the softening effect can be improved by adding phenols (as phenol, resorcinol, cresol).

The Perchrome colors of D. & H. Carbic, are selected chrome dyestuffs which fix readily in short steaming and therefore are adaptable for printing alongside vat colors, Rapidogens, etc.

Another series of patents granted to D. & H. is related to methods of brightening mordant dyestuff by blending them with basic dyes: *U.S.P. 2,131,320*, *B.P. 484,836*, *F.P. 817,501*, *G.P. 656,879*, *Aus.P. 153,802*. In order to fix the basic color, and prevent bleeding in the rinsing operation, it is suggested to add 3% of the sodium salt of an oxycarboxylic acid (lactic, glycollic, or tartaric acid) to the print paste containing chromium lactate and urea.

For example:

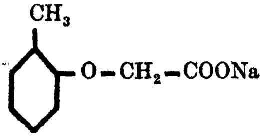
30 gm	dyestuff
200 gm	water
30 gm	sodium tartate
640 gm	gum arabic 1:1
40 gm	chromium lactate (Cr_2O_3–14.7%)
60 gm	urea
1000 gm	

The printed goods are aged one hour and rinsed in cold water.

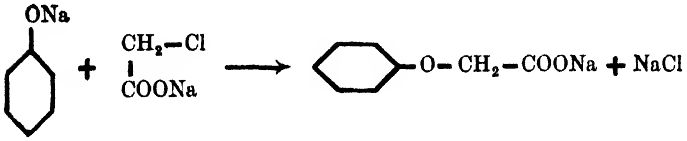
In *G.P. 683,952* (D. & H. 1937) a method of printing the chrome colors with short steaming is recommended. The print paste contains, besides dyestuff, the chromium salt of a lower aliphatic acid and a soluble salt of an aliphatic acid (for instance, sodium formate). By adding urea, phenol or a similar agent, greater stability is obtained. Prints are fixed in short ageing with soft hand. As example, the print paste contains chrome color, gum thickening, chromium formate, sodium formate, urea and triethanolamine formate.

A modification was proposed by D. & H. in *G.P. 732,682* (1943). The print paste contains dyestuff, chromium salt of a lower aliphatic acid (as formate), soluble salt of an organic acid (as sodium formate) and organic acids (or their salts), which form chromium complexes, as lactic, tartaric, glycollic, phthalic or citric acids. In this case it is claimed soft prints are obtained without using urea, which is contrary to disclosures in the earlier *G.P. 623,939* and *631,923*.

In the same line of thought, the I.G. patents *B.P. 543,348*, *S.P. 190,986*, *F.P. 801,765* and *G.P. 645,468* (*Rev. Gen. Mat. Col.*, **1938,** 346, *Bull Fed.*, **III,** 197, 311) find that coagulation of the gum thickening can be prevented by the addition of aminoacetic acid (glycocoll), hydroxyacetic acid (glycollic acid), or substitution products thereof, for example, the sodium salt of cresoxyacetic acid (tolylglycollic acid) or the sodium salt of phenyl oxyacetic acid (phenyl glycollic acid), to the printing paste. These acids are prepared by the reaction of chlorinated aliphatic acids with aromatic compounds such as phenol or cresol

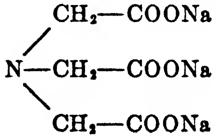


Sodium o-cresoxyacetate or sodium o-tolyl glycollate



Sodium phenyl oxyacetate or sodium phenyl glycollate

These compounds are added at the rate of 5 to 10% to the print paste, or used for pasting up the dyestuff. All chemical compounds containing the group $=\mathrm{N}-\mathrm{CH}_2-\mathrm{COO}-$ are within the scope of this invention, and it therefore includes such complicated derivatives as the sodium salt of triglycol amino acid (sodium nitriloacetate), sold as Trilon A.



Trilon A

This method yields better results as regards softness of the prints and stability of the pastes than that described in *F.P. 770,437* (see above).

In order to avoid coagulation of the gum thickening in a print paste of chrome colors and chromium acetate, *B.P. 499,377* (I.C.I.—1937) suggests the addition of 3% succinic or phthalic acid or their water-soluble ammonium or monoethanolamine salts. The printed goods are dried, steamed one hour and finished as usual.

Discharge and Resist Methods for Mordant Colors

These methods have been known for a long time. Persoz described a great many processes for discharges and resists, some of which are still used. But these styles have been for the most part supplanted by the development of the azo dyestuffs. The discharge style on Turkey red, called Koumatsch, was very popular with the peasant class in Russia and is probably still manufactured at present.

The discharge methods can be divided into five groups:

1. Citric acid discharge on mordanted material. (Haussmann, 1825).
2. Resists under Alizarine and chrome mordant print colors: citric acid and chlorate resists, half-resists with pyrophosphate.
3. Discharges on Turkey red.
4. Chlorate discharge on paddings of chrome mordant dyestuffs.
5. Discharges with sulfoxylate-formaldehyde.

The citric acid resist was used in manufacturing the red-white style under Alizarine Red blotch, which had a tremendous vogue for years. Much work was done in this field by such investigators as Haussmann, D. Koechlin, Schlieper and Baum, Schmidlin, etc.

From these investigations new processes of classic importance were developed. In chronological order these are

(a) Chromate discharges. Persoz, Vol. **III,** p. 231.
(b) Chlorate discharges (presse écossaise, England, 1810) Persoz, Vol. **III,** p. 232.
(c) Acid discharge (cuve décolorante, D. Koechlin, 1811) Persoz, Vol. **III,** p. 236–8, Depierre, Vol. **III,** p. 439–446.
(d) Discharge by alkali method (Schlieper and Baum, 1883; Triapkine, *Rev. Gen. Mat. Col.*, **1898,** Schmidlin, *Bull. Mulh.*, **1884,** 49).
(e) Hydrosulfite NF discharges, colored discharges with vat colors (Manual, Höchst, 1906; *G.P. 173,878, 179,454; Fischer's Ber.*, **1906,** 438; Ivanoff, *Bull. Mulh.*, **1913,** 87). Discharges with Hydrosulfite NF with silicate and caustic soda.

As already mentioned, this style has been almost entirely superseded by the discharge style on insoluble azo dyes.

Citric Acid Resist. Mordanted goods were first discharged by J. M. Haussmann in Lagelbach near Kolmar (Alsace) in 1825. The process consisted of printing an organic acid (oxalic, tartaric or citric) on a fabric prepared with aluminum, chrome or iron mordant. After storing for some time, the mordant is fixed and the goods dyed in a suitable dyestuff solution.

This style was manufactured for a long time with considerable success. Some of the formulas used are given here.

Black-White Print on Alizarine Garnet (Formula from Russia)

The goods are padded with the solution

50 l	aluminum acetate 9° Bé
30 l	pyrolignite of iron 16° Bé
20 l	water

and dried in the hot flue, then overprinted with an aniline black print paste and citric acid discharge.

Citric Acid Discharge

300 gm	citric acid crystals
130 gm	water
70 gm	caustic soda 38° Bé
500 gm	starch thickening
1000 gm	

After drying, the goods are aged 4 minutes in the rapid ager. To fix the mordant the material is treated first open width at 55°C, then in the rope form at 65°C in dung and chalk, and dyed at 60°C with

150 gm	Fuchsine
750 gm	nutgall extract 30° Bé
500 gm	quercitron bark extract 30° Bé
5100 gm	Alizarine 2A 20%

(recipe for 70 kg cotton cretonne)

The material is washed, steamed, and bleached lightly if necessary. The goods were often dyed cream color with Chrysophenine for maize, black and garnet combinations.

Logwood black can be resisted in a similar way. The logwood was dyed with added quercitron bark and nutgall extract in the presence of glue and chalk.

Chromium-mordanted material can be reserved in white and colors, and the method was used to obtain many varied colored effects.

By using mixed iron and chrome mordants it is possible to dye fast brown and blue shades according to a process described in *G.P. 97,686* (Rolffs & Co.).

Albert Scheurer disclosed in *Bull. Mulh.*, **1919**, 228, a discharge method using zinc lactate. Ammonium citrate is a good discharging agent for aluminum-, and chromium bisulfite mordants, and chrome mordants can also be discharged with a composition containing citric acid and sodium bisulfite. Calcium citrate can at the same time be used as a resist under aniline black and as a white discharge on mordanted fabrics (*Mell.*, **1926,** 615).

Mordant Resist. These resists are produced by printing a chlorate or citric acid paste on white cloth. The method is used principally for obtaining the so-called "Effets frappés", a kind of half-resist.

A citric acid paste is preprinted, for example, on white goods in stripes, dots or other geometric patterns. After drying, they are overprinted with a mordant dyestuff in another pattern, then aged and washed. The half discharge or resist effects are obtained where the patterns overlap, as here the mordant dyestuffs are only partly fixed. By adding tartar emetic to the citrate resist, basic colors can also be resisted.

Analogous effects are obtained by using a chlorate-ferrocyanide resist paste in place of the citrate paste. The overlapping mordant colors are partly destroyed by the oxidation during the ageing operation. Use of zinc lactate for the *effets frappés* was proposed by A. Scheurer. A similar style is produced by overprinting aged and washed prints with a chlorate discharge.

The citrate resist was popularly used to produce the red-white style under Alizarine Pink blotch print. The style has been known for a long time, as it was described by Persoz in Vol. II, p. 286, and has proved its worth by its good all-round fastness. It has been manufactured in great quantity, and was very popular with the Russian peasantry. It was often given a chintz finish. The procedure is as follows:

Alizarine Red is printed on white goods alongside the following resist:

140 gm	china clay
80 gm	water
160 gm	citric acid
388 gm	starch-trag. gum
2 gm	Indigo Carmine
230 gm	caustic soda 30° Bé
1000 gm	

After drying, the prints are overprinted with an over-all blotch with Alizarine Pink, treated in an ammonia solution, steamed twice one-hour, and soaped on the reel. The resulting print is red and white on a pink background. The same style is applied on iron-mordanted Alizarine Blue or Bordeaux.

Half Resists under Mordant Dyes. This style has been developed by Felix Binder (see Depierre, Vol. V, p. 581). It is based on the property of sodium pyrophosphate to prevent the fixation of chromium salts on fabrics. The goods are prepared with chromium sulfoacetate, dried and printed with a citric acid discharge printing paste and a "half-resist" containing sodium pyrophosphate (80 gm per kg). The material is aged and passed through a soda-ash solution at 60°C, dried and dyed as usual. Similar effects can also be obtained by printing sodium tungstate, sodium phosphate, tin lactate and especially sodium metaphosphate (Calgon) instead of sodium pyrophosphate.

Discharges on Turkey Red. This style occupied an important place in the textile printing art for a long time. It has been studied and developed for more than a century, and has had the attentive research of such chemists as Koechlin, Schlieper and Baum, Schmidlin and others. It has been popular in recent times for the manufacture of handkerchiefs, scarves and blouse material for the peasant trade, in white, yellow, blue and green combinations. In Russia the process follows the alkaline discharge methods developed by the Baranoff Company in Iwanowo-Wosnessensk.

The different methods by which Turkey red can be discharged have already been enumerated. One of the oldest is the discharge operation in the hypochlorite vat—*enlevage à la cuve décolorante*—invented in 1811 by D. Koechlin (Persoz, Vol. III, p. 236–8; Depierre, Vol. III, p. 439–446) and called the acid process.

The first trials were made by printing a thickened solution of calcium hypochlorite, then souring. This method proved to have too many inconveniences. The procedure was reversed, and was found to be practicable.

The discharge paste contains the acid. A typical formula is:

100 gm tartaric acid sol. 38° Bé
100 gm dextrin

The prints, after drying, are conveyed through a 5° Bé solution of chloride of lime in the quetsch, and washed.

Lactic acid was found to give equally good results by Düring (*Frb. Ztg.*, **1900,** 436). The formula in this case is:

400 gm lactic acid 50%
600 gm thickening

The printed fabrics are dried, treated in 3° Bé solution of chloride of lime, washed, soured and rinsed.

However, the most important process for discharging Turkey red dyeings is undoubtedly the alkaline discharge process. The method has been described in detail in many references.*

The first application was made by Schlieper and Baum who obtained indigo blue discharges on Turkey red dyeings using their well-known print formula.

The Turkey red dyed cloth is prepared with glucose and printed with a paste containing indigo and alkali. After drying, the prints are aged and washed through a three-compartment open-width washer, the first part containing 7° Bé sulfuric acid, the second water and the third a soda ash solution of 2° Bé.

Some years later Schmidlin rounded out the Schlieper and Baum process by developing yellow, green and white effects, and printed them alongside aniline black. For yellow he used pigment Chrome Yellow, for green, the Chrome Yellow together with indigo, and for white an alkaline paste containing caustic soda and sodium silicate. The whites are improved by the addition of sodium zincate or sodium stannite.

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* Triapkine, a thorough and detailed article in *Rev. Gen. Mat. Col.*, **1898,** 6; Diakonoff, *Frb. Ztg.*, **1898,** 199; Maslowsky, *Frb. Ztg.*, **1896,** 33; Oswald, *Rev. Gen. Mat. Col.*, **1897,** 184; Schlieper and Baum, *Bull. Mulh.*, **1884,** 49; Depierre, Vol. III, p. 370; Bourchart, *J. Soc. Chem. Ind.*, **1883,** 193; Schmidlin, *Bull. Rouen*, **1899,** 431; *Rev. Gen. Mat. Col.*, **1900,** 20; Depierre, Vol. V, p. 445–455.

White Discharge

55 gm	stannous chloride (tin salt)
35 gm	zinc sulfate
75 gm	glycerin
160 gm	gum thickening
535 gm	sodium hydroxide 50° Bé
125 gm	sodium silicate 30° Bé
15 gm	turpentine
1000 gm	

The yellow discharge is principally composed of a sodium plumbite solution and sodium silicate. During the ageing operation lead oxide is fixed upon the fiber and transformed in turn by passing through a bichromate solution into yellow lead chromate.

Yellow Discharge

2250 gm	dextrin
1750 gm	water
15000 gm	sodium hydroxide 50° Bé
2000 gm	glycerin
9250 gm	lead nitrate sol.
5000 gm	sodium silicate 38° Bé
400 gm	turpentine
35650 gm	

Blue discharges are obtained according to the Schlieper-Baum method with indigo, and green by combining the indigo with the yellow. Thus the discharge style encompassed white, blue, green, yellow and black on red. The procedure is as follows:

The Turkey red dyed fabrics are first prepared in a solution containing glucose, aluminum acetate and ammonium vanadate, dried and printed. Thereafter the goods are dried and passed for 3 to 5 minutes through the rapid ager at 102°C, treated in a sodium silicate solution of 2° Bé (10 to 15 gm of sodium silicate 38° Bé per liter) in order to remove the Alizarine in the form of soluble sodium alizarate. Thereupon the goods are chromed, washed and soaped. Freiberger succeeded in producing colored discharges with diazotizable direct dyestuffs upon Turkey red dyed fabrics (*Frb. Ztg.*, **1914,** 76; *Rev. Gen. Mat. Col.*, **1914,** 21; *Bull. Mulh.*, **1913,** 651).

Sulfoxylate Discharges on Turkey Red. In 1906 the sulfoxylate discharge process was promoted, and blue discharge was produced with strongly alkaline pastes containing indigo and Hydrosulfite NF (MLB).* This method was much simpler and less sensitive, and later completely re-

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* *G.P. 173,878, 179,454; Fischer's Ber.*, **1906,** 438.

placed the difficult Schlieper and Baum process. A typical formula follows:

75 gm Hydrosulfite NF extra	
125 gm water	165 gm dextrin
450 gm alkaline thickening →	835 gm caustic soda 50° Bé
150 gum indigo 20%	——
200 gm gum thickening	1000 gm
——	
1000 gm	

Sulfur colors can also be used to produce colored discharges on Alizarine Red dyed fabrics.

Vat dyestuffs are well suited for alkaline discharge effects. Ivanoff* appears to be the first to have worked with Indanthrene colors. He used a strongly alkaline paste thickened with dextrin, which in this case acts also as a reducing agent. However, the style was brought to complete success only with the creation of sulfoxylate formaldehyde. E. Zündel in Moscow launched the vat discharge style in 1914.

Print pastes containing vat dyestuff, alkali and alkali silicate, and Hydrosulfite NF were printed on dyed Alizarine Red material

Colored Discharge Paste	White Discharge Paste
200 gm vat dyestuff paste	180 gm dextrin
60 gm glycerin	100 gm gem thickener
300 gm gum thickener	600 gum NaOH 50° Bé
210 gm NaOH 38° Bé	100 gm Rongalite C extra
180 gm Rongalite C extra	20 gm sodium bisulfite 38° Bé
50 gm sodium silicate 36° Bé	——
——	1000 gm
1000 gm	

The printed goods are dried and aged in the rapid ager for 7 minutes' chromed in a bath containing 10 gm of bichromate plus 3 gm of hydrochloric acid per liter, washed, passed thereupon through a silicate solution of 1.5° Bé at 40°C, soaped and rinsed.

Chlorate Discharges on Pad-Dyed Mordant Colors. This style has been developed by Jeanmaire who used the known chlorate-ferrocyanide method which temporarily regained some importance.

Jeanmaire described in *Bull. Mulh.*, **1895,** 134; **1899,** 317; *Frb. Ztg.*, *1894–5*, 20 (sealed report from Koechlin Frères in Mulhouse, 1885) his discharge method on Alizarine Blue dyeing.

The goods are first padded with the dyestuff and mordant, aged, steamed and washed. The discharge prints are then made with chlorate, and aged.

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* *Bull. Mulh.*, **1913,** 87 (sealed report of 1901).

A formula used in practice is given here. The white goods are padded with:

42 gm	Modern Blue CVI (D. & H.)
609 gm	boiling water
3 gm	Hydrosulfite NF
10 gm	tragacanth gum
20 gm	glycerol
20 gm	formic acid 85%
196.5 gm	water
120 gm	chromium acetate 20° Bé
1.5 gm	oxalic acid
75 gm	logwood paste
1102 gm	

The padded goods are aged, then steamed one hour without pressure in the cottage steamer, finally chromed and chalked, rinsed and washed. The dyed goods are then printed with the following white discharge:

375 gm	starch-gum thickening
200 gm	sodium chlorate
200 gm	china clay
50 gm	potassium ferrocyanide
100 gm	citric acid
75 gm	water
1000 gm	

The printed goods are dried and treated for 6 minutes in the rapid ager, passed in the open width through an acid bichromate solution, rinsed and dried.

A complete color range can be produced, comprising the lightest to the darkest shades. The most suitable dyestuff brands which can be used in this process are:

Alizarine Blue, Gallocyanine, Modern Violet, Alizarine Brown, Coerulein, Alizarine Cyanine, Anthracyanine, Alizarine Viridine and so on.

The range of dyes which can be used for producing the colored discharges is restricted, however, to pigments (Chrome Yellow), some insoluble Azo dyestuffs and some direct dyestuffs of the Stilbene group (Diamine Fast Yellow A, Stilbene Yellow) or to some Thiazole derivatives (Primuline Yellow, Diamine Fast Yellow FF, B and C).

Sulfoxylate Discharges on Padded Colors. Some of the mordant dyestuffs are dischargeable with Hydrosulfite NF, for example, Eriochrome Yellow (Geigy), Chromal Blue (Geigy), Chromocitronine (D. & H.), Chrome Brilliant Violet BD (I.G.). The discharge method is similar to the discharge process of direct color dyeings.

The procedure consists of padding the chrome mordant dyestuff with mordant, and steaming for one hour. The white and colored discharges are printed, and the goods aged 7 minutes, and washed well.

Dyeing with Mordant Dyestuffs

Dyeing with mordant dyestuffs was an important art in the past, especially cotton yarn dyeing with Alizarine Red. However, the vat colors and especially the insoluble azo (naphthol) dyes have almost completely supplanted them. It is for this reason that little research has been done on the mordant color application to cotton in recent years. A brief review of the dyeing methods follows.

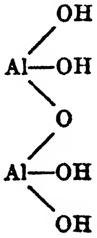
Dyeing on Aluminum Mordant—Turkey Red. The most important shade produced on aluminum mordant is Alizarine Red (Turkey red, Rouge Turc) which is obtained by dyeing Alizarine, oil mordant and lime on aluminum mordant.

Theory of the Turkey Red Process[*]

Undoubtedly Liechti and Suida deserve credit for having discovered the composition of the Alizarine Red lake. They proved beyond any doubt that this lake consisted of a double salt of Alizarine with aluminum and calcium, and they were able to explain fully the part played by the calcium salts in the formation of the Alizarine Red lake complex.

Dr. Haller published in *Mell.*, May, June and July, **1938,** 448, 504 and 595, a detailed and very interesting study regarding the constitution of Alizarine Red. He first quoted the theories of his predecessors, Fischli, Sansone and Kornfeld and disclosed thereupon his own experiments which led to a full explanation of the process taking place in the Alizarine Red lake formation.

Fischli[**] assumed that ricinoleic acid reacts with aluminum hydroxide having the constitution



and that this reaction product is dyed with Alizarine Red.

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[*] Haller-Glafey, "Technologie der Baumwolle" (The Technology of Cotton Fibers), in Herzog's "Technology of Textile Fibers," p. 91–94; Dr. Haller, "le Rouge d'Alizarine," *Bull. Fed.*, III, 381.

[**] *Bull. Mulh.*, 1888, 731; see also Haller, "Kolloidchemische Beihefte," 1920, 109.

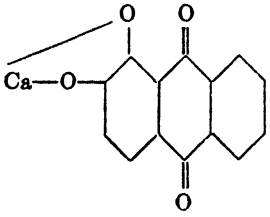
Witt shared this idea and supposed like Fischli that the ricinoleic acid radical was an essential part of the Alizarine Red lake.

But Prof. Haller's research furnished a result quite contrary to that indicated by Fischli. Haller could state that aluminum ricinoleate formed a red color with an Alizarine suspension but that neither the sodium salt of ricinoleic acid nor the sodium salt of Alizarine was obtained by reacting sodium hydroxide with this aluminum ricinoleate.

According to Haller, Alizarine behaves like an acid when combined with aluminum ricinoleate. This acid, *i.e.*, Alizarine, sets free the ricinoleic acid and forms aluminum alizarate.

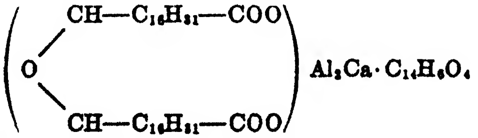
Sansone constructed a formula which was intended to give the constitution of the Red lake and to explain the connection between Alizarine, aluminum and fatty acid. He assumed that the fatty acid combined chemically with the lake and that the cellulosic fiber had something to do with this lake formation also. But even the author himself seemed to be doubtful whether this theory was correct.

In 1910 and 1912 Kornfeld offered a new theory.* He assumed that aluminumoleate formed a complex compound with calcium alizarate, having the formula



He assumes that an anhydride of the fatty acid is formed, giving with the alizarates of calcium and aluminum the Alizarine Red lake which might have the constitution: $Al_2 \cdot Ca(C_{14}H_6O_4)(CHOH)(C_{16}H_{31}COO)_6$.

The proper lake formation occurs according to his opinion during the process under excess pressure in the presence of water: one molecule of water is split off from two molecules of fatty acid and ring formation occurs with the alizarate. The following compound is supposed to result:



Prof. Haller stated, however, that a colloidal solution of Alizarine Red is formed by reacting aluminum hydroxide with Alizarine and he regards this colloidal solution as the parent substance of the Alizarine Red lake.

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* *Z. f. angew. Chemie*, 1910, 1273; *Chem. Ztg.*, 1911, 29, 42, 58.

Calcium alizarate and the complex calcium aluminum alizarate is formed only during the steam treatment in the cottage steamer whereby the oil present is essential as a dispersing agent.

Haller again presented, also in Z. f. ges. Tex. Ind., **41,** 298 (1921), the problem of Alizarine Red formation. He emphasized that the function of the fatty substance does not consist in forming a chemical combination with the dye-lake but that it is a dispersing agent for the aluminum calcium alizarate. It could definitely be proved that after the dyeing process three heterogeneous compounds are deposited within the fiber, *i.e.*, the polymerizates of the fatty acids (of ricinoleic acid or of lactones thereof), the alizarate of aluminum and the alizarate of calcium. Both of these alizarates combine in the steam atmosphere to form the complex Alizarine Red lake. The polymerizates of fatty acids occurring here have a melting point of 105 to 107 °C, and they offer therby only the dispersing agent which is the medium necessary for the double salt formation, while the two alizarates exist as separate compounds alongside each other before the steam treatment.

The quality of the Turkey red dyeings and especially the fastness to crocking and kier boiling depends principally on the nature of the oil applied and on the degree of the fixation.

Four different dyeing procedures can be enumerated:

(1) The dyeing process of the older type (old red process, "Altrot-Verfahren") using rancid olive oil ("tournant oel", "huile tournante") as a fatty mordant.

(2) The dyeing process of the new type (new red process, "Neurot-Verfahren") using Turkey red oil as fatty mordant

(3) The Erban-Specht method (mordanting and dyeing in the same bath, lake formation by subsequent ageing operation) (*G.P. 128,997* and *133,719,* M.L.B.).

(4) The Schlieper-Baum method, using sodium aluminate.

The process called the old red process gives a very fast red shade, satisfactory in every respect but the procedure is extremely time-consuming. The process requires about 20 days while the new red process takes only 5 to 8 days.

The Alizarine Red Dyeing Process—Old Method. This method has been almost completely abandoned because of the very complicated procedure. It is based on the use of rancid olive oil, known in the trade as rank olive oil, or "huile tournante". The rancid oil is produced by treating the oil with small amounts of alkali, not by the natural process of deterioration. The material is impregnated with the emulsion obtained in this way.

Some more recently developed processes of Turkey red dyeing are based on this first procedure:

(1) *Preparing:* the fabrics are boiled with a soda ash solution, washed and dried. A chlorinating operation should be omitted because it was found in practice that chlorinated goods cannot readily be dyed with Alizarine. Complete absence of iron salts is absolutely necessary (a preliminary condition).

(2) The *first oiling operation* with a mixture of emulsified olive oil or rank olive oil and cow dung: 15 kg of rank olive oil and 1¼ kg of cow dung in 200 liters of water are used for 100 kg of white cloth. The goods are oiled at 40°C in a vat until they are thoroughly impregnated. Thereupon they are first dried by skying in the open air and then hung in a heated chamber.

(3) A *second oiling operation.*

(4) A *third oiling operation.*

(5) *Treating* in a lukewarm soda-ash solution of 1¼° Bé for 5 to 6 hours in order to remove the unfixed portions of oil, thereupon rinsing in lukewarm water.

(6) "*Galling*", that is, treating with a gallic acid solution (for instance with sumac or nutgall extract) for 6 hours at 50°C.

(7) *Mordanting* with an alum solution neutralized with chalk or soda ash, absolutely free from iron. The material is immersed for 44 hours in a solution of alum 5° Bé containing 5 to 6 gm of stannous chloride per kg of alum, neutralized by adding one part of sodium carbonate crystals and ¼ part of aluminum acetate 15° Bé for 4 parts of alum. The fabrics are quetsched thereafter and dried in the open air or on the can.

(8) *Dyeing:* the water should have 5-degree hardness (German scale). The dye bath has to contain 8 to 10% Alizarine 20% paste, 3% bran, and 3% tannic acid calculated from the material's weight. The goods are entered at room temperature and treated for one hour without warming; thereupon the temperature is raised within an hour to 85 to 90°C and finally to the boil. The goods have a brownish shade after dyeing.

(9) *Clearing or brightening:* this treatment has for its purpose changing the shade into a bright red. The dyed goods are treated in a closed vessel at 15 lb of pressure with 4 to 5 kg of olive oil, 5 kg of Marseille soap and a soda ash solution of 2° Bé per kg of material. Thereupon the goods are cooled down, removed from the vessel and rinsed.

(10) *A similar supplementary treatment,* called pink shading ("Rosieren"), has been proposed by Arvers and St. Ervon in Rouen for giving the desired bluish and bright red shade. The pieces are aftertreated for 1 to 2 hours in a closed vessel at 15 lb of pres-

sure in a solution of 2.5 gm of soap and 0.15 gm of stannous chloride per liter.

Steiner (Manchester and Rappoltsweiler, Alsace) developed a modified simpler old style Alizarine Red process by impregnating the fabric with 100°C warm olive oil instead of rank olive oil. The oiled and dried material was passed seven times through a soda ash solution of 2–3° Bé and hung in a heated chamber for another 2 hours. It is possible to fix 10% oil calculated on the fabric's weight. Thereupon the goods are mordanted in an alum solution and dyed as reported here above.

It might have some historic interest to indicate here a method developed by Horace Koechlin and installed practically in the Gros-Roman plant in Wesserling (Haut-Rhin). The process was later on assigned to Walter Crum (1876). The procedure consists of the following steps:

(1) Padding with 30% ammonium sulfoleate solution.
(2) Drying and steaming for one hour.
(3) Padding in an aluminum sulfate solution 20° Bé and drying.
(4) Treating in a cold solution of sodium silicate plus ammonia for three minutes (1 liter sodium silicate 20° Bé + 10 liters of water + ½ liter ammonia conc.).
(5) Dyeing: 10 kg of material dyed in a bath containing

800 gm Alizarine 20%
800 gm calcium acetate 18° Bé
100 gm tannic acid
1.6 gm blood albumen 100/1000

rinsing, drying.

(6) Padding in a 10% ammonium sulfoleate solution,* drying and steaming for one hour.
(7) Rinsing, soaping at the boil, rinsing and drying.

Dyeing of mixed yarns of cotton and spun rayon by the old style Alizarine Red was a new problem for the dyer, and one which has not been satisfactorily solved. Such blends give poor results because the fibers dye up different shades. Microscopic investigation showed that staple fibers of different origins behaved differently, while only one, Vistra HB, dyed in similar fashion to cotton (W. Hees, *Mell.*, **1939,** #3).

In order to obtain level dyeings with blended yarns, Turkey red dyers developed special procedures.

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* *Ammonium sulfoleate preparation:* 4 kg of sulfuric acid 66° Bé are gradually stirred into 4 kg of olive oil under constant cooling. The mixture is kept standing for 12 hours and diluted thereupon with 80 liters of cold water. The supernatant liquid is neutralized in a separate vessel with ammonia: 18 kg of ammonia correspond to 165 kg of this liquid.

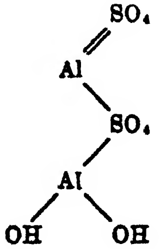
The so-called "predyeing" method was found satisfactory for mixtures of cotton and rayon such as 20–80 and 30–70 blends. The yarns are first oiled as described above and dyed on the pad in an Alizarine solution before mordanting with aluminum acetate. The Alizarine is dissolved in an alkali, such as potash, ammonia or borax, Alizarine being soluble in alkalis with a violet color, in borax with a brown shade. The absorbed solution then produces the red aluminum lake with the basic aluminum salts of the mordant. The dye bath contains Alizarine and calcium salts, so that the true Turkey red lake is formed by the aluminum alizarate on the fiber in combination with the calcium salts and Alizarine.

Staple fiber blends can also be dyed by another method, which makes use of preparation with tannic acid. In this way a tannate of aluminum is precipitated within the fiber and this mordant produces a lake with Alizarine and the calcium salts during dyeing. The disadvantages of this method is surface formation of the red lake, and consequent removal of much of the shade in the oil brightening operation.

The inequalities in dyeing mixed yarns have also led to overdyeing the Alizarine Red with naphthols of good light-fastness and wash-fastness. The naphthols, having better affinity to the rayons than to the cotton tend to compensate for the results obtained with the Alizarine Red, but the higher cost of such procedure will no doubt limit its use.

A patent for predyeing rayon and cotton mixed fabrics with naphthols was issued to A. Römer in Zittau in 1936 (*G.P. 696,448*), after which the goods are dyed as usual with Alizarine Red.

Excellent results can be obtained on all kinds of spun rayon qualities regardless of their origin, by the new ("Neurot") method of Alizarine Red dyeing. Uniform formation of the red lake depends on proper selection of mordant, and on the specific conditions of fixation. The usual mordants for dyeing by the old method are aluminum sulfates of low basicity, having little affinity for viscose rayon fibers. These mordants correspond approximately to the formula



They are generally applied in a concentration of 5° Bé equal to 50 gm $Al_2SO_4 \cdot 12\ H_2O$ per liter.

Aluminum mordants of higher basicity, produced by further treating aluminum sulfate with alkali carbonates offer greater advantage in dyeing rayons. Since they dissociate readily on dilution, they must be applied in relatively high concentrations, for example, about 12.5° Bé equal to 120 gm of $Al_2SO_4 \cdot 12\ H_2O$ per liter. The pH of such solutions is about 4. The I.G. developed a basic aluminum compound for dyeing Alizarine Red on rayon and cotton, called Mordant Salt TR ("Beizsalz TR"). The special mordant can be used in the old method for red without otherwise altering the procedure, and gives uniform results on mixed fibers. This salt has a high percentage of active alumina, is readily soluble in water, and in dilute solutions has a pH value of 5.2.

Alizarine Red Dyeing process—New Method.[*] Dyeing of Alizarine Reds was simplified by the introduction of water-soluble sulfonated oils. The long oiling operations could be replaced by a single passage through a solution of a sulforicinoleate. The credit for introducing this method into practice must be given H. Koechlin in Mulhouse.

The process consists of three steps: (1) oiling, (2) mordanting and (3) dyeing.

(1) The goods are treated with a solution of ammonium sulfoleate or sodium sulforicinoleate (100 to 150 gm per l) at 60°C, and dried at 40 to 50°C, then steamed two hours.

(2) The goods are padded at room temperature with an aluminum mordant, such as basic aluminum acetosulfate 6° Bé or basic aluminum sulfate 8°Bé. The pad liquor can be prepared according to the formula:

7.6 kg aluminum sulfate
2.76 kg sodium carbonate crys.
60 l water

The goods are then dried and aged 2 minutes in the rapid ager. Polyricinoleic acids and aluminum ricinoleate are formed in this operation. After this the goods are chalked in a bath of

36 kg arsenic acid 81%
17 kg sodium carbonate crys.
20 kg chalk
—
to 400 l

at 50°C, or in a chalk and phosphate bath at 80°C.

(3) Dyeing is carried out for one hour at room temperature then for ¾ hour at 60 to 75°C.

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[*] F. Weber, *Bull. Mulh.*, 1909, 275.

Formula for 700 m cotton, total weight 170 lb:

1200 gm Alizarine SX 100% or 7000 gm Alizarine GFX 20%
6000 gm sodium ricinoleate
6000 gm albumen 1:1 sol.
1000 gm sumac
3000 gm stannic hydroxide
500 gm chalk

The dyed goods are dried, padded with sulfonated castor oil again, steamed one hour, soaped, rinsed and dried.

Erban-Specht Method. This method has been mainly used for pink shades. The goods are padded in an ammoniacal solution of Alizarine, together with Turkey red oil. This solution must be free of iron and calcium salts. The goods are dried in the hot flue at 55°C. The material is then padded in a mordant solution of aluminum and calcium acetates, dried, steamed 2 hours in the cottage steamer under 2 atmospheres of pressure, washed and brightened as usual.

Schlieper-Baum Method. This process* is entirely different from the foregoing. It is characterized by the use of sodium aluminate as mordant.

The procedure is as follows:

(1) *Mordanting* with sodium aluminate and drying in the hot flue. Formula of the mordant solution: 41 kg aluminum hydroxide gel, 64 l sodium hydroxide 35°Bé, diluted with water to 450 liters. Add 8 liters of hydrochloric acid (density 1.15) and fill up to 600 liters.

(2) *Fixing* this mordant with ammonium chloride and washing.

An acid reacting aluminate is formed which is transformed by a chalk treatment into the corresponding calcium aluminate.

(3) *Dyeing* in the roller box with a dye liquid containing Alizarine and a clear calcium hydroxide solution.

(4) *Oiling* (20 to 25 gm Turkey red oil per liter).

(5) *Drying and ageing* in steam of 0.5 atmosphere pressure for 1 to 2 hours.

(6) *Brightening oil treatment* as usual.

Meister, Lucius & Bruening described in *G.P. 133,719* a process which combined the mordanting and dyeing operations in one bath by using aluminum formate or sulfite.

In *U.S.P. 1,895,019* (Barnes, Thomas, Scott) another rapid method for dyeing Alizarine is proposed. An Alizarine sulfoester, having the sulfo group linked to one of the hydroxyl groups in β position is prepared by treating Alizarine with a tertiary base such as pyridine and a sulfo derivative of this base. The sulfoester can be dyed together with aluminum sulfate and calcium acetate and the dye is fixed by subsequent steaming.

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* *Bull. Mulh.*, **1903, 193.**

In an interesting experiment, Dr. R. Haller* produced Alizarine Red in a single bath process. The work is based on the fact that ricinoleic acid ethyl ester, which undergoes saponification in subsequent steam treatment, can be combined with the metal mordants in the Alizarine dye bath, without precipitation of metallic soaps. The formula of the dye bath is given as

50 gm	ricinoleic acid ethyl ester, *emulsified in*
100 gm	tragacanth mucilage 60/1000
100 gm	Alizarine 20% paste
100 gm	aluminum thiocyanate 12° Bé
50 gm	calcium acetate 13° Bé
30 gm	tin acetate 6° Bé
570 gm	water
1000 gm	

A sample impregnated with this dye bath is dried and aged for 1 to 2 hours at 0.5 atmosphere, rinsed and soaped. A red shade fast to washing and to chlorine is obtained which is, however, not as bright as the normal Alizarine Red. Castor oil (which is the glycerin ester of ricinoleic acid) can be used instead of ricinoleic acid ethyl ester. The appearance of the dyed goods is approximately the same in both cases. This method, however, apparently did not proceed beyond the experimental phase.

G.P. 582,378 (Oranienburg-Lindner). According to this patent, the metal mordants can be combined in one bath with the fatty acids without precipitation of heavy metal soaps, provided that high alkyl-substituted benzene sulfonic acids, for instance palmityl benzene sulfonate, are used together with the metal mordants.

Dyeing Chrome Mordant Dyestuffs. The most important mordant for dyeing of cotton with chrome colors is Chrome Mordant GA II, 35° Bé (M.L.B.), developed by v. Gallois. It is a chromium chromate obtained by dissolving chromium hydroxide in chromic acid. By simply padding this mordant on the fabric a considerable quantity of chromium oxide is fixed on the fiber.

The dyeing of chrome mordant colors on cotton fabrics is of little importance today, but some use is made of these colors in yarn dyeing. For this purpose chromium chloride 20° Bé, chromium bisulfite and alkaline chrome mordant is employed.

Preparation of alkaline chrome mordant is made with:

25 l	chromium acetate 20° Bé
1 l	glycerin
32 l	caustic soda 30° Bé
42 l	cold water
adjust to 20° Bé	

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* *Mell.*, 1942, 86.

Cotton cloth may be dyed for white discharge printing with chrome colors, using the dyestuff in combination with the mordant, impregnating, drying in the hot flue and then steaming one hour in cottage or continuous steamer. This style can be carried out with a wide variety of ground colors. White discharges are obtained by printing chlorate discharge pastes. Chromocitronine yields a dischargeable yellow, while Modern Blue can be used for a navy ground.

Examples of other dyestuffs suitable for this purpose are given here, with impregnating formulas:

Tobacco Brown	
30 gm	Alizarine Red 20% paste
2.4 gm	Alizarine Brown 20% paste
70 gm	Persian berries extract 30° Bé
500 gm	cold water
30 gm	gum trag. paste
70 gm	dextrin 25% paste
45 gm	chromium acetate 30 Bé
—	
to 1 liter	

Olive Green	
7 gm	Alizarine Viridine
4 gm	Alizarine Cyanine GG
10 gm	borax
500 gm	boiling water
36 gm	Persian berries extract 30° Bé
300 gm	cold water
70 gm	dextrin 25% paste
30 gm	gum trag. paste
30 gm	chromium acetate 30° Bé
—	
to 1 liter	

According to *B.P. 481,854* (D. & H.), mordant dyestuffs can be dyed in a single-bath operation by employing chromium chromate. Cotton or rayon fabrics are entered at room temperature, the dye bath heated to 90°C gradually over ¾ hour, then dyed ½ hour at this temperature. It was observed that the lake formation takes place only on the fiber and not in the dye bath. Additions of chromium tartrate or lactate proved favorable.

The use of chromium chromates for mordanting cotton is recommended in *G.P. 672,328* (D. & H.). These chromium chromates are made by mixing bichromate with chromium chloride. The fibers are first impregnated with a solution of this product, then fixed in a bath of soda ash, and dyed with chrome mordant colors. The same process can be applied to rayon, and has been shown to be practicable in a single-bath process. The fabric is entered at the boil, the dye bath containing dyestuff, mordant and common salt. Acetic acid is gradually added and the dyeing continued to exhaustion of the bath. It is very likely that this patent covers the manufacture of "Chromate DH", which has been discussed previously under printing of chrome mordant colors (*Mell.*, **1939**, 585).

According to *G.P. 587,584* (Hankey) chromium hydroxide may be fixed on cotton material by padding a solution of sodium or potassium bichromate with Hydrosulfite NF and ageing. The compound $Cr_2(OH)_6 \cdot 4H_2O$ results. This is not only an efficient mordant, but acts as a fire-retardant also.

Stripping Mordant Dyes

F.P. 771,349 and *U.S.P. 2,019,124** (I.C.I.) disclose that mordant colors can be stripped with sodium hydrosulfite in the presence of substituted amines. The process is as follows:

Materials dyed with mordant colors are boiled for 15 minutes in a bath (liquor ratio 40 : 1) containing

4 gm caustic soda 38° Bé
3.75 gm sodium hydrosulfite
2 gm trimethyl cetyl ammonium bromide
—
per liter

The color is destroyed by this treatment, and the cloth cleared in subsequent passage in sodium hypochlorite solution of $\frac{1}{2}$° Bé.

MORDANT DYES ON ANIMAL FIBERS

Wool Dyeing

Dyeing wool with mordant dyestuffs, and particularly with chrome mordants, is one of the most important processes in the textile industry. Mordant dyes, for example, the well-known Eriochrome colors of Geigy, are dyed on wool in all forms and stages from the loose material to finished woven fabrics.

There are three methods which are used in dyeing the mordant dyestuffs:

(1) Dyeing, then aftertreating with the mordant in form of bichromate, chromium fluoride, alum or copper sulfate (after chrome method).

(2) Dyeing and mordanting in the same bath (single bath or chromate method).

(3) Mordanting with metal salt, then dyeing.

Afterchrome or Top Chrome Method.** The wool is first dyed, using acetic acid and Glauber's salt to exhaust the dyestuff, then aftertreated with bichromate.

The chrome lake is thus formed in the second bath. Dyeings obtained in this way are conspicuous by their excellent fastness properties.

The dyestuffs suitable for dyeing by this process are:

Acid Chrome, Chromoxan, Diamond, Acid Alizarine, Acid Anthracene and Palatine Chrome colors (I.G. and G.D.C.)
Chromate and Superchrome colors (N.A.C.)
Chromaven colors (A.A.P.)

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* *Rev. Gen. Mat. Col.*, **1935**, 138.

** Seiferth, *Frb. Ztg.*, **1907**, 84, 98, 185; von Kapff, *Frb. Ztg.*, **1907**, 130; **1908**, 49, 69, 236; Lengfeld, *Frb. Ztg.*, **1907**, 133; Mueller, *Frb. Ztg.*, **1908**, 142; Kertesz, *Frb. Ztg.*, **1909**, 213, 249; **1908**, 137; Theis, *Frb. Ztg.*, **1908**, 240; Gavard, *Frb. Ztg.*, **1908**, 270.

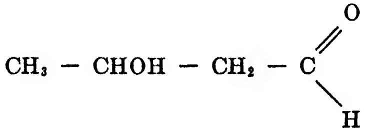
Chrome Fast, Naphtochrome colors (Ciba)
Calcochrome colors (Calco)
Altochrome colors (Althouse)
Eriochrome colors (Geigy)
Omega Chrome colors (Sandoz)
Coomassie and Solochrome colors (I.C.I.)
Diadem Chrome of L.B.H., etc.

Most of these dyes are sulfonated or carboxylated azo compounds which are dyed in the acetic bath, and developed in a bath with potassium bichromate. Some of them can also be dyed according to the single-bath method.

In some cases the bichromate can be substituted by chromium fluoride, as with Gallocyanaine, Erio Fast Brilliant Blue 3R; by alum, as with Alizarine Red, Alizarine Orange and Alizarine Yellow; or by copper sulfate, as with Neochrome Black, Eriochrome Violet B.

The so-called "combination black" is dyed with Acid Black and Logwood in one bath, and developed in a second bath with ferrous sulfate and copper sulfate.

The fastness to crocking of afterchrome dyeings can be improved by a slower absorption of the chrome salt. For this purpose Claflin recommends (*U.S.P. 1,911,307*) the use of aldol



which when added to the bichromate solution retards the rate of lake formation.

Bucherer discloses an interesting dyeing method (*G.P. 587,361*) for colors sensitive to excess chrome mordant. Wool is dyed in an acid bath with the chrome dyestuff, rinsed and then treated in a cold solution of chrome salt, washed, rinsed in bisulfite, and finally treated with hot water, where the lake formation takes place. In this case both dyestuff and chromium oxide are fixed on the fiber, but the lake is formed only by the application of hot water. In this way the tensile strength of the fiber is preserved.

In a modification of this process (*G.P. 591,212*) Bucherer suggests dyeing the colors in a single bath with the mordant, in the presence of ammonium salts, such as ammonium carbonate.

Mixed fabrics of spun rayon and wool can be dyed uniformly with certain colors containing a group which can be chromed, as Gallo Navy Blue S and Chrome Fast Yellow RD. The fabric is first prepared with chromium acetate together with a protective colloid like sulfite waste liquor, then dyed at the boil and afterchromed as usual. The prechroming retards dye absorption on the wool while it accelerates it on the rayon, thus leveling the dyeing on the mixed fibers (*Bull. Fed.*, **III,** 438)

Bichromates, besides acting as mordants, also have an oxidizing effect on wool, which by its nature exerts a slight reducing action. Because of this slow reducing action, it is assumed that faster color lakes are formed, although a slight weakening of the fiber accompanies the process.

Of the different mordant processes, the top chrome has proved to be best in practice. Complex metal-salt compounds are formed with the dyestuff which exhibit excellent all-round fastness properties. It is superior to the chrome mordant (chrome bottom) method in that the time necessary to treat the wool at the boil is shorter, thus preserving the strength of the fiber and effecting a saving in steam.

General Procedure for Afterchrome Dyeing. The dye bath contains the dissolved dyestuff, 10 to 20% Glauber's salt and 2 to 4% acetic acid 30%. It is warmed at 60–70°C. The material is entered and the bath is slowly warmed up to the boil and dyeing is thereupon continued for ½ to ¾ of an hour. Acetic acid (3 to 5%) is added thereafter and dyeing proceeds further until the bath is completely exhausted. The bath is cooled down, the bichromate solution is added, the solution is brought up to the boil again and the goods are treated in this boiling solution for another ¾ to 1 hour.

Single-Bath Method. This procedure is also called metachrome, synchromate, chromate and monochrome method.

Certain specially selected dyestuffs are suitable for this method, the trade names of some of which are:

Metachrome and Monochrome colors (I.G. and G.D.C.)
Synchromate colors (Ciba)
Eriochromal colors (Geigy)
Metomega Chrome colors (Sandoz)
Solochromate colors (I.C.I.)

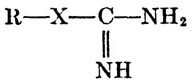
Chrome Yellows, Alizarine Cyanine Greens, Cloth Reds and other colors are also adaptable to the single bath process.

These dyestuffs are dyed in a bath together with the mordant, which may be ammonium chromate or a mixture of potassium chromate and ammonium sulfate or any of the special chromate mordants, such as Metachrome, Eriochromal, Synchromate, etc., mordant. (*Mell.*, Fr. ed., **1937,** 28).

Procedure: The dyestuff is boiled up in the liquor, it is then cooled to 35 to 40°C, 3 to 5% of Metachrome mordant well dissolved in water added and the material entered. After 10 minutes the bath is heated to the boil and dyeing continued until the dyestuff is exhausted. The addition of ammonium acetate and 1 to 2% of Leonil S is recommended for dyestuffs which are difficult to level.

Bichromate was formerly used as mordant in the single bath method. After the dyestuff has been dissolved, potassium bichromate (⅓ to ½ of the weight of the dyestuff) is added in solution. The material is entered at 60 to 70°C, the bath heated to the boil, and after one hour, 2 to 5% acetic acid or ½ to 1% formic acid is added, and the bath boiled for another hour.

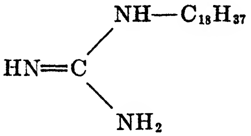
In *Aus. P. 153,489* (I.G.) a special adaptation of this method is explained for dyeing a wool and spun rayon blended fabric. The spinning mass of the rayon is blended with condensates of polyamines with higher chlorinated paraffins, such as polyethylene diamine and trichloroparaffin. Mixed fabrics composed of such fibers can be dyed with Metachrome colors, the colors being fast to milling (*Bull. Fed.*, **III,** 439). Other examples of condensates are given in *U.S.P. 2,121,337* (I.G.—Brodersen). The spun rayon is pretreated with organic bases which act as mordants for the Metachrome dyestuffs. The general formula of these bases is



$$R—X—\underset{\underset{NH}{\|}}{C}—NH_2$$

where R is an alkyl of high molecular weight, and X a bivalent radical such as NH =; O=; etc.

As an example, stearyl guanidine is mentioned:



The single-bath method cannot be used with the majority of chrome dyestuffs. On the other hand sampling is difficult in the two-bath methods, because shades change noticeably in the second bath. The following method of the I.C.I. (*F.P. 821,992*) augments the number of dyestuffs which can be dyed by the one-bath process. High-molecular substituted quaternary ammonium bases such as cetyl trimethyl ammonium bromide are added to the dye bath. Dyeing is carried out ½ hour warm and one hour at the boil.

Another one-bath method has been proposed by Sandoz. In this process, Chromosol ($CrNa(C_2O_4)_2$) chromium sodium oxalate, is used. This double salt decomposes slowly in hot acetic acid bath.

Chrome Mordant or Chrome Bottom Method. Dyeing on premordanted fabrics is one of the oldest dyeing processes for wool. The procedure consists of preparing the goods with an aluminum-, chrome-, or iron mordant and subsequently dyeing in a bath containing acetic acid. This process is especially suitable for dyeing Alizarine, logwood, Persian berries or synthetic Alizarine dyestuffs such as polyoxyanthraquinone dyestuffs or salicylic acid dyestuffs, etc. The mordants generally used are: alkali bichromates for chrome mordants (chrome bottom) and alum for aluminum mordants. These metal salts are applied combined with tartaric, lactic and formic or sulfuric acids for mordanting wool.

The use of titanium dioxide for mordanting purposes has also been suggested.* *U.S.P. 1,675,459*, 1929, of Federal Phosphorus Co. claims that very bright shades can be obtained by mordanting wool with sodium bichromate together with sodium pyrophosphate.

Procedure:

Mordanting. The bath contains 2 to 4% potassium bichromate + 2.5% or 1.5% sulfuric acid 96% or 1.5% potassium bichromate + 3% lactic acid + 1% sulfuric acid 96%. The goods are immersed in this bath at 70 °C which is then heated to the boil; boiling is continued for 1½ hours, whereupon the material is rinsed.

Dyeing. The dye bath contains 2 to 4% acetic acid (30%) or 5% ammonium acetate. The material is entered at 30 to 40 °C, treated at this temperature for ½ hour, whereupon the bath is warmed for ¾ hour at the boil. Dyeing is continued to exhaustion of the dye bath.

Potassium bichromate and copper sulfate mixtures are used for mordanting textile goods in dyeing with logwood.

The chrome mordant method requires two operations. However, it is also possible to combine them in a single bath. The following procedure is employed:

The dye bath contains dyestuff, bichromate and Glauber's salt. Dyeing is carried out at the boil with additions of acetic and sulfuric acids. The chrome colors, Chrome Fast, Monochrome, Eriochrome and Acid Chrome colors are suitable for this process.

Baumheier Co. recommended Formollactine, an acidic, water-miscible liquid as an assistant in the dyeing of wool with chrome colors. It has the property of slowly reducing the chromium salts, and of improving the level dyeing of the colors.

Aluminum mordants are used only for the dyeing of some brands of Alizarine, for red and orange. The wool is mordanted for ½ hour in a bath with 10% alum, 3% tartaric acid and 2% oxalic acid, rinsed and dyed with Alizarine.

Iron mordants were important at one time for mordanting logwood, which for a long time was the fastest black on wool. Alizarine Black and Diamond Black have replaced its usage.

The chrome mordant method is seldom employed today, having been replaced by the top chrome and monochrome dyeing methods.

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* Barnes, *Rev. Gen. Mat. Col.*, **1896**, 73; Gavard, *Frb. Ztg.*, **1909**, 8; compare *F.P 571,195* (1923).

Slubbing Printing. The chrome mordant colors are rarely used for printing silk or wool. They find use however in the printing of slubbing, or vigoureux. The print pastes are prepared with dyestuff, solvent, thickening (generally British gum) and chrome mordant. Addition of ammonium thiocyanate or urea has proved favorable. As acidic agents, organic acids like oxalic, tartaric or formic are used.

Slubbing is also printed with fast acid dyestuffs without mordant.

Formulas for print pastes with and without mordant are given here:

60 gm	chrome dyestuff
50 gm	glycerin
120 gm	hot water
620 gm	British gum paste 1:1
20 gm	ammonium oxalate
20 gm	sodium chlorate
100 gm	chrome acetate 20° Bé
10 gm	olive oil
1000 gm	

250 gm	Alizarine Viridine FF paste
50 gm	glycerin
20 gm	sodium chlorate
20 gm	ammonium oxalate
630 gm	British gum paste 1:1
30 gm	olive oil
1000 gm	

The material is steamed one hour, and washed well. Durand and Huguenin mention in several patents* that the ageing time can be considerably shortened by incorporating in the print paste a sufficient quantity of ammonium salts of nonvolatile organic acids, and by using a neutral chromium compound as mordant. Fixer WDHL of D. & H. and Carbic Color is a mixture containing ammonium oxalate and urea.

Stalder (Geigy) recommends the following print formula

20 gm	dyestuff
50 gm	glycerin
408 gm	water
500 gm	starch-trag. thickening
12 gm	ammonium oxalate
10 gm	neutral ammonium chromate
1000 gm	

The prints are steamed one hour. (Compare, Niederhäusern, *Mell.*, **1932,** 412; *Mell.*, **1933,** 20; *Text. Col.*, **1933,** 624, *Tiba*, **1933,** 35.)

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* *U.S.P. 2,018,436, B.P. 412,391, F.P. 755,351, G.P. 623,939.*

Table 8. Metal Salt Mordants

Mordant	Composition	Preparation	Application
Chromium acetate Chromium acetate green 24° Bé Chromium acetate S green 20° Bé (I.G.) Chromium acetate AS green 20° Bé (I.G.)	$Cr(C_2H_3O_2)_3 \cdot 5H_2O$ (Mol. wt. 229.1) Sold as green solution of 20–24° Bé, yields 8.4% of its chromium content. Does not precipitate with NaOH at room temperature. Also sold as powder. Contains a certain amount of sulfate and formate.	(1) By dissolving freshly precipitated $Cr(OH)_3$ in acetic acid. 20 parts $Cr(OH)_3$ of 22.5% Cr_2O_3 content + 30 parts acetic acid 7° Bé. Adjust to 20° Bé = 11.2% Cr_2O_3. (2) Double decomposition of chrome alum and lead acetate. 12.2 parts chrome alum + 12 parts lead acetate, adjust to 20–24°Bé. (3) Reduction of bichromate with glucose in the presence of acetic acid. 48 parts $Na_2Cr_2O_7$ + 72 parts acetic acid 40% + 27 parts glucose = 270 parts chromium acetate solution.	Used in printing wool, cotton, rayon and silk. For padding with chrome colors for the chlorate-discharge style.
Chromium acetate violet Chromium acetate violet in powder Chromium acetate A 20° Bé, violet (I.G.)	$Cr_2(C_2H_3O_2)_4(OH)_2$ Yields 25.7% of its chromium content. Available as solution or powder.	By addition of soda ash to normal chromium acetate. Contains more chromium oxide than the green form, and no combined sulfuric acid.	As mordant in printing cotton fabrics.
Chromium sulfoacetate, normal	$Cr_2(C_2H_3O_2)_4(SO_4)$	By reduction of bichromate in the presence of acetic and sulfuric acids. 12 parts $Na_2Cr_2O_7$ + 9 parts H_2SO_4 66° Bé + 4 parts glucose + 24 parts acetic acid. Adjusted to 50° Bé = 15.5% Cr_2O_3 content.	For printing cotton fabrics.

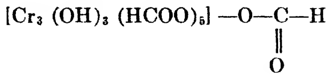
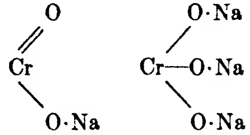
Chromium sulfoacetate basic	$Cr_3(SO_4)(C_2H_3O_2)(OH)_6$ Yields 84% of its chromium content.	Double decomposition of chrome alum with insufficient amount of lead acetate. 11 parts chrome alum + 7 parts lead acetate. Adjust to 25° Bé.	For printing cotton fabrics.
Chromium nitroacetate	$Cr_2(NO_3)_3(C_2H_3O_2)_3$ . . . . (Green solution)	By reducing bichromate with glucose in the presence of nitric and acetic acids. 3 parts $K_2Cr_2O_7$ + 2.6 parts HNO_3 (Sp. gr. 1.33) + 4 parts acetic acid 30% + 0.75 part glucose 28° Bé. Adjusted to 39° Bé.	Used in printing cottons.
Chromium nitroacetate basic	$Cr\ (NO_3)\ (C_2H_3O_2)_2$ $Cr_3(NO_3)_2(C_2H_3O_2)(OH)_6$		Does not decompose starch nor coagulate gum.
Chromium nitrate	Green solution of 50° Bé.	Reduction of bichromate with glucose and nitric acid. 20 parts $K_2Cr_2O_7$ + 31 parts HNO_3 (Sp. gr. 1.33) + 5 parts glucose.	For printing cotton in special cases only.
Chromium nitrosulfoacetate		By double decomposition of chrome alum with lead nitrate and lead acetate. 6 parts chrome alum + 2.5 parts lead acetate + 2.5 parts lead nitrate. Adjust to 21° Bé.	Rarely used.
Chromium formate, normal	$Cr(HCOO)_3$ (Mol.wt. 187) Green, water-soluble needles, not as readily hydrolyzed as the acetate.	By solution of chromium hydroxide in formic acid. 235 parts $Cr(OH)_3$ 30% + 150 parts formic acid 85%, adjusted to 20° Bé. *G.P. 228,668; 244,320; 252,833; 262,049*	Used for printing cotton in skeins.
Chromium formate, basic	$Cr(OH)\ (COOH)_2$		
Chromium formate, complex	 $[Cr_3\ (OH)_3\ (HCOO)_5]-O-\underset{\substack{\Vert \\ O}}{C}-H$ Does not dissociate as readily as the acetate.		

Table 8. Metal Salt Mordants (*Continued*)

Mordant	Composition	Preparation	Application
Chrome oxide T extra pst. (I.G.)	$Cr(OH)_3$ (24%) Readily soluble in acetic acid.	18 kg Na_2CO_3 are dissolved in 100 l water and a solution of 60 kg chrome alum in 300 l water (55°C) added until evolution of CO_2 ceases. Yields 75 kg $Cr(OH)_3$ of 12.5% Cr_2O_3 content.	Basic product for preparation of many chrome mordants.
Chromium sulfocyanide	$Cr(CNS)_3$ (Mol.wt. 226.22) Green salt, sold as a 20° Bé solution.	Double decomposition of chrome alum with barium thiocyanate. Warm 31 parts chromium oxide T with 63 parts water + 10 parts H_2SO_4 66° Bé + 30 parts $Ba(CNS)_2$ crystals. Adjust to 12° Bé.	
Chromium lactate		(1) By dissolving chromium hydroxide in lactic acid. 800 parts $Cr(OH)_3$ of 22% Cr_2O_3 content + 440 parts lactic acid. Adjust to 15% Cr_2O_3. (2) By double decomposition of chromium sulfate and calcium lactate. 480 parts $Cr_2(SO_4)_3$ 30° Bé + 220 parts calcium lactate + 300 parts water. A 20% solution of chromium lactate is obtained, equal to 4% Cr_2O_3.	Used in printing cotton, silk and rayon.
Universal Mordant 9333 **Universal Mordant 9333 conc. and 9333 extra conc.** **Universal Mordant RC (D. & H.)**	Mixtures of chromium lactate, urea and glycerin.	The "concentrated" brand is about 25% stronger than the "9333". *G.P. 583,204; 623,648; 631,923 F.P. 770, 437 (1934) Rev. Gen. Mat. Col.,* **1935**, 138	Used in printing rayon and silk. Prevent coagulation of gum pastes, preserving soft hand of the fabric. "9333" not efficient on cotton, "RC" fixes well on cotton and rayon.

Chromium chromate	$Cr_2(CrO_4)_3 \cdot 9H_2O$	100 parts chrome alum + 86 parts soda, and dissolving the $Cr(OH)_3$ formed in 30 parts CrO_3.	Mordanting of yarns by immersion and fixation in a chalk or warm soda ash bath.
Chrome Mordant GA I, 35° Bé. **Chrome Mordant GA II, GA III (M.L.B.)**	Solution of chromium chromate plus some sulfate and acetate. Chrome Mordant GA I is chromium chromate and chloride.	By dissolving $Cr(OH)_3$ in a mixture of chromic, acetic and sulfuric acids.	Used for the padding of chrome colors.
Eriochromal Mordant (Geigy)	Sodium-chromium oxalate.		For dyeing chrome colors by the Eriochromal method.
Chrosozine N (Geigy)	Inorganic chromium salts.		For improving the fastness to water and perspiration of deep dyeings aftertreated with metal salts.
Chromosol (Sandoz)	Sodium-chromium oxalate		For dyeing chrome mordant dyestuffs on wool.
Metachrome Mordant (I.G.) **Synchromate Mordant (Ciba)**	Ammonium chromate, or a mixture of ammonium sulfate and potassium chromate.	*Mell., Fr. ed.*, **1937**, 28	For dyeing chrome colors on wool by the one-bath method.
Chromium sulfochromate	$Cr_2(OH)_2(SO_4)(CrO_4)$ Solutions are stable.	1 part chrome alum + 0.86 part soda, and dissolving the $Cr(OH)_3$ in 0.2 part H_2SO_4 66° Bé then adding 0.15 part $Na_2Cr_2O_7$ (Gallois)	Used in printing cotton, wool and rayon.
Chromate DH (D. & H.)	Probably ammonium chromate.	*Mell.*, **1939**, 587 *B.P. 481,854* *Wengraf's Ber.*, **1938**, 11	Print pastes have improved stability. Not suitable for silk printing, or with gum thickenings.

Table 8. Metal Salt Mordants (*Continued*)

Mordant	Composition	Preparation	Application
Chromium bisulfite	$Cr_2(SO_3H)_6$ Known only as green aqueous solution. Sold in solutions of 21°, 28° and 40° Bé corresponding to Cr_2O_3 content of 9%, 12% and 18%.	(1) By reaction of calcium bisulfite with chromium sulfate. (2) By reaction of a saturated solution of chrome alum with sodium bisulfite 38° Bé. (3) By introducing a stream of SO_2 gas into freshly precipitated $Cr(OH)_3$ until complete solution results.	For dyeing cotton by padding the mordant and drying in the hot flue, and fixing in a chalk bath. For fixing chrome colors in steaming which have been printed with tartaric and oxalic acid resists.
Mordant pour soie SF (D. & H.)		Von Niederhäusern, *Mell.*, **1934**, 362 *Rev. Gen. Mat. Col.*, **1936**, 202	For dyeing silk in single bath.
Chrome Mordant S (Geigy)	Organic chromium salt.		For silk dyeing with chrome colors.
Chrome - ammonium sulfite	$Cr(NH_4)(SO_3)_2$	45 gm $K_2Cr_2O_7$ + 20 gm Na_2CO_3 + 100 cc $(NH_4)_2SO_3$ 36° Bé + 100 cc ammonia + 1000 cc water.	
Sodium chromite **Alkaline chrome mordant** **Sodium-chromium oxide**	Unstable compound, readily depositing $Cr(OH)_3$ on the fiber.	H. Koechlin: 250 parts green chrome acetate 20° Bé + 10 parts glycerin + 420 parts NaOH 38° Bé. H. Schmid: 150 parts chrome alum precipitated with 50 parts soda ash, the $Cr(OH)_3$ is dissolved in 540 parts NaOH 38° Bé. Erban, *Chem. Ztg.*, **1913**, 709	For dyeings which are to be discharged with oxalic acid.

Chromium chloride (Chlorchrome)	$CrCl(OH)_2$ $CrCl_2(OH)$ Basic salts, sold as green solution of 20° Bé or 30° Bé.	By dissolving $Cr(OH)_3$ in $CrCl_3$.	Mordant for cotton yarn. For dyeing cotton in one-bath method. Mordant for silk in dyeing Alizarine and Gallocyanine colors.
Chromium fluoride (Fluorchrome)	$CrF_3 \cdot 4H_2O$ (Mol. wt. 181.1) Green powder, readily soluble in water. The solutions attack glass, copper and zinc.		Mordant for cotton skein printing. In dyeing used only as an after-treatment of substantive colors.
Aluminum hydroxide gel **Gelée d'alumine**	$Al_4(SO_4)\ (OH)_{10} \cdot 2H_2O$ Insoluble in water, soluble in acids.	48 parts soda + 100 parts $Al_2(SO_4)_3 \cdot 18H_2O$ or 142 parts alum. The precipitate is set at 16.4% Al_2O_3.	Basic product for preparation of aluminum mordants.
Aluminum acetate, normal **Red mordant**	$Al(C_2H_3O_2)_3$ The solutions are very stable, and can be heated to 100°C without decomposition. Transfers only 15% of its Al_2O_3 content to the fiber.	(1) Solution of aluminum hydroxide in acetic acid. 1250 parts $Al(OH)_3$ 12% + 1000 parts acetic acid 6° Bé. Adjust to 10° Bé. (2) Double decomposition of aluminum sulfate with calcium or lead acetate. 665 parts $Al_2(SO_4)_3$ of 18% Al_2O_3 + 1127 parts $Pb(C_2H_3O_2)_2$. Filter and set at 10° Bé = 5.2% Al_2O_3	Used in dyeing cotton yarn, seldom in printing.
Basic aluminum acetate	$Al(OH)\ (C_2H_3O_2)_2$ $Al(OH)_2\ (C_2H_3O_2)$	(1) By dissolving $Al(OH)_3$ in normal aluminum acetate. (2) By addition of soda to a solution of normal aluminum acetate.	Similar to above.

Table 8. Metal Salt Mordants (*Continued*)

Mordant	Composition	Preparation	Application
Aluminum sulfoacetate	$Al_2(C_2H_3O_2)_4(SO_4)$	By double decomposition of aluminum sulfate with insufficient amount of lead or calcium acetate.	Very good mordant for printing Alizarine Red and Alizarine Pink.
Red Mordant	$Al_2(C_2H_3O_2)_2(SO_4)_2$	(1) 136 parts lead acetate + 120 parts aluminum sulfate. $Al_2(SO_4)_3 + 2Pb(C_2H_3O_2)_2 \rightarrow 2PbSO_4 + Al_2(SO_4)(C_2H_3O_2)_4$. (2) 120 parts aluminum sulfate + 63 parts lead acetate. $Al_2(SO_4)_3 + Pb(C_2H_3O_2)_2 \rightarrow PbSO_4 + Al_2(C_2H_3O_2)_2(SO_4)_2$	
Basic aluminum sulfoacetate	$Al_2(SO_4)(C_2H_3O_2)_2(OH)_2$ (Schlumberger, Crum, Liechti, Suida, Schwitzer)	Double decomposition of aluminum sulfate or alum with an insufficient amount of lead or calcium acetate.	For printing and dyeing Alizarine Red.
Mordant Salt TR (I.G.)	Very basic aluminum salt, having a high percentage of available alumina.	1908 parts alum or 1336 parts $Al_2(SO_4)_3$ + 1590 parts $Pb(C_2H_3O_2)_2$; filter and add 150 parts soda. Adjust to 12° Bé.	
Aluminum nitroacetate	$Al_2(C_2H_3O_2)_4(NO_3)_2$ (Mol. wt. 414) More easily hydrolyzed than the normal acetate.	Double decomposition of aluminum sulfate with lead or calcium acetate in the presence of lead or calcium nitrate. 66 parts $Al_2(SO_4)_3$ + 78 parts $Ca(C_2H_3O_2)_2$ 15° Bé + 88 $Ca(NO_3)_2$ 36° Bé. Adjust to 10° Bé. Or 6 parts alum + 4 parts lead acetate + 2 parts lead nitrate.	For printing Alizarine Red

Basic aluminum nitroacetate	$Al_2(C_2H_3O_2)_2(NO_3)_2(OH)_2$	102 parts barium nitrate or 130 parts lead nitrate + 74 parts aluminum sulfate of 18% Al_2O_3 content, dissolve and mix; filter, wash and add 12 parts soda. Set at 15° Bé.	For printing Alizarine Red
Aluminum formate **Aluminum triformate crys. (Dölau brand, Zschimmer & Schwarz)** **Aluminum triformate SN in pdr. (Soc. Normande)**	$Al(COOH)_3$ $Al_2(COOH)_6$ $Al_2(COOH)_6 \cdot 3H_2O$ (23% Al_2O_3)	By dissolving aluminum hydroxide gel in formic acid. 235 parts $Al(OH)_3$ gel 30% + 100 parts HCOOH + 450 parts H_2O. Set at 20° Bé. *Bull. Mulh.*, **1911**, 153 . *G.P. 133,719* (M.L.B., 1902)	For printing Alizarine colors. Does not attack the fiber in steaming. Does not tend to form the lake prematurely.
Aluminum sulfoformate		Similar to the sulfoacetate.	
Aluminum tartrate	$Al_2(C_4H_4O_6)_3$ (Mol. wt. 498.33)	1500 parts aluminum hydroxide gel 30% + 2200 parts H_2O + 720 parts tartaric acid + 1500 parts water. Dissolve and set at 15° Bé. *Bull. Mulh.*, **1911**, 153	For printing Alizarine colors, especially Alizarine Orange.
Aluminum sulfocyanide **Aluminum thiocyanate**	$Al_2(CNS)_6$ (Mol. wt. 402) Transfers about 33% of its alumina content.	630 gm aluminum sulfate + 1000 cc H_2O + 850 gm $Ba(SCN)_2$ + 1000 cc H_2O. Mix filter, adjust solution to 12° Bé. = 6.2% Al_2O_3.	For printing Alizarine Pink. Does not attack the doctor blade. Protects Alizarine Pink against damage caused by iron salts. No fiber attack in steaming operations.
Basic aluminum sulfocyanide	$Al_6(CNS)_2(OH)_{16}$	(1) 50 parts $Al_2(SO_4)_3$ + 50 parts $Ca(CNS)_2$. Adjust to 15° Bé (2) by dissolving aluminum hydroxide in an aluminum thiocyanate solution. *G.P. 42,682*, Hauff	

Table 8. Metal Salt Mordants (*Continued*)

Mordant	Composition	Preparation	Application
Aluminum lactate **Lacktalut (Böhringer)** **Lactinium (Byk, Guldenwerke)**	$Al_2(C_3H_5O_3)_6$ White mass	50 parts aluminum hydroxide gel (10% Al_2O_3) + 25 parts lactic acid 50%. Adjust to 17° Bé (4% Al_2O_3)	For printing Alizarine Red. Prevents premature lake formation.
Aluminum nitrate, normal Nitrate mordant	$Al_2(NO_3)_6 \cdot 15H_2O$ Not hydrolyzed by heating or dilution.	(1) By dissolving $Al(OH)_3$ in nitric acid. 24 parts $Al(OH)_3$ (10% Al_2O_3) + 0.6 part HNO_3 (sp.gr. 1.33). Set at 19.5° Bé = 4.8% Al_2O_3. (2) By double decomposition of aluminum sulfate and lead nitrate. 70 parts $Al_2(SO_4)_3$ + 104 parts $Pb(NO_3)_2$. Adjust to 15° Bé.	For printing Alizarine Red and for mordanting natural silk for dyeing with Alizarine colors.
Aluminum nitrate, basic		75 parts $Al_2(SO_4)_3$ + 100 parts barium nitrate or 130 parts lead nitrate; dissolve separately, mix, filter; add 8 parts soda ash and adjust to 15° Bé.	As for the normal nitrate.
Aluminum chloride	$AlCl_3 \cdot 6H_2O$	(1) By double decomposition of aluminum sulfate with calcium or barium chloride. 10 parts $Al_2(SO_4)_3$ + 11 parts $BaCl_2$. Set at 22° Bé. or 58 parts $Al_2(SO_4)_3$ + 140 parts $CaCl_2$ 21° Bé. Adjust to 12° Bé. (2) By dissolving $Al(OH)_3$ in HCl 19° Bé.	Rarely used as a mordant.
Aluminum chloride, basic	Al_2Cl_5OH $Al_2Cl_4(OH)_2$	By dissolving $Al(OH)_3$ in an aluminum chloride solution.	

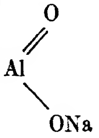
Aluminum chloroacetate	$AlCl(C_2H_3O_2)_2$ Resistant to dilution and boiling.	$Al_2(SO_4)_3 + BaCl_2 + 2Pb(C_2H_3O_2)_2 \rightarrow 2AlCl(C_2H_3O_2)_2 + BaSO_4 + 2PbSO_4$	For dyeing Alizarine Pink.
Sodium aluminate	 $Al(ONa)_3$ $Al_2Na_4O_5$	By dissolving Aluminum hydroxide gel in caustic soda. 500 gm $Al(OH)_3$ of 10% Al_2O_3 content + 328 gm NaOH 38° Bé. Set at 22° Bé. By solution of aluminum powder in caustic soda. Erban, *Chem. Zig.*, **1913**, 709	For mordanting cotton in the cold. Not suitable for animal fibers
Iron pyrolignite **Black liquor** **Iron liquor**	Liquors of 12–15° Bé are available, corresponding to iron content of 5–5.5%.	(1) By dissolving scrap iron in pyroligneous acid. (2) Double decomposition of ferrous sulfate with calcium pyrolignite.	For printing Alizarine and Nitroso dyestuffs. Used for dyeing wool, silk and cotton with logwood.
Ferrous acetate **Ferrous sulfoacetate**	$Fe(C_2H_3O_2)_2 \cdot 4H_2O$	By double decomposition of ferrous sulfate with lead acetate. 34 parts $FeSO_4$ + 36 parts $Pb(C_2H_3O_2)_2$. Set at 10° Bé.	For printing Alizarine Violet.
Ferrous sulfocyanide **Mordant for Fast Printing Green**	$Fe(CNS)_2$	280 parts $FeSO_4$ + 290 parts $Ba(CNS)_2$ or 192 parts $Ca(CNS)_2$. Filter and set at 10° Bé.	For printing Nitroso dyes, Vert d'Alsace, Fast Printing Green.
Ferrous nitrate		(1) By dissolving iron in nitric acid. (2) 175 parts $FeSO_4$ + 208 parts lead nitrate. Solution of 45° Bé = 22% $Fe(NO_3)_2$	

Table 8. Metal Salt Mordants (*Continued*)

Mordant	Composition	Preparation	Application
Basic ferric sulfate **Black liquor** **Iron mordant** ***Also, erroneously:*** **Iron nitrate** **Ferric nitrate** **Basic iron nitrate**	$Fe_4(SO_4)_5(OH)_2$ $Fe_2(OH)_2(SO_4)_2$ Avaliable as a liquor of 45–50° Bé. Dark brown syrupy liquid having 13–14% iron content and 26–28% H_2SO_4.	By reaction of nitric acid on ferrous sulfate. 150 parts HNO_3 (36° Bé) + 70 parts H_2SO_4 (66° Bé) + 400 parts $FeSO_4$. Heat and add 30 parts HNO_3. Adjust to 52° Bé.	For dyeing wool with logwood. Also in printing cotton.
Stannous hydroxide	$Sn(OH)_2$ Mol. wt. = 152.	Precipitation of stannous chloride with soda ash. 10 parts $SnCl_2$ dissolved in 50 parts water + 6.7 parts Na_2CO_3 dissolved in 40 parts water. Set at 23% solid content.	As addition to the print pastes for brightening Alizarine Red prints.
Stannous citrate **Ammoniacal stannous citrate**		35 parts $Sn(OH)_2$ + 65 parts citric acid. 50 parts $Sn(OH)_2$ + 47 parts citric acid + 65 parts NH_4OH 12.5%. Set solution at 32° Bé.	
Stannous acetate	$Sn(C_2H_3O_2)_2$ (Mol. wt. 236)	(1) 10 parts stannous hydroxide + 12 parts glacial acetic acid + 12 parts acetic acid 30%. (2) Double decomposition of stannous chloride with lead acetate. 100 parts $SnCl_2$ + 80 parts CH_3COOH + 100 parts $Pb(C_2H_3O_2)_2$ + 80 parts CH_3COOH 6° Bé. Dissolve separately and mix.	For discharging substantive black dyeings.
Stannous thiocyanate	$Sn(CNS)_2$	By reaction of potassium thiocyanate with stannous oxalate.	As addition to Alizarine printing pastes.

Stannous oxalate	$Sn(C_2O_4)$ 16° Bé	By dissolving stannous hydroxide in oxalic acid. 100 parts $Sn(OH)_2$ + 8 parts oxalic acid 1:1 with water. Warm to dissolve, set at 16° Bé.	As addition to Alizarine print pastes.
Stannous lactate	$Sn(C_3H_5O_3)_2$	By dissolving stannous hydroxide in lactic acid 50%. 180 parts $Sn(OH)_2$ 23% + 600 parts lactic acid 50% + 220 parts glycerin. Adjust to 25° bé.	Sometimes used for replacing stannous oxalate. Does not tender cotton in the steaming operation. Retards lake formation and improves the fastness of Alizarine Red.
Stannic hydroxide **Metastannic acid**	$Sn(OH)_4$ $SnO(OH)_2$	(1) By dissolving stannic chloride in ammonia or soda ash. 100 parts $SnCl_4$(66%) + 2500 water + 183 parts Na_2CO_3 in 2500 water. Filter. Yield 250 parts $SnO(OH)_2$ 17%. (2) By neutralizing stannic oxychloride with soda ash. 10 parts $SnOCl_2$ + 3 parts Na_2CO_3 = 28 parts stannic hydroxide 17%.	As addition to Alizarine print pastes.
Stannic oxychloride **"Stannic nitrate"**	Sold as a 50° or 55° Bé solution.	50 parts tin salt $SnCl_2 \cdot 2H_2O$ are slowly added to 30 parts nitric acid, sp. gr. 1.33. Yield, 100 parts stannic oxychloride sol. 55° Bé.	For Alizarine dyeing to brighten Alizarine Red and Pink.

Table 8. Metal Salt Mordants (*Continued*)

Mordant	Composition	Preparation	Application
Stannic oxalate **Mordant OX**	$Sn(C_2O_4)_2$ Available as a 16° Bé solution.	(1) By dissolving stannic hydroxide or stannic oxychloride in oxalic acid. 100 parts $Sn(OH)_2O$ 23% + 4 parts oxalic acid, warm, set at 16° Bé. (2) 500 parts stannic oxychloride, 55° Bé, in 2000 H_2O + 150 parts soda ash in 1000 H_2O and add 70 parts oxalic acid.	For printing and dyeing Alizarine dyestuffs, to brighten the reds and pinks.
Tin sulfoleate **Ammoniacal tin sulfoleate** **Stannic sulfoleate**	A. Scheurer, *Bull. Mulh.*, **1893**, 95 P. Wilhelm, *Bull. Mulh.*, **1908**, 78 H. Sunder, *Bull. Mulh.*, **1921**, 137 *Z. f. Frb. Ind.*, **1906**, 15–16	(1) 50 parts sodium sulfoleate 25% + 3.2 parts $SnCl_2$ + 20 parts H_2O. Filter. (2) 25 parts sulfoleic acid + 25 parts stannic sulfoleate + 10 parts NH_4OH 12.5%. (3) 100 parts sodium sulfoleate 25% + 90 parts $SnCl_4$ 55° Bé.	For brightening dyeings of Alizarine Red and Pink.
Calcium acetate	$Ca(C_2H_3O_2)_2 \cdot H_2O$	By dissolving lime in acetic acid. 5 parts CaO slaked in 25 parts H_2O + 25 parts CH_3COOH 6° Bé. Adjust to 15° Be.	As addition to Alizarine Red.
Calcium thiocyanate	$Ca(CNS)_2$		

Table 9. Fatty Mordants

Mordant	Manufacturer	Composition	Preparation	Application
Sodium sulfoleate		Mixture of di- and triglycerides of olein, oxystearic acid soaps and their sulfoesters, also of free fatty acids, such as stearic and palmitic acids.	78 parts oleic acid + 38 parts conc. H_2SO_4 added gradually so that the temperature does not rise above 35°C. Neutralize with caustic soda or ammonia.	For preparation of the goods for dyeing and printing Alizarine.
Turkey red oil **Sodium sulforicinoleate** **Ammonium sulforicinoleate** **Huile Rhéolane** **Huile pour rouge** **Huile Topaz**	Flesch Stockhausen Oranienburg S.P.C.M.C. Laroche & Juillard Fournier	Mixtures of triricine, triricinoleic and polyricinoleic acids and dioxystearic acid and their sulfoesters. $C_{17}H_{32}(O \cdot SO_3H) \cdot COOH$ Erban, *Frb. Ztg.*, **1915**, 187 Beyer, *Tiba*, Nov. 1927 *G.P. 128, 691* (1902) *Fischer's Ber.*, **1922**, 515	Prepared in three steps: (a) Reaction of 100 parts castor oil with 35 parts sulfuric acid 66° Bé. The acid is added slowly to prevent temperature rising over 35°C. (b) Removal of excess acid with brine, followed by water. (c) Neutralization of the sulforicinoleic acid with caustic soda or ammonia.	For preparing the goods for dyeing or printing. with Alizarine colors. 30 to 65 gm sulforicinoleate 50% plus 2.5 gm ammonia per l.
Sodium ricinate **Turkey red oil D** **Huile pour rouge** **Para Soap PN** **Alsatine** **Sapoleine** **Paranaphthaleine** **Turkey red oil PO** **Ricinate de soude**	Stockhausen M.L.B. Wegelin-Tétaz F.P.C.T.M. I.C.I. Laroche & Juillard	Ricinoleic acid soap of acid reaction. Mixtures of more or less hydrated oxy fatty acids, solubilized with ammonia.	(1) 100 parts castor oil + 59 parts NaOH 36° Bé + 100 parts H_2O. Boil one hour, add 22 parts HCl 19° Bé., and partly neutralize with 2 parts NaOH 36° Bé. (2) 100 parts castor oil + 100 parts NaOH 19° Bé, Boil one hour, then add slowly 15 parts H_2SO_4 66° Bé until solution is acid. Decant the ricinoleic acid (95 parts) and neutralize at 30°C with 0.12 parts ammonia 25%.	For oiling fabrics which are to be dyed or printed with Alizarine or Nitroalizarine dyes.

Table 9. Fatty Mordants (*Continued*)

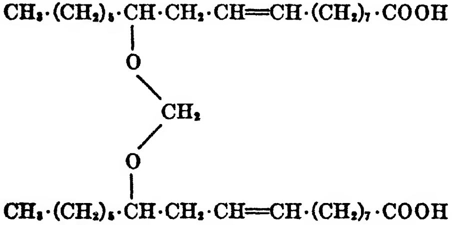
Mordant	Manufacturer	Composition	Preparation	Application
Chlor oil	M.L.B.	Lauber, 1887 *Depierre*, Vol. II, p. 229	By reaction of hypochlorite on olive or castor oil. 1 part castor oil + 1 part $Ca(ClO)_2$ 2° Bé or 1 part rank olive oil + 1 part $Ca(ClO)_2$ 6° Bé or 4 parts olive oil + 1 part H_2SO_4 66° Bé; then mix with 3 parts $Ca(ClO)_2$ 8° Bé.	As addition to Alizarine color print pastes.
Calcium sulfoglycerate **Mordant G**	Havraneck	Reaction product of glycerin and concentrated sulfuric acid.	48 parts glycerin 30° Bé + 48 parts H_2SO_4 66° Bé. Pour into 160 parts water, neutralize with 47 parts chalk and filter. Yield: 160 parts sulfoglycerate solution.	As addition to print paste of Alizarine, brightens the shade.
Lizarol **Lizarol D, D conc.** **Ricinol** **Lizarine** **Rhodenol** **Direct Red Oil** **Isodruckoel** **Purpur Oil**	M.L.B. I.G. Laroche & Juillard Pfeiffer Mulhouse Wacker & Schmitt Bayer L. Blumer Pott	Condensate of 2 mols. sulfonated castor oil with 1 mol. formaldehyde. *G.P. 226,222* (1908, M.L.B.) Viscous oil, insoluble in water. $\begin{array}{l} CH_3\cdot(CH_2)_5\cdot CH\cdot CH_2\cdot CH{=}CH\cdot(CH_2)_7\cdot COOH \\ \quad\quad\quad\quad\quad\quad\; \vert \\ \quad\quad\quad\quad\quad\quad O \\ \quad\quad\quad\quad\quad\quad\quad\; \backslash \\ \quad\quad\quad\quad\quad\quad\quad\quad CH_2 \\ \quad\quad\quad\quad\quad\quad\quad\; / \\ \quad\quad\quad\quad\quad\quad O \\ \quad\quad\quad\quad\quad\quad\; \vert \\ CH_3\cdot(CH_2)_5\cdot CH\cdot CH_2\cdot CH{=}CH\cdot(CH_2)_7\cdot COOH \end{array}$	10 parts castor oil + 10 parts NaOH 19° Bé, add 3.2 parts H_2SO_4 66° Bé. Rinse the ricinoleic acid so formed and sulfonate with 3 parts H_2SO_4 66° Be. Condense with 3 parts HCHO 40% and wash with brine. Or sulfonate castor oil in the cold, add formaldehyde and leave for some time.	For printing Alizarine Red on unoiled goods. Addition: 40 to 50 gm Lizarol per kg print paste.
Lizarol R conc.	M.L.B.	Substitute for Lizarol D (1918) Stable emulsions in water		
Elisol		Chlorinated oil.		

Table 10. Auxiliary Agents for the Mordant Dyestuffs

Name	Manufacturer	Composition	Literature	Application
Fixer CDH	D. & H., Carbie	The principal constituent is urea. Paste of fine crystals, readily soluble in water.	*G.P. 528,262* *U.S.P. 1,942,774* *B.P. 318,469* *F.P. 680,832* *Rev. Gen. Mat. Col.*, 1931, 146; 1934, 111; 1936, 202 *Bull. Fed.*, I von Niederhäusern, *Mell.*, 1933, 412; 1934, 362	Aids fixation of mordant colors in printing. Decreases time of steaming, improves the wash-fastness.
Dehagen S	D. &. H. Carbie	Colorless liquid, containing ammonium thiocyanate, urea and glycerin.	*G.P. 583,204* *U.S.P. 1,942,774* *F.P. 744,137* *Rev. Gen. Mat. Col.*, 1933, 306	Prevents coagulation of gums when printed with metal mordants. Preserves soft hand of prints on silk and rayon.
Dehapan O	D. &. H. Carbie	Thin paste.	*G.P. 601,860* (1933) *F.P. 769,171* *Tiba*, 1935, 58 *Rev. Gen. Mat. Col.*, 1936, 65,104 von Niederhäusern, *Mell.*, 1934, 362	Solvent for chrome colors.
Fixer WDHL	D. & H., Carbie	Ammonium oxalate and urea, sparingly soluble in water.	*G.P. 623,939* *U.S.P. 2,018,436* *F.P. 755,351* (1935) *B.P. 412,391*	For printing wool.
Débéchromol A, B **Débéchromordant**	L.Z.J.	Ureides plus pyridine derivatives.		Improve fixation, shorten time of steaming.

Table 10. Auxiliary Agents for the Mordant Dyestuffs (*Continued*)

Name	Manufacturer	Composition	Literature	Application
Solution Salt CN	I.G.	60% formamide, 40% urea.	*Teintex,* 1941, 83	
Universal Mordant 9333, 9333 conc., 9333 ex. conc. Universal Mordant RC	D. & H., Carbic	Chromium lactate + urea + glycerin.	*G.P. 655,445; 623,648; 631,923; 656,879* *B.P. 435,701; 489,836* *U.S.P. 2,131,320* *F.P. 770,437* (1934); *817,501* *Tiba,* 1936, 23, 94, 411 *Rev. Gen. Mat. Col.,* 1935, 138 von Niederhäusern, *Mell.,* 1934, 15 Britt, *Mell.,* 1935, 188 *Mell.,* 1939, 584	Mordants to replace chromium acetate. Do not coagulate gum thickenings. For printing on rayon and silk.

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