VAT DYESTUFFS AND VAT DYEING

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AND
VAT DYEING

By

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Huddersfield

LONDON
CHAPMAN & HALL LTD.
37 ESSEX STREET W.C. 2
1948

First published 1946
Reprinted . . 1948

THIS BOOK IS PRODUCED IN COMPLETE
CONFORMITY WITH THE AUTHORISED
ECONOMY STANDARDS

Catalogue No. 306/4

PRINTED IN GREAT BRITAIN BY JARROLD AND SONS, LTD., NORWICH

AUTHOR'S PREFACE

As a result of the rapid growth of the synthetic dyestuffs industry and, more recently, of the rayon industry, present-day dyeing has become very much more complicated than it was even a generation ago. In consequence of such rapid advances, it is wellnigh impossible for any one person to provide a detailed survey based on personal experience of the whole vast field of dyeing, and, as in other branches of industry, a need has arisen for books dealing with separate aspects of the subject.

Current Board of Trade statistics reveal how rapidly has the manufacture and employment of the vat dyestuffs risen, and it is conjectured that the present-day ranges of these dyes, which even now are already comprehensive, will increase still further during the years that lie ahead. The value of the vat dyestuff has been fully realised both by consumer and manufacturer. In short, the application of vat dyestuffs now provides a topic which is sufficiently large to justify the publication of a book devoted entirely to it.

Incorporated in this volume are a large number of correlated practical facts which have been collected during the author's ten years' experience with vat dyestuffs. Despite this experience, however, the author does not claim to be expert in all branches of their application. Where aspects of the subject have been described in detail elsewhere, suitable references have been included in the text.

It is hoped that this book will prove valuable to all who are connected with the practical application of vat dyestuffs, as well as to students of dyeing. Besides describing the application of vat dyestuffs, the book includes a brief description of their history and chemistry, for without this background a proper understanding of vat dyeing is impossible. The main section of the book describes, as far as possible, the application of vat dyestuffs to all forms of textile materials, with the inclusion of working recipes to illustrate the various processes. A brief chapter has been included relating to the various types of machinery employed; this has been written purposely for the assistance of students. There is also a short chapter concerning the non-textile uses of vat dyestuffs, and finally there is a section on their identification, alone or in mixtures, on the fibre or in substance.

As an appendix, a list of commercial vat dyestuffs grouped into equivalent, or analogous, products is included. The list purposely includes many obsolete dyestuffs of historical interest, for the benefit of students. It is not meant that this should be a catalogue of the various colour-makers' dyestuffs, but it is hoped that it will render some assistance in the identification of the various competition products. For the sake of simplicity, all the German products have been listed as belonging to the I.G. Farbenindustrie A.-G.

M. R. F.

ACKNOWLEDGMENTS

THE author desires to record his thanks to the following engineering firms who have so kindly given permission for the reproduction of photographs and diagrams of their dyeing and printing machines:

John Dalglish & Sons, Glasgow.
Samuel Pegg & Son (Mellor, Bromley & Co., Ltd.), Leicester.
Franklin Process Company, Rhode Island, U.S.A.
The Longclose Engineering Co., Ltd., Leeds.
Mather & Platt, Ltd., Manchester.
Benninger Engineering Co., Ltd., Uzwil, Switzerland.

Thanks are also due to the *Textile Recorder*, Manchester, for Fig. 17, and to the Deputy Trade Commissioner for information regarding Indian Indigo Exports, and also to Messrs. L. E. Morris; C. L. Bird, M.Sc., F.R.I.C.; and F. H. Marsh, B.Sc., F.R.I.C., for the help and advice they have given. Special acknowledgment must be made of the assistance given by Messrs. Bard and Wishart (Bollington) for the wealth of information they have given regarding the Indigosol dyestuffs of Durand & Huguenin, S.A.

To my wife also, I express my gratitude for the time spent in checking and secretarial work.

M. R. F.

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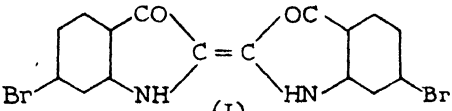
CHAPTER I

INDIGO AND RELATED DYESTUFFS

(*a*) **Tyrian Purple.**—The Purple of the Ancients was essentially a vat dyestuff as we understand the term to-day. Early this century, Friedländer proved that its main constituent was a derivative of indigo, viz. 6:6′-dibromoindigo (**I**).


(I)

Tyrian Purple was obtained from certain species of molluscs which thrived on the shores of several European, African and Asiatic countries, those countries whose seaboard fringed the Mediterranean sustaining the most abundant growth. The shellfish families chiefly concerned were *Murex* and *Buccinum*, the varieties found to yield the colouring matter in largest quantities being *Murex brandaris* and *Murex trunculus*.

According to Huebner (*J.S.D.C.*, Jubilee Issue, 1934, 1) the colouring matter obtained from such shells was used in the island of Crete as far back as 1600 B.C., and it is certain that the purple mentioned in the Bible (Ezekiel, Chapter 27, verse 16): "... they occupied thy fairs with emeralds, purple, and broidered work ..." is that produced from the molluscs. Purple was held in the highest esteem, and in the early period of its use was confined to the dyeing of royal raiments and for the robes of those connected with the highest offices of the Church.

As to its discovery, there are several legends, but the most illustrious is probably that referred to in the poem of John Dyer quoted on page 5 of this book. Thorpe and Ingold, in their book *Vat Colours* (1923, Longmans, Green & Co.), say that it was discovered about 1500 B.C., but Huebner (*loc. cit.*) states that it was used in 1600 B.C. The legend has the following outline. One day, Hercules and Tyros (a nymph) were strolling on the beach accompanied by a dog. In keeping with canine custom, the dog was nosing amongst the pebbles and shells scattered along the shore when he found a small shell which he subsequently crushed between his teeth. The juice from the fish stained his mouth a handsome purple, the shade of which was admired by both Tyros and Hercules. Tyros expressed the desire to have a robe so dyed for herself, and Hercules, anxious to prove his devotion, at once set to work and is thus credited with having dyed the first Tyrian Purple.

Scanty references to purple, or red as it was sometimes called, are to be found throughout the ancient and medieval literature, and an excellent collection of these references may be found in Thorpe and Ingold's *Vat Colours*.

In the fourteenth century, Ronulph of Chester wrote that "there is plenty of shell fish that men dye therewith fine red. The redness thereof is wonder fair and stable, staineth never with cold or with heat, nor with wet, nor with dry, but ever the older the colour is fairer." Interest in the purple-yielding mollusc waxed and waned. There are long periods in which nothing is to be found on the subject and it seems to have been quite forgotten, then someone would rediscover the properties of the various shells found on the shores of England or France and interest would once more be aroused. During the latter half of the last century and at the beginning of this century Friedländer, in particular, made a study of the colouring matter and finally proved that the main reason for its dyeing properties lay in the fact that it consists chiefly of 6:6′-dibromoindigo.

(*b*) **Woad.**—As far as we know, the woad plant (*Isatis tinctoria*) was the earliest source of indigo in Western Europe. When the Romans first visited Britain, they reported that the natives decorated or wholly covered their bodies with a blue colouring matter, which may be assumed without much doubt to have been woad, since Pliny in his writings of the period said that the Britons were acquainted with the art of applying woad to yarns and fabrics.

It was also known to the ancient Indo-Germanic tribes of the Stone Age, and it is believed that the art of cultivation and methods of application had spread to them from India. Gradually, the primitive industry travelled farther west, either by way of Egypt and North Africa to Gaul, or by way of the Indo-Germanics into the west of Europe and, consequently, to Britain.

There are several European plants which contain indigo, but *Isatis tinctoria* is the most important, since the exotic indigo plant will not thrive here. The woad plant is supposedly indigenous to the countries of the Levant and to South-East Russia. Although species of woad are to be found at various places all over Asia and Europe, those in Western Europe at least may be assumed to be cultivated aliens from warmer regions. However, the plant as we know it has every characteristic of belonging to a temperate zone, and examples found growing wild may be offsprings of earlier cultivated plants. Woad was cultivated in Egypt as far back as the early Christian era.

The woad plant, which is biennial or perennial, consists of an erect stem varying from 2 to 5 feet in height and bearing small yellow flowers and ovate or lanceolate leaves. The plant possesses a tap-root which is woody and deeply seated, penetrating the soil to a depth of 12–18 inches. It rapidly exhausts suitable nutrient matter from the soil, and this fact explains the nomadic habit of the early cultivators, who were persistently on the move in search of fresh terrain.

The flowers, although small, are very attractive, and up to recent times they have found a place in the herbaceous borders of our country and town gardens. The bloom measures about one-sixth of an inch in diameter and consists of four bright yellow petals which at the end of the flowering season (July and August) fall away with the formation of a hanging seed-pod. The latter is at first green, but on ripening it takes on a violet-brown colour.

During the first year after the planting of the seeds root development becomes well advanced, and in the following season flowering and fruiting takes place, whilst the foliage lives on through the winter.

The production of the dyestuff depends essentially on fermentation, and in principle the methods employed have varied little from the times of the Ancient Briton of 2,000 years ago to the time its use came to an end a little over ten years ago. Woad contains only a very small amount of indigotin (about 1 %), and after the introduction of natural indigo to the British Isles its importance as a dyestuff was gradually superseded by its use as a ferment in the application of its successor (see page 59, Woad Vat for Indigo). In fact, the cultivators of the plant are said to have lost the art of preserving the small quantity of indigo in woad during the latter half of the last century.

Molisch (*Ber. der Deutsch. Botan. Gesellsch.*, 1899, **17**, 228) demonstrated the presence of indican in woad by producing a deposit of indigo in the following manner. He subjected a number of fresh young leaves plucked from the woad plant to a 24-hour exposure in a closed vessel containing ammonia. This was done in order to precipitate the indican in the leaf cells. The leaves were then removed and treated for a further 24 hours with absolute alcohol. The alcohol treatment dissolved out the green colouring matter of the leaves, i.e. chlorophyll, and subsequent microscopic examination then showed the presence of indigo deposits in the chlorophyll-bearing leaf tissues.

Throughout the early literature relating to the subject, woad is variously named oad, glastum, vuadde, wad, wod, watchet, pastel and dyer's isatis. A more complete list of these variants is to be found in J. B. Hurry's *The Woad Plant and its Dye* (Oxford Univ. Press, 1930), p. 280. The most important districts in England cultivating woad were Somerset, Cambridgeshire and Lincolnshire, and relics of the trade are still to be found in these areas, for example the place names of Glastonbury and Watchet are obviously connected with this ancient trade.

The use and production of woad was the subject of many disputes and disturbances in medieval times. From the time of the Ancient Britons until the twelfth century, little is known as to the state of dyeing in Britain, but about this time there appeared a Merchant Guild which banned the use of woad, and disobedience of the ban was answered by expulsion from the Guild. In 1259, the use of woad "as you please" was apparently dangerous, since several dyers were fined heavily (one cask of ale each) for topping up woad-dyed wool with madder and bran to obtain a darker shade. In the reign of Edward I, however, things seem to have been a little more stable, on account of the law passed which stated that no long cloth shall be dyed except in woad. This may or may not be considered to amount to the same kind of restriction. Woad was mentioned by Chaucer in 1374.

About the year 1415, the town of Coventry was renowned for its production of blue-dyed materials, but its inhabitants evidently found something to grumble about. Their grievance took the form of a petition of complaint against the dyers, in which they said "that the dyers were great common cloth makers and use in their cloths, all the flowers of the woad and the remainder which settles down must serve the common people."

Communications to Burleigh in the sixteenth century from Caspar Vosbergh show that the woad industry was still flourishing, and at a later period we find the first printed book on the subject of dyeing in the English language. The author of this book, Leonard Mascall, whose work is said to have been translated "out of Dutche and englished" by him, gives an accurate description of the woad vat.

Reference to purple and woad was made by John Dyer in his poem "The Fleece," written in 1757, in the following lines:

Tyrian Melcartus thus (the first who brought
Tin's useful ore from Albion's distant isle,
And, for unwearied Toils and arts, the name
Of Hercules acquired), when o'er the mouth
Of his attendant sheep-dog he beheld
The wounded murex strike a purple stain,
The purple stain on fleecy woofs he spread,
Which lur'd the eye, adorning many nymph,.
And drew the pomp of trade to rising Tyre.
Our vallies yield not, or but sparing yield,
The dyer's gay materials. Only weld,
Or root of madder, here, or purple woad,
By which our naked ancesters obscur'd
Their hardy limbes, inwrought with mystic forms
Like Egypts' obelisks.

During the fifteenth century, small quantities of indigo came into the hands of European dyers and slowly its fame spread. The Italians were reputedly the first to use it, but the indigo trade had no substantial footing in Europe until the sixteenth century when the ding-dong struggle between woad and indigo began.

In eighteenth-century France, the cultivation and use of woad was only on a very small scale, the last woad field to be planted there, according to J. B. Hurry, was at Cannevière near Alby, in 1887. Germany, too, gradually allowed woad to fall into disuse, the last woad mill at Pferdingsleben near Gotha, being demolished in 1910. England was the last country to discontinue this declining trade, and Lincolnshire is credited with having taken the last woad harvest in 1931 (Clement Bolton, *Dyer*, 1935, 74, 391).

Towards the end of the last century the following method of preparing woad for the dyer was employed. The crop was harvested by plucking off the leaves at the base of the plant and leaving the root in the ground to produce a second crop. The leaves thus gathered were transported to the near-by "roller-house" where they were crushed to a pulp by a crude arrangement of rollers which were caused to rotate on a central point in a shallow pan set in the ground. Each roller was horse-drawn. The rollers each weighed 15–25 cwt. and were obtusely conical in design; their inner sides were about 6 feet in diameter and their outer sides 7½ feet. The outer and inner faces, which consisted of heavy wooden discs, were bound together by substantial iron bands which formed cross-pieces and constituted the roller face proper, each rod presenting a cutting edge as the wheel revolved.

After crushing the leaves to pulp, the mass was allowed to drain until it had attained the correct consistency. The pulp was next rolled by hand into balls which were about the size of a cricket ball and weighed about 1¼ lb. The diameter of the balls varied in different districts between 2 and 6 inches. After the "balling" operation, the balls were placed on trays and transported to the drying ranges. These consisted of roofed open-air structures beneath which a series of frames was arranged in tiers. The balls took from one week to a month to dry, depending on the weather; when dry, they were returned to the roller-house to be crushed into powder.

The woad powder was then removed from the pan and placed on the floor of a so-called "couching house" to a depth of 2–3 feet. The couching operation was one of fermentation and took approximately nine weeks. From time to time the woadmen would control and encourage fermentation by sprinkling water on the woad until it was in the form of a paste. Fermentation was at first vigorous, the woad steaming and becoming quite hot and at the same time giving off an objectionable smell which only the practised woadmen seemed to be able to endure. Careful check on the temperature (125° F.) of couching was kept, in order to obtain a uniform product of good quality. The final dark clay-like mass was then thoroughly dried and sifted into wooden casks ready for the dyehouse. Approximately 9 parts of woad leaves yielded 1 part of woad dye.

The preparation of the woad vat for dyeing varied little in principle during the whole 2,000 years of its use. However, as time went on, more chemical methods of fermentation began to be employed. In medieval times, before the introduction of indigo, the vat was prepared by first making an aqueous suspension of woad and then adding various agents ("mordants"), e.g. wood ashes (potash) or alum. The liquor was then heated for 3 hours, with or without the addition of additional ferments, e.g. bran and madder. Depending on the weather chiefly, as well as the quality of the woad, the bath would eventually become correctly reduced and dyeing could then be commenced. By varying the number of immersions of the cloth and their duration, and by regulating the concentration of the vat, blues of different depths were obtained. The cloth, after dyeing, was allowed to hang in the open air so as to oxidise the dyestuff, and the pieces were then washed. The dyers of the period appear to have carried on a profitable side-line by selling the skimmings of the woad vat (flowers of woad) to painters for use as pigments.

In combination with other natural products, woad was also employed for the production of woaded greens and blacks. The former were produced by taking woad-dyed wool and, after it had been mordanted with bichromate, dyeing it with a yellow colouring matter, e.g. fustic. Woaded blacks were obtained similarly by first dyeing the fabric blue with woad and then topping with logwood, which was finally fixed with ferrous sulphate.

The employment of woad as a ferment for indigo will be described in the section on the application of indigo (see pages 57–61).

Another indigo-yielding plant which should be mentioned before passing on to indigo proper is *Lonchocarpus cyanescens.* This plant yields a crude dyestuff, containing approximately 0·5% indigotin, which is prepared by certain African tribesmen. The dyestuff so obtained is named Gara. The young leaves, or buds, are taken from the plant and, in a manner analogous to the production of woad, are pulped, sun-dried and worked into balls.

(*c*) **Indigo.**—No colouring matter has been valued higher than indigo, but despite the fact that its history has been well recorded in a number of places, it is not well known. All the early writings seem to agree that India was the birthplace of indigo.

The art of dyeing this time-honoured veteran—which shows little sign of becoming obsolete with the fact that it can now be produced synthetically—probably had a very simple beginning. It may be that some tribesman of distant times discovered a pool into which leaves from an indigo-bearing plant had fallen. Fermentation conditions had been favourable and perhaps he dipped his hand or accidentally dropped a part of his scanty clothing in it and found that a firmly fixed blue stain appeared. He liked it, and therefore spread the story of his mystic pool. The art developed, gradually no doubt, and eventually it found its way through ancient trade routes to Egypt, where 5,000-year-old mummy cloths have been found which were indigo dyed. From Egypt, the mystic art spread northwards, doubtless first to Phoenicia and then to Italy. It was known to the Ancient Greeks and Romans, who appeared to value indigo more as a paint pigment than as a dyestuff for textiles.

The Indian methods of applying indigo do not appear to have spread to China and the East until about the seventh century A.D., probably on account of the fact that there were practically no trade routes.

From the fifth to the twelfth century very little indeed seems to have been known about indigo in Europe, and apart from its use in a few Italian towns it appears to have died out entirely. Then, from the twelfth century onwards, it became a commercial article in Europe. The Portuguese and the Dutch sailing vessels introduced it directly to the western ports, whilst, according to Benjamin the Jew, it apparently spread from India to the Levant and from there to Italy and France and finally to Flanders. Its gradual introduction was accompanied by much controversy and there was a great deal of propaganda put up against its use. It was described as a "devouring devil" and was said to eat the cloth. Edward III, however, encouraged its use, despite the weight of "evil prejudice," by importing a number of Flemish dyers during the fifteenth century. This sect of dyers established a Guild in London in 1472.

As the demand for indigo gradually increased, many countries in suitable climates started the cultivation of indigo-bearing plants. The most important countries concerned were India, China, Japan, Central America, West Indies, Brazil, South and Central Africa, Madagascar, Java and the Philippines. The various plants cultivated to supply the ever-increasing demand all belonged to the genus *Indigofera* and to the natural order of *Leguminosae*, various species of which, viz. *Indigofera tinctoria*, *I. anil*, *I. sumatrana*, *I. disperma*, *I. arrecta* and *I. argentea*, are to be found throughout the above-named areas. The plants are easily cultivated when a suitable soil and an appropriate climate are available; they are of prolific growth, hardy, and little affected by the ravages of disease or by the attacks of insects.

Seeds of the indigo-bearing plant, *Indigofera sumatrana*, were introduced to what was probably India's most fruitful indigo-growing area, namely Behar, in 1782, and in another ten years there were nine indigo factories in this district under European supervision. The cultivation of the area at this time was only to the extent of 670 acres, however, whilst a hundred years later (1893) there were 76 large indigo factories with a cultivation area of some 250,000 acres. Natural indigo production was then at its peak, but with the introduction of German synthetic indigo, which became commercially available on a menacing scale in 1900, there came a rapid decline in trade. Between 1902 and 1914 the planters and natural-dye producers were on the verge of ruin, but, with the temporary stoppage of the synthetic product, trade revived almost to the extent of a boom. Improved methods of production were worked out which, largely owing to the introduction of Javanese seed, gave an increase of 25% on the yield of dyestuff. The extent of the rise and fall in trade may be grasped when it is realised that in 1913 only 8,000 maunds were produced at a selling price of 140/- per maund, as against 200,000 maunds made in

1890 at a price of 300/- per maund. Germany produced 100,000 maunds of the synthetic product in the first nine months of 1914. The yearly consumption of indigo at that time was 200,000 maunds and, since the Germans were unable to supply their quota of 100,000 maunds, and Behar had only 8,000 maunds to offer, prices soared from 140/- per maund in 1913 to between 600/- and 700/- at the end of 1914. However, the impetus to increased production of natural indigo was damped by the fact that, in August 1916, Messrs. Levinstein Ltd. acquired the Ellesmere Port factory (which had belonged to the German firm Meister, Lucius and Brüning before the outbreak of war) and had begun the production of synthetic indigo in Great Britain.

Systematic inquiry was being made into the production of the natural product, and it was found that yields could be increased a further 25% by correct manuring (superphosphates) of the Behar soil. Further, by the removal of the damaging bacteria found to be present in the steeping process, a more profuse growth of the indoxyl-producing bacteria was promoted, and a further 25% increase in yield was obtained.

Manufacture of Natural Indigo.—The method of production of the dyestuff varied somewhat with the locality of the fields and the nature of the plants, and more recently it was modified in accordance with the results of scientific research. All the methods employed, however, whether belonging to the pre-Christian era or to this century, included the following three operations: (i) Steeping the harvested indigo plants in water, so as to extract the dyestuff-yielding substance. (ii) Removal of this aqueous infusion and precipitating the dyestuff by oxidation. (iii) Finally collecting the precipitated indigo and converting it to a merchantable form, viz. a dry cake or powder.

During the prosperous years of the natural indigo industry (late nineteenth century) there were apparently two schools of thought regarding the extraction of indoxyl. The opinions of one school are voiced by J. Bridges-Lee (*Indigo Manufacture*, 1892), who thought that the indoxyl was soluble in water and its extraction from the plant was in no way connected with fermentation. Although he was wrong in the main, he put forward some very sound arguments to prove his views. Christopher Rawson (*J.S.D.C.*, 1886, **2**, 140) definitely allied the process with bacterial fermentation. The colouring principle of the plant is a glucoside of indoxyl named indican, which by enzymatic action yields free indoxyl by hydrolysis and then by subsequent oxidation indigo is produced.

At this period, the principal methods of production depended on whether the starting material was fresh or whether it had been dried. A series of large stone- or cement-lined vats were arranged in two rows so that the bottom of one row was in line with the top of the next. Each vat covered an area of approximately 400 square feet and had a depth of 3 feet. The freshly cut indigo plants, tied up in neat bundles, were carefully packed in the upper row of vessels and were then weighted down so that they would not float, e.g. with stout wooden beams, or iron girders resting on a bamboo trellis. Water of good quality was then run in so that the upper surface of the indigo bundles was just covered. The vats were left in this condition for 10–15 hours, depending on the condition of the weather, the quality of the water and the nature of the plants. Fermentation commenced almost immediately and, after a careful check on the conditions, the liquor was run off into the lower series of tanks. When fermentation slowed down, the liquor was ready for removal. When fermentation was complete, the liquor became slightly greenish and muddy, and a greyish scum collected around the corners and edges of the vat.

The liquor, on running off from the steeping tanks, presented the appearance of an indigo vat, that is, it was yellow to golden-yellow in colour. The lower tanks were called the beating-tanks, because the method of oxidation consisted of beating up the bath with paddles for 2–3 hours. This process entailed very hard work for the natives, who waded waist-deep in the tanks and tossed the liquor vigorously by means of paddles until oxidation was complete. Several other methods of oxidation were later employed. Among the more successful was that involving a shower arrangement which allowed the liquor to fall from a height in tiny droplets, thus encouraging precipitation. Compressed-air bubbling was also widely employed in later days.

As the oxidation continued, the yellow liquor gradually became green, and finally the whole indigo content of the bath was precipitated in flakes. The vats were then allowed to settle, the indigo mal or paste being collected and placed in a separate vessel and raised to the boil in water. The object of the boil was to arrest any harmful prolongation of fermentation which might still be going on. A second important reason for the boiling operation was to remove water-soluble yellow impurities which were invariably present. The latter were in all probability oxidation products of chlorophyll. After standing for a further 20 hours and boiling for a further 3–4 hours, the indigo suspension was filtered through canvas or woollen cloth and washed with fresh water. Excess water was allowed to drain away from the filter, and the dry cake was then cut into cubes and thoroughly dried in a free passage of air.

When the starting material consisted of sun-dried plants the following procedure was followed. Firstly, the plants were threshed in order to separate the stems and the leaves. The latter, during drying, took on a bluish-grey appearance. The leaves were placed in the upper row of tanks and stirred into water until they had become thoroughly wetted and had settled. The remainder of the process was identical with the one described above.

At the end of the nineteenth century, the processes could be further divided into (*a*) the Cold Water Process and (*b*) the Boiling Water Process. The first method consisted, after the usual steeping and letting off the liquor into the beating vats, of raising the temperature of the liquor by means of steam pipes to 45° C., and then adding 250 lb. of 0·880 ammonia per 1,000 cubic feet of pressed plant being extracted. Five lb. of sodium nitrate or potassium nitrate were then added (per 1,000 cu. ft. of pressed plant) and air-blowing or paddle-beating completed the oxidation stage. The use of ammonia in these processes facilitated granulation of the precipitate and prevented side-reactions taking place at the expense of the indoxyl during its oxidation.

In the Boiling Water Process, shallower vats were employed (2 ft. 6 ins. deep) and the water used for the steeping was raised to the boil before adding the indigo bundles. After a few minutes immersion the greenish-yellow liquid was run off into the beating tanks and the procedure described for the Cold Water Process was then followed from this stage.

Fermentation in a boiling bath does not seem possible, and the Bridges-Lee theory of non-fermentation appears to hold good for the boiling process. However, for the cold processes, the theory of fermentation must certainly be the correct one, and it has been shown that the encouragement of bacterial growth or the introduction of artificial cultures gives increased yields of dyestuff. The Agricultural Research Association at Pusa did much valuable work in this connection, and interested readers may follow the subject in the Pusa Reports of 1917–18 and 1918–19 (Hutchinson, "The Importance of Bacterial Action in Indigo Manufacture").

Indigo is now produced in India on a comparatively small scale, but the bulk of production is consumed in domestic markets and the export trade has practically ceased. The following extract[1]

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[1] Kindly communicated to the author by the Deputy Trade Commissioner for India

from the *Annual Statement of the Sea-borne Trade of British India with the British Empire and Foreign Countries for the Fiscal Year Ending* 31*st March* 1940 shows the extent of recent trade.

EXPORTS OF INDIAN INDIGO

	Total British Empire		Total Foreign Countries	
	Quantity (cwts.)	Value (Rs.)	Quantity (cwts.)	Value (Rs.)
1935–36	103	23,268	247	43,206
1936–37	47	7,610	431	68,967
1937–38	99	16,799	326	55,561
1938–39	8	950	333	40,086
1939–40	Nil	Nil	158	17,473

In Japan, too, the trade appears to be only of a domestic nature. The source of present Japanese indigo, however, is of a different kind to that of India. The plant cultivated is *Polygonium tinctorium*, and the method employed in the production of the dyestuff is slightly different. Only the leaves are used, and these are subjected to fermentation by packing in straw-rope sacks for 70–80 days. The leaves are then moistened with water and placed under mats for 3–5 days, this operation being repeated several times. The resulting mass is placed in a large wooden mortar, worked into a dark blue doughy mass and finally worked into balls. A fuller description of this method has been given by H. Leopold (*Dyer*, 1936, **75**, 119).

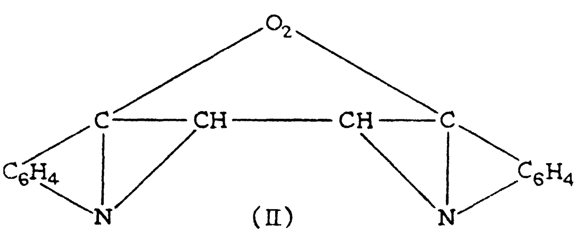
Before passing on to artificial indigo, it is worth while to record a note about indigo production in China in 1888. The Chinese indigo farms (there were only a few large plantations) possessed large earthenware jars or kongs about the size of a barrel in which steeping and beating took place. Slaked lime was largely used in the operation. The most interesting fact about Chinese indigo production, however, appears to be that the planters had a fear of women with flowers in their hair! The wearing of flowers amongst the female sex of the Chinese was a common custom, but it was believed that the quality of the indigo would be low if these ladies of fashion came near. The Chinese planters, therefore, removed the kongs to some position protected from the atmosphere of the fields which may have had flower-wearing females present!

Synthetic Indigo.—Early in the nineteenth century important investigations into the chemical constitution of indigo had already begun. The great importance attached to this universally employed dyestuff naturally led workers in organic chemistry to probe into its chemical nature.

As early as 1826, Unverdorben obtained aniline by the distillation of indigo. Incidentally, "anil" was one of the Indian native names for exotic indigo, hence the term aniline was given to the new product obtained from indigo. Fritsche, in 1841, by fusing indigo with caustic potash, obtained anthranilic acid and, although it was not realised at the time, this was an excellent clue to the raw material needed for the synthesis of the colouring matter. Both Laurent and Erdmann, by different routes, succeeded in preparing isatin from indigo; the former used chromic acid to oxidise indigo, whilst the latter employed nitric acid.

The year 1865 saw the beginning of Baeyer's classical researches directed towards the synthesis of indigo. Having rapidly conquered isatin, he finally succeeded in his epic synthesis of indigo in 1879. How wrong was Noelting when, as late as 1886, he said: "Notwithstanding the enthusiasm which this discovery raised, we are still unable to make the artificial product at such a rate as to compete with the natural one; in fact, *it is very doubtful whether this will ever be done*"! His opinion was without doubt based on the fact that Baeyer and Drewson's original commercial début (1882) had been anything but a success; on the contrary, it had been a lesson.

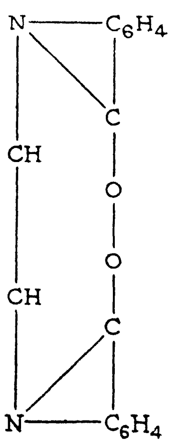
The great difficulties in the initial stages of Baeyer's researches are illustrated by the fact that amongst numerous other attempts, the following formulae (**II** and **III**) were laid down as representing indigo:



(II)

Known as the "Umbrella" formula

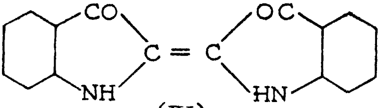
and



(III)

Known as the "Tower" formula

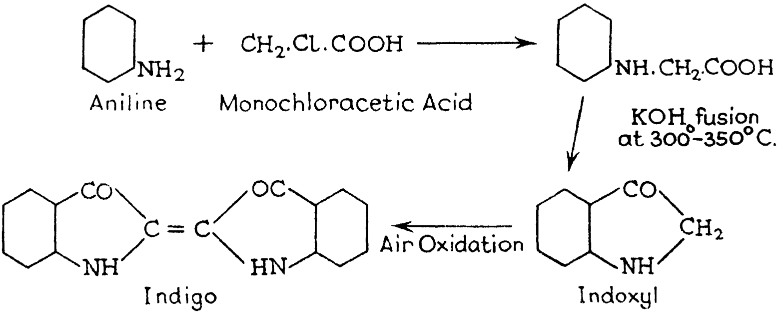
The number of carbon, hydrogen, oxygen and nitrogen atoms in the molecular formula for indigo had been correctly and definitely fixed, but it was not until 1883 that Baeyer was able to publish the correct formula (**IV**), now familiar to every student of colour chemistry.



(IV)

For his first synthesis, Baeyer used *o*-nitrocinnamic acid (from *o*-nitrophenylpropiolic acid) as his starting material. Later, an improved yield of the *o*-nitrocinnamic acid was obtained by nitrating ethyl cinnamate. In collaboration with Drewson he achieved another synthesis by way of *o*-nitrobenzaldehyde, which was prepared from *o*-nitrophenyllactomethyl ketone.

It was Flimm's discovery, in 1890, that the caustic potash fusion of monobromoacetanilide yielded oxindole (which in turn gave a small quantity of indigo by oxidation) that led to Heumann's important discovery a little later in the same year. Heumann's synthesis was responsible for the commercial production of synthetic indigo. He employed a caustic potash fusion of phenylglycine, and later a better yield of the dyestuff was obtained by starting from the *o*-carboxylic acid of phenylglycine. The principle of the discovery is self-explanatory in the following series of reactions:

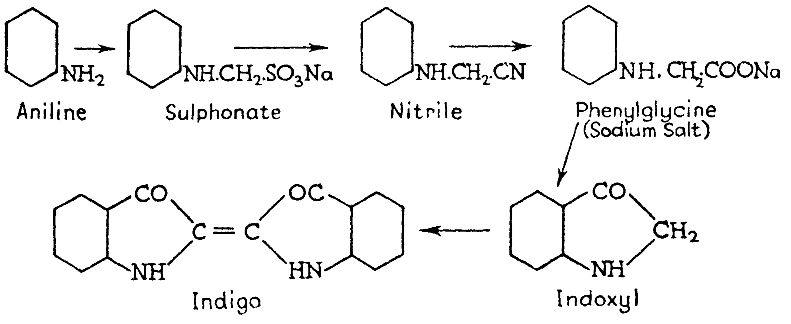


The Badische Anilin- und Soda-Fabrik (B.A.S.F.) first undertook the commercial manufacture of indigo by the *o*-carboxylic acid route, but found it necessary to cheapen the process of producing phthalic anhydride which was necessary for the preparation of anthranilic acid. There were available great quantities of naphthalene, i.e. the raw material for phthalic anhydride, but the production of phthalic anhydride did not become a large-scale success until 1896. In this memorable year a thermometer was broken, and what had seemed to be almost a worthless dream became a reality. Sapper succeeded in oxidising naphthalene in sulphuric acid monohydrate simply because of the presence of the mercury catalyst provided by his inadvertent clumsiness. The phthalic anhydride thus obtained was transformed into the imide and thence into anthranilic acid by the employment of alkaline hypochlorite. The reaction then proceeded in a parallel manner to Heumann's laboratory synthesis, that is the anthranilic acid was condensed with monochloracetic acid to yield phenylglycine-*o*-carboxylic acid.

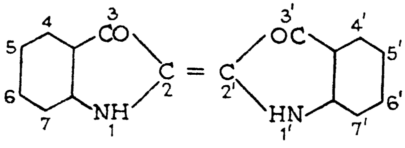
A further reduction in cost was made possible by the development of electrolytic plant for the production of chlorine from common salt, since chlorine is essential for the manufacture of monochloracetic acid.

In 1897, the B.A.S.F. put Indigo Pure on the market, some eighteen years after the first laboratory synthesis. Work did not stop here. Meister, Lucius & Brüning, then a competitive firm, were able to offer Indigo MLB shortly after the launching of the B.A.S.F. product. This was made possible by Roessler's discovery that an addition of sodamide to the alkaline fusion of phenylglycine itself gave increased yields of the dye. Further modifications have resulted in the following synthesis, which is now the most widely used commercial process. Aniline is condensed with formaldehyde bisulphite to yield the ω-sulphonate, which, by treatment with sodium cyanide, is converted into the nitrile. Hydrolysis in caustic soda solution then gives phenylglycine which, when fused in a mixture of caustic potash and sodamide, yields indoxyl, from which indigo is finally obtained by air oxidation.

The above method is now employed in the dyestuff factories of the U.S.A., Germany, France and Great Britain.

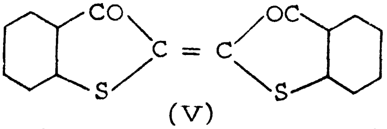


Derivatives of Indigo.—Before proceeding to the indigoid dyestuffs, it is well for the reader to familiarise himself with the following system of numbering the parent substance—indigo.



With the advent of synthetic indigo the required impetus was supplied to research workers all over Europe, and very quickly a range of new products with analogous structures was presented to the dyeing trade. The dyeing properties of these new compounds were virtually the same as those of the parent substance, but their shades were different, as well as being attractive. The first of these new products was the tetrachloro-derivative (5:7:5′:7′-tetrachloroindigo), placed on the market by the B.A.S.F. as Brilliant Indigo B.

Thioindigo (V) was probably the most important early discovery in this range of dyestuffs. In 1906, Paul Friedländer discovered this red dyestuff in which the NH groups of indigo are replaced by sulphur. It is chemically termed 2:2′-bisthionaphthenindigo.



(V)

By means of halogenation, alkylation, amination and benzoylation, and through condensation with other compounds, a great many dyestuffs with excellent fastness properties can be obtained.

Halogenation by means of chlorine produces brighter blues as more chlorine atoms are introduced. Thus, the 5-monochloro-derivative of indigo is little different in shade from indigo itself, but the 5:7:5′:7′-tetrachloro-compound is a decidedly brighter dyestuff. In the case of bromine there is a slight change towards greenness as the number of bromine atoms is increased, but the increasing greenness is accompanied by a decrease in the solubility of the *leuco*-compound, i.e. the dye is more difficult to vat. The following list of commercial dyestuffs will serve to illustrate these points:

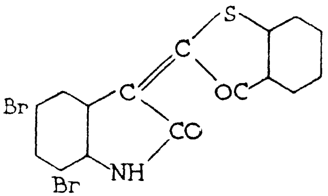
Increasing Greenness ↓

5-Monobromoindigo	Indigo Pure R
5:5′-Dibromoindigo	Indigo RBN
5:7:5′-Tribromoindigo	Indigo BB
5:7:5′:7′-Tetrabromoindigo	Brilliant Indigo 4B
4:5:7:5′:7′-Pentabromoindigo }	Obtained as a mixture,
4:5:7:4′:5′:7′-Hexabromoindigo }	viz. Ciba Blue G.

Mixed halogen compounds, i.e. dyes containing both chlorine and bromine, are also marketed. The 6:6′-dibromoindigo (the colouring matter of Tyrian Purple) is a red-violet dyestuff, but unlike the above bromo-derivatives, it is prepared by indirect synthesis and cannot be obtained by direct bromination of indigo.

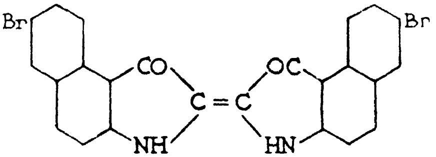
Halogenation of thioindigo yields various shades of red, e.g. 5:5′-dichlorothioindigo and 6:6′-dichlorothioindigo are sold as Thioindigo Red BG and Ciba Red B, respectively. When 6:6′-diethoxythioindigo (Thioindigo Orange R) is chlorinated, 5:5′-dichloro-6:6′-diethoxyindigo is formed, which is marketed as Helindone Fast Scarlet R.

Other chemically related compounds are Ciba Brown R, which is 6:6′-diamino-5:7:5′:7′-tetrabromoindigo; Hydron Pink FF, which is 6:6′-dichloro-4:4′-dimethylthioindigo; and Ciba Red G (**VI**), which is a condensation product with dissimilar nuclei prepared from 5:7-dibromoisatin and thioindoxyl.



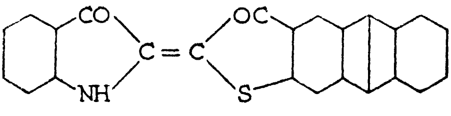
(VI)

Ciba Green G is the dibromo-derivative of β-naphthalene indigo (**VII**).



(VII)

More recently, complex condensation products containing both the indigoid nucleus and the anthraquinone nucleus have been placed on the market. In general, these compounds show better fastness properties than other indigoid vat dyestuffs.[1] Cibanone Green GC (**VIII**), for example, is reported to possess both an anthracene ring and an indigo ring:



(VIII)

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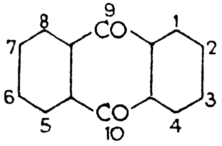
[1] See e.g. *B.P.* 398,053.

CHAPTER II

ANTHRAQUINONOID VAT DYESTUFFS

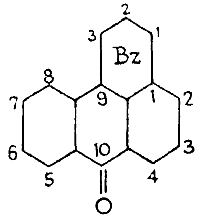
THE numbering of anthraquinonoid vat dyestuffs is based on that of anthraquinone:



If two anthraquinone nuclei unite to form a compound, then the positions in the second nucleus are indicated by the number of the specific position and accompanied by one dash ('). If a third nucleus is present, then two dashes ('') are added. Study of the formulae illustrated in this chapter will make these points clear.

Benzanthrone is numbered similarly:

Bz=Benzene



Benzanthrone

The parent substance of anthraquinonoid vat dyestuffs is anthracene, which was discovered in the higher-boiling fractions of coal tar by Dumas and Laurent, 110 years ago. One of the earliest and most important uses to which this compound was put was in 1868–9, when Graebe and Liebermann (and W. H. Perkin, independently) synthesised the colouring matter of madder. The synthesis of Alizarin revolutionised the dyeing trade in much the same way as did the synthesis of indigo in later years, and it resulted in the development of a whole range of acid and mordant dyestuffs from the same source.

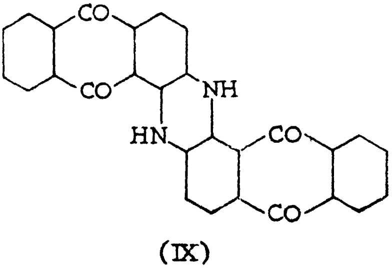
Indanthrones.—Probably the first vat dyestuff prepared from anthraquinone was one patented by Meister, Lucius & Brüning towards the end of the nineteenth century. This was a brownish-black dyestuff prepared from anthrachrysazine, but it possessed no attractive properties and was of little value. The synthesis of anthraquinonoid vat dyestuffs of commercial importance was not realised until René Bohn discovered indanthrone in 1901.

It was a natural sequence to the researches which had aimed at the synthesis of indigo to attempt to prepare an anthraquinonoid analogue. In fact, Bohn originally worked on the principle underlying the preparation of indigo. He endeavoured to make diphthaloylindigotin by the alkaline fusion of the glycine of β-aminoanthraquinone. Instead of the anticipated compound, however, he obtained a brilliant blue vat dyestuff with exceptionally high fastness properties. The constitution (IX) of the newly formed dyestuff was soon established as N-dihydro-1:2:1′:2′-anthraquinoneazine. The Badische Anilin- und Soda-Fabrik manufactured this compound under the name of Indanthren Blue R. The present Brilliant Blue RS types are chemically the same compound, but are in a much higher state of purity.

It was soon realised how large was the field for development laid bare by this discovery. Derivatives of indanthrone followed rapidly. Bromo-, chloro-, methyl-, and hydroxy-compounds followed quickly in the shape of more blue dyestuffs of increased fastness. The halogenated derivatives yielded Blues of high fastness to the chlorine bleach, examples being Indanthrene Blues GC and GCD, and Caledon Blue RC. Indanthrene Blue RK and Algol Blue RK, the monomethyl- and dimethyl-derivatives, were found to be applicable from a cold dyebath.

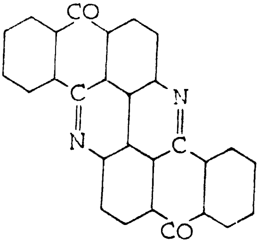
A more recent and very interesting synthesis of indanthrone involves treatment of the di-ester of β-aminoanthrahydroquinone, first with alkaline oxidising agents and then with acid oxidising agents.

Members of the indanthrone class all show excellent fastness to light and the chloro-derivatives, especially 3:3′-dichloroindanthrone or Caledon Blue RC, exhibit very good fastness to bleaching.



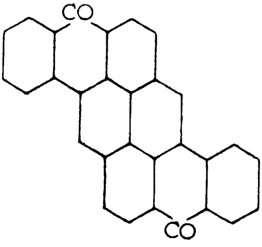
(IX)

Pyranthrones.—Flavanthrone (X), or Indanthrene Yellow G, was discovered by Bohn very shortly after he had prepared indanthrone. By varying the conditions of temperature in his experimental work on the blues he found he was able to produce this yellow dyestuff. Manufacture of this colour was commenced in this country by the Solway Dyes Co., in February 1915, only six months after the outbreak of the 1914–18 world war.



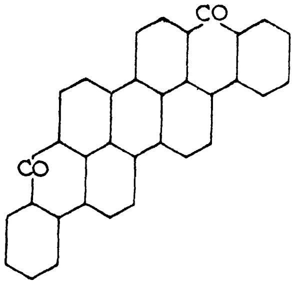
(X)

While Scholl was trying to establish the above formula (X) in 1905, he discovered that a fast orange vat dyestuff could be prepared by the caustic potash fusion of 2:2′-dimethyl-1:1′-dianthraquinonyl. This dyestuff became known as pyranthrone (XI) or Indanthrene Golden Orange G. On the introduction of bromine into the molecule, this compound yielded dyes of redder shade which were sold as Indanthrene Oranges 2RT and 4R.



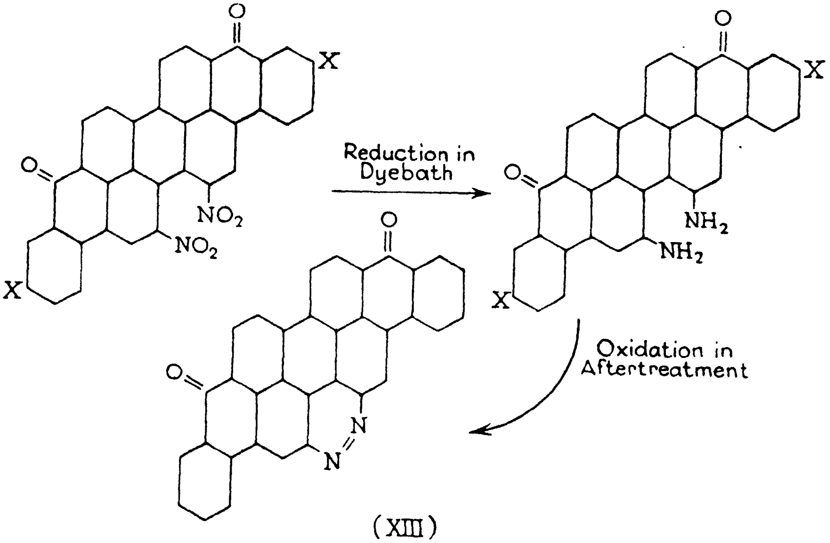
(XI)

Benzanthrones.—A large number of very important vat dyestuffs belong to the group known as the benzanthrone series. The first of these, Indanthrene Dark Blue BO or violanthrone, was dibenzanthrone (XII), prepared by alkaline fusion of benzanthrone, during which two molecules of benzanthrone unite to give a nine-membered ring compound. Besides being a valuable dyestuff in itself, violanthrone is a most useful intermediate product for the preparation of other vat colouring matters.



(XII)

The dinitro-derivative of dibenzanthrone is sold as Indanthrene Black 2B (**XIII**), which first dyes green on the fibre and is then converted into a black by oxidation with hypochlorite or sodium nitrite. During the application of this vat dyestuff it is known that the nitro-groups become reduced by the hydrosulphite of the dyebath to amino-groups. In the hypochlorite after-treatment, the amino-groups are oxidised, with probable formation of dibenzanthroneazine (**XIII**).[1]



(XIII)

The positions "*x*" have recently been suggested as more likely positions for the nitro-groups.[2]

This last reaction may be reversed and the green diamino-compound re-formed by a further treatment in alkaline hydrosulphite solution.

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[1] See Maki, Nagai and Hayashi, *J. Soc. Chem. Ind., Japan*, 1935, **38**, 710B–720B.

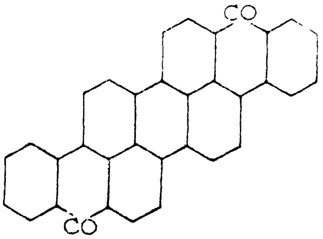
[2] See Bennett, Pritchard and Simonsen, *J.C.S.*, 1943, 31–33.

Indanthrene Direct Black RB,[1] however, is a direct-dyeing black, probably obtained from the last-mentioned compound by oxidation in substance, so that the reaction is irreversible. Direct-dyeing blacks and greys have also been produced from dibenzanthrone by oxidation, or by treatment with hydroxylamine salts. Halogenated derivatives are dyestuffs of great value.

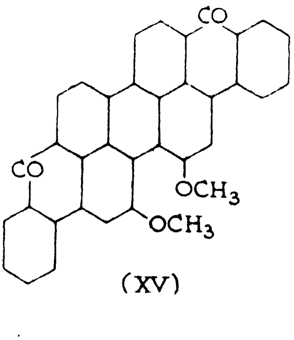
Two molecules of benzanthrone, besides being able to unite to give violanthrone, may be brought together in a different manner, by using benzanthrone which has been substituted in the Bz-ring by chlorine. In this case, a violet vat dyestuff, *iso*violanthrone or *iso*dibenzanthrone is produced. Commercially, it was first known as Indanthrene Violet R, and was discovered in 1906 by Bally and Wolff. Improved processes of manufacture have since been established, using the sulphides or selenides of dibenzanthronyl. Formerly, this dyestuff was widely employed in the dyeing of cotton, but its place has now been taken by more suitable products; it is still available as Paradone Violet B, etc.

*iso*Violanthrone (**XIV**) is of exceptional interest as an intermediate product for the production of Indanthrene Brilliant Violets 2R, 4R, B and 3B, which are halogen derivatives of greater tinctorial value than the starting material.

Of all the vat dyestuffs, the most valuable is probably 12:12′-dimethoxydibenzanthrone, or Caledon Jade Green (**XV**), prepared by methylating the oxidation product of dibenzanthrone, i.e. dihydroxydibenzanthrone.



(XIV)



(XV)

This compound was a British discovery, and was first made by Davies, Fraser-Thomson and Thomas in 1920 from a German discovered intermediate—dihydroxydibenzanthrone (Max Isler). Many derivatives are now obtained from the same raw materials, e.g. the Jade Greens 2GS, 4GS and 3BS and Caledon Dark Blue

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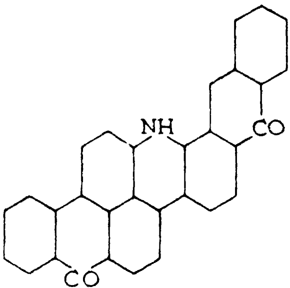
[1] *B.I.O.S., Final Report No. 987* now states that this is a condensation product of amino-violanthrone, α-amino-anthraquinone and tetra-bromo-pyranthrone (1947).

GS; Caledon Ming Blue is obtained similarly from *iso*dibenzanthrone.

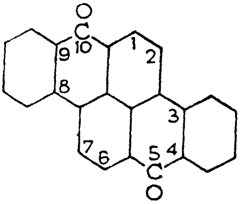
Indanthrene Olive Green B is a benzanthrone derivative belonging also to the acridone class. It consists chiefly of benzanthrone acridone (**XVI**).



(XVI)

Benzanthrone-pyrazolanthrone is obtained by the alkaline fusion of the condensation product of bromobenzanthrone and pyrazolanthrone and is an important Indanthrene Navy Blue showing almost unrivalled fastness to light.

Although the dibenzpyrenequinones are usually classed separately, they really belong to the benzanthrone group. Indanthrene Golden Yellow GK, or 3:4:8:9-dibenzpyrene-5:10-quinone (**XVII**), is probably the best example of this very important sub-group; the RK brand is the dibromo-derivative.



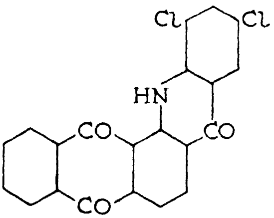
(XVII)

Other dyestuffs closely related to the pyrenequinones, although not of the benzanthrone class, belong to the *Anthanthrone group*. Anthanthrone itself is valueless as a dyestuff, but when halogen atoms are introduced into the molecule the very powerful Indanthrene Brilliant Oranges GK and RK are produced.

Acylamino-Anthraquinone Group.—This large class of vat dyestuffs, although not as popular as when first discovered, is still important for many purposes. Deinet is credited with the discovery of most of these compounds. Algol Yellow WG

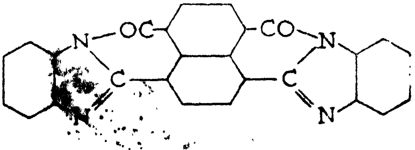
(1-benzoylaminoanthraquinone) was one of the first members of this group to be discovered. It is now obsolete as far as its use as a dyestuff is concerned, but it still finds employment as an intermediate product for the manufacture of other vat dyestuffs. Algol Brilliant Violet R, Algol Red 5G, Algol Brilliant Red 2B, Algol Bordeaux 2B and Indanthrene Yellow GK all belong to this class.

Acridone Group.—Important members of this group are Indanthrene Violet RN, Indanthrene Red Violet RRN (**XVIII**), Indanthrene Red BN and the Indanthrene Turquoise Blues. Mention has already been made of the benzanthroneacridone, Indanthrene Olive Green B. Anthraquinoneacridone vat dyestuffs are noteworthy for their excellent fastness to light and non-tendering properties (see p. 47).

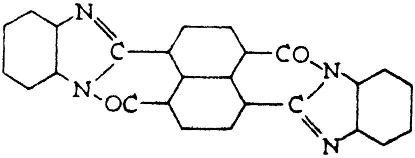


(XVIII)

Iminazole Group.—Although Indanthrene Orange FFRK belongs to this group (as an iminazole) it is an anthraquinonoid compound. The most interesting members of this class are derivatives of naphthalenic acids: Indanthrene Scarlet GG and Indanthrene Brilliant Orange GR are naphthoylene dibenziminazoles, the former being a mixture of two isomeric forms (*cis*- and *trans*-) of the naphthoylene dibenziminazole. When the *trans*-isomeride (**XX**) is isolated from this mixture it yields Indanthrene Orange GR; the pure *cis*-form (**XIX**) is of little value and is bluish-red in colour.[1] Dyestuffs belonging to this class possess high tinctorial value and give clear saturated shades which are non-tendering.



(XIX)



(XX)

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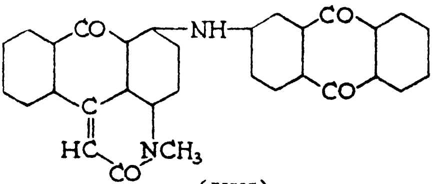
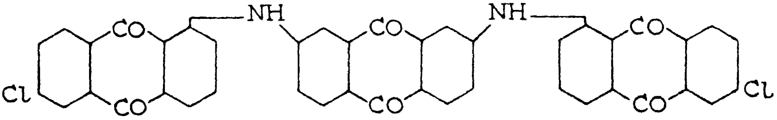
[1] *B.I.O.S., Final Report No. 1088* now states that this compound is Indanthrene Bordeaux RR (1947).

Anthrimide Group.—Anthrimide or anthraquinonylamine vat dyes contain two or more anthraquinone nuclei connected by imino-groups; they constitute a very important group of vat dyestuffs. One of the first red vat dyestuffs produced (1906), viz. Algol Red B (**XXI**), belongs to this class.



(XXI)

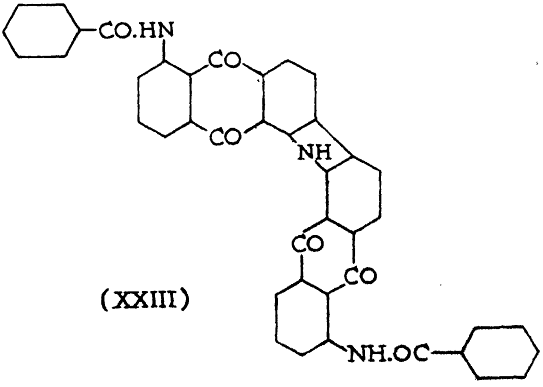
An example containing three molecules of anthraquinone, i.e. a trianthrimide, is Indanthrene Bordeaux B extra (**XXII**), obtained by condensing 2 mol. 1-amino-6-chloroanthraquinone with 1 mol. 2:7-dichloroanthraquinone.



(XXII)

The Society of Chemical Industry in Basle were first responsible for the production of vat dyestuffs containing the *Cyanuric Ring*; this class is exemplified by Cibanone Red G and Cibanone Orange 6R.

Carbazole Group.—Dyestuffs containing the carbazole ring are very important, e.g. the group includes Indanthrene Golden Orange 3G (**XXIII**), Indanthrene Brown BR, Indanthrene Olive R and Indanthrene Khaki 2G.

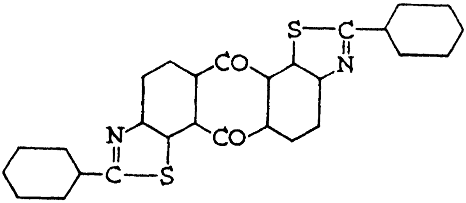


(XXIII)

The anthraquinone carbazoles exhibit excellent fastness to light and good all-round fastness and dyeing properties.

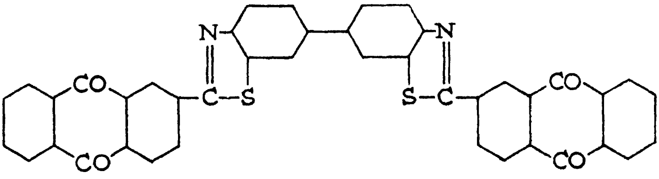
Vat Dyestuffs containing Sulphur.—When attempting to distinguish vat dyestuffs from sulphur dyestuffs, it is found that there are many border-line cases. Thus, there are several anthraquinonoid vat dyestuffs which contain sulphur; on the other hand, there are compounds such as Hydron Blue which may be dyed by either the vat process or by the sulphide process, or by a modified method combining the two principles. Such colouring matters have been classified as the sulphurised vat dyestuffs, a class which is further subdivided into anthraquinone derivatives and indophenol derivatives.

Two important anthraquinone thiazole compounds belonging to this class are Anthra Yellow GC and Indanthrene Yellow GF. Both these dyestuffs have high fastness properties (although failing in resistance to light) and are very widely used on account of the wide range of conditions under which they may be applied to the fibre. Anthra Yellow GC (**XXIV**) was first made in 1912 by Isler and Kačer; it is obtained by refluxing 2:6-diaminoanthraquinone, sulphur and benzotrichloride with naphthalene.



(XXIV)

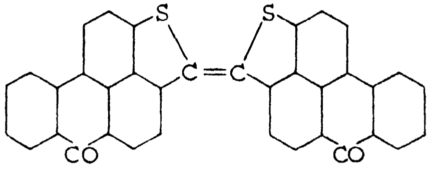
Indanthrene Yellow GF (**XXV**) is prepared similarly from 2-methylanthraquinone, sulphur and benzidine.



(XXV)

A very beautiful colouring matter belonging to this class is Cibanone Blue 3G, which is a sulphur derivative of benzanthrone. It was originally prepared by the Society of Chemical Industry in Basle from 2-methylbenzanthrone, sulphur and naphthalene in 1908. Its constitution remained a mystery, however, until the I.G. chemists synthesised Indanthrene Blue Green FFB in 1927.

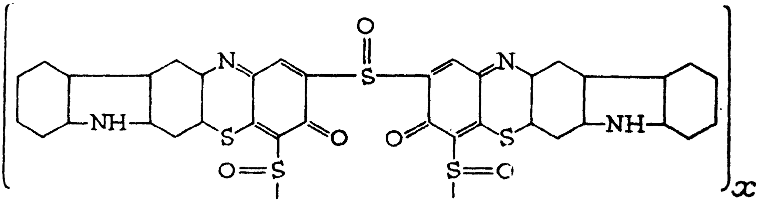
The two dyes are identical, and the method of manufacture of Indanthrene Blue Green FFB elucidated the structure of Cibanone Blue 3G (**XXVI**).



(XXVI)

Many other Cibanone dyestuffs belong to this class, e.g. Cibanone Green B, Cibanone Orange R and Cibanone Yellow R.

Indo Carbon S is a black sulphur dyestuff which, although it does not actually belong to this class, must be mentioned because it may be considered to be the parent of the most important dyestuff of the indophenol class of sulphurised vat dyes, viz. Hydron Blue R (**XXVII**). Both compounds are derived from *p*-nitrosophenol and carbazole. Fierz-David and Bernasconi have established the constitution of Hydron Blue R as:

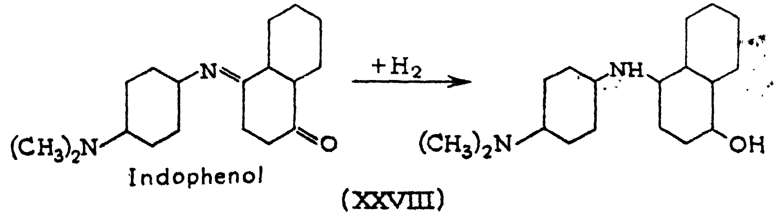


(XXVII)

There are several other Immedial and Pyrogene dyestuffs which are similar in dyeing properties and constitution to the above compound, e.g. Immedial Pure Blue and Pyrogene Green, but these dyes are almost always dyed by the normal sulphide process.

Hydron Blues, Hydron Black and the Indocarbons have been called the sulphurised derivatives of carbazole.

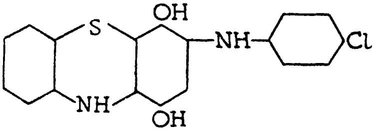
Before closing this section it is as well to mention Indophenol Blue (**XXVIII**). This compound has very similar dyeing properties



(XXVIII)

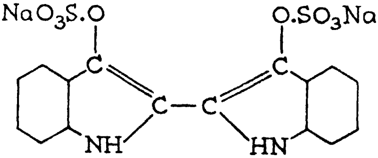
to indigo itself and is almost as fast to light, alkali and milling, but it is extremely sensitive to acids. Indophenol reduces to indophenol white, in which form it is applied to the fibre and is then re-oxidised to the original compound.

The diarylaminobenzoquinones and their thionated products are related to indophenol and may be considered to belong to the class of sulphurised vat dyestuffs. Examples are provided by several of the Helindon vat dyestuffs for wool, e.g. Helindon Yellow CR and Helindon Brown CM (**XXIX**).



(XXIX)

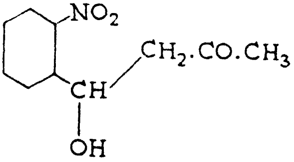
Solubilised Vat Dyestuffs.—The first solubilised vat dyestuff was produced by Bader and Sunder in 1921. This product, known as Indigosol O, was prepared by subjecting *leuco*-indigo to the action of chlorosulphonic acid in the presence of pyridine. The disulphuric ester so formed was then converted into the water-soluble sodium salt (**XXX**).



(XXX)

In the application of the Indigosols to the fibre, the water-soluble product is first dyed or padded on to the fibre directly, and subsequently oxidised in acid solution to the original insoluble vat dyestuff. A number of previous attempts had been made in the hope of finding some method whereby vat dyestuffs could be applied without the vatting process. Thus, one method involved drying the stabilised *leuco*-compound of indigo in presence of agents such as glucose and molasses so as to prevent oxidation. This was not a commercial success, and later the Badische Anilin- und Soda-Fabrik took out patents dealing with the stabilisation of *leuco*-indigo by forming the carbonic ester. These products, in contrast to the Indigosols which are developed in acid solution, had to be developed in alkaline solution, which proved to be difficult in practice because the reaction on the fibre was too slow.

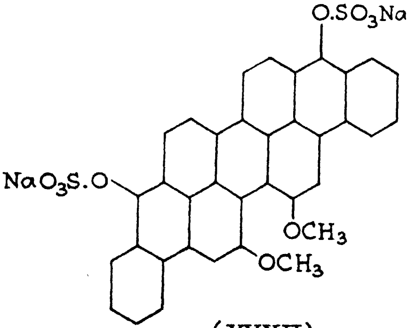
Kalle & Co. A.-G. marketed Indigo Salt T (**XXXI**), or the bisulphite compound of *o*-nitrophenyllactomethyl ketone, which liberates indigo on the fibre at 50°–80° C., but difficulties in practical manipulation were too great to make the use of this compound a success.



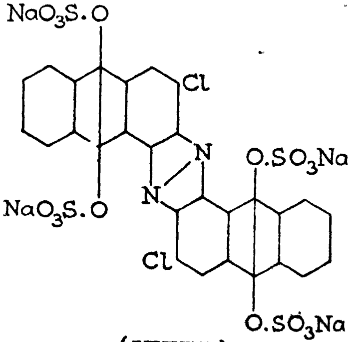
(XXXI)

Durand & Huguenin A.-G. and the I.G. Farbenindustrie A.-G. commenced research on Bader and Sunder's initial discovery with the result that a range of Indigosol dyestuffs based on the soluble sulphato-compounds was quickly evolved from the indigoid and anthraquinonoid vat dyestuff families. Scottish Dyes Ltd. (now I.C.I.) were responsible for improving the method of manufacture of these products, the new products appearing under the name of Soledon dyestuffs. In the Soledon process, the *leuco*-compounds of the dyestuffs are not employed as the starting material, but the dyestuffs themselves. The latter are converted into metal-tertiary base complexes of the sulphuric esters of the *leuco*-compounds, which are then transformed into soluble sodium salts. The vat dyestuff is first finely suspended in a tertiary base, e.g. pyridine, and then treated with a metal, e.g. copper, zinc or iron, and a source of sulphuric anhydride. The work was first accomplished in 1924 by Morton, Jones, Wylam, Harris and Wilson.

Soledon Jade Green (**XXXII**), for instance, has the formula:



(XXXII)
(cf. page 22)



(XXXIII)

The dyestuff Soledon Blue 2RC (**XXXIII**), which is a tetra-ester, cannot be prepared in the above manner and is synthesised by way of the ester of *leuco*-2-amino-3-chloroanthraquinone.

CHAPTER III

INTRODUCTORY TO APPLICATION

DISCUSSION on the theories of colour and the effect of chemical constitution on shade is not within the scope of this book. The classical theories of Witt and Armstrong are described in standard works on colour chemistry, whilst more recent views are contained in Wizinger's *Organische Farbstoffe* (Berlin, 1933) and in Chapters V and VI of Branch and Calvin's *The Theory of Organic Chemistry* (New York, 1941).

According to Witt's theory, every intensely coloured organic compound contains within its molecule at least one grouping which is responsible for the colour. Such a grouping is termed a chromophore. In the case of vat dyestuffs the chromophore is the keto group ($\rangle C=O$), whilst azo dyestuffs contain the azo chromophore ($-N:N-$).

Any substance which contains a chromophore in the molecule is called a chromogen. Before such a compound can become of use as a dyestuff, however, further supplementary groups, or auxochromes, are necessary in order to intensify the colour and so render an otherwise inert compound of use as a tinctorial agent. Anthraquinone itself, for example, although capable of reduction to a soluble *leuco*-compound, like the vat dyestuffs, is of no use as a colouring matter for textiles; but if an auxochrome or a combination of auxochromes such as $-NH_2$ or $-NH.CO.C_6H_5$ is introduced, the compound acquires a definite shade which is of value to the dyer.

If the various formulae for vat dyestuffs set out in the foregoing chapters are examined, it will be noticed that each one of them contains at least one keto group, i.e. $\rangle C=O$.[1] It is upon this group that the whole system of vat dyeing depends; it is in fact the chromophore.

All vat dyestuffs in their normal condition are water-insoluble products, and so are incapable of being applied directly to the fibre. It is for this reason that they must be converted into water-soluble sodium salts of their *leuco*-compounds (i.e. reduction

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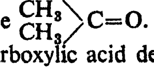
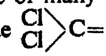
[1] This group is variously called the keto or carbonyl group. It is contained in all ketone molecules (hence "keto"), e.g. acetone  $\begin{matrix}CH_3\\CH_3\end{matrix}\rangle C=O$.

It is also the essential feature of many carboxylic acid derivatives, e.g.:

carbonyl chloride  $\begin{matrix}Cl\\Cl\end{matrix}\rangle C=O$ and urea  $\begin{matrix}H_2N\\H_2N\end{matrix}\rangle C=O$·

products) which, in the dyehouse, are prepared by the process of vatting with sodium hydrosulphite and caustic soda. During this process the $>\mathrm{C{=}O}$ group becomes $>\mathrm{C.OH}$. The appearance of the *leuco*-compound varies with the dyestuff in use. The majority of indigoid vat dyestuffs yield a pale yellow, orange or brown *leuco*-compound, whilst dyestuffs of the anthraquinone series change to a wide variety of hues which are usually very different in colour from the original dyestuffs. Thus, the "vat" or *leuco*-compound of Anthra Yellow GC is violet and that of Indanthrene Yellow G is blue. On blowing air through such a solution, the dyestuff becomes precipitated as the original insoluble compound due to oxidation. Vat dyes in the form of solutions of their *leuco*-compounds are more or less substantive to cellulosic fibres, and if fibres are dyed in such solutions and then exposed to air or subjected to oxidation by chemical agencies, the dyestuff is similarly converted to the oxidised insoluble form within the fibre itself. After oxidation, the dyed textile fibres are soured in dilute acid solution in order to neutralise the caustic soda and, in many cases, to assist in the development of the true shade. Boiling in soap solution completely develops the shade, ensures full brightness and removes any loose particles of dyestuff which may have oxidised on the surface of the fibres. The very high fastness properties of most of the vat dyestuffs is attributed to their total insolubility in ordinary solvents and the great stability of the dyestuff molecules.

Physical Condition of Vat Dyestuffs.—In order to secure the greatest tinctorial yield from vat dyestuffs it is essential that the physical condition of the pastes and powders should be of a high standard for all types of application, viz., padding, dyeing, printing, as well as when using vat dyestuffs as pigments (see page 228). This is especially important in fabric printing processes in order to ensure smooth homogeneous pastes and to enable rapid reduction of the dyestuff to take place during the steaming operation.

The dyestuff manufacturers have fully realised these requirements and the present-day ranges of vat dyestuffs are very satisfactory. Specially prepared brands appear under the various denominations of—"Powder Fine," "Micro Powder," "Suprafix Paste," "Paste Fine for Printing," etc., besides being available in the form of "Grains" so as to facilitate easier handling and more accurate weighing out. The different kinds of pastes and powders are prepared in a number of ways and the methods of preparation apparently vary widely from one manufacturer to another.

Special attention is paid to the fineness of form of the dyestuff particles and to the employment of dispersing agents. In order to bring certain dyestuffs into a very fine state of division, a solution in sulphuric acid is first prepared, and this is then poured in a thin stream into ice-cold water, thus producing a very fine precipitate of the dyestuff. Certain vat dyes can be obtained in an exceedingly fine form by first vatting the dyestuff completely and then oxidising the *leuco*-compound by an addition of *m*-nitrobenzene sulphonic acid. Precipitation of the insoluble pigment is instantaneous and very finely divided particles are formed. The suspension is then filtered and washed free from alkali and *m*-nitrobenzene sulphonate.

Dispersing agents have been the subject of very many patent specifications; the products employed are widely diverse in chemical nature and include such substances as betaine and pyridine derivatives, sulphonated aliphatic and aromatic compounds, quaternary ammonium compounds, polyhydric alcohols and their derivatives, and sulphamides.

Dyeing Methods.—Experience in handling vat dyestuffs has enabled them to be grouped into various dyeing classes, as distinct from chemical classes. Vat dyestuffs may be divided into two large classes, viz. (1) strong alkali and (2) weak alkali, depending on whether the dyestuff has the property of being reduced best in a strongly alkaline or a weakly alkaline bath. The solubility classes are further divided into groups depending on the actual dyeing conditions required to obtain maximum results as regards colour value, fastness, levelling and penetration. The main methods for cotton dyeing were probably first established by the Germans, who called them the IN, IW, and IK classes. The IN or Indanthrene Normal method of dyeing consists essentially in applying the dyestuff from a strongly alkaline bath at 60° C.; perhaps the majority of vat dyestuffs at present available belong to this class. The IW or Indanthrene Warm method involves the use of a weakly alkaline vat at 45°–50° C., usually with the addition of an exhausting agent such as common salt or Glauber's salt. Most of the homogeneous brown anthraquinonoid vat dyestuffs are best applied by this method. The IK or Indanthrene Cold (Kalt) method is employed for cold-dyeing vat dyestuffs, which usually require a weakly alkaline bath and rather more salt for exhaustion than dyes applied by the IW method.

Other methods have been evolved to cover, for instance, the application of the indigoid vat dyestuffs to cotton and wool. This class of dyestuffs belongs to the weakly alkaline dyeing group, but they possess various individual properties which call for special attention. In general, they require more hydrosulphite than the weakly alkaline class of anthraquinonoid vat dyes, and, unlike the latter, which are vatted directly in the dyebath, they are usually prepared for dyeing in the stock vat. The Helindon dyestuffs for wool are dyed by the HW or HN processes, which are discussed in a later section (see pages 71–72). All the above methods are later dealt with in detail.

Affinity.—It has been established by various workers that the water-soluble alkali salts of the *leuco*-compounds of vat dyestuffs behave towards cotton like the substantive direct cotton dyestuffs, the degree of substantivity varying with the chemical and physical nature of the fibre, as well as with the individual dyestuff under consideration. Thus, Engi, in 1907, showed that although the affinity of *leuco*-indigo for cotton is low, it is greatly improved by substitution, as in the case of tetrabromoindigo or Ciba Blue 2B. Attention was drawn more closely to the varying affinity of *leuco*-vat dyes by Pummerer and Brass (*Berichte*, 1911, **44**, 1651). These workers tested the fastness to washing of the absorbed compounds in an atmosphere of carbon dioxide. *leuco*-Indigo, they showed, was easily washed out, whereas *leuco*-indanthrone was firmly retained by the cotton fibre. The *leuco*-compounds of the weak alkali dyestuffs are naturally much more soluble than those of the strong alkali dyestuffs and are therefore much more likely to be washed off the fibre or to bleed during oxidation, soaping, and other subsequent processing.

Boulton and Morton (*J.S.D.C.*, 1939, **55**, 481) have discussed the application of vat dyestuffs to viscose rayon and have shown that the process consists of adsorption of the *leuco*-compounds by cellulose, followed by relatively slow diffusion into the interior of the fibre.

Measurements of the rate of exhaustion, the degree of exhaustion and the rate of diffusion, made on a large range of commercial vat dyestuffs, revealed that the vat dyeing of viscose rayon consists of two phases. Primarily, there is the adsorption of the dyestuff by the fibre, which quickly and almost completely exhausts the dyebath; secondarily, there is a levelling process, the speed of which depends upon the ease of diffusion of the dyestuff molecules within the fibre. The importance of temperature as a controlling factor is stressed.

The "strike" test is a valuable indicator of the properties of vat dyestuffs from the point of view of diffusion and levelling. This test was developed by Courtaulds Ltd., and its use is to be recommended to all viscose rayon dyers. The test is based upon the fact that, in many cases when dyeing viscose rayon in hank form with vat dyes, the dyestuff is absorbed by the areas of easy access, e.g. the outside of the hank, and that if the inside is examined it is found to be very lightly dyed or in many cases totally undyed. This state of affairs is described as a "bad strike" and, in order to classify dyestuffs in the order of their good and bad "striking" qualities, the following test is made, using the procedure of Courtaulds Ltd., as described by Boulton and Morton.

The One-Minute Strike Test.—Five small identical dyebaths are prepared, using the formula which is to be employed on the subsequent large-scale run, and two skeins of yarn or slips of fabric are entered one after the other with a one-minute interval between the first and second skein. Dyeing is then carried out for periods of 5, 20, 40, 60 and 80 minutes and the two skeins from each of the five dyebaths are compared and the results tabulated.

The "strike" differences between the two skeins after dyeing for 5 minutes are then classified by the use of letters indicating the appearance of the yarn: A=Negligible, B=Appreciable, C=Considerable, and D=Gross. The time required to obtain a solid shade (i.e. both skeins level and of equal depths of shade) is noted, as well as the classification letter of difference. For example "A5" shows that levelling is accomplished within 5 minutes of the introduction of the second skein. "B80" indicates that after 5 minutes there is an appreciable strike difference which levels out after 80 minutes. "C20" indicates a considerable difference after 5 minutes, but levelness after 20 minutes. The mark ∞ is used by Boulton and Morton to show that the strike difference does not level out after dyeing for 80 minutes.

The Ten-Seconds Strike Test.—Considered as a class, the strong alkali vat dyes exhaust rapidly, and therefore require the use of a modified strike test. In this case the second skein is introduced after an interval of only 10 seconds; otherwise, the strike differences are estimated in the same manner, using dyebaths for 5, 10, 20, 40, 60 and 80 minutes and recording the time required to obtain the same shade on both hanks.

In the original publication, Boulton and Morton provide a useful list of weak and strong alkali vat dyestuffs, classified according to strike properties. This list serves as an excellent guide to the dyer who is formulating compound shades. Wherever possible, dyestuffs which level after the same time should be employed, the original strike difference being only of secondary importance.

Animal Fibres.—When dyeing wool with vat dyestuffs it is necessary to control the alkalinity of the dyebath, on account of the destructive effect of alkali on animal fibres. Apart from this danger, too much alkali would retard the exhaustion to a greater or smaller extent, depending on the particular dyestuff. Sufficient caustic soda to dissolve the dyestuff completely is all that is necessary and, since the strong alkali vat dyestuffs are only very rarely used on animal fibres, the amount of alkali required is usually very small. If extra alkalinity is desirable in vats prepared for wool dyeing, further quantities of caustic alkali should not be added, but instead an addition of either soda ash or, preferably, ammonia should be made. An indication of the degree of alkalinity of the vat can be obtained by using phenolphthalein paper (or solution), which should turn only slightly red. The adverse effect of alkali on wool is inhibited to a large extent by adding glue or some other protective colloid to the dyebath.

It is also essential that correct souring should follow oxidation, in order to remove the last traces of alkali which, if not neutralised, would concentrate on drying the material and cause localised or complete damage to the fibre. Such damage is very likely to occur in the subsequent decatising process to which vat-dyed wool is often subjected. The decatising treatment, either wet or dry, is exceedingly drastic and a change in shade is often noted. The dyestuffs used should therefore be carefully chosen, in order that they may withstand this treatment.

During wool dyeing, the temperature of the vat should not be allowed to become too high or danger of alkali damage will become imminent. The dyestuff manufacturers are fully aware of these important details, and the figures given in their pattern cards may be regarded as reliable guides. Control of temperature is also a very important factor during vatting, if correct and repeatable shades are to be obtained. In its reduced form in the dyebath, the vat dyestuff should always show the correct colour characterising perfect formation of the *leuco*-compound. Sufficient sodium hydrosulphite should always be present, but, as in cotton dyeing, any excess will hinder the exhaustion of the dyestuff. Insufficient hydrosulphite, on the other hand, leads to results which show inferior fastness to rubbing. An indication of the amount of reducing agent present can be obtained by spotting a sample of the dyebath on "yellow paper." This paper may be prepared quite easily by the dyer himself by immersing a sheet of filter paper in a suspension of Indanthrene Yellow G paste (or equivalent product) and drying. When sufficient hydrosulphite is present in the dyebath the yellow paper becomes blue, i.e. the Indanthrene Yellow G, which is very easily reduced, is converted to its *leuco*-compound.

Vats for dyeing wool invariably require the use of exhausting agents in order to obtain the full colour value. The agents employed for this purpose are ammonium sulphate and ammonium chloride. These compounds gradually neutralise the alkalinity of the dyebath and thus promote more rapid exhaustion.

Silk.—The indigoid vat dyestuffs are largely used for dyeing silk, and many of the weak-alkali anthraquinonoid types are also employed. In fact, from the point of view of fastness properties, the latter are to be recommended. A method for dyeing weighted silk successfully with vat dyestuffs is not yet available.

When dyeing silk with vat dyes it is necessary to employ a protective agent, in order to prevent the deleterious action of alkali on the fibre. These agents also act as restrainers, thereby promoting better penetration and easier levelling. Common salt and Glauber's salt are employed as exhausting agents where necessary. Working details for dyeing silk with vat dyes are given in Chapter V.

We follow now with a list of the chemical assistants and auxiliaries employed in vat dyeing. A brief description of each agent is given in an endeavour to bring out the salient features and acquaint the student with the vat dyer's raw materials.

Alkalis

Caustic Soda or sodium hydroxide (NaOH; mol. wt., 40) is employed in the preparation of stock vats and dyebaths. In its purest form it is a white crystalline substance which absorbs moisture from the air. Caustic soda is available as lumps or flakes, as well as in the form of sticks for laboratory use. In the dyehouse, however, it is usually employed in liquor form, and is purchased as Caustic Liquor or Soda Lye in strengths varying from 64° to 72°Tw.; the 72°Tw. strength is equivalent to a 33% solution of NaOH in water. It is also possible to obtain 106°Tw. caustic liquor, which contains 76·65% NaOH.

Sodium Carbonate or soda ash (Na_2CO_3; mol. wt., 106) is marketed as calcined soda, soda ash or Solvay soda. Soda crystals or washing soda ($Na_2CO_3.10H_2O$) is rarely employed in the dyehouse. The chief uses of sodium carbonate in dyehouses where vat dyeing is carried on are for the preliminary boiling out of cotton goods, neutralisation, in the final soap and soda boil, and in setting certain vats for wool dyeing.

Lime, in the form of caustic lime (CaO) or slaked lime ($Ca(OH)_2$) is a mild alkali used in the preparation of indigo vats.

Ammonia (NH_3) is a gas which is extremely soluble in water and is usually handled in the dyehouse as a 25% or 33% solution in water (NH_4OH); the latter strength, which has a sp. gr. of 0·880, is bought as 0·880's ammonia. Ammonia is a volatile base and is capable of causing asphyxiation, so care is necessary when handling it. It finds employment in the application of Helindon dyestuffs and indigo on account of its mildly alkaline nature..

Potassium Carbonate or Potash ($K_2CO_3.2H_2O$) has a milder action than soda ash and is therefore employed in wool scouring baths. Its main use from the point of view of vat dyestuff application is in textile printing, e.g. in the Potash–Rongalite (Formosul) process.

Reducing Agents

Sodium Sulphide (Na_2S) is available as crystals ($Na_2S,9H_2O$) and in the anhydrous rock form as rock sulphide or sulphide conc. The latter is approximately twice the strength of the crystals. It is employed as a reducing agent in the application of sulphur dyestuffs and Hydron Blues. It is strongly alkaline in nature.

Sodium Bisulphite ($NaHSO_3$; mol. wt., 104) is obtainable in the form of crystals or as ground powder. It is usually handled in the dyehouse as 72°–77°Tw. liquor. It finds use in the preparation of hydrosulphite (see page 62) and also as an anti-chlor.

Sodium Hydrosulphite ($Na_2S_2O_4$; mol. wt., 174) is probably the dyer's most valuable aid to vat dyeing. At one time it was customary for the vat dyer to prepare his own hydrosulphite by the action of zinc dust on sodium bisulphite. As the crystals obtained by this process are unstable, the hydrosulphite was always prepared for use as a solution. To-day, such methods of preparation are almost obsolete. The stable anhydrous salt is now obtained by boiling the hydrated salt with alcohol, the resultant powder being the Hydros (Bro.) or Hydrosulphite Conc. powder (I.G. and L.B.H.) employed by the dyer for reduction purposes. In the following pages this compound is referred to simply as "hydrosulphite."

When a solution of hydrosulphite is boiled it decomposes fairly quickly, so hydrosulphite is unsuitable for the comparatively high temperatures used in textile printing operations, a fact which led to the production of hydrosulphite compounds of increased stability. Sodium hydrosulphite-formaldehyde is such a compound and is prepared by the action of formaldehyde solution (formalin) on sodium hydrosulphite; it has the formula:

$$Na_2S_2O_4.2HCHO.4H_2O.$$

This is really a mixture of sodium bisulphite-formaldehyde ($NaHSO_3.HCHO$) and sodium sulphoxylate-formaldehyde ($NaHSO_2.HCHO$). The latter compound is a powerful reducing agent and is commercially available as Erasol C (L.B.H.), Formosul (Bro.), and Rongalite C (I.G.). Further derivatives with reducing properties suitable for specific applications have been developed, and the zinc-formaldehyde sulphoxylate compounds are probably the most noteworthy. (See "Stripping," Chapter VIII, page 144.)

Zinc Dust appears as a grey powder in the dyehouse and, besides metallic zinc, it often contains a small quantity of the oxide. It is used as a reducing agent in the preparation of indigo vats and in the manufacture of hydrosulphite compounds.

Ferrous Sulphate or copperas ($FeSO_4.7H_2O$) is available as green crystals which readily lose water of crystallisation. It finds use in the now rarely employed Copperas Vat for indigo.

Exhaustants

Sodium Chloride or common salt ($NaCl$) is soluble in 2·5 parts of water and is employed for exhaustion purposes in the application of vat dyestuffs by the IN and IK processes.

Sodium Sulphate or Glauber's salt is available as crystals ($Na_2SO_4.10H_2O$) and as calcined Glauber's salt. One part of the calcined product is equivalent to 2·25 parts of the crystals. It has the same use as common salt from the point of view of vat dyeing and appears to be preferred when viscose rayon is being processed.

Ammonium Chloride (NH_4Cl) is used for exhausting the dyebath when applying indigoid vat dyestuffs to wool. It is fed slowly into the dyebath, where it gradually neutralises the alkalinity and promotes the exhaustion of the alkali-soluble *leuco*-compound.

Ammonium Sulphate ($(NH_4)_2SO_4$) is employed similarly to ammonium chloride and finds further use in the dyeing of the solubilised vat colours on animal fibres.

Souring Agents

Sulphuric Acid (H_2SO_4; mol. wt., 98) is sold in various strengths, e.g. 168°Tw. or "double oil of vitriol" (D.O.V.) which contains

95·6% H_2SO_4, and as "brown oil of vitriol" (B.O.V.) which contains 76–80% H_2SO_4. It is used in souring and developing operations.

Heat is generated when sulphuric acid is diluted, and precautions should be taken against splashing. Goggles and rubber gloves should be worn and sulphuric acid should always be diluted by pouring it into large quantities of cold water.

Hydrochloric Acid (HCl) or muriatic acid is an aqueous solution of the gas hydrogen chloride. The commercial acid usually contains about 28% HCl. It is only occasionally used for souring purposes as it is more expensive than sulphuric acid.

Acetic Acid (CH_3COOH) is an organic acid marketed in various strengths, e.g. 30%, 40%, 60% and 80%. It is used in souring and in developing certain Indigosols, as well as in the correction of hard water.

Formic Acid (H.COOH) is a pungent-smelling organic acid which finds use in the application of the solubilised vat dyestuffs to animal fibres. The commercial acid has a sp. gr. of about 1·2 and contains 80–85% formic acid.

Oxidants

Chemical oxidation is not always necessary for the development of vat dyestuffs, and skying or hanging in the air is invariably resorted to. Many vat dyestuffs, however, oxidise slowly and require the use of certain chemicals to speed up the process. Chemical oxidation of dyeings is especially necessary when employing certain types of dyeing machines.

Hydrogen Peroxide (H_2O_2) is a colourless liquid marketed in various strengths, e.g. 100 Vols (=30% H_2O_2) and 10 Vols (=3% H_2O_2). The "volumes" represent the number of cubic centimetres of oxygen which can be obtained from one cubic centimetre of the liquid. Hydrogen peroxide is often employed for the development of vat dyeings. It is supplied in a stable, slightly acid condition and, when made slightly alkaline with ammonia, oxygen is liberated.

Sodium Peroxide (Na_2O_2) is sold as a yellowish powder or in lumps and is widely employed as a source of oxygen in the dyehouse. It should always be handled with great care, because inflammable materials are easily ignited when moisture and sodium peroxide come into contact with them. It should always be kept in a tightly closed container. When it is dissolved in ice-cold water, hydrogen peroxide and caustic soda are formed; with hot water, however, the hydrogen peroxide formed is easily decomposed with the liberation of oxygen. Cold dilute solutions of acids also cause a rapid liberation of oxygen *via* hydrogen peroxide.

Sodium Perborate ($NaBO_3.4H_2O$) is a white crystalline powder containing 10% available oxygen, and is soluble in 40 parts of cold water. On dissolving, it yields borax and hydrogen peroxide thus: $4NaBO_3+5H_2O=4H_2O_2+Na_2B_4O_7+2NaOH$. By reason of its strong oxidising character sodium perborate finds occasional use in vat dyestuff development.

Sodium Nitrite ($NaNO_2$) is available as readily soluble crystals which have oxidising properties in the presence of acids. It is used for developing the solubilised vat dyestuffs.

Sodium Bichromate ($Na_2Cr_2O_7.2H_2O$) is a deliquescent, orange, crystalline substance possessing strong oxidising properties in acid solution. It is used in the development of the solubilised vat colours and for certain vat dyes which oxidise with difficulty, e.g. Indanthrene Yellow G.

Potassium Bichromate ($K_2Cr_2O_7$) is slightly less soluble than the sodium salt and finds similar uses in vat dyeing. The two salts are commonly known as "bichromate," "bichrome," or "chrome."

Ammonium Sulphocyanide (NH_4CNS) is available as colourless hygroscopic flakes and finds employment in developing baths for Indigosols on wool. Its use enables purer shades to be obtained, and it prevents the *over-oxidation* of certain easily developed dyestuffs.

Some Auxiliary Compounds

Fullers' Earth is a naturally-occurring greenish-brown clay with a greasy handle; it is insoluble in water but easily forms pastes and fine suspensions. It is employed in the removal of surface colour from indigo dyeings, which would otherwise have poor fastness to rubbing. Various auxiliary compounds, e.g. Indigosol Soap SP (D.H.), have been offered to replace this compound.

Turkey Red Oils.—Under this denomination several different brands of "soluble oils" appear on the market. They are sulphonated fatty acids of the castor oil type (e.g. sulphoricinoleic acid) and are totally miscible with water. Solutions of these oils in water which are milky require neutralising with ammonia or soda ash to give clear solutions. Turkey Red oils are employed in the pasting up of vat dyestuffs in powder form, and they also act as levelling and wetting agents in the dyebath.

A useful, though fairly crude, sulphoricinoleic acid can be prepared by adding 5 lb. of D.O.V. (95·6% H_2SO_4) very slowly to 20 lb. of castor oil at 30°C. This mixture should stand for 24 hours and then be washed by decantation, using a solution of 6 lb. of common salt in 6 gallons of water. The fatty acid will rise to the top and the aqueous liquor should be run off from below on settling. The washing process should be repeated two or three times with fresh salt solution. Approximately 2·5 lb. of sulphonated oil are thus obtained. The reliability and regularity of commercially available Turkey Red oils, however, makes the use of such a process unnecessary in a dyehouse of small size.

Monopol Brilliant Oil and *Monopol Soap* are compounds which have a neutral or slightly acid reaction; they are moderately stable to hard water and dilute acid solutions. In dyeing animal and vegetable fibres with vat dyestuffs, these products are used in the preparation of the stock vats and, in addition, may be used in the dyebath as wetting and penetrating agents. They prevent excessive frothing in machine dyeing.

Glue may be purchased as brown tablets or beads which vary in transparency. It is employed in solution as a protective colloid in the vat dyeing of animal fibres, and is believed to improve the fastness to rubbing of indigo dyeings. It has a restraining action when dyeing cellulosic fibres with vat dyestuffs and is widely used in the dyeing of viscose rayon. Glue solutions keep only for a short time, and salicylic acid or phenol is occasionally added to preserve them.

Waste Sulphite Cellulose Lye.—This is a waste product from the manufacture of paper pulp and is usually obtained in the form of a dark brown treacle-like mass or solution.

Dekol, a German product, is a special brand of this substance prepared specifically for dyehouse use. Several other proprietary sulphite lyes are available. These products should be practically neutral and should not contain more than a trace of iron and calcium. Freedom from other inorganic matter and SO_2 is also essential.

These compounds are employed as restrainers or retarding agents in the application of rapidly exhausting vat dyestuffs. They are especially suitable for use in rayon dyeing. Various protective colloid agents, e.g. the Protektols (I.G.), appear to be based on waste sulphite lye.

Nekal B extra (I.G.) is a wetting agent especially suitable for use in acid or alkaline liquors, hence its recommendation for vat dyeing purposes. Several products of a similar type are available, e.g. Perminal W (I.C.I.). Nekal B extra is reported to be sodium *iso*propylnaphthalene sulphonate.

Albatex PO (S.C.I.) is a water-soluble liquid paste which is employed in vat dyeing as a levelling and penetrating agent. It is an anion-active salt of a high-molecular organic sulphonic acid which possesses a neutral reaction, and is not precipitated by the calcium and magnesium salts in hard water. Under certain conditions this compound may be employed as a stripping agent for vat dyestuffs.

Peregal O (I.G.) is a water-soluble dispersing, wetting and penetrating agent which is especially suitable for vat dyeing, although it is not generally recommended for use with indigoid vat dyestuffs. It finds a wide usage in stripping baths and, when used in large quantities in the dyebath, exhaustion is retarded to a marked degree. It is a paraffin-chain derivative of the polymerisation products of ethylene oxide.

Prestabit Oil V (I.G.) and *Calsolene Oil HS* (I.C.I.) probably consist of highly sulphonated ricinoleic acid. They find extensive use in the application of vat dyes by the pigment padding process (see page 133) and are very stable to acids and concentrated salt solutions.

CHAPTER IV

PROPERTIES OF VAT DYESTUFFS

AN intimate knowledge of the vagaries of individual vat dyestuffs takes a lifetime to acquire. Such knowledge is desirable, however, if the dyer is to obtain maximum fastness and full colour value. Although successful achievement of these objectives largely depends upon the chemical constitution of the dyestuffs employed, much depends upon the care exercised during dyeing. Slipshod dyeing methods yield inferior dyeings, and particular care should be taken to see that the properties of the colouring matters being handled are thoroughly understood.

A common example is provided by indigo dyeings of poor wet and dry rubbing fastness. This is clearly a case of careless or inexperienced handling and not a fault of the dyestuff itself. Badly dyed indigo dyeings also show a lower resistance to light than properly dyed materials, and the secret of overcoming such defects lies solely in careful scouring and dyeing.

In all cases of vat dyeing great care should always be given to vatting details, so that complete solution of the dyestuff is obtained, but without the presence in the stock vat or dyebath of too much or too little caustic soda or sodium hydrosulphite. It will be found by experience that some dyestuffs give better solutions if they are reduced to the *leuco*-state in a short or concentrated liquor for a prolonged period, whilst others need only a comparatively short time and may be vatted in a long liquor or directly in the dyebath.

Dyebaths should always be tested before and during use (particularly when handling the more sensitive dyestuffs indicated in the ensuing text) by the use of several easily applied tests commonly employed by all vat dyers. Such tests as the Flavanthrone (or "Yellow Paper") test for the sufficiency of hydrosulphite (page 35), the Phenolphthalein colour test showing the degree of alkalinity, the glass-plate test for perfection of solution, and the use of a thermometer and a watch, are reliable guides to success.

In order to ensure thorough penetration, effective exhaustion and good levelling, attention must always be paid to the duration of dyeing, the regulation of temperatures and the judicious employment of auxiliary agents. The treatment which the goods receive after they have left the dyebath is also extremely important.

For instance, improperly oxidised goods yield poor results, not only from the viewpoint of fastness, but also from the angle of levelness and shade. Careful rinsing should always be given, taking care to see that as little as possible, if any, of the agents used in the preceding processes are carried on into the next bath; rinsings between souring and soaping are the most important.

Some vat dyestuffs do not require a souring treatment, but the majority, particularly the anthraquinonoid types, only yield the correct result after they have undergone this treatment. The soaping of dyeings at the boil is an essential feature of all vat dyeings on cellulosic fibres; this process is designed to remove all surface colour, the presence of which would affect the fastness to light and rubbing of the dyed goods. Soaping has the secondary effect of producing the maximum brilliance of shade.

Many of the above precautions are of course dependent upon the type of material and nature of the equipment in use. Where special attention is required, suitable notes and hints will be given in the following pages.

Fastness and Constitution.—It has already been stated that the fastness of vat dyestuffs is largely dependent upon the nature of the dyestuff molecule. The anthraquinonoid vat dyestuffs are by far the most resistant to the usual agencies met with during the processing and wear of a textile fabric. Wherever the highest degree of fastness is demanded on cellulosic goods this class of dyestuffs is employed. All the anthraquinonoid vat dyestuffs, however, do not possess the same degree of all-round fastness, but the dyestuff manufacturers usually provide a specific name or indicative letter which denotes those members of their ranges which show the best fastness properties. The I.G. Farbenindustrie A.-G., for instance, have made the term "Indanthren" world-famous as a mark of high quality as regards fastness and durability. Other denominations employed by the same firm, such as Anthra and Algol, are generally used to indicate anthraquinonoid types which show a slightly lower degree of fastness, but compared with dyestuffs of other dyeing classes, e.g. the direct cotton colours, they still possess a notably high degree of resistance. The mark "P," indicating "paramount fastness" is used by the Society of Chemical Industry in Basle (S.C.I.) to distinguish their best brands.

After the anthraquinonoid class, the sulphurised vat dyestuffs of the Hydron Blue type rank next in importance as regards high fastness. The indigoid class comes next on the list but although they find a wide application on cellulosic fibres, they do not seem to have been seriously adopted by wool dyers in Great

Britain, the excellent acid and mordant dyestuffs available being preferred.

As previously noted, the general high fastness to wet processing and light of the vat dyestuffs is due to their insolubility, but the presence of certain groupings in the dyestuff molecule and the arrangement and size of the molecule are also important. It [illegible] on such knowledge that the dyestuff research chemist is able to plan the dyestuffs of the future. To dyers, progress in the direction of perfect dyestuffs may seem painfully slow, but it should be borne in mind that the knowledge concerning these important details is still very meagre, and so far it has been impossible to set up hard and fast rules governing constitution and fastness.

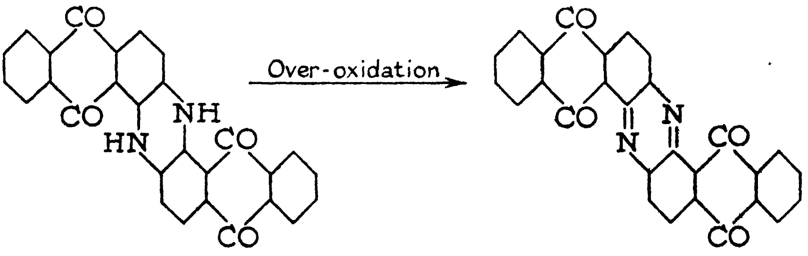
Influence of Hydroxyl Groups.—With dyestuffs containing hydroxyl (OH) groups, e.g. Caledon Red FFS and Indanthrene Blue 5G, great attention must be paid to effective souring of the dyeings. Hydroxyl groups are in general highly susceptible to alkaline conditions, having a natural tendency to form more or less soluble alkali metal salts. In the case of Caledon Red FFS (1:5-dibenzoylamino-8-hydroxyanthraquinone), bluer and duller shades are obtained on cotton if the souring operation is omitted or carelessly carried out. Such dyestuffs will not withstand the boiling soda solutions which are occasionally used by some dyers to replace the final soap boil.

The chemical intermediate product for the production of the Caledon Jade Greens is dihydroxydibenzanthrone, which, by virtue of its hydroxyl groups, is soluble to a large extent in alkali, forming the disodium salt. This compound, however, despite the fact that it yields excellent yellow-green dyeings of good body and would otherwise be a valuable dyestuff, is rapidly turned very much bluer in the presence of even a trace of acid. Even an acid atmosphere is sufficient to convert the $-ONa$ groups to $-OH$ groups and yield the true colour of the blue-green dihydroxydibenzanthrone. In order to produce a dyestuff from this sensitive intermediate product, the chemists of Scottish Dyes Ltd. (now I.C.I.) blocked the solubilising $-OH$ groups by methylation and obtained the remarkably fast dimethoxy compound known as Caledon Jade Green (see page 22).

Fastness to Soda-Boil.—The fastness to boiling soda of the majority of the vat dyestuffs is unsatisfactory, particularly when pressure is employed, as in kier-boiling, and the principal cause is the fact that boiling soda ash exerts a reducing action on the dyestuff, with the result that it is transformed into its soluble *leuco*-derivative. The theory put forward by Max A. Kunz (in a lecture at the École Supérieure de Chimie de Mulhouse in 1934) is that fastness to soda boiling increases with the number of reducible keto groups present in the dye molecule, i.e. fewer $>C=O$ groups mean that the dyestuff will be more quickly reduced under the conditions of the soda boil. From this point of view, therefore, fastness is not attributable to the number and type of substituted groups. A plurality of keto groups is also thought to exercise a levelling effect on the dyeings, and this is borne out to some extent by many of the carbazole–imide type of dyestuffs, which usually contain more keto groups than do the vat dyestuffs of the other classes. Indanthrene Khaki 2G, for example, contains ten such groups and exhibits a remarkable resistance to soda boiling. Other dyestuffs with similar properties are exemplified by Indanthrene Brown BR, Indanthrene Golden Orange 3G, Indanthrene Olive R and Indanthrene Yellow 3RT. In weak shades, however, the above-mentioned khaki and the yellow dyestuffs do not level well.

The employment of agents which prevent the reduction of vat dyestuffs during soda boiling, e.g. Resist Salt L (I.C.I.) and Ludigol (I.G.) (which consist of sodium *m*-nitrobenzene sulphonate), is advisable in all kier-boiling operations.

Over-oxidation.—Several vat dyestuffs are sensitive to over-oxidation, with the result that dull dyeings are often obtained. The blue dyestuffs derived from indanthrone are notable examples, and to obviate this defect they are rinsed in cold water containing a little sodium hydrosulphite before souring. These dyestuffs also give greener and duller shades when over-oxidised; it is therefore necessary to avoid the use of chemical oxidants such as bichromate in any after-treatment. During hypochlorite bleaching the dyestuff is oxidised; in the case of indanthrone itself with formation of the yellow-green azine:



The correct blue shade of the dyestuff may be obtained from over-oxidised dyeings by treatment in a solution of sodium hydrosulphite.

The low fastness to chlorine of indanthrone (Blue R types) was overcome very early in the history of the anthraquinonoid vat dyestuffs by the introduction of halogen groups into the dyestuff molecule. Thus, Caledon Blue RC and Paradone Blue GCD, which contain chlorine in their molecules, show a resistance to chlorine bleaching, although they are still sensitive to over-oxidation to some extent. When applying chlorine-fast Blues of this type, it is essential to control the temperature during vatting and dyeing; 50° C. must not be exceeded if their fastness to bleaching is to remain unimpaired.

Accelerated Tendering produced by Vat Dyestuffs.—Many vat dyestuffs, particularly Yellows and Oranges, have a harmful effect upon cellulose when their dyeings are exposed to light; the tendering of cotton by these dyestuffs has been the subject of a great deal of research work. Tendering may occur in the dyehouse during dyeing operations, as well as during the life of such vat dyed materials as curtains and other fabrics which are continually exposed to sunlight. In the dyehouse, the action of light upon the *leuco*-compound of the susceptible dyestuff often takes the form of an alteration in hue; in rare cases, complete disintegration of the fibre occurs, often accompanied by breakdown of the dyestuff itself. The loss in strength of the fibre is due to the production of oxycellulose, and the oxidising agent responsible for this harmful result has been shown to be hydrogen peroxide. Schönbein (*J. pr. Chem.*, 1860, **81**, 16) observed as early as 1860 that hydrogen peroxide is one of the products of oxidation of *leuco*-indigo in air, particularly when alkali is present.

There are, however, a great many factors which influence the degradation of cellulose. Thus, the atmosphere of districts near the sea is less deleterious than that of industrial areas, whilst outside exposure is less degradative to vat dyed goods than is exposure behind glass. Sunlight, humidity, industrial fumes and atmospheric impurities are catalytic factors involved in the production of the oxidising agent. It is curious that the dyestuffs which are harmful to cellulose in this respect are mainly Yellows and Oranges, with some Reds and some Browns. E. Baur (*Helv. Chim. Acta*, 1937, **20**, 879–81) has put forward a theory based on sensitisation and desensitisation in order to explain the action of these dyes and the non-tendering action of certain other dyestuffs such as Indanthrene Yellow G.

The following dyestuffs are liable to tender cellulose (particularly regenerated cellulose, e.g. viscose rayon):

Yellows.—Indanthrene Yellows 3RT, 5GK, FFRK and 3GF;

Indanthrene Golden Yellows GK and RK; Cibanone Yellow R and Hydron Yellow NF.

Oranges.—Indanthrene Orange 2RK; Indanthrene Golden Orange G; Indanthrene Brilliant Orange GK; Caledon Orange 2RTS and Cibanone Brilliant Orange 4RS.

Browns.—Ciba Browns G and 2R.

Pinks and Reds.—Indanthrene Red FBB; Indanthrene Magenta B; Indanthrene Brilliant Pinks and Cibanone Red 4B.

These examples do not provide a complete list, but they appear to be the most common offenders and, if possible, should be avoided for use on curtain materials. Undue exposure of the material during dyeing should always be avoided when applying these dyestuffs. The Blues, homogeneous Violets, Greens and Blacks do not cause cellulosic degradation, but shades containing harmful dyestuffs often tender, although certain mixtures can be found which partially inhibit the harmful effect.

Kunz's theory regarding these dyestuffs is that they "exercise the harmful effect by transmitting oxygen by catalysis due to their paraquinonoidic structure." On the basis of this theory, Kunz produced a large number of pyridine vat dyestuffs which were unable to "transmit oxygen." These dyestuffs, however, do not appear to have been placed on the market, probably on account of manufacturing difficulties and high cost.

Further work relating to the subject of tendering has been described by Scholefield and Patel (*J.S.D.C.*, 1928, **44**, 268), and by Whittaker (*ibid.*, 1933, **49**, 9). A report of Kunz's work can be read in the *Dyer* (1934, **72**, 27).

Physical Changes.—The change in shade shown by many vat dyestuffs on hot pressing, water spotting or soap boiling are essentially physical effects. Dyeings of dyestuffs of the dibenzanthrone series in particular exhibit these shade changes; in general they tend to become redder or yellower when wet. These colour changes are not permanent; usually the normal shade returns when the dyeing has cooled or become dry again. By effective soaping at the boil, colour changes of this nature are very often made less evident, because the dyestuff assumes the more stable crystallised form within the fibre.

Various workers have attributed such changes to oxidation, aggregation of the pigment in the fibre, dispersion, and hydration and dehydration. The most modern theories on the subject are described by Kornreich (*J.S.D.C.*, 1942, **58**, 177), who has shown that, although the above factors exert their influence, crystallisation is the most important factor. Vat dyestuff particles, when first completely oxidised within the cellulose fibre are in varying states of aggregation. The fibres become swollen in boiling solutions of dispersing agents such as soap, so that the aggregates are loosened as a preliminary to eventual dispersion. Subsequent crystallisation, which produces a light-scattering effect, is the real cause of apparent shade changes.

When dyestuffs within the fibre walls show a great tendency towards crystallisation, they are least affected by hot pressing and water spotting. Boiling in soap solution is therefore essential for all vat dyeings, both in order to develop the final shade of the dyestuff (which exhibits the best fastness to physical agencies), and in order to remove any loose surface colour which would diminish the resistance to sunlight and result in fading.

Choice of Dyestuffs.—In choosing dyestuffs for a specific purpose it is essential to consider—(*d*) the type of fibre, (*b*) the structure of the yarn or fabric, and (*c*) the purposes for which the finished material is to be employed.

(*a*) The choice of the class of dyestuffs for any particular fibre is an easy matter. Sufficient has already been said to indicate that the anthraquinonoid vat dyestuffs require too much caustic soda to be used for animal fibres and, consequently, they are not usually employed for this purpose, at any rate under ordinary conditions. The indigoid vat dyestuffs may be applied to either animal or vegetable fibres, but dyestuffs of the Hydron Blue class are reserved for the latter alone. Although the indigoid vat dyestuffs may, as a class, be applied to both types of fibres, individual members show greater suitability for one fibre or the other.

(*b*) The structure of the material, e.g. when it is tightly twisted or closely woven, very often decides the dyeing conditions, including the type of machine to be used. With tightly twisted goods, etc., and for machine dyeing, dyestuffs showing good solubility and penetrative properties should be chosen wherever possible. As regards penetration, it is often possible to regulate the temperature and other conditions of the vat so that greatly improved results can be obtained with normally poor-penetrating dyestuffs. Judicious employment of retarding and penetrating auxiliary compounds is also important in this respect.

(*c*) From the point of view of ultimate use, the deciding factor in the choice of dyes is of course the fastness performance of the dyestuffs. When high demands are made, particularly as regards fastness to light and washing and resistance to weather, only the dyestuffs of the highest grades should be used, for example the "P" brands of Ciba, the Indanthrene brands of the I.G., or equivalent products of other dyestuff manufacturers. These dyestuffs, besides showing the highest obtainable fastness to light, washing and weather, usually exhibit a high degree of resistance to bleaching and soda boiling and are thus very suitable for the production of coloured bleaching goods, provided that (*a*) they are carefully employed and (*b*) the soda boil is carried out in the presence of a reduction-resisting agent.

Anthraquinonoid vat dyestuffs of the Algol type, and analogous products, possess the same dyeing properties and, in general, the same high fastness characteristics as the above-mentioned brands, except as regards fastness to light. They are therefore avoided as far as possible for such fabrics as awnings, curtains and deck-chair covers. As a class, however, these dyestuffs are very suitable for the production of coloured bleaching goods.

The Hydron dyestuffs, e.g. Hydron Blue R, on account of their chemical composition, occupy the special position of being applicable by a cheap dyeing method involving the use of sodium sulphide. Their dyeings show very good fastness to light and washing, and are produced very economically, hence these dyestuffs are very popular for the coloration of workmen's overalls and similar goods.

The Indigosols are used in the production of fast dyeings in pale shades on cotton piece goods and embroidery yarn, and are used where special attention must be paid to levelling and penetration. The various methods of application, which include both padding and dyeing processes, cater for all types of goods, including linen, natural silk, rayon, wool and union materials, a modified dyeing procedure being available for each individual application.

As a general rule, it is inadvisable to use dyestuffs from different chemical and dyeing classes when formulating mixture shades, but this is often necessary when difficulties arise in shade matching. Whenever possible, too, dyestuffs which are to be employed in combination shades should be chosen so that their dyeing peculiarities are similar. Their rates of exhaustion, strike values and degree of penetration should also be as nearly similar as possible. Occasionally, mixture formulae provide problems from the point of view of fastness. Thus, to quote a well-known example, the individual fastness properties of Cibanone Orange R and Caledon Jade Green BS are almost unimpeachable. But when these dyestuffs are used together for the production of a sage-green shade the orange dyestuff, acting in a manner which has not yet been explained, causes the green dyestuff to fade. When Paradone

Yellow GC is used as a shading agent with the Jade Greens, however, it does not appreciably lower the light-fastness of the resultant shade until approximately 25% is added, despite the comparatively poor light-fastness of this yellow dyestuff.

Even with the very large range of vat dyestuffs at present available, the dyer of mode shades often finds it difficult to obtain certain shades and at the same time satisfy the fastness demands. In general, the yellow vat dyestuffs (although so very numerous) exhibit a lower fastness to light than the other colours and, if pale lemon or straw shades are required to show excellent fastness to light on cotton, it is found that there is no really suitable dyestuff. Indanthrene Yellow FFRK, although exhibiting excellent fastness, is liable to tender the goods; Yellow G (Flavanthrone) brands show good all-round fastness, but are apt to be reduced to a dirty green-black shade on long exposure to brilliant sunlight. Indanthrene Yellow 3R is probably the fastest vat yellow dyestuff available, but its shades are far from clear, and it is difficult to dye it level in such pale shades. The dyestuff exhibiting the best possible properties for this specific purpose is probably Indanthrene Yellow 4GK.

Blues, greens, browns and blacks are shades which are fairly well represented in the vat dyestuff range and, in general, they do not cause much trouble, but the violet and navy blue vat dyes give rise to difficulty on account of their almost universal habit of reddening by water spotting, and very often they possess rather poor fastness to light. Indanthrene Brilliant Violets 3B, BBK, RK, 2R and 4R, as well as Paradone Violet B, all show reddening when spotted with water and, although the colour change is not permanent, this defect produces a bad impression in the eyes of the customer. Indanthrene Violet FFBN is a little better in this respect, but it lacks the brilliance of the Brilliant Violet 2R and 4R types and, further, it is of no use for soda boiling.

Paradone Dark Blue and equivalent brands also show bad water-spotting effects, as does also Indanthrene Navy Blue R. This last-mentioned dyestuff is remarkable for its really high degree of resistance to light, and it is unfortunate that it does not show the very good resistance to water spotting possessed by the less light-fast Cibanone Navy Blue RA.

The ranges of Pinks and Reds have been greatly improved during the last twenty years, but they still lack the required body (and cheapness) that is so characteristic of the azoic combinations derived from members of the Naphtol AS (I.G.) and Brenthol (I.C.I.) series.

The Evaluation of the Fastness Properties of Vat Dyestuffs.—A great deal has been done to create standard fastness tests for the evaluation of dyes and dyed textile materials. Notable in this direction is the work of the Society of Dyers and Colourists, who have produced fastness standards for light, washing and perspiration which are published in the Society's *Report on the Work of Its Fastness Tests Committee* (1928).

The American Association of Textile Chemists and Colorists have grappled with the problem of standardised fastness tests in a similar manner, and their reports have appeared from year to year in the official *Year Book* of the Association, as well as in the *American Dyestuff Reporter.* In the following brief survey of fastness tests, tests for fastness to light, washing and perspiration have been purposely omitted and the reader is strongly recommended to adopt the methods published by the above societies.

The following tests are intended merely as guides and, wherever the conditions of the various processes through which the dyed goods have to pass are known, the mill details should be imitated as closely as possible. In their own interest, textile chemists and dyers should familiarise themselves with the processes which are applied to the goods when they have left the dyehouse. The fastness figures supplied by the dyestuff manufacturers in their pattern cards are usually very reliable indications as to the behaviour of individual dyestuffs. These should be employed as a preliminary guide, but whenever new dyestuffs are introduced or dyeing recipes are changed careful fastness tests should always be carried out. This is particularly important when dealing with mixture formulae, and small trials should always be made before the bulk is dyed.

Fastness Tests for Vat-dyed Cellulosic Fibres

Fastness to Chlorine.—The dyed pattern is immersed in a cold solution of bleaching powder or sodium hypochlorite of the same specific gravity as that to be employed in the works bleaching process. The treatment usually lasts for 30 minutes and the amount of available chlorine varies from approximately 0·4 g. to 2·0 g. per litre. The treated dyeing is rinsed well in running water, soured, rinsed again and allowed to dry. The dried sample is then compared with the original pattern.

A test involving saturation of the pattern in a bleaching solution containing the measured amount of available chlorine, squeezing well and allowing to lie wrapped in a strip of cotton cloth at room temperature for one hour, is often employed.

Fastness to Hydrogen Peroxide.—The pattern is immersed in a solution of 3 vols. hydrogen peroxide at 40°–50°C. for 24 hours and then examined for change of shade. Although bleeding of the dyestuff rarely occurs in this test, it is advisable to make sure by placing a small pattern of undyed material in the solution alongside the test piece.

Fastness to Soda Boiling.—The conditions of soda boiling or kier boiling vary widely in different works and works practice should always be followed in testing. As an example, a 1 g. pattern is plaited with 9 g. of grey material and boiled for 3–5 hours in a solution containing 1 g. soap and 10 g. soda ash per litre of water. The volume of the liquor should be kept at the same level throughout the test. The plait is finally washed off well and dried.

Tests may also be made in the presence of Resist Salt L and similar compounds, and care should always be taken to ensure that both the grey and the dyed goods are thoroughly desized, otherwise some reduction is likely to occur.

The soda boil and chlorine tests are usually carried out consecutively in this order when testing dyestuffs for suitability for coloured bleaching fabrics.

Fastness to the Combined Chlorine–Peroxide Bleach.—The pattern may be plaited with an equivalent weight of desized grey material and treated in a cold solution of sodium hypochlorite containing 1·75 g. active chlorine and 0·2 g. of sodium bicarbonate per litre for 30 minutes. After thorough rinsing and souring, the pattern is again rinsed and placed in a cold solution (1 : 50) containing 3 g. sodium peroxide per litre of water. This solution is then raised to 75°C. in 30–40 minutes and maintained at this temperature for 1 hour. After washing, souring and rinsing, the pattern is dried, allowed to cool and then compared with the original for shade, and any bleeding is noted.

Fastness to Mercerising.—The pattern is immersed in 52°Tw. caustic soda liquor for 10 minutes, squeezed, rinsed, soured and rinsed again before drying. Shade changes, noted by comparison with the original dyeing, are used as a measure of the fastness.

Fastness to Vulcanising.—Many types of vulcanisation are now employed with rubber-treated textiles, and these should be imitated in the laboratory as closely as possible. The usual hot-cure test involves the use of a 2% solution of rubber containing 10% sulphur on the weight of the rubber. The pattern is immersed in this solution until it is thoroughly penetrated and then dried. It is finally steamed for 40 minutes at 3 atmospheres pressure at approximately 140°C.

The cold-cure test is carried out by first treating the pattern in rubber solution and drying. The pattern is then passed through a 3% solution of sulphur chloride in carbon disulphide, rinsed in carbon disulphide, dried quickly and washed in water containing a trace of ammonia.

Whenever vat dyestuffs are required for dyeing goods which have subsequently to be rubber-proofed, colour orders from the dyehouse should be accompanied by a note to that effect. Most dyestuff firms issue special metal-free brands for the purpose.

Fastness to Milling.—This test is carried out in the manner described for wool (see page 55).

Fastness to Cross-dyeing.—The dyed yarn is boiled for ½–1 hour with 10% Glauber's salt and 4% sulphuric acid on the weight of the material and shade changes are noted. If the extent to which the wool colours will bleed on to the cotton is not known, the wool should be dyed in the presence of the vat-dyed cotton yarn under dyehouse conditions. Most of the triphenylmethane acid wool dyes transfer themselves to the cotton with a consequent change in shade of the cotton.

Fastness to Hot Pressing.—A sandwich of the dyed pattern should be made between two pieces of white cotton and then pressed for 20 seconds with a hot iron. The iron should first be heated so that it will just singe a piece of wool in 20 seconds; it should then be allowed to cool until it will no longer singe before applying it to the cotton test-pieces. Marking-off and shade changes should be noticed immediately, as well as the time taken for the original shade to return.

Fastness to Rubbing, Acids and Alkalis.—These tests are carried out as described for wool (see page 56).

Laundering Tests.—Laundering is difficult to imitate, because conditions in laundries vary very widely. However, a vigorous test is always advisable and may be based on the following example.

The pattern is stitched in between a piece of white cotton and a piece of white wool flannel. It is then shaken in a glass-stoppered bottle for 30 minutes with a solution (starting at 85° C.) consisting of 50 ccs. water, 0·5 g. soap and 0·2 g. soda ash for every 1 g. of fabric. The test may be made even more rigorous by adding very small amounts of bleaching powder or other chlorine-containing washing agents, as these are often employed in laundries. The pattern is finally washed several times in hot water to remove the soap and then dried by means of a moderately heated iron. Bleeding and shade changes are noted.

In order to obtain a mechanical and therefore reproducible test, the Society of Dyers and Colourists have developed a wash-wheel, and the American Association of Textile Chemists and Colorists put forward the Launderometer. It is strongly recommended that all washing and laundering tests should be carried out in some such standard machine in order to obviate the personal element which is bound to yield results of a varying character.

Fastness Tests for Vat-dyed Wool and Silk

Fastness to Carbonising.—The dyed wool is thoroughly saturated at room temperature in 5°–6°Tw. sulphuric acid and excess acid squeezed out through tight-nip rubber rollers. The pattern is then dried at 80°C. for about 10 minutes and baked at 110°C. for 20 minutes. Finally, the dyeing is neutralised with soda ash solution, washed well and dried. Where hydrochloric acid or aluminium chloride are used, works details must be imitated in the laboratory.

Fastness to Milling.—The wool is plaited alternately with white wool and cotton, and placed in a solution containing 2% soap and 1% soda ash for 3–4 hours at 50°C. Systematic rubbing between the hands is then applied for 3 minutes in every 20 minutes.

Acid milling tests are made by immersing a plaited pattern in a solution of sulphuric acid (2 ccs. D.O.V. per litre) for 4 hours at 50°C. Rubbing is carried out as above, either by hand using rubber gloves, or with a wooden roller on a wooden board.

Fastness to Potting.—The dyed pattern is rolled between white wool and silk cloths, fixed firmly with string and then boiled for 1 hour in hard water. An immersion in cold water is given before unrolling.

Fastness to Decatising.—A sample of white wool and the dry pattern, in contact with each other, are steamed at ¾ atmosphere for 1 hour.

Fastness to Stoving.—The pattern is wetted thoroughly in a 0·5% solution of soap, squeezed well and suspended in an atmosphere of sulphur dioxide for 12 hours.

Fastness to Cross-dyeing and Peroxide.—These fastness properties are estimated in the same way as described for cotton (above).

Fastness to Chlorine.—This is usually carried out on wool to indicate the suitability of the dyestuff for the non-shrink process. The pattern is immersed for approximately 10 seconds in a solution of sodium hypochlorite (containing 0·1 g. available chlorine per litre) to which a trace of dilute hydrochloric acid has been added. It is then rinsed and anti-chlored in a solution of sodium bisulphite.

Fastness to Acids.—The dyeing is spotted with solutions of sulphuric, hydrochloric or acetic acid (5%, 10% and 40% respectively) or with acid from scrooping baths, and allowed to dry without rinsing.

Fastness to Alkalis.—The pattern is spotted with a 10% solution of soda ash or a 20% milk of lime suspension and allowed to dry without rinsing.

Fastness to Rubbing.—This is usually estimated by rubbing the dyed material 30 times in a brisk manner on white cotton. Various types of rubbing apparatus have been designed to standardise this test, e.g. the "Crockmeter" of the American Association of Textile Chemists and Colorists and the abrasion machine of the Wool Industries Research Association.

CHAPTER V

APPLICATION—ANIMAL FIBRES

Indigo on Wool.—Throughout the history of dyeing there must have been at least a score of different processes used for dyeing wool with indigo. It is impossible to describe in this book all the diverse methods employed in the days of natural indigo, and this section deals only with the more important methods, paying particular attention to those employed to-day. Although the old fermentation vats have been almost entirely superseded by the hydrosulphite vats, fermentation processes still find occasional use in oriental countries, the nature of the vat varying greatly from place to place. The type of fermentation vat used depends chiefly on the type of natural dyeing assistants obtainable in that particular district. Wood ashes, lime and soda are usually employed as the alkaline agents, whilst for reduction or fermentation a wide variety of products are employed, such as bran, treacle, flour, sliced fruits and vegetables, woad and madder.

About fifty years ago the most popular indigo vats employed in European countries were the Suint Vat, the Soda Vat, the Woad Vat and the Bastard Vat. It is believed that the former is still employed in certain districts in the Balkans for domestic dyeing. It is claimed that in this process the wool is scoured simultaneously with dyeing on account of wool fat being employed as the ferment. Potash or wood ashes are employed to supplement the alkalinity of the suint. The Soda Vat employs molasses, madder and bran as ferments in the presence of soda, or lime and soda. This process was at one time widely used in Central Europe.

The Woad Vat is probably the best of all the fermentation vats for wool, and it owes its success mainly to the developments made by former dyers of this country. Its popularity, however, gradually waned on account of the introduction of the simpler chemical vats, and it has not been used on a commercial scale in this country for over ten years. The Bastard Vat appears to have been a combination of the Woad and Soda Vats, originating on the Continent; this vat is never employed to-day.

Practically all the methods involving the use of fermentation for reduction are now obsolete, at least as far as industrialised countries are concerned. The early types of hydrosulphite vats, such as the Schützenberger-Lalande Vat, are also very rarely employed to-day, even in their most recent modifications. The Glue–Ammonia–Hydrosulphite Vat is now the chief method employed.

Indigo possesses less affinity for wool than do the derivatives of indigo, i.e. the indigoid vat dyestuffs; consequently, indigo is now used to a smaller extent than in the past. Indigo, in fact, is never employed in mixtures with other vat dyestuffs, and where a blue component is required for the production of mode shades the brominated indigo brands are invariably used. The parent vat dyestuff, however, is still used as a "bottom" for subsequent topping with mordant and fast acid dyestuffs, but the latter have for many purposes entirely replaced indigo, owing to the increased availability of faster dyestuffs of this type.

Loose wool is still occasionally dyed with indigo, particularly for bottoming purposes. The old methods of dyeing, involving the use of nets and gallows, have been replaced by improved methods employing pumping machines of the circulating-liquor type; slubbing is now more commonly dyed. In the old days, after dyeing, the nets were raised above the vat and the liquor allowed to drain, oxidation was then effected by shaking the nets in air.

Woollen and worsted yarn is now only occasionally dyed with indigo, but the chief consumer of indigo is without doubt the piece dyer. Like loose wool, pieces are usually only bottomed with indigo, and only for very special jobs is it customary to dye full indigo shades on cloth. Yarn may be dyed in circulating-liquor machines or on bent rods in the open vat. Piece dyeing is carried out either in the winch-beck with submerged winches, or on modernised hawking machines.

Whenever wool is dyed with indigo, no matter what the stage, it is essential for it to be free from grease and other impurities if the best possible fastness to rubbing and the brightest results are to be obtained. Rubbing fastness is improved in many cases by the use of fullers' earth and myrabolan baths. When vats which contain sediment are being employed, the use of the old-time trammel nets is advisable in order to keep the wool out of contact with the "mud." Carbonised wool should always be perfectly neutralised with soda ash before entering the vat, for the obvious reason that residual acid is bound to throw the indigo out of solution.

Dyeing should never be carried out above 50°–55°C., or the wool will be damaged, as higher temperatures increase the deleterious action of the alkali. Wool is generally entered into the vat in a wet condition, so as to avoid introducing oxygen into the reduced liquor. For heavy and medium shades it is usual to build up the shade in three and two dips, respectively, of half an hour each, with thorough oxidation in the air between each dip. Light shades can usually be obtained in one dip without the danger of poor rubbing fastness. By this dipping procedure, redder and brighter shades are also obtained.

"Woaded" shades are only rarely dyed at the present time. At the time of their popularity these were obtained by first bottoming with indigo from the woad vat and then, for "woaded greens," topping with fustic and logwood or Alizarine Yellow; "woaded blacks" were produced by topping with logwood and fixing with iron. Alizarine Red on a chrome mordant has also been employed for bottoming indigo, so that red-shade blues could be obtained.

Details concerning many of these points are mentioned in the pages which follow.

The Woad Vat.—At the time of its popularity, the woad vat probably required more skill than any other textile finishing treatment. It is said that once the vat was in good condition it could be employed without a break for periods varying from six to ten months, i.e. before it became necessary to run off the vat and set a new one. The woad vat required a great amount of care, both in preparation and use, and throughout its whole life it had to be tended like a child; indeed, if insufficient attention was given, the vat would often go "sick."

The task of the dyer was to produce and maintain conditions in the vat which would suitably and continually supply the bacteria requisite for bringing about the fermentation which caused the reduction of the dyestuff. This was made possible by the dyer's skill and his experience in handling the vat, for, in those days, little was known about bacteriology and nothing of hydrogen ion concentrations. With the arrival of synthetic indigo, difficulties were experienced in obtaining the correct degree of fermentation and, in many cases, new vats had to be set with old liquors from the natural product.

Sugary compounds (carbohydrates) such as treacle, honey, raisins, flour and bran were added to the dye vat to encourage the growth of bacteria, as well as to prolong their life. The bacteria, during growth, split up the carbohydrates present into various organic acids, e.g. lactic and butyric acids, as well as carbonic acid, which liberated the reducing agent hydrogen. The acid conditions produced by such a reaction, however, would not render possible the formation of indigo white, and it was therefore always necessary to add alkali (e.g. lime, soda, potash and vegetable ashes) for two reasons, viz. (*a*) in order to neutralise the acids of fermentation and (*b*) to promote the formation of the indigo white.

Excess alkali had always to be avoided, on account of the fact that it retarded the growth of bacteria. On the other hand, insufficient alkali resulted in too vigorous liberation of hydrogen, causing a loss in indigo, as well as stirring up the bath to such an extent that dyeing was impossible.

Each dyer had his own carefully guarded recipes and no hard and fast rules as regards the setting of the vat were ever established. Hence, no fixed materials, weights, proportions and conditions can be set down as ideal. Fortunately, dyers' notebooks and a few published handbooks have helped interested dyers of to-day to gain an insight into these early methods. Quite a few old dyers, mostly retired and getting on in years, are still able to tell the tale of the woad vat they "could walk on"!

An example of a woad vat now follows, but other excellent accounts of this vat have been described by Hurry (*The Woad Plant and its Dye*, 1930) and by Stansfield (*Jubilee Issue of the Society of Dyers and Colourists*, 1935, 159–160).

A dye vessel of 2,000 gallons capacity (usually circular and constructed of wood) was set with:

Woad	120 lb.
Madder	40 lb.
Wheat Bran . . .	50 lb.
Syrup	20 lb.
Chalk	6 lb.
Soda Ash	20 lb.
Indigo 20% paste . .	45 lb.

Before the ingredients were added, the water was first run into the vessel and heated to 60°–70°C.; the woad was usually broken up the day before and steeped in warm water overnight. The remainder of the ingredients were then added and, after a good stirring, the vat was covered up and allowed to stand for 24 hours. During this time fermentation commenced, the liquid acquired a greenish hue, a sweet smell could be noticed, and, when the rake was pushed down into the sediment, bubbles would rise to the top. After another gentle stir up, the vat was again covered and left to stand once more until the liquor became pale green. Small quantities of slaked lime were then added and the vat once more stirred and covered.

Two days after the first addition of lime, the vat would (if everything was going well) become yellowish-green. If this was so, it was said to be "coming on," i.e. after four days or more! The sharpening process was then commenced, which involved making small additions of lime at two-hourly intervals, stirring up the vat carefully at each addition. During the sharpening, the sweet smell would gradually disappear, giving rise to a more pungent odour. The vat was ready only when this characteristic odour had appeared and the liquor was a clear greenish-yellow exhibiting blue veins and streaks. The surface of the vat had a rich coppery flurry which had to be skimmed off before the dyeing was commenced.

During the course of its long life, the woad vat was kept in good condition by additions of lime, bran and indigo paste. These additions were made at regular intervals during the evening, so that the baths were ready for use on the following morning.

During dyeing a temperature of 55°–60° C. was maintained, and dyeing was done in several dips. Indigo dyeings, especially when dark shades are required (and this was the chief use of the woad vat), are better dyed in short dips; more even dyeings, better fastness to rubbing and more bloomy and redder dyeings result from the short-dip process.

The disadvantages of fermentation vats are obvious. Quite apart from the lengthy time required for reduction of the indigo, there was always a great deal of sediment and the baths were consequently never clear during dyeing. Small particles of sediment always attached themselves to the wool, and difficulties in the spinning sheds were quite common occurrences. The formation of sediment led to the use of deeper dyeing vessels; liquors therefore took longer to heat and required a greater expenditure of steam.

The soda fermentation vat was preferred to the woad vat in continental countries where woad was more difficult to obtain than in Great Britain; syrup was employed in place of woad in this process.

The Older Hydrosulphite Vats.—At the close of the nineteenth century the introduction of chemical methods for the reduction of indigo, as distinct from the fermentation processes, represented a remarkable advance in the technique of dyeing. Although the new methods were not readily accepted by the old rule-of-thumb dyers, the advantages of chemical reduction were gradually realised and the fermentation processes began their decline. The *Schützenberger and Lalande Vat* was introduced in 1871 and Read Holliday & Sons bought the British rights·to the patent; for this reason it was known in England as the "*Read Holliday Vat.*" This process involves the preparation of hydrosulphite in the dyehouse from zinc dust and sodium bisulphite, which results in an accumulation of zinc in the dyevat with a consequent loss of indigo. The alkali originally recommended was lime, but the process was soon modified for the use of other alkalis, e.g. ammonia and caustic soda. Various names were given to the modified vats, e.g. the Hydrosulphite–Lime Vat, the Bisulphite Vat, the Bisulphite–Zinc–Lime Vat, etc.

The hydrosulphite was prepared in a separate vessel by "killing" 7 gallons of 57°Tw. sodium bisulphite liquor with approximately 7 lb. of zinc dust. These ingredients were thoroughly mixed together for about 15 minutes and, when the bisulphite was properly "killed," i.e. when the evolution of sulphur dioxide had ceased, milk of lime was added until the paste became thick; stirring was then continued until it became thin again. This mixture was next added to the vat (usually, for loose wool, a cast-iron vessel, 6 feet diameter and 7 feet deep) which had been prepared with water at 50°C. The stock vat of indigo was prepared in a separate vessel as follows: 7 gallons of bisulphite liquor and 7 lb. zinc dust were mixed as above, and milk of lime added. About 15 lb. of indigo powder, previously worked into a smooth paste with water, were then stirred in and agitated gently by hand until the liquor acquired a yellowish-brown appearance. After it had been allowed to stand for a short time until the characteristic blue flurry appeared, the liquor was made up to 40 gallons with warm water. The requisite amount of stock vat was charged into the prepared dyevat and, after a thorough stirring, was allowed to stand for a few hours before dyeing.

The Bisulphite–Zinc–Lime Vat, with the exception of the fermentation vats, gives the greatest amount of sediment of all the vats yet used for indigo. When dyeing, care must be taken to see that the vat is in good condition. A bright yellow vat indicates an excess of alkali, whilst a blue or green-blue vat indicates a shortage of killed bisulphite. After dyeing, owing to the use of lime, a thorough souring with acid should follow. These vats are never worked for longer than 18–20 days, and are replenished with further charges of killed bisulphite and stock indigo vat.

Zinc reacts with the bisulphite in the following manner, forming a very impure solution of sodium hydrogen hyposulphite:

$$Zn+3NaHSO_3 \longrightarrow ZnNa_2(SO_3)_2+NaHSO_2+H_2O.$$

The Hydrosulphite-Soda Vat was developed from the original Schützenberger–Lalande Vat by the use of caustic soda in place of lime. This led to the production of vats which were far superior as regards the amount of sediment produced, especially when the "killed bisulphite" form of hydrosulphite was replaced by the ready-prepared Hydrosulphite O solution of Meister, Lucius and Brüning. It was at this time, also, that Badische and M.L.B. introduced stable sodium hydrosulphite powder—the greatest boon yet experienced by the vat-dyeing trade.

Unfortunately, there was always a great danger of alkali damage to the wool when the hydrosulphite–caustic soda vat was employed. By carefully avoiding an excess of alkali, however, dyers soon gained sufficient experience to reduce alkali-damage to a minimum.

A stock vat for dyeing indigo on wool by the hydrosulphite–soda method is prepared as follows:

Fifteen lb. of 20% indigo paste, after first diluting with 2½ gallons of water at 60°C., are thoroughly mixed with 3 pints of 77°Tw. caustic soda. Three lb. of hydrosulphite (90%) are then sprinkled in steadily with stirring, and the whole is allowed to stand for 30 minutes.

When using powder brands, the following procedure is carried out. Three lb. of indigo powder are made into a paste with ¼ pint methylated spirits, and 3 gallons of water at 60°C. are added. The same amounts of caustic soda and sodium hydrosulphite are then added as for indigo paste. The stock vat must be clear and yellow and, if specks of reduced indigo can be seen on a slip of glass dipped in the vat, a small addition of hydrosulphite (2–3 oz.) is made in small portions until a clear liquor is obtained. If the stock vat is pale green in colour and exhibits a turbid or cloudy appearance, the temperature is noted and, if necessary, corrected; if the cloudiness persists very small amounts of caustic soda should be added. Cloudiness indicates the presence of undissolved indigo white.

A dyebath (for 300 gallons) is prepared at 50°C. and sharpened with an addition of 1 pint of 25% ammonia and 4 oz. hydrosulphite. The requisite amount of stock vat is added, the amount depending on the depth of shade desired, followed by 1¼ lb. of previously dissolved glue. Three lb. of indigo powder should be regarded as a maximum charge for a 300 gallon vat. The scoured and wetted wool is dyed in dips of 20–30 minutes each and completely oxidised before being subjected to a second dip, if this is required. Throughout dyeing the bath should show a faintly alkaline reaction to phenolphthalein test-paper, and the condition of the vat should be controlled by judicious additions of alkali and hydrosulphite as required.

The most useful and easily worked indigo vat for wool was introduced in 1902 by the Farbewerke Hoechst, who first placed Indigo Solutions, i.e. ready-reduced indigo, on the market. This firm (Meister, Lucius & Brüning) found that, although ammonia itself was incapable of dissolving indigo with the formation of indigo white, the indigo was not precipitated in the presence of glue and ammonia. In the colloidal form thus obtained, indigo was found to possess a greater affinity for wool than that shown by the calcium and sodium salts of indigo white. It was in this ammoniated *leuco*-form that the ready-reduced indigo brands appeared, and the same firm issued methods for working the *Ammonia-Glue-Hydrosulphite Vat.* Indigo MLB/Vat I and the similar competing brands which followed consist of indigo white, ammonia and a minimum of fixed alkali. Their use by this method ensures the production of perfectly clear vats which show no sediment. They provide an easy and convenient method of working to pattern, and the introduction of the R Vat brands (which quickly followed the original indigo solutions) led to the production of redder shades.

Stock vats are totally unnecessary as the Indigo Solution or Vat Grains (a later and more convenient innovation) are simply added to the dyevat prepared as follows:

A 300-gallon dye vessel is set with water at 50°C., 1½ pints 25% ammonia and ¾–1 lb. hydrosulphite and then the measured quantity of Indigo Solution is stirred in. One lb. of dissolved glue is next added and the bath raked up and dyeing commenced. The procedure during dyeing is the same as for the Hydrosulphite-Soda process just described.

For standing baths, 6 oz. glue, 8 oz. hydrosulphite and 3 pints ammonia are added each evening. The reduced indigo is then added in the morning, immediately before dyeing. A slightly alkaline reaction should always be shown on phenolphthalein test-paper and the bath should be kept clear by small additions of hydrosulphite. When dry wool is being dyed it will be found necessary to increase the amount of hydrosulphite to counteract the oxygen carried into the vat by the wool. The wool should appear pale green when leaving the bath and should be thoroughly oxidised before the next dip. After thorough oxidation, souring at about 75°C. is given, followed by a final rinsing. Ammonia-glue-hydrosulphite vats can usually be run for about six days, averaging about ten dips per day.

When using Vat Grains or Vat Powder, the dyevat is set with 1½ pints 25% ammonia, ⅓ pint caustic soda and 1 lb. of hydrosulphite. The procedure is then the same.

When dyeing light shades it is customary to use rather more hydrosulphite and caustic soda, and the following table, quoted from an early M.L.B. handbook, may prove useful:

Shade	*Indigo MLB/Vat I*	*Hydro-sulphite*	*Ammonia*	*Appearance*	*Reaction*
Dark	Much	Little	None	Dark Green	Only slightly alkaline
Medium	Equal	Equal	Little	Green	Weakly alkaline
Light	Little	Much	Much	Yellow	Alkaline

A slight excess of ammonia usually retards the rate of dyeing to such an extent that increased penetration is obtained. A large excess, however, is to be avoided as it produces uneven and washed-out shades.

Dyeing Various Forms of Wool with Indigo

The following particulars concern the application of indigoid vat dyestuffs, as well as indigo itself.

Shoddy and Loose Wool.—Loose wool is usually dyed in rectangular dyevats provided with a cage to hold the wool. The cage or basket is generally constructed of sheet iron and is so arranged that it can be raised clear of the vat when charging the vat or removing the wool. At the front of the vessel, or at the side in some cases, there is an adjustable squeezing device consisting of wrapped rollers through which the dyed wool is passed on leaving the cage. Squeezing must be as effective as possible so as to encourage even oxidation; the excess liquor drains back into the dyevat.

Machine dyeing of indigo on loose stock is carried out in a circulating-liquor machine. The wool is contained in a removable cage which, when loaded, is let down into the machine, and the indigo vat solution is drawn through the wool by means of a reversible pump. All additions should be well diluted and added in front of the pump so as to promote thorough mixing. The dyed wool is squeezed immediately after being discharged from the cage. The gradual accumulation of dirt in circulating-liquor machines calls for more frequent renewal of the vat liquor, but the output of these machines is often four times that of an open vat.

Loose wool is still occasionally dyed with indigo in ordinary open vessels constructed of wood, iron or copper. Particular attention has to be paid to the stirring, which should be done as smoothly and as effectively as possible. If squeezing or hydro-extracting arrangements are not available to work in conjunction with the open vessel, oxidation may be carried out in the exhausted liquor by gradually filling up with cold water from the top of the vessel while the spent dye liquor is being run off below. After cooling, the goods are lifted and allowed to drain and oxidise in the air. Hydrogen peroxide baths may also be used for the purpose of oxidation.

The following process has recently been developed in America (von Bergen, Crowley and Brommelsiek, *Amer. Dyestuff Rep.*, 1945, **34,** 53–62). Loose wool is dyed in a continuous process on two modified wool scouring sets consisting of four bowls each. The bowls are interconnected with squeeze rollers and mobile aprons along which the wool is propelled by means of rakes specially designed to obviate vigorous movement of the liquor. The wool is dyed by two dips of 4% and 3·5% indigo respectively.

The loose wool is wetted out in the first bowl into which it is fed by means of a hopper at the rate of 550 lb. per hour. In the second bowl it receives its first indigo dip during six minutes. In the third bowl the dyed wool is rapidly oxidised by a treatment with hydrogen peroxide or sodium perborate. In the fourth bowl, the wool is rinsed free from oxidising agents and is then placed in a second hopper which feeds the fifth bowl which contains the second indigo vat. The sixth bowl contains an oxidising bath, and the seventh and eighth bowls are used for rinsing operations. Each indigo dip takes place during six minutes and the temperature is maintained at a fixed level by the employment of thermostatically controlled coils.

The indigo vats are prepared with caustic soda, hydrosulphite, soda ash, ammonia and glue, and a constant concentration is maintained in each vat by an elaborate circulating and feeding system. During the continuous operation of the dyeing range, oxidation products of hydrosulphite are formed. When the equivalent of 8 g. oxygen per litre is reached the vat ceases to be effective. The oxidation products react with the alkalis present to form sodium bicarbonate with a consequent build up of alkali content. Maintenance of a fixed carbonate concentration is necessary for effective operation. The full process, including control data, is described in the original article. The latter has been abstracted in *J.S.D.C.*, 1945, **61**, 180.

Wool Balls or Tops.—These are dyed in circulating-liquor machines with one- or two-way circulation. Oxidation is generally carried out in the machine by first cooling with water and then circulating an oxidising liquor through the goods at 30° C. for about 10 minutes. The oxidising liquor consists of 2% hydrogen peroxide (30%). After circulation, this liquor is run off and the wool is rinsed with water and then soured by passing 2–5% acetic acid (30%) through the machine at 80° C. for 10 minutes. If this method of oxidation is not employed, the goods are cooled down with water to about 30° C., and then rapidly hydro-extracted and allowed to oxidise in the air; or, alternatively, simply dropped into skips after squeezing and allowed to oxidise there. Sometimes, the squeezed wool is allowed to fall directly into a tank of cold running water, thus effecting a gradual and even oxidation. It is only necessary to sour indigo-dyed goods when they are required to show the maximum resistance to decatising.

Slubbing and Woollen and Worsted Yarns.—Wool in these forms is usually dyed in hank form in an open dye-beck supplied with bent iron rods designed to keep the yarn beneath the liquor. After dyeing, the hanks are passed separately through a nip, while still on the sticks.

Yarn is also dyed in specially constructed yarn-dyeing machines designed to afford gentle circulation of the liquor.

Wool Piece Goods.—These are dyed on the hawking machine (Fig. 17), which works the goods through the vat below the surface of the liquor. The construction of the cloth determines the time of dyeing; several half-hour dips are employed for deep shades of indigo, whilst indigoid vat dyestuffs are dyed for times varying between half an hour and two hours, depending on the thickness of the cloth and the nature of the weave. Even squeezing of piece goods, followed by an effective air passage before cuttling, is essential for thorough oxidation. Continuous full-width machines supplied with squeezing rollers and an airing device may also be used for standard shades. A new process for the continuous dyeing of woollen piece goods with indigo at the rate of 5,000 lb. wool per eight hours has recently been described by Linberg (*Amer. Dyestuff Rep.*, 1943, **32**, 33).

Very fine wool fabrics are often dyed in winch machines with the winch set below the surface of the liquor.

Details concerning dyeing apparatus are given in Chapter X.

Derivatives of Indigo on Wool.—Each individual indigoid vat dyestuff in its application to wool requires special treatment; and details of each dyestuff cannot be given in this book. The weights and proportions of the various agents required for vatting given by the dyestuff manufacturers in their folders, pattern cards and handbooks will be found to be reliable guides for dyehouse procedure.

Apart from indigo dyeing, which is considered a specialised trade even to-day, the dyeing of wool with vat dyestuffs has never received a great deal of attention in this country, although the dyestuffs have been employed to a comparatively large extent on the Continent. They are occasionally dyed in this country, however, usually for the overseas trade. In the past there has been a decided prejudice against the use of vat dyestuffs for wool and, besides the question of the high cost of the colours, the following arguments have been put forward. The deciding question is that of the comparative wearing and weathering properties of vat-dyed and chrome-dyed wool goods. In addition, the fact that the majority of dyers in this country, particularly in the woollen districts, look upon the special procedures for which vat dyeing calls as alien to their usual dyeing processes has also had a strong influence. These dyers have been accustomed to dyeing methods which involve the use of water-soluble dyestuffs in a neutral or slightly acid bath, and the use of alkaline reducing liquors has been something of a bogy to them. The possibility of alkali-damage to the wool has also made the wool dyer avoid vat dyestuffs; by the use of correct methods, however, this possibility may be rendered very unlikely.

On the Continent such bogies have not been feared, probably because of the army of technicians sent out by the dyestuff firms (particularly the I.G.) for the purpose of instructing dyers in the art of dyeing wool with vat dyestuffs. Such materials as overcoatings, suitings and dress goods, tapestry, carpets, upholstery, and even hosiery, are not uncommonly vat dyed in Germany, and particular interest has long been shown in the vat dyeing of wool intended for military cloths. Similar goods are dyed in England with fast acid, Neolan and mordant dyestuffs.

In connexion with the wearing properties of dyed goods there is always a large number of factors to consider, including the fineness and quality of the wool, the extent of injury to the wool caused by processes other than dyeing, the structure of the cloth, the variations in the various manufacturing and finishing processes, as well as the depth of shade. Sommer (*Melliand Textilberichte*, *Engl. Edn.*, 1939, **20**, 25) has shown that vat dyes, in general, particularly navy blues on military cloths, give better value than chrome dyes. It is claimed that vat dyestuffs leave the wool with a greater tensile strength than mordant-dyed wool of identical shade, whilst in resistance to light and other atmospheric influences vat dyestuffs are claimed to be superior to mordant dyestuffs. Sommer states, however, that with navy blue shades, at least, after-chromed mordant dyestuffs exhibit better fastness to rubbing and greater resistance to abrasive wear.

Indigoid vat dyestuffs for wool appear on the market under various brand names. The names Durindone (I.C.I.), Ciba (S.C.I.) and Helindon (I.G.) are probably the most familiar, and other examples will be found in the last chapter of this book. These dyestuffs are available either as pastes or as powders, whilst specially reduced forms are also available under the denominations of Ciba-Leuco (S.C.I.), Vat Powder, Vat Paste and Vat Grains (I.G.).

When preparing the stock vat, the dyestuff in ordinary paste or powder form is worked into a smooth paste with Turkey Red oil, Monopol Soap, Solapol Oil F, methylated spirits or other wetting agent and then diluted with soft or condensed water at the prescribed temperature. The requisite quantity of caustic soda is then added, the amount being based on the weight of the dyestuff. Just sufficient alkali to dissolve the dyestuff is employed, and the alkalinity is later increased slightly by adding ammonia to the dyevat. After the caustic soda has been thoroughly mixed with the colour paste, hydrosulphite is sprinkled in and the vat stirred and allowed to reduce for 15 minutes. The appearance of the vat should coincide with the dyestuff maker's description, and a glass plate dipped into the solution should show the characteristic shade of the *leuco*-dyestuff, be free from specks and slowly oxidise to the correct shade.

The dyevat is set with 8 oz. freshly dissolved glue, 1 pint of 25% ammonia and 4 oz. hydrosulphite per 100 gallons of dyeliquor at 50°–60°C. When dyeing pale shades small additions of caustic soda and hydrosulphite are added to the vat during dyeing. The required amount of stock vat is then added to the dyevat, preferably through a fine-mesh sieve. The bath is well raked up, the wetted wool entered and dyeing carried on for 30–45 minutes at the prescribed temperature. During dyeing, the vat should be only slightly alkaline to phenolphthalein test-paper.

A shortage of hydrosulphite yields dyeings of poor fastness to rubbing, whilst an excess results in incomplete exhaustion. The use of Flavanthrone paper will indicate whether or not there is a sufficiency of hydrosulphite present.

In most cases the bath exhausts quite well, but certain dyestuffs require the gradual addition of ammonium sulphate or chloride to effect complete exhaustion. At the end of the dyeing time the goods are lifted, squeezed or hydro-extracted and allowed to lie in skips for an oxidation period of ½–2 hours. Rinsing and then souring follows. The souring is done with acetic or formic acid at 60°C., or, occasionally for certain dyestuffs, at 80°C., or at the boil. The goods are then rinsed and dried.

Vat Powders and Vat Grains (i.e. ready-reduced dyestuffs) simply require dissolving in boiling water to which 5% glue and 5% hydrosulphite on the weight of the colour have been added. The solutions are then allowed to stand for a short time before they are added to the sharpened dyevat. Vat Powders and Grains, as well as Vat Pastes (reduced), may also be added directly to the prepared dye vessel.

When dyeing mode shades from combinations of indigoid colouring matters it is essential to choose those dyestuffs which have similar dyeing properties and require similar amounts of alkali and hydrosulphite. It is always best to dye mixture shades by completely exhausting the bath; standing baths are only employed for single dyestuffs and for shades of the "bread and butter" category, e.g. dark browns and dark blues. When mixtures of dyestuffs are present there is always a strong possibility of one of the colours lingering behind the others and upsetting matching in subsequent baths. When dyeing to pattern, small samples should be taken from the vat, squeezed and aired, and then either steamed or developed in 1% acetic acid for about 10 minutes at 80°C. The sample should then be rinsed, dried and allowed to cool before comparing it with the pattern.

Small samples, or "bits," taken for matching purposes may be rapidly dried and cooled with the aid of a domestic electric hair-dryer over the end of which is fitted a funnel-shaped attachment. The sample is placed in the funnel and held in position by a wire-gauze lid, the heat is turned on for a few minutes until the sample is dry, and then cold air is used for a further short period.

In order to illustrate the preparation of stock vats, the following examples are given:

(*a*) Ciba Orange R Paste (1 lb.) is mixed with 1 oz. of Solapol Oil F, diluted with 4 pints of water at 75°C., and $\frac{3}{16}$ pint of 72°Tw. caustic soda are added. Next, 2½ oz. hydrosulphite are strewn in steadily with stirring and the vat is allowed to stand, with occasional stirring, for 15 minutes. The vat should be free from specks or cloudiness and should show a pale yellow-orange colour. This dyestuff is dyed at 60°C., and developed after oxidation by souring at 80°–100°C. with 1 pint of 90% formic acid per 100 gallons of water.

(*b*) Ciba Yellow G Powder (1 lb.) is pasted with 2 lb. of Solapol Oil F and 10 gallons of water at 75°C., and 1½ pints of 72°Tw. caustic soda are added. Next, 1½ lb. of hydrosulphite are added and vatting is allowed to proceed for 10–15 minutes before testing. The *leuco*-compound of this dyestuff has a dull red-violet colour. After dyeing at 60°C. and oxidising, souring is carried out at 60°C.

The makers of the Helindon dyestuffs (I.G.) have conveniently divided their products into two distinct dyeing classes, viz. the HN Group and the HW Group.

Dyestuffs of the HN Group.—The Helindon dyestuffs of this group, which are all dyed between 50°C. and 65°C., include yellows, browns, khakis, reds, scarlets, greens, indigos and blacks, and they are available as ordinary pastes and powders and in the ready-reduced form. Soft or condensed water should always be employed if possible, since hard water speeds up the rate of dyeing to some extent. With soft water, however, a few of the dyestuffs of this group may be found difficult to exhaust, but the addition of small amounts of ammonium sulphate (dissolved) will completely exhaust the dyebath. The dyevats are set with glue, ammonia and hydrosulphite, as described above, and the dyeing procedure is also the same.

Helindon Scarlet GG powder (1 lb.), for example, requires pasting with an equal weight of Monopol Soap or a similar agent and then diluting with 3½ gallons of water at 55°C.; 1¼ lb. of 72°Tw. caustic soda, and 1 lb. of hydrosulphite are then needed for the reduction. After 20 minutes, a glass plate dipped into the stock vat should show a bluish-violet coloration and no specks; this shade slowly passes through wine red to a final shade of brick red. Wetting oils for pasting can be omitted when "powder special" brands are being employed.

For exhaustion, the HN dyestuffs may require the addition of up to 3% ammonium sulphate, depending on the condition of the water and the depth of shade. If the dyevat is found to be too strongly alkaline when tested with phenolphthalein paper, it can be corrected by adding a little ammonium sulphate or chloride. At the commencement of dyeing the vat should show a pink coloration on the test-paper, and at the end of the dyeing the bath should be practically neutral.

Dyestuffs of the HW Group.—These dyestuffs, which must always be dyed at 60°–65°C., include Helindon Orange R, Brown 3R, Pink R, Red B, Red BR, Violet BBN and Blue 3G; Indigo MLB/4B and Brilliant Indigo BASF/4B. The method of preparation of the stock vat is identical with that used for the HN Group. The dyevat is similarly set with glue, ammonia and hydrosulphite, and a dyeing period of 30 minutes is usually employed.

Owing to the poor exhaustion exhibited by the HW dyestuffs, even when ammonium sulphate is used, dyeing by the exhaustion method is seldom practised, but standing baths are used. Indeed, ammonium salts should never be employed with members of this group because they are liable to precipitate the dyestuff and produce washed-out shades of poor fastness to rubbing. These dyestuffs are also dyed in rather more alkaline vats than the HN Group, and their vats should react red rather than pink to phenolphthalein paper.

Hard water is probably the most suitable for dyeing HW dyestuffs; it apparently increases their rates of dyeing without causing precipitation. When soft water is used it is advisable to add 5–10% calcium chloride crystals before sharpening the vat. With Helindon Blue 3G, however, soft or condensed water should always be used.

Acid development is essential for dyestuffs of the HW group. This is carried out after thorough air-oxidation, using 2–3% D.O.V. or 4–5% acetic acid (30%) on the weight of the goods. Souring is commenced at 30°–40°C. and the bath is then raised to the boil; boiling is continued for 10 minutes before the wool is finally rinsed off.

Mixtures including HN and HW dyestuffs may only be applied in standing baths at a temperature of 60°–65°C.

The Trisodium Phosphate Method of Dyeing Wool with Indigoid and Anthraquinonoid Vat Dyestuffs.—This method was originated by Imperial Chemical Industries Ltd. In this process, caustic soda is replaced by crystalline trisodium phosphate; it is imperative that crystalline and not anhydrous trisodium phosphate should be used. Dyestuffs from both the indigoid and anthraquinonoid classes may be applied by this method.

The dyestuff is reduced with one-fourth of the total volume of the required dye liquor with 0·5% trisodium phosphate crystals and 0·15% hydrosulphite (the quantities are here expressed as percentage weights on the total volume of the liquor). Anthraquinonoid vat dyestuffs are reduced at 60°C., and indigoid vat dyestuffs at 90°C. Vatting is allowed to continue for 15 minutes and the reduced solution is then added to the dyebath containing 0·5% trisodium phosphate crystals and 0·02% hydrosulphite. Dyeing is carried out at 60°C. for 30 minutes. Dyeings with anthraquinonoid dyestuffs are squeezed and oxidised in air, and when oxidation is complete they are rinsed and treated for 15 minutes at 50°C. in a solution containing 0·25% Lissapol C and 0·25% acetic acid (30%). Finally, the goods are given a thorough rinsing. Dyeings with the indigoid vat dyestuffs are oxidised by a 15-minutes treatment in a solution containing 0·25% potassium persulphate and 0·5% acetic acid (30%). On completion of oxidation, the goods are treated in a solution of 0·25% Lissapol C for 15 minutes at 50°C.

Dyestuffs recommended for application by this process are:

(a) Anthraquinonoid—
Caledon Reds 5GS, BNS and X5BS
Caledon Brilliant Purple 2RS
Caledon Purple RS
Caledon Khakis RS and 2GS
Caledon Olive RS
Caledon Jade Greens 4GS, 2GS, XS, BS, and 3BS
Caledon Navy Blue 2R
Caledon Red Violet 2RNS
Caledon Brilliant Violet RS
Caledon Violet XBNS
Caledon Grey 3R
Caledon Greens RCS, 2BS, G and 2G
Caledon Dark Blue GS
Alizanthrene Navy Blue R

(b) Indigoid—
Durindone Orange RS
Durindone Pinks FFS and FBS
Durindone Brown GS
Durindone Scarlets YS, 2B and 3B
Durindone Reds BS and 3BS
Durindone Blues 4BCS and 4BS

Indigoid Vat Dyestuffs for Natural Silk.—When shades which are fast to light, washing, wear, weather and water are required on embroidery yarns, furnishings and curtains composed of natural silk, the indigoid vat dyestuffs fulfil the requirements very well indeed. Natural silk is always vat-dyed in an unweighted state, and it is usually dyed in hank form. Vat-dyed silk also finds employment as effect threads in dress goods, as well as for the production of coloured woven goods which are subsequently to be degummed and bleached.

The introduction of vat dyes to the silk industry has led to the production of striped crêpe-de-chine fabrics which were previously unobtainable, except by printing. The vat dyes, being fast to the degumming process, have proved to be exceptionally suitable for the production of checks and other fancy woven designs on this type of fabric, on which only self-shades were previously obtainable.

So far, the dyeing of weighted silk has not been developed, on account of the varying affinity imparted to the goods by the various metallic compounds employed in weighting. The affinity of natural silk for vat dyestuffs can be increased by treatment with solutions of certain salts of nickel, copper, iron and aluminium, or with ammoniacal copper hydroxide solutions.

Individual dyestuffs require individual treatment, but it is customary to proceed as follows. The stock vat is prepared by pasting 1 lb. of dyestuff powder (or an equivalent quantity of paste) with 2–16 oz. of neutral Turkey Red Oil and diluting it with 2½–10 gallons of water at 60°C.; 1½–4 pints of 70°Tw. caustic soda, followed by 2–2½ lb. of hydrosulphite, are then added, and vatting is allowed to take place for 30 minutes.

The dyevat is set at 40°–60°C. with ¼–1 pint of 70°Tw. caustic soda and 4–12 oz. hydrosulphite per 100 gallons, depending on the depth of shade. Weak shades need 1 pint of caustic soda and 12 oz. of hydrosulphite; medium shade dyevats are set with ½ pint caustic soda and 8 oz. of hydrosulphite; whilst strong shades require less alkali, viz. ¼ pint of caustic soda and only 4 oz. hydrosulphite powder. Glue (1–2 lb.) or waste sulphite cellulose lye (1 lb.) is employed as a protection against alkali damage.

Exhaustion is effected in most cases by adding common salt or Glauber's salt half-way through the dyeing process, which takes from ¾–1 hour. Pale shades and certain dyestuffs in any depth of shade, e.g. Ciba Violet B, can be dyed satisfactorily without adding salt.

Ciba Brilliant Pink B powder (1 lb.), for example, is vatted by first mixing to a paste with 1 lb. of Turkey Red Oil and 10 gallons of water at 80°C.; 2¼ pints of 70°Tw. caustic soda and 2½ lb. of hydrosulphite are then added, and vatting is allowed to take place during 30 minutes. By this time the vat liquor should be clear and free from specks and be reddish-yellow in shade. The required amount of this stock vat is then added through a fine sieve to the sharpened dyevat, which is set at 60°C. and made up to 100 gallons. A solution containing 10–30 lb. of Glauber's salt is added during dyeing, according to the depth of shade.

Effective squeezing or hydro-extraction follows the dyeing, and the goods should then be allowed to oxidise in the air for about 1 hour before soaping for 30 minutes at the boil with 3 lb. soap per 100 gallons of water.

Many of the indigoid vat colours may also be applied to natural silk by the IN, IW or IK processes used for vat dyestuffs of the anthraquinonoid class, as described in Chapter VI. When using these methods the dyestuffs are usually employed in conjunction with anthraquinonoid colours for the production of mode shades; they must, however, always be vatted separately in the stock vat.

Solubilised Vat Dyestuffs on Wool.—For application to wool the solubilised vat dyestuffs possess great advantages over the ordinary vat dyestuffs. The possibility of alkali-damage to wool entailed by the use of ordinary vat dyestuffs is absent with the solubilised vat dyes of the Algosol, Indigosol and Soledon ranges, which are applied from an acid bath with subsequent acid development.

Wool in any form, for example loose stock, slubbing, yarn and pieces, may be dyed with these dyestuffs, and the dyeings show a fastness equal to or closely approaching that of ordinary vat dyeings. The dyeing of piece goods for the United States Navy has absorbed a large amount of solubilised indigo, which, on account of its excellent affinity for wool, will produce dark shades in one operation. When this is compared with the three or even four dips which are required to produce navy blue dyeings from ordinary indigo applied from the alkaline vat, the advantages are immediately apparent. Taken as a unit process, the method is on the whole dearer than the continuous process for dyeing ordinary indigo, but it possesses the advantages of speed, and cleanliness of the machines and finished goods. Another advantage lies in the fact that Indigosol O and similar products can be dyed on machinery normally used by wool dyers, whereas indigo requires special ranges. Indigosols O and OR are also employed in weaker shades for bottoming wool serges and uniform cloths, and for such garments as bathing costumes.

These water-soluble dyestuffs may be applied in an open vessel in the following manner. The bath is set with the requisite quantity of dyestuff (previously dissolved in hot water), 10% Glauber's salt, 1% Rongalite C (I.G.) (or equivalent product, e.g. Formosul (Bro.), Erasol C (L.B.H.), etc.) and 3–6% formic acid (80%), depending on the depth of shade, all percentages being on the weight of the goods.

The scoured goods are entered at 40°C. and steadily raised to the boil. After boiling for 30 minutes, 2% well-diluted D.O.V. is added and boiling is continued for a further 40 minutes. During dyeing the wool should appear light green; if this colour changes to blue during dyeing a small quantity of Rongalite should be an acid bath. Subsequently, they are developed in a bichrome-sulphuric acid bath, neutralised and soaped. The dyebaths are prepared with the requisite amount of dyestuff (up to 5%), 1–2% Rongalite C (or equivalent product) and 2–5% acetic acid (80%), depending on the depth of shade. After the silk has been dyed cold for 15 minutes, the bath is raised slowly to 85°–90°C. and dyeing is continued at this temperature for a further 30 minutes.

After oxidation, the dyeings are rinsed, neutralised with a little ammonia or soda ash, and then soaped at 80°–90°C., using 5 lb. Marseilles soap per 100 gallons of water.

Several dyestuffs not mentioned in the above list may be applied to silk, but they are not suitable for dyeing by the above process. Indigosol Green IBA is applied in the same way as it is dyed on wool (see page 77) and may be developed either with nitrite or bichromate. Indigosol Printing Black IB and Indigosol Yellow HCG are dyed in the same way as the main body of Indigosols, but, after dyeing in the cold for 15 minutes in presence of formic acid, an addition of 2% D.O.V. is made to secure exhaustion. The remaining procedure is then identical, but the ammonium sulphocyanide is omitted from the developing bath.

Tin-silicate-phosphate weighted silk (up to 20% weighting) may be dyed in the following manner. The bath is first set with 1–2% Rongalite C and then the dissolved dyestuff is added. Dyeing is commenced in this cold bath and no further additions are made for about 10 minutes, when 10–20 lb. Glauber's salt per 100 gallons of liquor are added. Dyeing is continued cold for 15 minutes and then 2–4% formic acid (80%) is added for exhaustion purposes. After a further 15 minutes of cold dyeing, the bath is raised slowly to 85°–90°C. and maintained at this temperature for 30 minutes. Development is carried out as for unweighted silk.

When thick silk goods are being dyed, some difficulty in penetration may be experienced, but this can usually be overcome by the use of Gardinol, Melioran, Nekal BX, or other acid-stable wetting agent. Closely woven and thick silk piece goods are often dyed by the padding method. For this purpose, the pad-liquor is set at 30°–40°C. with the required amount of colour, 5 parts of 6% tragacanth thickening and 0·2–1·5 parts of Glyecine A (or similar product), the whole being made up to 100 parts with water containing 10% of an acid-stable wetting agent. After single or double padding, the goods are dried and steamed for 20 minutes in the cottage steamer. The paddings are finally developed for 5 minutes at 60°C. in a winch beck or washer containing 3–3½ oz. potassium bichromate and 5–7 lb. D.O.V. per 100 gallons of water.

CHAPTER VI

APPLICATION—CELLULOSIC FIBRES

ALL types of vat dyestuffs and their solubilised derivatives may be applied to cotton, linen and regenerated cellulose. The various methods of application of the different classes of vat colouring matters, which have been outlined in the foregoing chapters, will now be discussed in more detail. As far as possible this chapter is subdivided into the following sections, but some overlapping is unavoidable.

(*a*) Indigo on Cotton
(*b*) Hydron Blues on Cotton
(*c*) Indigoid Vat Dyes on Cotton and Rayons
(*d*) The Faster Anthraquinonoid Vat Dyes (as exemplified by the Indanthrenes) on Cotton and Rayon
(*e*) The Less-fast Anthraquinonoid Vat Dyes (as exemplified by the Algols) on Cotton and Rayon
(*f*) The Indigosols on Cotton and Rayons (Chapter VII)

(*a*) Indigo on Cotton

There are still four main methods of dyeing indigo blues on cotton goods, the most important of these being by way of the Hydrosulphite Vat. The other methods, occasionally used, are known as the Fermentation Vat, the Ferrous Sulphate Vat and the Zinc–Lime Vat.

Cotton may be dyed at any stage during the manufacture of cloth, i.e. in loose form, hanks, warps or pieces. The method chosen is largely dependent upon the form of the goods and the type of machine available; occasionally local conditions play their part. This last factor applies to the fermentation process, the use of which is now almost confined to Oriental countries.

The *Hydrosulphite Vat* provides the most productive, simple and scientific method of dyeing indigo on cotton goods. It is quicker and easier to prepare than the alternative vats, is perfectly free from sediment and yields faster results. It is economical in use, so far as wastage of indigo and time are concerned, but the cost of the hydrosulphite and caustic soda is very slightly higher than that of the agents used for the less scientific types of vats. The high-grade results obtained warrant general usage of the hydrosulphite process. Hydrosulphite vats may be employed in three ways, viz. the cold process, the warm process, and the potash process. These are worked, in general, as follows.

The *Cold Hydrosulphite Vat* is usually employed for cotton yarn and the lighter piece materials and is probably the most commonly used indigo vat for cotton. Practically all indigo and indigo "pure" brands are applicable by this method.

A 200-gallon dye-vessel is prepared with 3 oz. of 70°Tw. caustic soda and 5 oz. of hydrosulphite. The liquor, thus sharpened, is then stirred well and 7–8 lb. of Monopol Soap, or a similar product, are added, followed by 40 lb. of common salt. The dissolved indigo from a stock vat prepared as follows, is then added.

To prepare a stock vat using 20 lb. of Indigo Paste (20%), 4 gallons of water at 50°–60°C. are used for diluting the weighed out colour. Next, 7 lb. of 70°Tw. caustic soda are added, followed by 4 lb. hydrosulphite, with stirring between each addition. The vat is maintained at 55°C., for 30 minutes, after which time the indigo should be in solution. If the reduced liquor shows a clear yellow colour when running from a glass slide which has been dipped in the vat, the vat is ready for use. The yellow solution from the slide test should oxidise to a greenish colour in about 20 seconds. If the vat is not clear, a small amount of hydrosulphite (½ oz.) should be added and a further glass-slide test made before the stock vat is added to the dyeing vessel.

The charged dye-vessel should be stirred well after adding the reduced indigo, and allowed to stand for some time before skimming off the surface flurry and commencing dyeing.

The ready-reduced, or "vat," indigo brands are simply added to the prepared dyebath, a stock vat being unnecessary. The dyevat (200 gallons) is prepared by filling up to the 200 gallons mark with cold water and priming with 2¼ oz. of 70°Tw. caustic soda and 4½ oz. of hydrosulphite. About 8 lb. of Monopol Soap and 40 lb. of common salt are then stirred in and, finally, 30 lb. of "vat indigo solution" are added. Dyeing details are given on pages 84–90.

The *Warm Hydrosulphite Vat* is employed for the brands of indigo which show a higher affinity for cotton, i.e. more rapid absorption, than the ordinary types. As examples of this type of indigo, Indigo MLB/R and Indigo BASF/R and their equivalent products may be mentioned. Such products give indigo blues of purer and redder tone and exhibit superior fastness to rubbing and washing than the ordinary types.

The warm vat is also often employed for goods which are difficult to penetrate, e.g. heavy pieces and tightly twisted mercerised yarns. The dyestuffs are dissolved in the stock vat and then added to the dyeing vessel set at 50°C., and containing 2 pints of 70°Tw. caustic soda and ½ lb. of hydrosulphite per 500 gallons of soft water. For example, 15 lb. of Indigo MLB/R Powder are dissolved in the stock vat by pasting up with hot water and a little methylated spirits, diluting the thin even paste so obtained to 35 gallons with water at 50°C., and then adding with careful stirring 4 gallons of 70°Tw. caustic soda, followed by 15 lb. of hydrosulphite. The vat is allowed to stand at 50°C. for 20 minutes, or until a clear vat of good condition is obtained.

The amount of stock vat required for dyeing is then added to the sharpened dye-liquor, and 2 gallons of 10% glue solution are added. The glue solution assists absorption of the *leuco*-indigo, and slightly brighter results are always obtained by its use. The dyevat is allowed to stand for some time, and the conditions are carefully checked before removing the scum and entering the goods for dyeing. Dyeing details will be found on pages 84–90.

The *Hydrosulphite-Potash Vat* has for some reason not been as well received as its advantages merit, probably on account of the slightly increased costs entailed. It is mainly recommended for dyeing yarn in hank form and it has the advantage of not attacking the hands of the labourers who turn the sticks. It is also chiefly used in conjunction with indigo "vats" (reduced) and indigo solutions, dyeing and preparation being carried out cold. A 750-gallon beck is charged first with water and then with 7½ lb. of potassium carbonate previously dissolved in hot water. While dissolving the potash care must be taken to avoid caking, as the lumps so formed are difficult to dissolve. Hydrosulphite (2¼ lb.) is then added and the requisite amount of reduced indigo, e.g. 50 lb. of 20% Solution, is finally stirred in. The potash vat presents a greenish-yellow appearance when in correct condition; a dark green or bluish-green colour shows the vat to be incorrectly reduced, and further additions of hydrosulphite (e.g. 1¾ lb.) and potassium carbonate (e.g. ¾ lb.) should be made.

The so-called "*Brilliant Indigos*" are applied to yarn and piece goods which are required to show a pure bright shade and to exhibit a higher degree of fastness to rubbing, as well as good fastness to washing and light. These dyestuffs, e.g. Indigo MLB/6B and Brilliant Indigo BASF, are dyed by the hydrosulphite process, and vatting takes place in the stock vat.

For example, 1 lb. dyestuff powder is pasted with 1¼ pints of

50% Turkey Red oil and a little water at 60°C. The paste is gradually diluted to give 5 gallons of thin paste and then, at 50°–60°C., 2 pints of caustic liquor 70°Tw. and 2½ lb. of hydrosulphite are added while stirring. Amounts of reducing agent and alkali naturally vary with the depth of shade, dark shades requiring less alkali and hydrosulphite than medium or pale shades. Vatting is usually completed in 20 minutes and the reduced liquor should appear dark or light yellow, according to the amount of dyestuff employed. The "G" brand Brilliant Indigos require approximately twice as much caustic soda as the other brands, and it is always wisest to carry out laboratory trials in every case, under machine conditions if possible, in order to ascertain the formulae for reduction and dyeing which are most suitable for the particular conditions.

When dyeing with Brilliant Indigos soft or softened water should always be used, and it is usually advisable to add 1–2 lb. soda ash to the dyebath in order to precipitate any lime. The dyebath is set at 50°C. with a small quantity of hydrosulphite, and dyeing is carried out for 30 minutes at 30°–50°C., depending on the type of goods and depth of shade. Pale shades, for instance, are best dyed by entering the goods at the lower temperature and gradually raising to the higher temperature during the course of the dyeing. Finally, the goods are squeezed and oxidised in the air and rinsed in hot water before soaping at the boil. The hot-water rinse ensures full shades, and a thorough soaping is always necessary if maximum brightness is to be obtained.

The *Fermentation Vat*, as previously stated, is now obsolete, except in certain backward Eastern countries where it is used for domestic dyeing. For a long time after the general adoption of hydrosulphite vats, however, several firms continued to employ this process on account of the characteristic smell which it imparts to the goods. In certain markets "genuine indigo" is judged by its odour. Latterly, however, goods have been given this characteristic odour by the use of marketed auxiliary products especially designed for the purpose.

A fermentation vat is difficult to set and control, except by experienced men, and the introduction of the easier chemical methods soon led to the decline of its use. As in the case of wool dyeing with indigo by the fermentation process, the choice of reducing agents and alkalis largely depends upon the availability of materials. The ferments chosen are usually fruits or syrup, whilst the alkali used may be wood-ashes, soda ash or lime. German dyestuff firms, in particular, appear to have done a fair amount of trade with native dyers by the sale of their ready-reduced indigo brands for use with a fermentation dyevat.

The following outline illustrates the use of a fermentation vat for cotton. The vat is set at 50°C. with 7–9 lb. of bran, 2½ lb. stale bread and 2 lb. soda ash per 100 gallons of water. After 10–12 hours, when fermentation begins, about 7½ lb. of indigo solution are added and the vat is sharpened with further quantities of soda ash or lime. After a further 2 hours the vat will have settled and, if conditions are favourable, dyeing may be commenced.

The *Ferrous Sulphate* or *Copperas Vat* is now little used on account of the large losses of indigo incurred; much sediment is formed in the vessels and only deep equipment is suitable. The reduction of indigo by this process takes about 3½ hours and the dyevats themselves constantly require renewing. The preparation of the stock vat varies greatly, but the following formula is a typical example. Thirty pounds of 20% indigo paste are diluted with about 6 gallons of water at 55°C., and then 24 lb. of ferrous sulphate dissolved in 10 gallons of warm water are added. A thin paste of 32 lb. quicklime is next made with water and sieved into the indigo-ferrous sulphate mixture, and the whole diluted to 30 gallons and adjusted to 50°C. After thorough stirring, the vat is covered up and allowed to stand for 4–8 hours (often overnight) with occasional stirring. The reduced liquor should be yellow and clear before it is added to the dyevat, which has been previously set with 2 lb. of pasted lime and 1 lb. of copperas per 100 gallons of liquor at 50°C. and allowed to stand for 1 hour. After the addition of the reduced dyestuff, the bath is stirred well and allowed to settle for about 3 hours. If the dyevat appears greenish, more lime and copperas should be added; if bluish-green, more lime is usually required. Excess of lime or ferrous sulphate, however, should always be avoided, or the rate of dyeing will be lowered so much that weak dyeings will result. A correct vat should show a slightly brownish-yellow colour and be veined with dark blue streaks. Before dyeing, the surface scum is removed. Standing baths are not usually recommended, but in the interests of economy the old vats are always exhausted before a new vat is used.

The *Zinc-Lime Vat* is still employed extensively for yarn dyeing and reserve printing. Slightly redder shades of indigo blue are yielded by its use, and this is particularly evident when dyeing pale shades. As with the ferrous sulphate vat, there is a large loss of indigo and considerable sediment. Stock vats cannot be employed with success for more than three days, but the dyevats can be fed for a longer period than the ferrous sulphate-lime vats.

A great many recipes are used, and the following example is quoted not as a rigid formula, but merely as an indication of the amounts of materials and conditions employed.

Six pounds of zinc dust are pasted with 10 gallons of water at 60°C. and added to 40 lb. of indigo 20% paste previously thinned with 10 gallons of hot water; 20 lb. of quicklime paste are then stirred in and the whole diluted to 50 gallons at 60°C. The temperature is maintained during vatting (which takes about 5 hours) by means of a closed steam pipe. The vat should be frequently stirred up, and when in correct condition it presents a characteristic yellow appearance.

The stock vat is finally added to the dyeing vessel which has been primed with 1 lb. of slaked lime and ½ lb. zinc dust per 100 gallons. Before dyeing is commenced, the bath is allowed to stand for about 30 minutes until the sediment has settled. The scum is then removed and dyeing commenced. The vats are kept in condition by judicious feeding with zinc and lime when the state of the vat requires it.

Dyeing Piece Goods with Indigo.—In general, cotton piece goods are indigo-dyed on the under-water or immersion jig, ordinary jiggers being unsuitable on account of the fairly rapid oxidation of the *leuco*-indigo. Although similar in principle, different immersion jiggers vary widely in details of construction. The vessel usually consists of a cast-iron trough containing two rollers. A back-grey is employed to carry the fabric and is permanently fixed to the rollers. Two further rollers are also fixed above the machine to facilitate the winding on and off of the fabric. Tentering frames, expander bars or rollers, cuttlers and plaiters are generally arranged to work in conjunction with the jigger, so as to assist in the leading in and out of the fabric, which must be done carefully.

The main pair of rollers is always set to work below the surface of the indigo vat liquor, in order to prevent the fabric from coming into contact with the air during dyeing. The rollers turn in such a manner that they convey the back-grey (to which the fabric is attached) in alternate directions from one roller to the other. Various devices for reversing the direction of the pieces have been developed; one of the simplest employs iron rods which are fixed a few yards from the end of the back-grey. The iron rod, at the termination point of one particular direction of travel, engages a lever connected with the shaft operating and controlling the gearing which effects reversal of the direction of travel.

On completion of the dyeing, or "dip," the stitched seam which is used to fasten the fabric to the back-grey is unfastened and the end of the piece is led through a squeezing arrangement. The extracted liquor flows back into the vat and the piece is skyed for oxidation in open width over a series of small rollers. The pieces are finally plaited down into a truck and allowed to lie for some time before after-treating on an ordinary jigger.

Stock vats are usually prepared in a steam-heated wooden tub kept for the purpose. Fourteen pounds Indigo MLB powder pasted with methylated spirits (or Turkey Red oil, etc.) are added to 11 gallons of water at 75°C., and then 3 gallons of 70°Tw. caustic liquor are added. After mixing well, 11 lb. hydrosulphite are sprinkled in carefully, taking care to stir steadily so as to avoid admitting too much air below the liquor surface. After vatting and, if necessary, correcting the condition of the solution, the required amount is poured into the jig vessel which itself has been previously primed with water, caustic soda and hydrosulphite. For every 100 gallons of dye liquor about $\frac{3}{4}$ oz. of hydrosulphite and about $\frac{1}{10}$ pint of caustic liquor are employed. With goods which have not been alkali-boiled before dyeing, it is advisable to add 1–2 pints Turkey Red oil to assist wetting and levelling. Dyeing is usually carried out at 30°C., in from four to six ends.

Whilst the immersion jigger can be employed quite successfully for lightweight to medium-heavy goods, the *Dipping Frame* is largely employed for thicker cloths. In this process the goods are stretched on a star-shaped frame fitted with tenter-hooks for the cloth selvedges. The frames are slung, usually on rope-and-pulley blocks, so that they may be raised or lowered into a rectangular, round or octagonal liquor-container. The size and shape of the vat are designed to suit the dimensions of the star-frame. The time of immersion of the cloth varies with its thickness and with the nature of the weave; very thick goods require 8–10 one-hour dips for a full shade in a vat of medium concentration. Each dip is followed by squeezing or hydro-extraction; and the cloth is allowed to oxidise and is then rinsed before the next dip. The hydrosulphite process is invariably used for dipping-vat methods, but dark shades are best obtained from the zinc–lime vat, which has a lower alkalinity and is thus more suitable for the longer process involved.

A battery of several dipping vats is often employed, the goods being treated in the weakest, i.e. the oldest, vat first; very heavy goods such as heavy linens and moleskins may be left in this weak vat overnight. The shades are then built up by several dips in fresh vats during the next day. The stock vats and dyevats are prepared by the methods described in the early pages of this chapter.

Another use for which the dipping frame is admirable is the dyeing of fabrics which have been previously printed with resists, the use of this machine affording the best protection against mechanical damage to paste resists. Indigo, however, is now much less commonly employed for this purpose, having been replaced almost completely by anthraquinonoid vat dyestuffs, particularly Blue RS types.

The *Continuous Machine*, or *Roller Vat* as it is sometimes called, is employed for the dyeing of indigo on thin and easily penetrated fabrics. This machine consists of several units, each unit or compartment consisting of wooden or iron dye vessels fitted with a squeezing device, usually two bowls fitted above and at the end of the vessel so as to allow the extracted liquor to drain back into the vat. The latter contains an upper and a lower series of guide rollers through which the fabric is threaded so as to guide it through the vat in open width below the surface of the liquor. Stirring devices are also generally fitted in vessels intended for this class of work.

For indigo dyeing, squeezing arrangements and air passages are imperative before the cloth enters the second unit for its second dip, and similarly for subsequent dips. The widely used skying method involves the use of a system of guide rollers which lead the cloth high up above the vat and then down into the next unit. A system using an overhead winch which leads the cloth down on to an endless apron and then back over another winch and down into the next vessel is also employed.

Two to four such units are employed for dyeing, the number varying with the concentration of the vats and the depth of shade required. Dyeings obtained by several passages through weak vats are usually far superior in fastness to washing and rubbing than similar shades produced by one or two passages through more concentrated vats. Twenty pounds of 20% indigo paste per 100 gallons of dye liquor should be the highest concentration used; a much weaker concentration is normally employed. The vats are always fed daily, so as to maintain an even concentration until it becomes necessary to exhaust them. Indigo Solutions, i.e. the ready-reduced form, are therefore highly recommended, because they save time when preparing stock vats.

A 1,500-gallons dyevat is sharpened with 1⅛ pint of caustic liquor and ¾ lb. of hydrosulphite and left to stand for 1 hour before adding the stock vat (i.e. when using the ordinary unreduced indigo brands), which is prepared in the same way as described for the under-water jigger.

When using Indigo Solutions a similar vat would be set initially as follows. Two gallons of 70°Tw. caustic liquor are stirred into the water and 5 lb. of hydrosulphite strewn in. This is followed shortly by 1½ gallons of Turkey Red oil. Finally, 110 lb. 20% Indigo Solution are added and the stirrers allowed to work for several minutes. The condition of the vat should then be tested and corrected. The above quantities are suitable for the production of a medium-shade indigo, but, when paler or deeper shades are required, the amounts of caustic liquor should be increased and decreased, respectively, by one-third of the above amount. The zinc–lime process may also be used on the roller vat.

When the vat is found to be satisfactory, dyeing may be commenced, the goods being entered wet or dry. It is claimed that dyeings which are faster to rubbing are obtained by pre-padding the goods with 3 oz. glue per gallon of water, but slightly redder shades result. On completion of dyeing the cloth is squeezed, thoroughly aired, and rinsed in a similar unit fitted with guide rollers and containing cold running water. The material is finally soured cold in 2°Tw. hydrochloric acid, rinsed and soaped at the boil. Souring with 1½°Tw. sulphuric acid is chiefly recommended for printed styles.

Cotton warps in rope form are very often dyed on the roller vat, conditions similar to those used in piece dyeing being employed. Several warps are run through the vat side by side, and porcelain eyelets are used for leading the warps in and out of the vats. Full shades are usually obtained with two or three dips, the after-treatment being similar to that employed for piece goods.

The feeding of indigo vats is a subject on which no hard and fast rules can be laid down, since so many factors need to be considered. Experience and trials are the only routes to a full knowledge of vat feeding. The most important factor involved is of course the amount of indigo absorbed by the cotton, and this in turn is dependent upon the nature of the fabric and the length of the dyeing time. A quarter of a gallon of 70°Tw. caustic liquor, 1½ lb. hydrosulphite, $\frac{1}{10}$ gallon Turkey Red oil and 22½ lb. of 20% Indigo Solution have been found suitable for a day's feeding of the above type of vat. Usually, ¼–⅕ of the original amount of indigo, ⅛ each of the caustic soda and hydrosulphite first used, and about $\frac{1}{20}$ of the original amount of Turkey Red oil are required.

Yarn Dyeing.—Pale and medium shades of indigo are usually obtained on cotton hanks by dyeing in an open beck by the hydrosulphite process. The zinc–lime vat is widely used for the production of dark blues, whilst the use of the ferrous sulphate vat is now almost obsolete. Practically all brands of indigo are suitable for yarn dyeing, and similar principles to those already described for fabric dyeing are employed.

For the hydrosulphite vat a liquor-goods ratio of 20:1 is employed, and the open vats or becks may be constructed of wood, iron, stainless steel or copper. After preliminary preparation the yarn is loaded on to sticks which are suspended across the narrow vessels. Straight or bent sticks may be employed, but the latter are usually recommended because they keep the goods below the liquor surface and thus effect a saving in reducing agents; further, the hanks require less turning. The vats are now usually fitted with a squeezing device and hand squeezing is rarely employed. For the latter purpose, the hanks were twisted on a pole fixed above the vat which caught the extruded liquor. Squeezing devices usually take the form of rollers which are designed and regulated to give even pressure throughout the batch; the yarn should contain its own weight of liquor when leaving the nip. The rollers should be arranged so that they turn at a regular speed.

Great attention should be paid to the preliminary preparation of the yarn. Grey cotton is usually employed for the production of medium to full indigos, whilst paler shades are dyed on bleached material. Avoidance of tight or twisted tie-bands in stringing up the hanks is necessary in order that there may be no obstruction to penetration. Grey goods are usually boiled out in soda ash solution or given a preliminary wetting-out treatment in a solution of a proprietary wetting agent. Wetting at 60° C., in a solution containing 5 lb. of Turkey Red oil and ½ gallon of 70°Tw. caustic soda per 100 gallons of water is very effective. Bleached goods require no wetting out if they are dyed immediately after bleaching, but if they are dry it is advisable to soak them for some time in warm alkaline Turkey Red oil, Monopol Soap or Lissapol before hydro-extracting and dyeing. Before loading the hanks on to the sticks it is important that they should be opened out well in order to assist even penetration of the cotton; 1½–2½ lb. of yarn per stick is sufficient, and overloading must be avoided in the interests of levelness.

The dyevats and stock vats are set as previously described in the general description of cotton dyeing, and the baths must at all times show a red spot on phenolphthalein paper. If acid, the liquor takes on a turbid grey appearance and this state must be corrected immediately by adding small quantities of caustic soda. Too much caustic soda, however, prevents exhaustion, and weak washed-out shades result; similar results are obtained with an excess of hydrosulphite. When this latter state exists the vat will appear bright yellow instead of the normal yellowish-green colour.

The hanks are dyed for 30 minutes by moving them backwards and forwards in the liquor with an occasional turn. Before lifting, the hanks should be given a few quick turns, then lifted and passed through the squeezing device (while still on the sticks) or wrung by hand over the vat. If a second dip is required they must be thoroughly oxidised and then immersed again in the dye liquor for a further 5–10 minutes. If more than 10 minutes are given it may be found that, instead of the shade building up deeper it will become paler, owing to the stripping action of the vat.

Cold water rinsing follows oxidation, after which the goods are usually hydro-extracted and dried without further treatment, souring being unnecessary. Approximately 20% of the original indigo is removed from the vat by one dip of 30 minutes; about 30% is removed in two dips. Feeding is based on such facts, and the corresponding amounts of caustic soda and hydrosulphite are used for reduction of the feed liquor. Brilliant Indigo brands exhaust much more quickly, up to about 70% being removed in one dip. A very small amount of Turkey Red oil may be added daily and about 2½ lb. of common salt. The specific gravity of the vats, however, should not be allowed to exceed 8°Tw.

The ferrous sulphate–lime and zinc–lime vats may be used for heavy shades, although use of the former has now been practically abandoned, as it is not very productive and contains much sediment. For dyeing by this method deep and narrow cement or cement-lined vats are employed, the proportionate measurements of which are—width, 1; length, 1·2; depth, 3. Zinc–lime vats are usually worked in deep iron vessels of 200 gallons capacity.

Apart from the preparation of the dyevats and stock vats, the dyeing procedures for hanks are similar for both these methods, as for piece dyeing. Usually a battery of vats is used, the hanks being first dyed for one dip in an old or weak vat (e.g. 3 lb. of 20% indigo paste per 200 gallons) and then built up in depth of shade in three to six subsequent vats of slightly increasing concentration (up to 30 lb. per 200 gallons), oxidising between each dip. Finally, the goods are oxidised, rinsed, soured in 3 pints D.O.V. per 100 gallons to remove the lime, and rinsed again before hydro-extracting and drying.

(Indigosol O—see page 125.)

(*b*) Hydron Blues on Cotton

The production of navy and dark blues on cotton in any of its forms is quite simply carried out by using the easily levelling products of the Hydron Blue class. The dyeings possess good fastness to light and washing, and the low cost of production, as well as the simple dyeing method, has done much to foster universal acceptance of these dyestuffs for certain types of materials. These dyestuffs constitute a fairly large range of blues and dark blues which may be employed singly or in combination with each other to produce any shade of dark blue. In many instances they may also be shaded with certain black sulphur dyestuffs, e.g. those of the Indo Carbon type, which are specially suitable for this purpose on account of their very similar chemical nature. Hydron Navy Blue C, however, is not recommended for mixture shades.

There are two methods of applying the Hydron Blues, viz. the Sulphide-Hydros Vat and the Hydros Vat. The former is the cheaper of the two and is very productive. It is especially suitable when dyeing thick and tightly woven yarns or fabrics, which, owing to the stability of the sulphide vats, may be dyed for some time at the boil. Brass and copper vessels and fittings must be avoided, owing to the deleterious and stain-forming action of the sulphide. The Hydrosulphite–Caustic Soda Vat, on the other hand, is clearer and, for this reason, far more suitable for use in machine dyeing.

Sulphide–Hydrosulphite Process.—Dissolution of the dyestuff in this process is carried out at 60°–70°C., using 4–15 lb. sodium sulphide crystals and 2½–6 pints 70°Tw. caustic soda per 100 gallons of dye liquor, depending upon the depth of shade required. Two to four pounds of hydrosulphite per 100 gallons are then strewn in with stirring, about 10 minutes before commencing the dyeing. Dyeing is carried out for ¾–1 hour at 60°–70°C., and the goods are then rinsed, oxidised and finished.

Yarn in hank form is usually dyed with a 20:1 liquor-goods ratio on straight or bent iron or stainless rods in an open vat fitted with a squeezing arrangement. For example, a 4·5% shade of Hydron Blue R Powder on 50 lb. of cotton yarn may be obtained in a 100-gallon dyebath prepared as follows. Two and a quarter pounds of Hydron Blue R Powder are smoothly pasted up with

Turkey Red oil (Turkey Red oil is unnecessary if corresponding amounts of 30% dyestuff paste are used) and 11 lb. of sodium sulphide crystals previously dissolved are added, followed by 5 lb. of 70°Tw. caustic soda at 70°C. The temperature of the vat should also be about 70°C., and the dyestuff–sulphide–caustic mixture should be sieved in. Three and a half pounds of sodium hydrosulphite powder are then strewn in with stirring and the bath allowed to stand for about 10 minutes.

Throughout the dyeing the vat should show a greenish-yellow colour; if this is not the case small additions of hydrosulphite should be made. The hanks should be boiled out in soda ash solution and hydro-extracted before the sticks are loaded and dyeing commenced. The hanks are worked below the surface of the liquor for ¾–1 hour at 60°–70°C., then given a few rapid turns in the liquor and finally passed through the nip. Where a squeezing device is not fixed to the vat, very careful even squeezing or wringing may be done on a pole over the vat. Evenness in squeezing is essential for good results and, instead of trusting to hand squeezing, it is always better to use some mechanical device. Where straight sticks are employed, part of the hanks are always out of the liquor and, consequently, the goods require more regular turning and the addition of a little more hydrosulphite.

The above vat may be maintained as a standing bath by careful feeding with approximately 3 lb. of dyestuff dissolved with 6 lb. sulphide crystals, 2 pints caustic soda and 2 lb. hydrosulphite.

Immediately after wringing or squeezing, the sticked hanks are plunged into lukewarm water containing about 1 lb. of sodium sulphide crystals and ½ lb. of hydrosulphite per 100 gallons of water. The goods are then given three separate cold rinses before being hydro-extracted, finished and dried.

Some difficulty may be experienced in obtaining the correct degree of penetration on tightly twisted yarns when using the above process. Better results may be obtained by dyeing first for about 30 minutes at 95°C. without the addition of the hydrosulphite, and then, after cooling to about 70°C., adding the hydrosulphite and continuing the dyeing for a further 30 minutes.

Piece goods may be dyed in the sulphide–hydros vat in an ordinary jigger, provided that an efficient squeezing device is fitted. It is essential that the pieces should be thoroughly desized, freed from all extraneous matter and thoroughly boiled out before dyeing is commenced. The goods must also be evenly batched up on the jigger without creases, and the edges of the piece must lie selvedge upon selvedge. When dyeing heavy shades of blue, bronziness at the selvedges is likely to occur if batching is done carelessly. Goods may be entered either dry or after a thorough hydro-extraction.

The dye liquor required for piece dyeing on the jigger is much more concentrated than that employed for yarn dyeing in the open beck. A goods–liquor ratio of 1:8 is commonly employed, and a heavy shade may be produced using 6% Hydron Blue dissolved with 25 lb. sodium sulphide crystals, 9½ pints 70°Tw. caustic soda and 6 lb. hydrosulphite per 100 gallons of liquor. For feeding, approximately two-thirds of the original amount of dyestuff is needed, with half the original sulphide, two-thirds of the caustic soda and two-thirds of the hydrosulphite.

Dyeing is first carried out by giving two ends at the boil before adding the hydrosulphite. Thin materials, however, can be dyed throughout at 60°–70°C., with the hydrosulphite added at the start. After the two ends at the boil, the bath should be allowed to cool by shutting off the steam for about four ends. Hydrosulphite is then added and the goods are run for a further four to six ends. If the correct yellow shade of the vat disappears during dyeing, further quantities of hydrosulphite must be added.

After completing the last end, the fabric is passed through squeezing rollers, which should be adjusted to give the most even and thorough squeezing possible, and then led directly into a second jigger containing warm water. Finally, the goods are given a cold rinse followed by a hot rinse.

Hydrosulphite–Caustic Soda Process.—Cotton yarn in hank form is dyed in a manner similar to that employed in the sulphide–hydrosulphite process. A 4·5% shade of Hydron Blue R may be produced on 50 lb. of cotton yarn in 100 gallons of liquor (i.e. 1:20), by using 5 pints of caustic liquor and 5 lb. hydrosulphite at 60°–65°C. The resulting vat is slightly brighter than the sulphide vat, but perfectly clear. The feeding requirements for this vat are two-thirds the amount of dyestuff first used, 2¾ pints caustic soda and 3½ lb. hydrosulphite (per 100 gallons).

Dyeing is carried out for ¾–1 hour at 60°C., and subsequent treatments are as for the sulphide–hydrosulphite method, although sodium perborate may be advantageously employed for oxidation. Brighter shades are obtained by after-treating the goods with 0·5–1·0% of perborate at 70°C., but slightly inferior washing fastness often results from this treatment, so before its use is adopted it is necessary to ascertain the effect upon the goods being dyed.

Warps may be dyed with the Hydron Blues on the roller vat by means of the hydrosulphite–caustic soda process. A liquor-goods ratio of 40 : 1 is used, and conditions are so arranged that the goods are dyed to shade by a 1–1½-minute immersion. Feeding of these baths depends chiefly upon the time of dyeing, as well as on the weight of the goods.

The well-wetted warps are hydro-extracted and passed through the system at 70° C. On leaving the dye liquor they must be effectively squeezed before being led into a cold rinsing bath fitted with spurt pipes, which more effectively remove any loosely adhering colour than a simple run through standing water; a hot rinse completes the process.

Warp beams, as well as cheeses, sliver, cops and loose stock, may be dyed in circulating-liquor machines by the hydrosulphite method. The vats for this purpose are prepared as for yarn dyeing, but, as more concentrated vats are required, owing to the shorter volume of liquor needed, the caustic soda and hydrosulphite content of the vat is increased.

Closed pack- or spindle-machines are used. The goods are first boiled out for 30 minutes with soda ash solution or a wetting agent, the liquor run off and the cage or frame lifted while the prepared dyevat is run in. The goods are then lowered into the machine and dyed for ¾–1 hour. Finally, the liquor is thoroughly removed by suction and the goods rinsed, first with hot water and then with cold water. Fifty pounds of cotton in cop form may be dyed to a medium blue shade, using 10 lb. of Hydron Blue G Paste as follows. The paste is dissolved at 60° C., using 5½ pints of caustic soda and 4½ lb. of hydrosulphite in 60 gallons of liquor. This liquor is circulated through the previously boiled-out goods for ½–¾ hour at 70° C. After exhausting the bath, a warm rinse followed by two cold rinses, or an after-treatment in hot perborate, is given. Finally, the dyed and oxidised cops are hydro-extracted and dried.

Cotton fabrics may be dyed on the jigger using 6% dyestuff for a heavy shade, with 12 pints of 70° Tw. caustic soda and 7½ lb. hydrosulphite per 100 gallons of liquor at 65° C., for periods up to 1 hour. A standing bath is fed with the usual two-thirds of the original amount of Hydron Blue and corresponding amounts of caustic soda and hydrosulphite. After dyeing, the goods are squeezed and rinsed cold and hot, with or without perborate or peroxide after-treatment.

Piece goods may also be dyed on the continuous machine, using two or three compartments of the machine and without the use of the usual skying arrangements used for indigo dyeing. A 40:1 bath is used, and the time of actual immersion in the liquor is 4–5 minutes. A bath of the following composition may be quoted as an example:

10 lb. Hydron Blue R Powder vatted with
5¾ pints Caustic Soda, and
5 lb. Hydrosulphite, per
100 gallons Water, at 65°–70°C.

The pieces must be carefully prepared before dyeing by desizing and boiling in soda ash solution, rinsing and drying. They are run into the machine in the dry condition at 70°C., the speed of the machine being regulated so as to keep the goods in the bath for 4 minutes. Feeding liquor of exactly the same concentration as that of the initial vat is added continuously, in order to maintain the volume and strength of the dye liquor. On leaving the vat, the goods are evenly squeezed and passed forward into a cold rinsing bath fitted with spurt pipes, and finally given a hot rinse before finishing.

The pigment padding process may be successfully applied to the Hydron Blues (see Chapter VIII).

(*c*) Indigoid Vat Dyestuffs on Cotton and Cellulosic Rayons

The indigoid vat dyestuffs are usually prepared for dyeing in the same manner as indigo, i.e. by the stock-vat process. Their method of application, however, is similar to that used for the anthraquinonoid vat colours. The Durindone (I.C.I.), Ciba (S.C.I.), and certain Algol (I.G.) and Indanthrene (I.G.) dyestuffs, are indigoid derivatives and differ from the Caledon (I.C.I.), Paradone (L.B.H.), Cibanone (S.C.I.) and anthraquinonoid Indanthrenes in that they require, in general, smaller amounts of alkali, i.e. they are weak alkali dyes and are prepared for dyeing by the stock-vat method. These dyestuffs may be applied to cotton, linen and viscose rayon in all forms, the majority being suitable for machine dyeing. They must be carefully selected from the viewpoint of fastness, however, and wherever high demands are made the Ciba (P) and Indanthrene types, or equivalent brands, must be chosen.

Individual dyestuffs require specific amounts of reducing agent and alkali, and individual attention must also be paid to particular temperatures and other conditions if the best colour value and fastness properties are to be obtained from these dyestuffs. They may be used as self shades or in combination with dyestuffs of similar dyeing properties. They may also be applied by the IN, IW and IK processes for shading the anthraquinonoid Algol and Indanthrene brands. For this latter purpose, however, it is always advisable to dissolve them separately in a stock vat before adding them to the dyebath set with anthraquinonoid vat dyestuffs.

The indigoid vat dyes provide a wide range of bright shades on cotton and cellulosic rayons. When the latter are being dyed it is usually necessary to add glue, or such products as Albatex PO (S.C.I.), in order to slow down the rate of dyeing and promote better levelling. The general procedure in preparing stock vats is first to thin the dyestuff paste with water, or paste up the powder brands, with a little methylated spirits or Monopol Soap and soft water; ⅓–1⅓ pints of 70°Tw. caustic soda and 1½–6 oz. Monopol Soap for each 1 lb. of dyestuff paste (or the corresponding amount of dyestuff powder) are required, depending upon the individual dyestuff. This mixture is then thinned further with 8–16 pints of soft water at 40°–75° C., the amount used again depending on the particular dyestuff being employed, and 4–6 oz. of hydrosulphite are stirred in. The vat is then allowed to stand at the prescribed temperature for 20–30 minutes, heating the vat by indirect steam. The vat should be clear and free from specks and show the characteristic shade of the alkaline *leuco*-compound, which in most cases will be yellow. Cloudy vats can usually be cleared by a small addition of caustic alkali; a little more hydrosulphite or an increase in temperature may also be required to clear the solution.

The dyebath is prepared by filling the vessel with soft water at 40°–60° C. and sharpening it with a little hydrosulphite and caustic soda. Salt additions, which are required for the exhaustion of several of these dyestuffs, are usually made at this stage. Viscose rayon and mercerised cotton, however, can generally be dyed, even in heavy shades, without the use of salt. The dissolved dyestuff from the stock vat is then sieved into the dye liquor with thorough, but not too vigorous, stirring or mixing up. Dyeing is carried out for ½–1 hour at the specified temperature, taking care that the good condition of the vat is maintained throughout. The goods are desized, bleached for pale and bright shades, and boiled out thoroughly before dyeing. After dyeing, the goods are squeezed and thoroughly oxidised in air for periods up to 1 hour; particular attention should always be paid to oxidation, especially when dyeing viscose rayon. Finally, the material is rinsed in cold water and soaped at or near the boil and rinsed before drying.

Viscose rayon is usually soaped at 70°–80°C., without the use of soda.

Detailed methods for dyeing cotton and viscose rayon with indigoid vat dyestuffs are given in the following examples, but the pattern cards issued by the dyestuff manufacturers should always be studied, as initial guides at least, since each dyestuff has its own characteristics.

Durindone Scarlet 3B Paste.—Dilute 1 lb. of dyestuff paste with 1½ gallons of soft water at 75°C. and add ½ pint of 70°Tw. caustic soda and ¼ pint of Turkey Red oil or Monopol Soap. Mix well and then sprinkle in 5 oz. of hydrosulphite powder. In 20 minutes the vat will be fully reduced and ready for adding to the dyevat, which has been previously set at 60°C. and sharpened with ¼ pint caustic liquor and 2½ oz. hydrosulphite per 100 gallons of dye liquor. The colour of the dye liquor should be pale greenish-yellow. Dye at 60°C. for 1 hour, squeeze, air for ¾ hour, rinse and soap.

Fish-glue may be added to the dyebath when dyeing viscose rayon, in order to retard the rate of dyeing and thus assist levelling. The addition of glue is specially recommended when dyeing pale shades on any cellulosic materials; soap, sulphite lye and proprietary agents may also be used for the same purpose.

Indanthrene Brilliant Pink R Paste.—For dyeing 100 lb. loose cotton in a pack machine of 80 gallons capacity, 2 lb. of dyestuff paste are dissolved in the stock vat by first diluting with about 2½ gallons of hot water and 1 gallon of caustic liquor. Seven ounces of Monopol Soap are then added and 9½ oz. of hydrosulphite are finally sprinkled in. The vat is adjusted to 75°C., allowed to stand for 30 minutes and then corrected, if necessary, before being sieved into the warm dyebath. The vat solution must be clear and golden yellow.

The dyebath is set at 55°C. with 6½ pints of caustic liquor and 6 oz. of hydrosulphite. The loose cotton, which has previously been well boiled out, is then dyed for 45 minutes with gentle circulation, the exhausted liquor being finally pumped off and the goods carrier hydro-extracted so as to ensure thorough oxidation. Finally, the goods are returned to the machine, rinsed well with cold water and then soaped for 30 minutes at the boil with 2–3 lb. of soap per 100 gallons. A final rinse with a little Lissapol or similar agent will leave the cotton with a satisfactory handle and in good condition for spinning.

Ciba Orange R Powder.—This dyestuff requires an addition of 1½ lb. soda ash for each 1 lb. of dyestuff powder, in order to assist solution. The dyestuff powder is worked into a smooth paste with a little methylated spirits and 4 gallons of soft water at 70°C., 1½ pints of 70°Tw. caustic soda and 1½ lb. of hydrosulphite are then added, and vatting is carried out during 20–30 minutes. The solution should be perfectly clear before adding to the dyebath, which has previously been sharpened with only a trace of alkali and hydrosulphite. Dyeing is carried out at 45°C. for periods of up to 1 hour, and the dyeings are finished as previously described.

(*d*) The Faster Anthraquinonoid Vat Dyestuffs

These dyes, as exemplified by the Indanthrenes, form the largest and most important group of vat dyestuffs.

Members of the Indanthrene range, and the corresponding equivalents of other dyestuff firms, are grouped together on account of their exceptionally high resistance to weather, wear, light and washing. The term "Indanthren" is well known throughout the Continent, and indeed throughout the world, as representative of "utmost durability." These dyestuffs therefore find employment on all cellulosic fabrics where a high resistance to such agencies is required. In general, they also possess a high standard of fastness to soda boiling and chlorine bleaching, and are consequently in great demand for dyeing yarn and fabrics which have subsequently to pass through these processes. The physical properties of the dyestuffs of this class have been carefully modified by the various dyestuff manufacturers so as to facilitate their use in cases where specifications are rigorous. For example, the majority are sufficiently soluble for use in all types of machine dyeing; in most cases they are equally suitable for printing and pigment padding.

The three general methods of application, which have already been mentioned in the foregoing pages, were originally developed by the I.G. Farbenindustrie A.-G. (the pioneers in this field) and were entitled IN, IW and IK. Other dyestuff manufacturers have variously named the three methods No. 1, No. 2 and No. 3; C1, C11 and C111; A, B and C; etc. The corresponding groups are very similar in detail.

The three methods, which have been chosen to suit the various classes of dyestuffs within the series, differ as regards temperature, the quantity of alkali employed, and the addition of exhausting salts. They may be more simply classified as (*a*) the strong alkali class, which requires a comparatively high dyeing temperature;

(*b*) the medium alkali class, needing medium temperatures and additions of salt; and (*c*) the cold dyeing class, which also requires the addition of salt. Apart from these groups, individual dyestuffs vary still further in their requirements, and it is necessary to fulfil these requirements if the best results are to be obtained. The following table, therefore, only indicates the limits.

Details for Open Vessels (20:1 *Liquor: Goods Ratio*)

	IN	IW	IK
Caustic Soda 70° Tw.(in pints per 100 gallons liquor) . . Dependent on the individual nature of the dyestuff.	8–13	3¼–6½	2½–5
Hydrosulphite Powder (in lb. per 100 gallons liquor) . . Dependent upon the weight of dyestuff taken, i.e. the depth of shade.	1–4	1–4	1–4
Glauber's Salt (calcined) or Common Salt (in lb. per 100 gallons liquor) . . . Dependent upon the rate of exhaustion of the individual dyestuff, as well as to some extent upon the nature of the goods.	None	5–25	7½–35
Temperature of dyeing. . . Depending on the requirements of individual dyestuffs, as well as to some extent upon the nature of the goods.	55°–60°C.	45°–55°C.	20°–30°C.
Time of dyeing (in minutes) . Depending on the rate of exhaustion, ease of levelling and the nature of the goods.	20–45	30–60	30–60

The above conditions are often modified to suit particular dyestuffs, dyestuff mixtures and specialised work. The process known as "IN Special" has been designed for the application of direct-dyeing black vat dyestuffs, as well as for those which require after-treatment with hypochlorite. In this process, temperatures up to 70°C. are employed, together with 50% more caustic soda.

Processes have also been modified to suit the application of vat dyestuffs at the boil. Modification is also necessary when dyeing in open and closed machines, the liquor length usually deciding the amounts of agents to be employed.

When using machines with a liquor–goods ratio of 8:1 to 12:1, the corresponding amounts of alkali and hydrosulphite are increased to the following figures:

	IN	IW	IK
Caustic Soda 70°Tw. in pints per 100 gallons liquor .	12–19	4–9½	4–8
Hydrosulphite Powder in lb. per 100 gallons liquor .	2–8	2–8	2–8

Stock vats for these dyestuffs are usually unnecessary, vatting being carried out in the dyebath. It is advisable, however, to reduce many of the dyestuffs in a short liquor. Although this may be done in the dyeing vessel before filling up to the required volume, it is often better to reduce the dyestuffs in a separate vessel and, when solution has been effected, to add them to the sharpened dyebath. As examples of dyestuffs which are best dissolved by short-liquor vatting, the following may be quoted:

Caledon Yellow 3GS
Paradone Yellow 5GK
Indanthrene Golden Yellows GK and RK
Cibanone Brilliant Orange 2G
Indanthrene Brilliant Oranges GK and RK
Indanthrene Oranges RRK, 7RK and 6RTK
Caledon Yellow Brown 3GS
Paradone Red Brown 2RD
Indanthrene Browns FFR and 3GT
Cibanone Browns BG and 2G
Caledon Brown RS
Indanthrene Olive 3G
Indanthrene Red Brown 5RF
Indanthrene Corinth RK
Indanthrene Bordeaux B
Benzadone Red 5GK
Indanthrene Reds BKand GG
Indanthrene Blues 8GK and RK
Indanthrene Greys BG and K
Caledon Brilliant Violet 2BS
Sandothrene Brilliant Violet ER

In contrast to the above examples, vatting in a long cold liquor is necessary for the Indanthrene Turquoise Blues.

In vatting the Indanthrene dyestuffs, the use of hard water is to be avoided. If the mill supply is hard, it is necessary to soften it with soda ash before use. After first adding the required amount of caustic soda to the water, the bath is regulated to the temperature required for vatting and the hydrosulphite is sprinkled in. Paste dyestuffs are then diluted with about ten times their weight of water and added to the alkaline hydrosulphite solution through a sieve. Powder fine brands. and dyestuff grains are handled similarly, but ordinary powder brands require careful pasting with Turkey Red oil or methylated spirits and gradual working into a thin suspension before being added to the dyeing liquor. Vatting should be allowed to proceed at a constant temperature for 15–30 minutes, powder brands always being given the full 30 minutes. By this time the liquor should have assumed the correct colour and be quite clear and free from undissolved dyestuff.

Medium and dark shades may be dyed in standing baths, with economic advantage. When mixture shades are being applied, however, the working of standing baths is likely to cause a great deal of trouble and, consequently, it is often better to use fresh baths each time. Nothing is saved by the employment of standing baths for pale shades.

Only an approximate indication of the amounts of dyestuff, caustic soda and hydrosulphite required for feeding purposes can be given, as the requirements vary with the duration of dyeing, the type of vessel and the individual dyestuff. Small-scale trials are essential, particularly when working with new dyestuffs. However, when using the IN Process, 80–90% of the original weight of colour, 20–50% of the original amount of caustic soda, and 75% of the original amount of hydrosulphite are generally required for feeding purposes. The corresponding amounts for the IW Process are—dyestuff, 60–80%; caustic soda, 50–75%; hydrosulphite, 75%; and for IK dyeings—dyestuff, 50–75%; caustic soda, 50–75%; hydrosulphite, 75%. Salt additions are usually controlled by means of Twaddel's hydrometer, the strength of the vat being regulated to a definite measurement after each dyeing. The use of sulphite cellulose lye greatly increases the stability of vat liquors, especially if the temperature is not allowed to fall more than 10°–15°C. below the temperature used for dyeing.

Most vat dyeings oxidise quite quickly in the air after squeezing, and many, e.g. dyeings of the indanthrone blues, may be rinsed immediately after dyeing; but some vat dyes require long airing treatments or even help from chemical oxidants. One very good example of a slow-oxidising colour is provided by Flavanthrone (i.e. Yellow G brands). In order to ensure thorough oxidation of this dyestuff, it is usual to employ ½ lb. of bichromate and ¾ pint D.O.V. per 100 gallons of warm water; or 2–3 lb. sodium perborate may be employed in place of bichromate for the same purpose. Bichromate should never be used with mixtures of the Indanthrene Blues, or green and dull results will be obtained. If quick- and slow-oxidising colours are employed together in mixtures, the use of perborate is recommended for oxidation.

The question of temperature is a very important one if the correct colour value and repeatable shades are to be obtained. Individual dyestuffs vary somewhat in their sensitivity to temperature, and it is always best, as far as possible, to employ the temperatures indicated in the dyestuff manufacturers' pattern cards. Classic examples of dyestuffs which vary in shade at different temperatures are Indanthrene Grey M, Indanthrene Navy Blue BRF, Paradone Brilliant Violet 2R and Caledon Khaki 2GS. The bleaching-fastness of the chlorine-fast blues is greatly lowered by dyeing at temperatures above 50° C.; after bleaching, if these blue dyeings exhibit a greener shade than before bleaching, they can be restored almost to the correct shade by running the goods through a dilute hydrosulphite solution. Shades restored in this way, however, are often slightly redder and duller than the correct dyeings.

Dyeings of vat dyestuffs which are sensitive to alkali should be carefully soured at 40° C. with 2 lb. D.O.V. per 100 gallons water, subsequently rinsing and then boiling in soap solution containing no soda ash. Examples of such dyestuffs are Caledon Red FFS, Indanthrene Blue 5G, Sandothrene Brilliant Violet ER, Caledon Brilliant Violet 2BS and Caledon Khaki 2GS. Caledon Red FFS should always be rinsed and soured (without any airing stage) immediately after dyeing if the full brightness of the shade is to be obtained.

Amongst the dyestuffs classified as unsuitable for machine dyeing on the grounds of insolubility are Paradone Dark Blue, Indanthrene Black BB, Indanthrene Grey K, Indanthrene Blue RK and Indanthrene Scarlet R. However, it is frequently possible to obtain machine-dyeing dyestuffs of the above types, although they differ very slightly in shade compared with the more insoluble originals, e.g. the BOA brands of the Dark Blues. Dyestuffs intended for machine dyeing are usually required to have a solubility of 99·5–99·7%.

The following dyestuff brands are generally recognised as being uneven-dyeing, usually owing to their too rapid exhaustion. The rate of dyeing can be considerably slowed down, with consequent improvement from the point of view of levelling by the employment in the dyebath of sulphite cellulose lye and such products as Albatex PO (S.C.I.); 2–20 lb. of the former and ½–2 lb. of the latter are required per 100 gallons of dye liquor.

Indanthrene Dark Blues
Paradone Greys B and R
Cibanone Greens B, 2G, 4G, 5G and GN
Caledon Brilliant Purples 2RS and 4RS
Indanthrene Blue Green FFB
Alizanthrene Navy Blue R

and all weak and medium dyeings of the "direct" black brands.

Sulphite lye should not be employed for levelling Caledon Khaki 2GS, Indanthrene Blue 5G and Hydron Green GT, or the shade will be adversely affected. In such cases, 2 lb. of Monopol Soap and 2 lb. dissolved glue should be employed.

Choice of dyestuffs for use in compound shades has been dealt with already in Chapter IV.

Loose Cotton and Sliver.—These are usually dyed in closed machines of the pack type, although dyeing is occasionally carried out in open vats, the loose cotton being packed into baskets which can be lowered or raised at will.

Loose cotton is prepared for dyeing by passing through an opening device (the "opener") which pulls the hard mass of packed stock apart and facilitates easier wetting and penetration. Even packing of the carrier is essential for level dyeing, and soft places which cause channelling should be avoided. It is a common practice to line the carrier with a linen cover in order to avoid clogging of the pump by bits of loose cotton which may be forced through the perforations in the carrier.

Wetting or boiling out is done in the machine by circulating non-oily solutions through the goods, e.g. mixtures of soda ash and agents such as Nekal BX (I.G.), Invadine N (S.C.I.), or Ultravon W (S.C.I.). The goods are then rinsed and hydro-extracted before being entered into the dye liquor. Alternatively, the cotton may be wetted in a dilute "blank" vat containing small amounts of alkali and hydrosulphite, e.g. quantities such as are normally employed for sharpening.

After dyeing (during which constant attention is paid to the condition of the vat), the goods carriage is drained by suction, and rinsing and soaping then follow in the same vessel. A final rinse with a softening agent which gives the cotton improved spinning properties, e.g. Lissapol (I.C.I.), is often employed.

For example, a 10% shade of Paradone Red Brown 2RD Paste may be produced on 100 lb. of raw cotton in a 1:8 bath as follows. The water is first softened with 1–2 lb. of soda ash and then 2 pints 70°Tw. caustic soda and 1½ lb. hydrosulphite are added. Half a pound of Albatex PO is next added and the liquor is allowed to circulate through the material for about 20 minutes.

In a separate vessel, a vat containing 10 lb. Paradone Red Brown 2RD Paste, 10 gallons of water, 3 pints caustic soda and 2½ lb. hydrosulphite is allowed to stand for 15 minutes at 50°C. The goods carrier is then raised from the sharpened dyevat and the dye liquor is added to the machine and allowed to circulate for a short while before the carrier is again lowered and dyeing is commenced. Dyeing is carried on at 50°C. for about 30 minutes and then 3 lb. of common salt (dissolved) are added. After a further 20 minutes, the exhausted liquor is run off and the basket and its contents are hydro-extracted vigorously. Rinsing and soaping at the boil for 30 minutes completes the process.

Cops, Cheese and Warp Beams.—These are usually dyed on perforated spindle or beam dyeing machines. Uniform packing, with particular attention to the winding of the cops, cheese or cones is essential. Spaces between the bodies may be filled with loose cotton packings, although this is unnecessary in most of the modern machines.

The procedure in dyeing the above type of goods is very similar to that described in the foregoing section, but the following example will illustrate the method.

A medium orange shade may be obtained on 100 lb. of cotton cheeses on the spindle machine (100 gallons liquor) by using 5% Cibanone Orange 2R Double Paste. The cheeses are first boiled out carefully so as to enable maximum penetration to be obtained, and then the dyebath is prepared by first softening the water with soda ash (1–2 lb.) or with Ultravon W (S.C.I) (1 lb.) or a similar agent. Two pints of 70°Tw. caustic soda, ¾ lb. hydrosulphite powder and 1 gallon Prosetol (S.C.I) liquor (or any similar agent, e.g. sulphite cellulose lye) are then added and the machine is run for a short time. The dyestuff is next dissolved separately at 50°C., after first diluting the paste with roughly ten times its weight of water, by adding 4 pints of 70°Tw. caustic soda and 1¼ lb. hydrosulphite. After allowing it to stand for some time, the characteristic brown-red vat becomes clear and all the dyestuff is in solution. It is then added to the machine, preferably through a fine-mesh sieve.

As the dyeing proceeds (at 50°C.), 10 lb. of previously dissolved Glauber's salt are added at two separate intervals. Dyeing should be allowed to continue for about 20 minutes after the last addition. The liquor is then drawn off and the vacuum allowed to operate so as to facilitate oxidation, or, depending on the machine, air may be allowed to blow through the dyed packages. Oxidation should be thorough if the best fastness to rubbing and washing is to be obtained. The cheeses are next rinsed well with cold and then, hot water and are finally treated for 30 minutes at the boil with 1 lb. Lissapol or similar auxiliary product.

Dyeing Yarn in Hanks

Yarn in hank form is usually dyed in the open beck or bark, using straight or bent sticks from which to suspend the hanks. Yarn-dyeing machines are also sometimes employed, but the procedure, as far as preparation and dyeing details are concerned, is practically the same as when using the open beck. The dyebaths are prepared as already described on page 98, and where either the IW or IK methods are being employed the salt is usually added at the start. The previously boiled-out hanks are then placed on the dyeing sticks, avoiding overloading, and dyeing is carried out for ¾–1 hour at the prescribed temperature.

When pale shades are being dyed by either of the warm processes, it is usually advisable to start dyeing at about 40°C. and gradually raise the temperature to 50°–60°C. When the cold-dyeing process is being employed, however, the procedure is reversed; dyeing is commenced at about 35°C. and the dyebath is then allowed to cool down. Cooling down in a large vessel takes a long time, and it is therefore customary to start dyeing with about four-fifths of the full quantity of liquor required and then to add cold water carefully and gradually until the correct volume is obtained. Salt additions, for pale shades, are best added after dyeing for about 30 minutes. Retarding agents and levelling compounds help greatly in the production of pale shades and are also useful when dyeing medium and dark shades of the uneven dyeing colours. The addition of auxiliary agents, such as glue, sulphite cellulose lye, Monopol Soap and dissolved soap, is advisable, but too large an addition will produce a sluggish vat which does not exhaust.

Throughout dyeing, attention must be paid to the state of the vat, which may require additions of small quantities of hydrosulphite. A deficiency of the latter, as previously stated, is indicated by the non-appearance of a blue spot on Flavanthrone paper.

After dyeing, the yarn is thoroughly and evenly squeezed or wrung, and then allowed to hang in the air or hydro-extracted to bring about oxidation. At this juncture, it is as well to remember those dyestuffs whose *leuco*-compounds are sensitive to strong sunlight and to take suitable precautions when the goods are being removed from the vat and being oxidised. Rinsing in cold water follows the oxidation treatment, and where heavy shades (e.g. blacks) are being processed an addition of 1½ oz. hydrosulphite per 100 gallons water is usually made. After a second rinse, the yarn is soured in a warm bath containing 1–2 pints D.O.V. or formic acid per 100 gallons water, rinsed thoroughly, and soaped at the boil for 30 minutes.

The following examples will serve to illustrate the preparation of the dyevats.

Process IN. Paradone Blue RS 1000% Powder

A medium shade of blue may be obtained on 100 lb. cotton yarn in a 200-gallon vat prepared as follows. One pound of Paradone Blue RS 1000% Powder is pasted with Turkey Red oil or methylated spirits and a small amount of water at 60°C. Three gallons of 70°Tw. caustic soda are then stirred in and the vat is filled up with hot water. Finally, 2¼ lb. of hydrosulphite are sprinkled in and, after stirring well, the vat is allowed to stand for 20 minutes at 60°C. before dyeing is commenced.

Process IW. Caledon Olive RS Paste

A 30% shade of this dyestuff is produced on 100 lb. yarn in a 200-gallon vat, using 1½ gallons caustic liquor and 6 lb. hydrosulphite at 50°C. for reduction. When the vat is ready for use, as indicated by the formation of the red-brown *leuco*-compound, 30 lb. of Glauber's salt are added before entering the boiled-out yarn. Dyeing proceeds at 45°–50°C.

Process IK. Paradone Yellow 5GK Double Paste

A 5% shade of this dyestuff may be used to give a clear lemon shade on 100 lb. cotton yarn in 200 gallons of liquor. Six pints of 70°Tw. caustic soda and 2¼ lb. hydrosulphite are used for reduction in 50 gallons of water at 40°C. After 20 minutes, the vat is made up to the correct liquor length with cold and slightly sharpened water. The *leuco*-compound of this dyestuff is a dull brownish-wine shade; 25 lb. of Glauber's salt are needed for exhaustion. Dyeing is carried out cold for 1 hour.

Process IN Special. Caledon Direct Black RS Paste

A stock vat is prepared at 60°C., using 40 lb. dyestuff paste which is first diluted with about 40 gallons of water and then reduced with 5 gallons of 70°Tw. caustic soda and 10 lb. hydrosulphite. Vatting is allowed to proceed for 15–20 minutes before the stock vat is added to the 200-gallon dye vat prepared with 150 gallons water, 2½ gallons caustic soda and 3½ lb. hydrosulphite. The bath is then stirred up, the temperature regulated to 60°C., and 100 lb. boiled-out grey yarn are entered. Dyeing is allowed to proceed for 45 minutes at 60°C. and then for 15 minutes at 65°C., before lifting.

With *Caledon Black NBS* and similar brands of "*Chlor-Blacks*" the vatting and dyeing proceeds as for the "Direct Blacks," but the dark green shades obtained are subsequently rinsed in cold water and treated in cold 1°Tw. sodium hypochlorite solution for 30 minutes. In this bath the green shade is converted into the desired black shade. The goods are then rinsed well, soured, rinsed again, and finally soaped at the boil, as with other anthraquinonoid vat dyestuffs. It is usual to employ about 4 lb. soap per gallon for black dyeings.

Mercerised Yarns.—The general procedure for dyeing hanks of mercerised cotton yarns is the same as for ordinary cotton, but slight modifications are usually necessary to obtain good results. Dyebaths exhaust at a much higher rate than when processing ordinary cotton, and for this reason it is usual to employ retarding agents of the Dekol or Albatex PO type. Compounds such as Igepon T have also proved advantageous, not only as levelling agents, but particularly from the point of view of preserving the lustre and soft handle of the yarns. With the IN Process it is often found that the usual large amount of alkali employed has a more or less marked dulling effect on the yarn and that the dyeings require an exceptionally long period for the completion of oxidation. For this reason it is necessary either to dye at a low temperature, e.g. 35°–40°C., or to use minimum amounts of alkali and reducing agent. Dyeing by the cold (IK) and the IW Processes gives rise to little trouble in this respect, but it is occasionally necessary to cut down the amount of salt required for exhaustion, or to use no salt at all when dyeing pale and medium shades, depending on the dyestuffs used.

Mercerised yarns are now largely dyed by the oil-padding method, or pale shades are produced by the use of the Indigosols.

Viscose Rayon Yarn in Hanks.—Apart from preparation, handling and manipulation, the dyeing procedure for viscose rayon yarns is similar to that employed for mercerised cotton, but it is necessary to pay particular attention to the very great affinity of viscose rayon for vat dyestuffs. Careful choice of dyestuffs, although important for all types of fibres, is perhaps more important when dealing with viscose rayon than when dealing with any other fibre. Comparatively small amounts of viscose rayon are dyed in the form of yarn. This fact is accounted for by the difficulties experienced in handling, and particularly on account of the problem of penetration. In consequence, the bulk of viscose rayon is dyed in fabric form.

Particularly great value must be attached to the use of the strike tests described in Chapter III, as well as to the use of restraining agents such as fish-glue, dissolved soap and sulphite lye. Most dyestuffs of the Indanthrene type exhaust very quickly on viscose rayon, but it is usually necessary to prolong the dyeing period for some time after the exhaustion of the bath in order to assist levelling and penetration.

An account of the dyeing of Fibro (Courtauld's viscose rayon staple) has been given by C. M. Whittaker (*J.S.D.C.*, 1938, **54**, 255).

Viscose Rayon Cakes.—The dyeing of viscose rayon yarn in cake form with vat dyes is still in its infancy. The mechanical aspects of this process present the most difficulty. However, the Longclose Engineering Co., Ltd., have recently developed a very efficient cake-dyeing machine.

Whittaker (*J.S.D.C.*, 1944, **60**, 113) reports that experimental work and bulk dyeings indicate that the temperature of the dyevat must be much higher than that used in the normal practice and recommends a dyeing temperature of 90°C. Such high temperatures naturally preclude the use of the anthraquinone azine chlorine-fast blues; this presents a major problem since blue dyeings with properties corresponding to Caledon Blue RCS are in heavy demand.

Cotton Warps.—Warps are usually dyed in rope form on the roller vat, but recently there has been an increase in the popularity of warp-beam dyeing in the circulating-liquor machines already described.

On the roller vat usually adopted for dyeing warps, a working width of about 40 inches is sufficient, and several warps are run side by side. The first two boxes of the machine contain the dye liquor, and a third box is used for rinsing. The capacity of each unit varies from 200–300 gallons, and as the warps are required to pass smoothly from one bath to another, efficient squeezing devices and porcelain eyelets are usually fitted. When pale shades are being dyed, it is usually only necessary to employ one dyeing unit. Heavy shades may require a double run through two units.

The dyeing time for warps is much shorter than for hanks, and consequently more concentrated vats are employed. It is also necessary to feed the vats during dyeing, in order to maintain a regular concentration of dyestuff solution throughout the process. A good guide as to the relative rates of feeding may be obtained by carrying out exhaustion tests at 12-second intervals, on the range of dyestuffs in use. The dyestuff which yields the greatest number of dyeings before the bath is finally exhausted is taken as the standard, and a factor of 1 is assigned to it. If the standard dyestuff—e.g. Paradone Red Brown 2RD—yields 52 dyeings before exhaustion, and another dyestuff—e.g. Paradone Yellow G New—yields only 37 dyeings, the factor for the second dyestuff is given as $52/37=1{\cdot}4$, and if it is found in actual practice that the vat requires feeding with 10 gallons of the standard dye liquor, it is therefore necessary to feed with approximately 14 gallons of the second dyestuff. On the basis of such tests it is possible to formulate mixtures and feed according to the ratio of the factors of the individual colours. The use of mixtures for warp dyeing, however, is a very difficult undertaking, and it is usual to employ homogeneous dyestuffs as far as possible.

Piece Dyeing.—Cotton fabrics are vat-dyed by several different methods, the choice of method depending partly upon the dyestuffs to be used, but mainly upon the nature of the fabric. The available methods include dyeing on the jigger, jig-padding, winch-beck dyeing, use of the padding mangle (see also Chapter VII), the continuous dyeing machine and dyeing in the dipping vat.

The preliminary treatment of cotton cloth is especially important, although cheap materials which are to be dyed in heavy shades are seldom prepared in any way, apart from preliminary wetting out or boiling out. On the other hand, the majority of fabrics require some, or all, of the following treatments in order that level, well-penetrated fabrics may be obtained. Desizing before dyeing is just as important as wetting or boiling out. Mechanical treatments, such as are employed in the removal of motes and in singeing and shearing, are necessary treatments in the production of fine-finish fabrics which may require subsequent printing or mercerisation. Kier-boiling, bleaching, and mercerisation are also general treatments essential for the production of particular qualities and effects.

The Jigger.—The Indanthrene vat dyestuffs are usually dyed on ordinary jiggers, although immersion and semi-immersion jiggers are often used. In all cases of jig dyeing, particular attention must be given to the preparation and batching of the goods. After desizing, boiling off and, if necessary, bleaching, the goods are squeezed as thoroughly as possible and then carefully and evenly batched up on the jigger roller with selvedge upon selvedge.

Jigger dyebaths are prepared by the IN, IW and IK methods, as described for machine dyeing (page 99). Hard water must be effectively softened, e.g. with 1–2 lb. soda ash per 100 gallons of liquor. Dyeing then proceeds during 8 to 10 ends at the prescribed temperature, the latter being regulated and controlled carefully by means of a closed steam-pipe inside the jigger. The following example illustrates a typical jigger dyeing.

A 40-gallon dyebath is prepared at 55°–60°C. for the treatment of 40 lb. cotton piece (i.e. a 10:1 liquor–goods ratio) by the IN Process, using 5–7 pints 70°Tw. caustic soda, ¾–2 lb. hydrosulphite and the requisite amount of paste or powder dyestuff. After dyeing for four ends at the correct temperature, 2–8 oz. hydrosulphite are added and the dyeing continued for a further four ends, when a further 2–8 oz. hydrosulphite are added. These small additions are to compensate for the slow destruction of hydrosulphite which is unavoidable in an ordinary jigger; where semi- or total-immersion jiggers are employed, such additions are not usually required.

Methods IW and IK are carried out at 45°–55°C. and at room temperature, respectively, and with smaller amounts of caustic soda and hydrosulphite, as described on page 99. Salt additions may be made either at the start of the dyeing or at intervals during dyeing, whichever method is most suitable for the goods being dyed. Dyeing and finishing procedure is then identical with that just described for the IN Process.

After dyeing, the pieces are thoroughly squeezed, preferably open-width, and then rinsed in another jigger. For dark dyeings it is advisable that the first rinsing bath should contain a small amount, e.g. 1 oz. hydrosulphite. A second rinsing precedes the oxidising treatment, which is usually accomplished (after an air passage) in four to six ends at 50°C. in a bath containing, per 100 gallons water, ½–1 lb. bichromate and 1–1½ pints D.O.V., or 2–3 lb. sodium perborate and 2–4 pints formic acid. Slow oxidising dyestuffs require the first of these alternatives, whereas for quick-oxidising colours, particularly the blues, the latter is always employed. Rinsing for two ends is then given to remove the acid before the final 4–6 ends in a boiling soap bath containing 2–3 lb. soap and 1–3 lb. soda ash per 100 gallons. For certain dyestuffs soda ash should not be used (cf. page 45). After final rinsing for soap removal, the goods are dried on a hot stenter or a cylinder drying machine.

When levelling and penetration difficulties are experienced in ordinary jigger dyeing, jig-padding may be resorted to. For this purpose it is necessary to employ fine pastes and finely dispersed powder dyestuffs, as the first operation consists in applying a short concentrated suspension of unreduced dyestuff to the goods. After the lower rollers of the jigger have been just covered with softened water, a restraining agent such as sulphite lye or Albatex PO is added, the thinned dyestuff paste is sieved in and the bath raised to 90° C. The boiled-off and, if necessary, bleached goods are then given two or three passages through the unreduced suspension at 80°–90° C. The bath is next filled with softened water and the temperature regulated to that prescribed for the particular dyestuff in use. The requisite amounts of caustic soda and hydrosulphite are then added and the goods dyed for about 8 ends, as in the ordinary procedure.

The Padding Machine.—For the production of pale shades on relatively thick materials the method of padding the goods with the dyestuff in the reduced state is often employed. For this purpose padding machines fitted with two or more rollers, a colour box and squeezing devices may be employed.

Padding liquors are prepared with soft water, levelling or restraining agents, e.g. glue or Monopol Oil, the dyestuff, and the requisite quantities of caustic soda and hydrosulphite. Thickening agents, e.g. 10% tragacanth paste, and additions of anthraquinone are also useful assistants for some dyestuffs. The quantity of caustic soda employed tends to be the controlling factor as the solubility, and consequently the affinity of the dyestuff for the cotton is largely dependent on it. The affinity of a padding liquor may therefore be increased or decreased at will by using, respectively, less or more caustic soda. Certain dyestuffs which are normally classed as not very soluble, or which are greatly affected by altering the standard dyeing temperature, are best avoided. The majority of the Indanthrene, Algol and indigoid types are quite suitable; particularly the latter, on account of their excellent solubility.

A padding liquor may be formulated as follows, the amounts varying slightly to suit individual dyestuffs. Two to five pounds of dyestuff paste ("paste fine" brands are usually preferred) are vatted in about 40 gallons of water at 55°–65° C., using 3–5 pints of 70° Tw. caustic soda and 1–2 lb. hydrosulphite; 25–30 lb. of freshly prepared 10% glue solution are then added, and the whole bulked to 100 gallons and allowed to cool. Salt is never employed, but in the interests of vat stability it may be advisable to add 3–4 lb. sodium sulphide crystals to the pad liquor.

The box is then charged and kept full throughout the operation by a feed liquor which maintains the correct concentration of the vat. A little extra caustic soda is usually employed in the feed liquor, so as to make up for the small amounts absorbed by the cotton during its passage. Padding is carried out at room temperature or a little higher, e.g. at 30°C., and after leaving the squeezing rollers a brief air passage is given. Finally, the goods are rinsed, oxidised, rinsed, soaped, and rinsed again, either in rope form on a winch beck, or in open width on a washing machine.

The Continuous Machine.—This machine, which is also called the *Roller Piece Vat*, consists of a sequence of roller vats and is usually employed for the production of "bread and butter" shades on cotton fabrics, e.g. browns, dark blues, heavy greys and blacks. The process is also particularly suitable for the production of medium and heavy shades on resist-printed goods. Ordinary straightforward piece dyeing is generally conducted in a similar manner to that described for warp dyeing and for Hydron Blues; the dyeing, and particularly the preparation, of resist–print styles, however, requires special technique. The dyeing process involved is usually described as the *Hydrosulphite–Glucose Process*, because glucose is employed to stabilise the reduced liquors and maintain them in good condition throughout the long period of their use.

Pieces for dyeing and printing by the resist process are usually given a preliminary singe and are desized overnight. After removing the agents used in these operations the pieces are boiled in 3°Tw. caustic soda in rope form in a continuous machine similar to the one employed for dyeing. Rinsing and souring follow, in order to free the goods from alkali, and the pieces are then boiled in soap solution containing a little resin. Finally, the material is thoroughly rinsed free from soap, soured again, rinsed and then sized. The latter operation is carried out in open width with the aid of glue and dextrine while the goods are still in the wet state. Printing with a resist paste then follows.

After the printed goods have stood for two or three days they are ready for dyeing on the continuous machine, the actual process varying with the quality and thickness of the goods. The depth of shade acquired is chiefly dependent upon the concentration of the dyebath; the duration of the dyeing, which is rarely more than 3–4 minutes, has little effect. In a sense, therefore, this is not a dyeing process, but a padding process similar to that just described (page 110).

Indanthrone (Blue RS types) is very popular for this style of ornamentation, and the machine is set as follows when using this dyestuff and similar products.

The dyeing vessel, which is the first in the series of vessels which constitutes a continuous dyeing machine of this type, varies in size from 200 to about 600 gallons. A vessel of 200 gallons capacity is prepared with 60 lb. Blue RS Double Paste, 7½ gallons of glucose (1 : 1) and the requisite quantity of hot water. The vat is then adjusted to 70°C., and 30 gallons of 70°Tw. caustic soda and 8½ lb. of hydrosulphite are added while the temperature is rising to 80°C. A vat of good condition is generally obtained within 15 minutes and the prepared goods may be entered immediately. During dyeing, a temperature of 80°–85°C. should be carefully maintained, and the concentration of the vat should be controlled throughout, by the use of a continuous feeding tank.

As the goods leave the dyeing vessel (after an immersion lasting about 40 seconds), they pass through squeezing rollers into the second vessel, where they are allowed to pile up in cold rinsing water containing a little hydrosulphite. The goods are allowed to lie here for at least 3 hours before being soured in the next vessel on the range. They are subsequently rinsed, soaped and rinsed again in rope form. Steaming is a popular finishing treatment which is employed particularly with Blue RS types in order to enhance the brilliance of their royal blue shades. Finally, the goods are finished and calendered.

Dyeing by this process is one of the most highly skilled jobs in the dyeing trade. Control of the feeding liquor demands much experience and skill, and maintaining the baths from day to day requires specialised technique only gained by long experience. Since the liquors become fouled very rapidly, they are allowed to settle during the night, and the surface liquor (about half the total amount) is removed on the following morning by a siphon arrangement; it is usually brown and contains decomposition products from the resist-prints. The liquor length is then adjusted with fresh water, the temperature of the bath raised and the vat reconditioned by adding caustic soda, glucose and, finally, hydrosulphite and dyestuff.

The Winch Beck.—The wince or winch beck is only employed for very light fabrics which normally give trouble on the jigger. Such fabrics as stockinette and voile are commonly dyed on this machine. A liquor–goods ratio of 30 : 1 or 40 : 1 is usually employed and the baths are prepared as described for jigger dyeing (page 108), with corresponding increases of caustic soda and hydrosulphite to suit the increased length of liquor.

On this type of machine the goods are dyed in rope form, after the pieces have been stitched together to form an endless belt, The back of the beck usually tapers slightly towards the bottom, and a perforated partition is fitted at the front of the machine in order to enclose the steam-pipe. Additions of salt or caustic soda and hydrosulphite, which may be required for conditioning during dyeing, are always made in the small compartment so formed. The design of the wince arrangement varies with the different makes of machine, round or (more commonly of late) elliptical winces being employed. Guide rollers lead the fabric over the winch and back into the dyevat and are arranged so as to prevent entanglement.

After the dyeing has been in progress for about one-third of its full duration, i.e. for ¾–1 hour, small additions of hydrosulphite are added in order to counteract losses due to oxidation; two of these additions are usually necessary. Rinsing can be carried out in the same vessel, by letting off the dye liquor below and allowing a considerable volume of cold water to enter at the top of the machine. After thorough rinsing, oxidation may be completed in the same vessel by using perborate; or the material may be run out of the machine, squeezed and allowed to oxidise in the air. The goods are finally soured and soaped as usual.

Star Frame or Dipping Vat—This machine has already been briefly described on page 85. It is often preferred to the continuous machine for dyeing resist-printed fabrics. This preference is due to the fact that there is less likelihood of mechanical damage to the resists. The dyeing process employed is usually the Hydrosulphite–Dekol Vat, although the Hydrosulphite–Glucose Vat and the Ferrous Sulphate Vat are also used for certain dyestuffs. The vat is prepared approximately as follows, the weight of hydrosulphite employed generally being about one-quarter of the weight of the dyestuff paste, pale shades requiring rather more.

A 200-gallon vat is set with hot water, 3 gallons of 70°Tw. caustic soda and 5 lb. of hydrosulphite. The dyestuff paste, e.g. 20 lb., is then stirred in and, finally, 4 gallons Dekol, or a similar quantity of sulphite cellulose lye stabilising and restraining agent, is added. After vatting for about 15 minutes at 60°C., dyeing can be commenced. The goods, which have previously been resist-printed, are dyed on the frame for about 5 minutes, after which they are rinsed, soured with diluted D.O.V. and soaped at the boil as usual.

The ferrous sulphate type of vat is more difficult to handle, and the metallic nature of the resist-prints calls for a variation in the quantity of alkali employed.

Dyeing at High Temperatures.—When insufficient penetration is obtained on viscose rayon or cotton fabrics at ordinary temperatures on the jigger, or even by the reduced padding-jig process, it is possible to dye at or near the boil, thereby obtaining improved results on thick materials. The pigment padding process is the ideal method to employ in a case of this kind, but equipment for this purpose is not always available and, therefore, a modified jig method involving boiling vat solutions may be employed. Dyebaths are almost completely exhausted, and shades which deviate somewhat from normal dyeings are obtained. The violet dyestuffs, in particular those of the chlorodibenzanthrone type (e.g. Violets 2R and 4R), show a change towards a bluer shade when dyed at these abnormally high temperatures. In general, a shade change towards blue is noted with a great majority of dyestuffs, e.g. certain greens, browns and scarlets are so affected.

J. Lanzer (*Melliand Textilberichte, Eng. Edn.*, 1939, **20**, 94) has stated that the change of shade is more evident when the goods–liquor ratio is high, e.g. 1:25, than when it is low, e.g. 1:5. This is explained by the fact that the agglomeration of finely dispersed particles to form coarsely dispersed particles is more likely in the longer baths. Lanzer further stated that 3% Indanthrene Brilliant Violet 4R Powder dyed at 85°C. matches a mixture of 4·25% Indanthrene Brilliant Violet 4R Powder and 0·35% Indanthrene Violet B dyed by the normal method. Similar results have also been experienced by the author. A large saving in dyestuff will be noted here, but this is not always the case, as several dyestuffs give a decreased yield in colour value at high temperatures. In the author's opinion, in the case of these violets the change in shade is due just as much to a migration of chlorine from the dyestuff molecule as to the change in dispersion state. *iso*-Violanthrone is bluer in shade than the chloro-derivatives, and removal of chloro-groups is apparently corroborated by *B.P.* 263,826.

Dyeing is carried out with the addition of approximately 2 lb. of glue, glucose, or sulphite cellulose lye per 100 gallons, and the prepared goods are entered into the boiling bath and dyed for about ½–1 hour. Sulphite cellulose lye is usually preferred to glucose, since the latter compound has undesirable effects on several dyestuffs, e.g. Indanthrene Yellow 3RT.

The quantities of hydrosulphite are necessarily greater by 20–30% than the amounts employed for dyeing at normal temperatures. During dyeing, also, it is necessary to observe carefully the degree of reduction of the vat and maintain the correct shade of the *leuco*-compounds by additions of hydrosulphite.

After dyeing, the finishing procedure, i.e. rinsing, oxidising, souring, soaping, etc., is carried out as usual. As regards choice of dyestuffs for this purpose, laboratory trials should always be made, and as a general rule it will be found that dyestuffs normally applied by the cold dyeing method are unsuitable.

(*e*) The Less-fast Anthraquinonoid Vat Dyestuffs

This group of colouring matters, which are exemplified by the Algol dyestuffs of the I.G. and equivalent products of competing firms, are widely employed where the high durability of the Indanthrene type is not demanded.

In general, these dyestuffs are applied in the same way as the Indanthrene colours. Vatting and dyeing details compare very closely with those described on pages 98–99.

Several dyestuffs under the denomination of Algol are in fact closely related to the indigoid dyestuffs, and these are therefore applied, using a stock vat.

CHAPTER VII

APPLICATION—THE INDIGOSOL DYESTUFFS

THE Indigosol dyestuffs have already been mentioned several times in the preceding text (cf. pages 75–78) and the general methods used in their application have been described. Working conditions vary slightly with different fibres, and the following section deals with their application to cellulose goods, viz. cotton, linen, and regenerated cellulose rayons.

Cellulosic fibres are, in fact, the largest consumers of the solubilised vat dyestuffs, which are applied either by dyeing, padding or by printing processes. By reason of their excellent penetration and fastness properties they are becoming increasingly popular.

Their main use in dyeing is in the production of pale shades on piece goods. Three methods may be adopted for this purpose and the choice of method depends upon the machinery available. The methods are: (1) Jigger Dyeing, (2) Padding and (3) Winch Dyeing. The last-named machine is chiefly employed for rayon piece goods and knitted fabrics, partially on account of the greater volume of liquor necessary for the careful handling of these more delicate fabrics. Jigger dyeing and machine padding both permit the use of short liquors, which is desirable on account of the general low degree of affinity of these dyestuffs for cellulose.

The actual dyeing process is no more difficult than dyeing with direct cotton dyestuffs of the type suitable for after-treatment. There are two stages, viz. the application of the often almost colourless dyestuff in aqueous solution to the cellulose, and the regeneration of the insoluble vat dyestuff by means of chemical oxidation. Although a two-bath process is usually employed, methods have also been devised whereby a single bath can be employed in open vessels or on the winch.

Three main processes, the names of which describe the oxidising or developing stage, may be employed. These are: (1) the Nitrite Process, (2) the Bichromate Process, and (3) the Ferric Salt Process. Individual dyestuffs require individual treatment from the point of view of application and development, and it is therefore impossible to give full details for all the colouring matters of this class. Examples of the application of individual dyestuffs, as well as the general methods, are given in this book. Readers who desire further information may safely consult the manufacturers' pattern cards relating to this class of dyestuffs, which includes, besides the Indigosol brands (D.H. and I.G.), several very important equivalent ranges, e.g. the Soledons (I.C.I.) and Tinosols (Gy.)

Dissolving.—Most of the solubilised vat dyestuffs are dissolved by merely adding water at 50°–60° C., direct steam being avoided. Indigosol Green IBA, however, is an exception; it is dissolved in cold water with the addition of 15% soda ash and 30% hydrosulphite, based on the weight of dyestuff taken. Further exceptions, viz. Indigosol Green IEGG, Indigosol Olive Green IB and Indigosol Brilliant Violet I4R, are dissolved in a 0·1% solution of soda ash. All Indigosol solutions should be protected from the deleterious action of acid fumes, as well as from direct sunlight.

The degree of solubility of almost all the range is sufficiently good to allow 5% solutions of dyestuff to be employed when using normal amounts of the electrolytes, sodium nitrite and common salt. This strength of dye solution is usually more than adequate for most requirements. There are, however, several exceptions to this high degree of solubility, viz.:

	Approximate Maximum Concentration of Solution (%)
Indigosol Golden Yellow IRK	1·5
Indigosol Scarlet HB	4·5
Indigosol Pink IR extra	3·5
Indigosol Red Violet IRH	3·5
Indigosol Brown IRRD	0·5

Solubility is also decreased by employing large concentrations of electrolytes, e.g. sodium nitrite, common salt and Glauber's salt, as well as by employing low temperatures. Such factors must be taken into account during the setting of the baths and during dyeing.

Jigger Dyeing

(1) **The Nitrite Process** is probably the most commonly used of all the three processes mentioned above, and the procedure, in general, is as follows. The liquor–goods ratio varies with local conditions from 4:1 to 10:1, the maximum colour value being obtained in the shortest baths.

The dyestuff is first dissolved in water, the temperature being below 80° C. and usually between 50° and 60° C. The use of small quantities of acid-stable wetting agents of the substituted naphthalene sulphonic acid or long-chain sulphated fatty alcohol type, although not essential, is usually recommended. The solution thus obtained is then added to the jigger vessel, which is prepared with the requisite short volume of soft water. Sodium nitrite (5–12 lb. per 100 gallons) and Glauber's salt (0–200 lb. per 100 gallons) are then added, the amounts used depending on the particular dyestuffs and on the concentration of the bath.

The cleansed and prepared goods may then be entered, either wet or dry, and dyeing allowed to proceed for ½–1 hour (minimum 4 ends) at a carefully controlled temperature lying between 15° and 60° C., the actual temperature depending upon the properties of the dyestuffs in use and upon the type of goods in the machine. The material is then squeezed as effectively and uniformly as possible and passed at once into a second jigger where development in dilute acid solution takes place. The amount of sulphuric acid used in development varies slightly with the depth of shade and with individual dyestuffs; 2–3½ gallons D.O.V. per 100 gallons water at 20°–70° C. are employed, and 2 ends (10–15 minutes) are given. A third jigger is utilised for rinsing with cold running water.

After the rinsing, neutralisation with dilute soda ash solution and a further rinse are given before finally soaping the goods at the boil, as for ordinary vat dyestuffs.

Modifications of this process have been designed to suit different types of fabrics and to obviate levelling difficulties. For example, since the amount of Glauber's salt present controls the degree and speed of exhaustion, Glauber's salt is often omitted at the start, particularly for heavy goods; instead, it is added slowly in small portions during the dyeing. The dyestuff solutions themselves may also be advantageously added in two or more parts, and this practice is strongly recommended when dyeing large pieces. When using these modifications it is always advisable to make additions of acid-stable wetting agents to the dyebath.

Temperature modifications also do much to assist the degree of penetration and, although the usual temperatures are in general the most suitable, thick materials will be better penetrated if they are entered at 50°–60° C. and allowed to dye in a cooling bath.

The addition of sodium nitrite to the dyebath in the first instance may be omitted. Nitrite has a salting-on effect and, therefore, in certain cases where control of the rate of exhaustion is essential its omission is advantageous. In such cases, however, the nitrite must be included in the acid developing bath for the purpose of oxidation. For this purpose, 1 lb. of sodium nitrite per 100 gallons of developing liquor is dissolved separately and then added to the cold bath before adding the cold diluted sulphuric acid and heating to the prescribed temperature. This procedure largely prevents the formation of obnoxious nitrous fumes. Cold development can also be carried out with the majority of dyestuffs in the range and, although slightly longer periods are required, the treatment is "kinder" to the fabric, there is less depreciation on the machine, and the inconvenience of nitrous fumes is almost totally eliminated.

With several Indigosol dyestuffs which are sensitive to over-oxidation, careful maintenance of the developing bath at 20° C. is advisable. Indigosol Blue IBC is an example of a dyestuff which is very sensitive to over-oxidation.

Matching to pattern is simplified by removing a small sample before oxidation and treating it for 1 minute at 70° C. in a small portion of the developing bath. The sample should then be rinsed, neutralised carefully, and finally boiled in soap solution in a boiling-tube for 2 minutes. After comparing the shade of cooled and dried sample with that of the pattern, the dyeing should be carefully topped to the required extent.

The use of three jiggers in sequence is advisable, so as to ensure effective continuity. The first jigger is used for dyeing, the second for development, and the last jigger is used for the final rinsing and soaping. The dyeing jigger, at least, should be provided with a very efficient set of squeezing rollers, and if possible a low cowl should be fitted over the vessel, so as to prevent direct sunlight gaining access to the pieces during dyeing. Provision should also be made so that the dyed pieces, in their passage to the developing bath, are protected from drops of condensed water from the roof and other fittings. Water-splashed areas result in weak patches or spots, owing to local washing-out of the *leuco*-ester of the dyestuff by the water.

The second jigger, which is employed for development, should be constructed of materials capable of resisting the action of solutions of nitrite and sulphuric acid. Wood is usually employed for this purpose, although, more recently, acid-resisting steel, in conjunction with rubber-covered rollers, has proved of exceptional value in this connection.

When the number of jiggers available in the dyehouse is restricted, it is always possible to carry out all three stages in two or even in one jigger, provided that the dyer can be relied upon for quick and careful manipulation. Open-width scouring machines can also replace the developing jigger quite successfully.

Specially designed V-shaped developing troughs, holding only about 2½ gallons, have been produced for continuous work. A detailed description of this type of trough has been given by Christ (*J.S.D.C.*, 1938, **54**, 96).

Examples of Jigger Dyeing with Indigosols on Cotton or Linen Fabrics by the Nitrite Process

Indigosol Golden Yellow IRK.—1½ lb. of dyestuff powder is dissolved in hot water and added to the jigger prepared with 12 lb. sodium nitrite and 70 lb. Glauber's salt per 100 gallons of dye liquor. Dyeing then proceeds at a temperature between 30° and 60° C., according to the nature of the goods, for ¾–1 hour. To prevent rapid and uneven exhaustion of this dyestuff, it is often advisable to add the Glauber's salt and nitrite in small portions during the dyeing. Since high temperatures also cause a decrease in affinity in the case of all Indigosol dyestuffs, it is advisable to commence dyeing at the highest temperature permitted, in this case 60° C. Dyeing is then allowed to proceed in a gradually cooling bath, in order to obtain the correct degree of exhaustion. It must be remembered, however, especially when dealing with dyestuffs of limited solubility, that a decrease in temperature corresponds to a decrease in solubility, and precautions based on laboratory trials should always be adhered to.

Development of Indigosol Golden Yellow IRK then takes place at 60° C., using 2½ gallons D.O.V. per 100 gallons of water.

Soledon Green GS.—The required quantity of dyestuff powder is dissolved in water at 50°–60° C. and added to the jigger previously set with 40 gallons of water at 60° C., ½ lb. soda ash and 4 lb. sodium nitrite. The fabric is dyed for four ends, feeding common salt or Glauber's salt into the dyebath very slowly, so as to effect gradual exhaustion. Development is then carried out at 60° C., using a 2% solution of D.O.V. in water. Neutralisation with soda ash and final soaping at the boil completes the process.

(2) **The Bichromate Process.**—Dyeing by this process is carried out as described for the nitrite process, without the addition of sodium nitrite. Development is then accomplished in baths containing sulphuric acid and potassium (or sodium) bichromate, e.g. a solution containing 1–2% potassium bichromate and 2–4% D.O.V. is employed at 35° C. This process of development is chiefly employed in padding and has not been widely adopted for jigger dyeing. It has the disadvantage of producing duller shades than the nitrite process, but objectionable nitrous acid fumes

are not produced. The bichromate process is very suitable for dark shades, since the salting-out effect of the nitrite is avoided.

(3) **The Ferric Salt Process.**—This method, which is seldom employed, possesses the disadvantages and the advantages of the bichromate process. Apart from the use of ferric chloride or sulphate and sulphuric acid, the procedure for development is identical with that of the nitrite method.

Other methods of development have been found suitable, but none has been so widely adopted as the nitrite process. In the *Chlorate Process*, the oxidising agent used is sodium chlorate; this method is preferred in the steam development of Indigosol prints. The use of aluminium chlorate in the presence of tartaric acid, or copper sulphate in the presence of lactic acid, is now only of academic interest.

Indigosols on the Winch Vessel.—Light-weight and delicate fabrics of cotton or rayon are best dyed on the winch, although it is not economical to dye heavy shades in this type of machine. The nitrite process is best adapted to the winch vessel, and the details regarding the preparation of the dyebath and the developing bath are the same as for jigger dyeing. The liquor–goods ratio is, of course, much greater, and corresponding increases in the amount of salt are usually required. After dyeing and removal from the winch, it is customary to hydro-extract the goods as uniformly as possible until they retain not more than 90% liquid, based on their original air-dry weight. The goods are then developed for 5–10 minutes in the usual quantity of acid, and finished as for jigger dyeing.

A slightly modified method for winch working, which has been reported as being satisfactory, is carried out as follows. The dissolved dyestuff is added in small portions to the dyebath, which has been set with the requisite quantity of water at 30° C. After running the goods on the winch for 45 minutes, 3–6 lb. of sodium nitrite, previously dissolved in water, are run in, followed by 10–50 lb. of Glauber's salt crystals in solution. Dyeing is then continued for 20 minutes, after which a sample is taken and examined for shade.

When the dyeing is complete, the pieces are run off the winch on to a clean board (which has been well wetted with exhausted dye liquor) and allowed to drain. Oxidation is then carried out, using a 2% solution of D.O.V. containing ½ lb. sodium nitrite and 20 lb. Glauber's salt per 100 gallons water, for 15 minutes at 50° C. Finally, the goods are rinsed and neutralised with soda ash, and then soaped at or near the boil (85°–90°C. for rayons) for about 15 minutes. During development it is often necessary to employ a temperature of 70°C. to obtain full oxidation. This is the case when using Indigosol Brilliant Pink I3B, Indigosol Pink IR extra, and Indigosol Red Violet IRH.

The One-Bath Process for the Winch Vessel.—For the production of pale pastel shades on vegetable fibres, especially rayons, this process has proved itself to be of exceptional value. Development is carried out in the same bath as the dyeing, i.e. at the end of the dyeing. Two-bath processes always result in a fair amount of Indigosol being washed out in the developing bath, especially if slow-developing dyestuffs are employed. By the use of a one-bath process, however, such a loss of colour is greatly reduced. A minimum of sulphuric acid is necessary for development and, consequently, there is less strain upon delicate fabrics. An addition of Setamol WS (I.G.) (a protective colloid), Unipan A (D.H.) or Peregal O (I.G.), is always recommended when using the one-bath process.

Not all the Indigosol dyestuffs may be applied by this process, and it is always safest to make small-scale trials before attempting bulk dyeings. The working details are as follows. The winch vessel is set at 18°–20°C. with ½ lb. Nekal BX (or similar product) and 1 lb. Peregal O (or 1 lb. Setamol WS) per 100 gallons of liquor. The fabric is then entered and allowed to run until thoroughly wetted.

After wetting out in this manner, the requisite quantity of dissolved dyestuff is added in a slow continuous stream during 30 minutes, followed by 1 lb. sodium nitrite (dissolved) and, finally, 25–50 lb. Glauber's salt, previously dissolved and then fed into the bath during a further 30 minutes.

After the piece has run for a further 15 minutes, a sample is cut and placed in about 1 gill of the dye liquor taken from the vessel at the same time as the pattern; about 5 ccs. of D.O.V. are then added while shaking vigorously. After 2 minutes in this liquor the pattern is withdrawn, washed in water, neutralised, and boiled in soap solution for 2 minutes. When the pattern has been dried and cooled, it is compared with the standard, and the necessary adjustments are then made to the dye liquor. When the piece is on shade, 2¾ lb. D.O.V. (previously diluted with about 4 times its weight of water) are added to the vessel while stirring vigorously. Development of the shade is complete after running the piece for about 15 minutes, and is followed by the usual after-treatment.

Examples of Shades Obtainable by the One-Bath Process

Pastel Ecru on Delustred Rayon.—The material is dyed in a 30:1 bath using, per 100 gallons dye liquor, 60 g. Indigosol Brown IBR, 18 g. Indigosol Golden Yellow IRK, and 9 g. Indigosol Olive Green IB. The dyeing procedure is as described above. A temperature of 20°C. is maintained throughout the process and an addition of 25 lb. Glauber's salt is made to the dyebath.

Pastel Beige Shade on Bright Rayon Fabric.—The material is dyed as described in the above example, using 71 g. Indigosol Brown IBR shaded with 7 g. Indigosol Grey IBL.

Ammonia–Acetic Acid Process (Durand & Huguenin A.-G. patent).—This process is specially designed for use with Indigosol Blue IBC, which, on account of its extremely low substantivity, is not very suitable for the ordinary one-bath process. Using the ammonia–acetic acid process, a completely exhausted dyebath can be obtained. Indigosol Blue IBC is a tetra-ester (cf. page 29, Soledon Blue 2RC) which is yellow in aqueous solution. Two of the ester groups are easily hydrolysed with the formation of a violet-coloured di-ester of high affinity. By the application of weak acids, therefore, development can be made to take place in two stages, *via* the di-ester intermediate stage. The gradual splitting off or hydrolysis of the ester groups is accomplished by means of a buffer, viz. ammonia.

Indigosol Blue IBC may also be used as the basis of combination shades, and is suitable for use in all forms of apparatus, including winches, yarn-dyeing machines and jiggers. The working method for this dyestuff is as follows.

For a 100-gallon dyebath (a 30:1 liquor–goods ratio is usually employed), ½ gallon of 25% ammonia is added at the start, followed by the dissolved Indigosol Blue IBC and 8 oz. of Setamol WS or 5 oz. of Nekal BX. The pieces are then entered at 20°C. and run for about 7 minutes, when 20 lb. of dissolved Glauber's salt are added in two portions, with an interval of 7 minutes between additions. At this stage the pieces and the dyebath appear bright yellow. After running for a further 7 minutes at 20°C., 2 lb. of acetic acid (30%) diluted with water are added and dyeing is continued for about 30 minutes with the temperature gradually rising to a maximum of 33°C. The fabric has by this time acquired a red-violet appearance. Three-quarters of an hour after the first addition of acetic acid a further addition of 1 lb. acetic acid (diluted) is made, and dyeing is continued for a further 20 minutes. The pieces will now be blue-violet.

At this stage 2 lb. of previously dissolved sodium nitrite are added, followed, while vigorously agitating the bath, by 5 lb. of D.O.V. (diluted). Development to the final pure blue shade is completed after 10 minutes at 33°C. Finally, the goods are rinsed, neutralised carefully and soaped at the boil as usual.

Fuller details regarding this somewhat complicated process may be obtained from Durand & Huguenin's pattern cards and handbooks. Details have also been given by Dietrich (*Melliand Textilberichte, Eng. Edn.*, 1936, **17**, 118).

Padding Piece Goods with Indigosol Dyestuffs.—Owing to the good solubility possessed by the Indigosols they are very suitable for application by the padding method of dyeing. Pale shades can be produced by a single passage through a two-bowl machine, and three-bowl machines are often retained for heavier shades. The goods are developed on a small roller-vat system, on a jigger, or in a V-shaped trough. Padding ranges have been specially designed for continuous working, but most types of available apparatus can be arranged to suit the process.

The padding machine itself should be fitted with a small liquor box, the capacity of which should never exceed 5 gallons. The box is heated by closed steam pipes or a double-bottom heating device. The padding bath should be maintained at a constant level throughout the operation, as in all other padding procedures. For this purpose a pipe from a separate feed tank operated by a valve is necessary, as is also an overflow pipe to run off any excess liquor in the event of too rapid feeding. The feeding liquor should always be of a higher concentration than the original starting bath, the strength of the replenishing liquor varying with the affinity of the dyestuffs in use, as well as with the travelling speed of the cloth and its nature. In the latter respect, it will always be found that rayons and mercerised cotton fabrics exhaust the padding bath much quicker than ordinary cotton, and the concentration of the feed liquor must be adjusted accordingly. Indigosols with low affinity require an excess of about 5% over the original strength, whilst those of higher affinity need up to 30% or even more.

The temperature at which the padding is carried out is also a decisive factor, and the ideal conditions for general work are a temperature of 60°–80°C. and a high working speed, e.g. 3–8 seconds padding time. Efficient squeezing of the goods after padding, e.g. 70–100% increase in weight, is essential, and when heavy shades are being dyed the goods should be dried in a hot flue fitted with steam chests or hot-air circulation. Drying is essential with heavy shades in order to minimise loss of colour in the developing bath. Cylinder drying is out of the question, since this leads to two-sided effects. After drying, the pieces are rolled up and developed later. With pale and medium shades development can take place straight away, i.e. without intermediate drying, and this is usually accomplished in the V-shaped trough, in the roller vat or on the jig. A temperature of 60°–70°C. is usually employed, with a minimum time of 3 seconds, provided that an air passage of say 20–25 seconds is given before rinsing If no air passage is given, the time of development should be increased to 6–8 seconds. Washing, neutralisation in tepid soda ash solution and soaping are then carried out as for ordinary jig or winch dyeing. For this purpose, jiggers or a continuous arrangement of roller vats can be employed.

Two main methods of padding are employed, viz. the so-called "rapid" nitrite process and the bichromate process. The former is the more popular, since fuller and brighter shades can be obtained. The bichromate process is probably the more suitable one for the production of heavy shades.

For the nitrite process, the padding solution is prepared by dissolving 4 oz. dyestuff in 1 gallon of warm water containing ¾ oz. soda ash. This is then thickened by adding ½ oz. Formosul, Rongalite C or Erasol C, and ¼ gallon of 5% gum tragacanth paste and worked into a smooth homogeneous mixture. Finally, 4 oz. sodium nitrite are thoroughly incorporated, and after straining the whole is diluted to 5 gallons.

The dry material, which has previously been desized and perhaps prepared with an acid-resisting wetting agent, is padded and then run directly into the developing bath, which consists of a 2% solution of D.O.V. in water at 65°C. After an immersion of 3 seconds, the goods are squeezed and given a 20-seconds air passage to complete the oxidation, before rinsing and finishing as usual.

For the bichromate method of development the padding liquor is prepared with 4 oz. dyestuff, 2 pints of 5% tragacanth thickening and 8 oz. of an acid-stable wetting agent, and then diluted with water to 5 gallons.

After padding, the dyed pieces are either dried or developed directly, using 2 lb. potassium bichromate in 10 gallons of a 4% solution of D.O.V. at 35°C. Pastel shades require only half as much bichromate. This method is widely employed in the application of Indigosol O.

For both processes it is essential to study the dyestuff manufacturers' pattern cards for special details concerning individual dyestuffs.

The steaming process of padding is more complicated than either of the wet processes which have just been described. It is very rarely used for the dyeing of plain shades, but the fabric printer finds it of great value in the production of special effects (Chapter IX). The following general formula illustrates the composition of the padding liquor:

5 parts Indigosol Dyestuff
150 parts Hot Water
50 parts Neutral Tragacanth (80:1,000)
757 parts Cold Water
8 parts Sodium Chlorate (1:3)
10 parts Ammonium Sulphocyanide (1:1)
Immediately before padding, add:
10 parts Ammonium Vanadate (1%) and
10 parts Acid-resisting Wetting Agent (10%)

1,000 parts

The goods are padded on the two-bowl or three-bowl mangle, dried in a hot flue, and then steamed for 8 minutes in the rapid ager. The goods are then rinsed and given a short treatment in boiling soap solution. Viscose rayon goods are soaped at 60°C.

Yarn and Cheese Dyeing.—For general hank-dyeing purposes, Indigosol dyestuffs possess little advantage over ordinary vat dyestuffs, but for very pale shades, and particularly for tightly twisted yarns of mercerised cotton or rayon, their use is to be recommended on the grounds of levelling and penetration. Development often presents difficulties, and it is advisable to use only those dyestuffs which develop rapidly and easily.

Hanks may be dyed in the open bath by stick turning or on any of the machines designed for the purpose. A liquor-goods ratio of 20:1 is usually employed, and the prepared goods, i.e. after boiling out, bleaching, etc., are entered into the bath in a dry condition. Dyeing and developing details are as described for jigger dyeing, and either the single-bath or two-bath process may be employed. For hard-spun yarns it is necessary to dye at the start without Glauber's salt, and to add this in small portions during the dyeing. Starting at a high temperature, e.g. 60°C., and then dyeing in a cooling bath is always advisable for tight-twist yarns. In general, development for 15 minutes at 70°C. is satisfactory, using nitrite in the developing bath and not in the dyeing bath.

Cops, cheeses and warp beams may be dyed in the usual type of circulating-liquor machine, provided that it is made of acid-resisting metal, under similar conditions to those previously described. After dyeing, using nitrite in the dyebath, the goods carriage is lifted and hydro-extracted while the developing bath is being prepared. When using brands which are sensitive to over-oxidation, e.g. Indigosol Blue IBC and Indigosol Olive Green IB, it is also advisable to rinse out the machine with water before the developing bath is made up. Oxidation in the 2% D.O.V. solution is allowed to continue for 15 minutes at 70°C., care being taken that the acid penetrates to the centre of the yarn packages. Rinsing, neutralisation and soaping must be thorough and may be carried out in the same machine.

The following brands are particularly recommended for use in circulating-liquor machines:

Indigosol Golden Yellow IRK
Indigosol Brilliant Orange IRK
Indigosol Brown IBR
Indigosol Olive Green IB
Indigosol Green IE3G
Indigosol Green IB
Indigosol Blue IBC
Indigosol Red IFBB
Indigosol Grey IBL

The ammonia–acetic acid process may be used with Indigosol Blue IBC. When using Indigosol Red IFBB, nitrite should be omitted from the dyebath in order to obtain better fastness properties.

Rayons and Mixed Fabrics.—Rayons are dyed with Indigosols in much the same way as cotton. The chief difference lies in the fact that the rayons possess a higher affinity for these dyestuffs than ordinary cotton, and more care is required in handling from the mechanical point of view. Soaping is never carried out at the boil, temperatures ranging between 60°–80°C. usually being sufficient.

The coloration of rayons, particularly lingerie goods and similar delicate fabrics, claims a large part of the total consumption of the solubilised vat dyestuffs. In union materials of the cotton–rayon type it is a fairly easy matter to obtain solid effects in pale shades. On the other hand, heavy shades present a great deal of difficulty when solid effects are required. The difference in affinity between the two fibres appears to exert more effect in the presence of larger amounts of dyestuff, and resort must therefore be made to other methods of dyeing.

In the case of a mixture fabric containing acetate rayon, cold dyeing with Indigosols results in the acetate rayon being fully reserved, although there are a few exceptions, e.g. Indigosol Green IBA and Golden Yellow IGK. In heavy shades, acetate rayon is slightly stained, but, when two-colour effects are required, this stain can usually be effectively covered by using the dispersed acetate rayon dyestuffs.

In order to obtain "shot" or "cross" effects upon mixture fabrics of acetate rayon and viscose rayon or cotton, the following procedure, which employs Indigosols to colour both fibres, is recommended. The fabric is first padded in a bath consisting of:

6–60 parts Indigosol Dyestuff dissolved in
800 parts Water
50 parts Tragacanth Thickening (80:1,000) and
10–20 parts Sodium Nitrite,
5 parts Ammonia (25%) are then added and the bulk is brought up to

1,000 parts

The goods are then dried and developed for 2 seconds in a bath containing 20 ccs. sulphuric acid (168°Tw.) per litre of water, at 65°–70°C. An air-passage of 20–30 seconds is then given before rinsing, soaping lightly, rinsing again and then drying. In this way, the viscose rayon or cotton is dyed, and the acetate rayon is completely reserved.

The acetate rayon may then be dyed in a different shade by a second padding in a bath containing:

6–60 parts Indigosol Dyestuff dissolved in
600 parts Water, and
30 parts Indigosol Developer D (D.H.)
200–250 parts Tragacanth Thickening (80:1,000)

Bulk to 1,000 parts

After padding and drying, the goods are steamed in the box for 20 minutes, and then rinsed and lightly soaped. Final development is achieved by passing the goods through a bath containing 20 ccs. sulphuric acid (168°Tw.) and 4 g. sodium nitrite per litre of water at 70°–75°C. Rinsing, soaping, rinsing and drying complete the production of the two-coloured or "shot" effects, It will be realised from the above that by using the latter half of the process it is possible to produce fabrics in which the acetate rayon is dyed and the viscose rayon or cotton is completely reserved.

Indigosols have proved to be extremely valuable for dyeing solid shades on union goods composed of viscose staple fibre (or cotton) and wool. For this purpose a padding method is employed, and all the Soledon dyestuffs, except Soledon Blue 2RCS and Soledon Red BNS, are reported to be suitable.

The process recommended by Imperial Chemical Industries Ltd. is as follows: 4–8 oz. Soledon Jade Green XS are dissolved in 7¼ gallons of water. To this are added, in the order given:

1⅜ pint Solaval B,
⅝ pint Soledon Developer T,
8 oz. Ammonium Sulphocyanide, and
1 gallon Perminal W (5% solution)

This mixture is bulked to 10 gallons with water and padded on to the goods at 60° C. The material is then dried and steamed for development for 30 minutes at 100° C., using moist steam. Final development is effected by means of an immersion for 3 minutes at 95° C. in a bath containing 1 lb. ammonium persulphate and ½ pint acetic acid (30%) per 10 gallons water.

Notes on Individual Indigosol Dyestuffs

Indigosol Blues O and OR are considered to be unsuitable for application on the jigger on account of their low affinity. Padding methods are usually employed for the production of pale, medium and heavy-shade blues. Further, these dyestuffs, as well as Indigosol Printing Black IB and Indigosol Yellow HCG, are not suitable for the production of mixture shades. The oxidation process for these dyestuffs is best conducted at ordinary temperatures with the nitrite in the developing bath.

Mixture shades should be formulated as far as possible from dyestuffs which exhibit the same degree of fastness, the same ease of development and, above all, the same degree of affinity. Beige and brown shades, for example, are preferably based on Indigosol Brown IBR, shading as required with Indigosol Golden Yellow IRK or Indigosol Brilliant Orange IRK, and saddening when necessary with Indigosol Olive Green IB. When redder shades of brown are required, the brown base employed should be Indigosol Brown IRRD, but, since this dyestuff exhibits dichroism and reddens considerably in artificial light, it should be avoided if at all possible.

Satisfactory yellowish-orange shades can be obtained by shading Indigosol Brilliant Orange IRK with Indigosol Golden Yellow IRK, whilst reddish-orange shades are obtained by shading with Indigosol Scarlet IB for weak shades, and Indigosol Red IFBB for heavier shades. Indigosol Red IFBB is less suitable than Indigosol Scarlet IB for padding processes.

In the production of green shades, matters are greatly simplified by the fact that the range is rich in homogeneous green dyestuffs. These, as a rule, only require a minimum of shading with Indigosol Blue IBC or Indigosol Golden Yellow IRK to obtain the desired shade. The latter dyestuff, if added to Indigosol Green IEGG or IB, should not exceed 20% of the total weight if maximum light fastness is to be retained. Olive green and drab shades may be based on Indigosol Olive Green IB, Indigosol Brown IBR and Indigosol Golden Yellow IRK.

Blue shades are invariably based upon Indigosol Blue IBC. This dyestuff may be toned to the green side by adding small amounts of Indigosol Green IE3G or Indigosol Olive Green IB. If redder shades are needed, traces of Indigosol Scarlet IB or Indigosol Red IFBB may be added. Blue shades which require saddening need a trace of Indigosol Grey IBL.

Greys can be based on Indigosol Grey IBL or Indigosol Blue IBC and shaded with Indigosol Brown IBR (which with Blue IBC yields greys of excellent tone and fastness), Indigosol Olive Green IB or Indigosol Brilliant Orange IRK. Black shades are obtained by padding with 10 lb. Indigosol Printing Black IB per 100 gallons of liquor.

Throughout this section the Indigosol brands of solubilised vat dyestuffs have been used to provide the main examples, chiefly because they represent the original range. Furthermore, this range includes the largest number of dyestuffs of this type, whilst the makers (Durand & Huguenin A.-G.) have done much pioneer work in fostering their use. Other brands, e.g. Soledon (I.C.I.), Cibantine (S.C.I.) and Tinosol (Gy.) brands are very similar to the Indigosols, and the foregoing instructions apply equally to the products of all the dyestuff manufacturers concerned.

CHAPTER VIII

APPLICATION—PIGMENT PADDING AND MISCELLANEOUS PROCESSES

THE pigment padding process was originally recommended for overcoming difficulties of penetration when dealing with tightly woven materials such as duck cloths, cotton drills and linen fabrics. Its use has now spread to finer fabrics such as spun rayons, viscose rayon–cotton unions, and poplins, as well as to the field of yarn dyeing and raw stock dyeing. Its popularity for almost every type of cellulosic fabric is a measure of the great value of the process, and dyeings produced by this method invariably bear the marks of fine-quality workmanship. However, the process is more expensive than ordinary dyeing, since a greater quantity of dyestuff is required for full penetration of the goods, whilst the cost of the padding oils which are necessary for the production of good results, although comparatively small when compared to the extra cost in dyestuff, further increases the price of the process.

In its simplest terms, pigment padding consists of first producing a finely dispersed layer of unreduced vat dyestuff in and on the mass of fibres which constitutes a yarn or fabric. The loose dyestuff is then reduced in a blank vat and subsequently fixed by the usual process of oxidation.

Four vital factors affect the final appearance and quality of the dyed fabrics, and all are of such consequence that it is impossible to list them in order of importance. They are, briefly, (*a*) the design of the padding mangle and associated apparatus, (*b*) the careful preparation and pre-treatment of the material to be dyed, (*c*) the correct selection of dyestuffs, and (*d*) the quality of the padding assistant.

The choice of the padding mangle is probably the most difficult question to settle, on account of the wide variety of machines available. Efficient mangles have been purposely designed to suit this type of padding, and the experience of the machine-makers is always worthy of consideration.

Probably the first essential in the choice of the machine is to make sure that it can be easily cleaned. The vertical mangle types are very suitable for the purpose and may consist of two or three bowls. An effective degree of expression is essential, and a combination of hard and soft rubber rollers gives the desired effect. One passage through the two-bowl padding mangle gives a single immersion of the goods, whilst with the three-bowl type a double immersion is given. The two-bowl type is often employed for certain types of fabrics and a double run through the machine is given, reversing the cloth at the second passage.

The capacity of the liquor troughs should be as small as possible and should not exceed 5 gallons; heating is provided by a closed steam-pipe or by means of a steam jacket. The feed-box for the trough should be similarly fitted with a heating device, as well as an easily controllable feed pipe and a system of agitation. Expander bars are necessary in front of the machine, in order to avoid creases in the goods, and after the padded fabric leaves the nip it should be rolled up on to an efficient batching roller, or arrangements should be made for plaiting down.

Special types of padding machines, as exemplified by the Haubold, "Fibe" and Zittauer machines (see Chapter X), should not be overlooked when installing new plant.

The method of preparing the goods to be dyed varies considerably in accordance with their nature, e.g. fabrics may be subjected to singeing, desizing, washing, kier-boiling, bleaching, souring, washing and mercerising. Finally, the fabrics must be dried. Drying to even width is essential, and the degree of drying must be thorough and uniform throughout the full length of the piece. Uneven drying will always express itself in uneven dyeing, and particular attention must be given at this stage. Heavy fabrics are processed in open width throughout, whilst with light materials the majority of the preparatory processes are best conducted in rope form. When dyeing grey goods, e.g. of the type required for the production of heavy overalls and service materials, it is necessary to remove all motes or burrs by a treatment in boiling caustic soda, prior to drying and padding.

Specially prepared dyestuffs are necessary for this particular type of dyeing, and the majority of firms manufacturing vat dyestuffs offer ranges suitable for pigment padding. Dyestuffs for this purpose must possess a very high degree of dispersion and fineness of form, so as to be effective even in weak liquors. "Paste fine," "grains" and "powder fine" brands are usually found to fulfil the requirements, but all untested dyestuffs should be subjected to sieving in suspension before making up the padding liquors. This precaution will remove any aggregated dyestuff particles which would otherwise cause undesirable effects. Powder brands should be stirred very carefully with ten to twenty times their weight of warm water, so as to avoid clogging. The advantages of the powder types are threefold in that (*a*) they are more stable than paste brands (no drying up can possibly occur), (*b*) they do not freeze in cold weather, and (*c*) they are more easily handled in the weighing-room.

Vat dyestuffs have been marketed which require no assistance from padding oils or other auxiliary products, but most of the available dyestuffs require a carefully selected assistant. Two oils which have established themselves by large-scale application and popularity are Calsolene Oil HS (I.C.I.) and Prestabit Oil V (I.G.). Such products have the ability to wet fibres effectively, suspend the dyestuff particles for almost unlimited periods, prevent aggregation of dyestuff particles, remain unaffected by large variations in pH, and, furthermore, they are free from any tendency to objectionable frothing.

The squeezing effect of the nip and the capacity of the padding box are the chief factors to consider when preparing the padding liquor, whilst the desired depth of shade and the weight of the fabric to be processed also play an important role. A formula for calculating the total amount of padding liquor required for a given weight of fabric has been provided by Hopkins (*J.S.D.C.*, 1941, **57**, 358) and is based on these four factors.

The volume of the liquor required is calculated from the equation:

$x = \frac{B \times A}{100 \times 10} + C$, where A = Weight of the cloth
B = Percentage expression of the rollers
C = Capacity of the padding box in gallons, and
x = The number of gallons of liquor required.

For example, in order to pad 128 lb. cloth to a 10% shade with Indanthrene Yellow 3RT double paste using $\frac{x}{100}$ gallons Calsolene Oil HS, the roller expression being 75% and the capacity of the box 5 gallons, the volume of pad liquor required would be:

$$\frac{75 \times 128}{100 \times 10} + 5 = 14{\cdot}6 \text{ gallons.}$$

This would contain $\frac{75}{100} = 0{\cdot}75$ gallons Calsolene Oil HS, and

$$\frac{128 \times 10}{100} = 12{\cdot}8 \text{ lb. of dyestuff paste}$$

The amount of dyestuff required for the production of a particular shade should be based on small-scale laboratory trials. If possible, these trials should be conducted on a small test-mangle which has been accurately set for speed and expression, so that precise details may be repeated with the larger machine. When lengthy pieces are being processed the padding liquor tends to become slowly weaker, and in order to counteract this the addition of ¼–½ gallon gum tragacanth (1:20) per 100 gallons of liquor is recommended. Excess of this agent, however, prevents the maximum wetting-out effect from being obtained.

The goods, in a dry condition, are allowed to pass through the padding trough and nip at a definite speed and temperature. These factors must be decided by the quality of the material, and conditions should be so regulated that the goods are perfectly wetted out, preferably in one passage. With the heavier type of fabric it is possible to obtain complete wetting only after several passages. Padding on the light side of the shade required is better than too heavy a pad; weak shades may always be topped up on the jigger.

Throughout the run, the pad box should be maintained at a constant liquor level and at constant temperature. The expression of the rollers should be as effective as possible, so as to prevent the carriage of too much of the padding liquor into the jigger. Temperatures of from 60° to 95°C. are employed, heavy goods requiring the highest temperatures in order to ensure penetration.

On leaving the nip, the fabric is batched up evenly on the beam, selvedge upon selvedge, or it may be plaited down. Hand-cuttling should never be allowed and the pieces should be touched as little as possible, so as to avoid removal of the unreduced dyestuff. For the same reason it is essential to avoid water splashes and thus prevent the local washing out of unfixed dyestuff.

If, for some reason, it is found necessary to dry the goods before development, drying must be very slow. Hot steam-cans are very liable to cause two-sidedness and speckled effects, particularly if the cans are at "sizzling" heat. Steam-cans are best kept at a low temperature, and it is advisable to cover the first cans in the range with calico.

For reduction on the jigger, the blank vat is set as it would be for the ordinary process of jigger vat dyeing, employing the quantities of caustic soda and hydrosulphite and the temperature recommended for the particular dyestuffs in use. Four to six ends, or more, are given, and if after this time a pattern is found to be off-shade, the goods may be topped in the same bath. Oxidation and finishing treatments are then carried out as for ordinary vat dyeings on pieces.

Example: Production of a pastel neutral-grey shade by the Pigment Padding Process:
110 lb. Mercerised Cotton Poplin (960 yds.)
Roller expression = 70%.
Use 13 gallons of pad liquor containing:
1 lb. 6½ oz. Indanthrene Grey BG Paste
6 oz. Indanthrene Orange 7RK Paste, and
3 pints Prestabit Oil V
bulked to 13 gallons with soft water

The pad box contains 5 gallons of liquor and is fed during the single passage of the goods with the remaining 8 gallons. Padding temperature: 80° C.

The developing jigger contains:

70 gallons Water
1¼ gallons Caustic Soda (70°Tw.)
5½ lb. Hydrosulphite
5 lb. Glauber's Salt, and
2 pints Padding Liquor

Run at 40° C. for 6 ends. Rinse, oxidise, sour and soap as usual.

A process described as the *Pad-Steam Continuous Dyeing Process* has recently been developed in the United States by E. I. du Pont de Nemours & Co., Inc. Full details of the process and the special equipment required have been described by Stribling and by Meunier (*American Dyestuff Rep.*, 1945, **34**, 99 and 206 respectively).

Briefly, the Pad-Steam Process is as follows. The prepared fabric is pigment-padded in the usual manner on a two- or three-bowl padding machine. The material is then uniformly dried in a flue dryer and then cooled by a passage over a cooling cylinder which leads it into a second padding machine. This machine contains a solution of caustic soda and hydrosulphite below 38°C. The migration tendencies of the dye are arrested by the addition of common salt and sodium formaldehyde-sulphoxylate to the first or second pad-box.

With a minimum exposure to air, the fabric next passes into a steaming chamber where it is treated in a saturated steam atmosphere at 100°C. or slightly higher. The vat dyestuff is thus rapidly reduced to its leuco-form which penetrates the fabric. The steaming operation is completed in about 10–60 seconds, and the *fabric is finally subjected to the conventional oxidation, soaping, rinsing, and drying.*

Dyeings carried out by this process are reported to show excellent penetration and fixation of the dyestuffs, all-round fastness properties, good colour value, and brilliancy of shade. Almost all the vat dyestuffs can be applied in this manner and pastel to deep shades can be produced with equal ease. Du Pont report that cotton fabrics of every type, rayon fabrics, blends of cotton and rayon, wool and rayon, and other combinations, have all been successfully dyed by the pad-steam method.

Loose Cotton, Loose Rayon Staple Fibre, Cheeses, and Viscose Rayon and Cotton Yarns.—The pigment padding process can be effectively applied to any of these forms of cellulosic fibres, with consequent ruling out of difficulties of penetration and levelling which are experienced when dyeing pale shades by the ordinary reduced vat method.

As in the case of piece dyeing, it is essential that the fibres should be perfectly cleansed and dried before padding. Rayon materials usually require desizing and scouring in soap and ammonia, whilst cotton fibres require boiling in alkali and, where necessary, bleaching.

Viscose staple fibre and raw cotton may be worked in open vessels, using a short boiling bath charged with the sieved dyestuff paste and about 2 lb. padding oil per 100 gallons of liquor. The dry goods are entered at the boil and allowed to boil for 15 minutes, with careful poling. The bath is then filled up with cold water and the temperature regulated to suit the particular dyestuff. Caustic soda and hydrosulphite are next added, and dyeing proceeds normally for about 1 hour.

Cotton yarns may be padded in the open beck in a similar manner, using 2¼–5 times more padding oil. Padding is carried out for 15 minutes at temperatures up to 90°C., after which the hanks are evenly squeezed. They are then replaced in the vessel, after it has been brought down to the correct dyeing temperature with water and the requisite amounts of caustic soda and hydrosulphite have been added.

Dyeing of cops and cheeses on open or closed circulating-liquor machines by this process possesses an advantage over reduced vat dyeing in that the cotton packages do not show "zoning" after dyeing. Machines must be packed with the usual meticulous care required for ordinary vat dyeing, and particular attention must be paid to the fine state of dispersion of the dyestuff suspension.

Pigment padding of cheeses and similar packages calls for extremely fine dispersions, and suspensions must therefore always be filtered before use. From 5–10 lb. Calsolene Oil HS are added per 100 gallons of liquor, and the dyestuff suspension is circulated through the goods for 10 minutes, adjusting the pressure in the machine meanwhile. The padding liquor is then pumped off and the cheeses are hydro-extracted or extracted by vacuum. Reduction with the blank vat solution then follows at the correct temperature, dyeing proceeding in the manner usual for this type of machine.

Union Fabrics of Viscose Rayon and Cotton

Imperial Chemical Industries, Ltd., recommend the Gum Tragasol Pigment Padding Process for the coloration of cotton–viscose rayon materials (cf. I.C.I., *Technical Circular*). The tendency for the dyestuff to bleed into the blank reducing bath and re-dye the viscose rayon preferentially is overcome by the employment of Gum Tragasol.

Gum Tragasol is a locust bean product which is easily coagulated by alkali; this property enables the unreduced dyestuff to remain static when the gum is coagulated in the caustic soda–hydrosulphite reducing solution. Excessive bleeding is therefore avoided and more solid results are obtained.

Padding liquors for this process are prepared according to the following recipe:

1 lb. Gum Tragasol is sprinkled slowly with continuous stirring, into
7½ gallons Cold Water, which contains
½ oz. Borax, and
⅛ pint Acetic Acid (40%)

The liquor is allowed to stand for 15 minutes and is then boiled for 15 minutes until a clear mucilage is obtained. One pound of Calsolene Oil HS is then added, followed by water to a bulk of 10 gallons. The solution is sieved through a fine cotton cloth before use.

The requisite amount of vat dyestuff (“paste fine” or “grains”) is pasted with a little water and then diluted to the required pad-box volume with the 1% solution of Gum Tragasol and Calsolene Oil HS prepared as described above. The rest of the procedure is then identical with the normal pigment padding process previously described; it is recommended, however, that common salt should be added to the reducing bath so as further to minimise bleeding. By drying after padding, it is possible with certain dyestuffs to produce a darker shade on the cotton than on the viscose rayon. Mixture shades cause little difficulty when applied by this process.

Although the pigment padding process is often recommended for the production of solid shades on viscose rayon–cotton union fabrics, it is not always possible to apply this process, and other methods have therefore been devised.

A process originally introduced by Imperial Chemical Industries, Ltd., consists of first treating the fabric in a cooling solution of tannic acid for 1 hour. The excess liquor in the fabric is then removed by squeezing, and the absorbed tannic acid is fixed in a solution of tartar emetic. The viscose rayon absorbs much more of the tannic acid than the cotton. Subsequently, in the alkaline vat, the insoluble antimony tannate is slowly decomposed. The cotton very quickly loses its smaller amount of mordant and begins to absorb the vat dyestuff some time before all the tannin has left the viscose rayon. Adjustments in the strength of the tannin bath and control of the temperature and alkalinity of the dyebath make it possible to obtain almost any desired result, e.g. cotton stronger in shade than viscose rayon or solid effects.

The temperature required for dyeing the IN and IW types of anthraquinonoid vat dyestuffs must be lowered to 35°–40°C.; cold-dyeing vat dyestuffs (IK) are best dyed with 50% more caustic soda than usual.

Approximately 3–4 lb. tannic acid per 30–35 gallons water are required to produce a solid shade on 100 lb. of viscose rayon–cotton fabric. The scoured pieces are treated on the jigger at 95°C. for 6–8 ends, the temperature of the bath is then allowed to fall, and a cold water rinse is given. The goods are next fixed by giving 4 ends with 2–2½ lb. tartar emetic in 30–35 gallons cold water, followed by 4 ends in warm water.

The length of this process is a disadvantage and there is a danger of damage; a minimum of 2% warp shrinkage may also be anticipated.

Pre-treatment of viscose rayon–cotton union fabrics with caustic potash results in improved dyeings from the point of view of solid shades, but the improvement is less pronounced with vat dyestuffs than with direct cotton dyes. For this purpose, a brief immersion of the goods in open width in cold 32°Tw. caustic potash solution is used. It is essential that the immersion should be as brief as possible, and it must be followed by rapid and thorough rinsing if shrinkage and swelling of the viscose rayon is to be cut down to a minimum.

Modified Rayons.—The vat dyestuffs have not received much attention from the point of view of application to resin-modified regenerated cellulose. This is probably due to the fact that the primary aim of treating cellulosic fibres with resins is to impart to them the property of dyeing with acid wool dyestuffs. Nevertheless, it is occasionally necessary to dye such fibres as Rayolanda (Courtaulds, Ltd.) with vat dyestuffs. The solubilised vat dyestuffs appear to be the most suitable for this purpose.

Solid shades or tone-in-tone effects may be produced on union fabrics containing Rayolanda and Fibro (Courtaulds' viscose rayon staple), the effect obtained being mainly dependent upon the temperature employed. High temperatures, e.g. 80° C., yield solid shades with most anthraquinonoid vat dyestuffs, whilst low temperatures, e.g. 30° C., result in a heavier shade on the Fibro.

It is interesting to note that Rayolanda treated in a blank vat of caustic soda and hydrosulphite does not lose its original affinity for acid dyestuffs.

The solubilised vat dyestuffs, as exemplified by the Indigosols and Soledons, are chiefly employed for tone-in-tone effects on Rayolanda-Fibro materials, and those dyestuffs which possess low affinity for viscose rayon yield the greatest degree of contrast. The difference in depth on the two fibres can also be regulated to a large extent by the use of varying quantities of salt and different dyeing temperatures. The lower the weight of salt and the higher the temperature employed the greater will be the difference in depth of shade between the two fibres, the Rayolanda being the darker.

Acetate Rayon.—Acetate rayon is very often encountered in the form of effect threads in fabrics. It may be desired to reserve these threads so as to leave a white pattern on a dyed ground, or to dye them a different or a similar shade to the ground. As is well known, acetate rayon becomes saponified in alkaline liquors, with consequent formation of a surface of regenerated cellulose which has a high affinity for vat dyestuffs. Saponification (or hydrolysis) is therefore undesirable, especially if the acetate effect threads are to yield their full contrast effect, and resist compounds must be employed in the dyebath. Many compounds have been suggested for this purpose, some of the more important ones being β-naphthol, sodium phenate, ammonium salts, Katanol WL (I.G.), Tibaline NAM (K.), Celascour (B.C.), and Resist for Acetate Silk Powder (I.G.).

β-Naphthol and sodium phenate are both capable of yielding good reserves on acetate rayon during the application of weak alkali vat dyestuffs. Low temperature (IK) dyestuffs yield the best results, since a smaller amount of caustic alkali is required in dyeing. An addition of 7 lb. β-napthol or 15 lb. sodium phenate per 100 gallons of dye liquor is recommended, and the dyeing time should be cut down to a minimum.

It has been stated (*Dyer*, 1943, **89**, 206) that if the quantity of caustic soda 70°Tw. employed in the preparation of the vat does not exceed 2 ccs. per litre, and if 20 g. of trisodium phosphate per litre are added, a high degree of reservation is obtained.

All vat-dyed goods containing acetate rayon effects should be soaped for at least 45 minutes at 80° C., in order to minimise any staining of the white effects during subsequent domestic treatments.

In *B.P.* 517,751, Courtaulds, Ltd., describe a successful process for applying vat dyestuffs to acetate rayon itself without causing harmful effects. Incidentally, this process may also be used for dyeing wool or nylon with vat dyestuffs. The method depends upon the fact that, previous to the entry of the material into the dyebath, all excess or free caustic alkali is converted into sodium carbonate by the addition of sodium bicarbonate.

The vat dyestuff is first reduced, using the quantities of caustic soda and sodium hydrosulphite employed for normal cotton dyeings. When thorough solution has been effected, sodium bicarbonate is added in amount just sufficient to convert to sodium carbonate any caustic soda present in excess of that required to form the sodium salt of the *leuco*-vat dye. The excess alkali is dependent upon the number of reducible keto groups in the particular dyestuff molecule, and a simple calculation based upon the following equation will indicate the quantity of bicarbonate required.

$$\underset{(40)}{NaOH} + \underset{(84)}{NaHCO_3} = Na_2CO_3 + H_2O$$

Thus, 40 parts of caustic soda require 84 parts of sodium bicarbonate for conversion into sodium carbonate.

Dyeing then proceeds in this bath for 45 minutes at 60°–70° C., and the shade is subsequently developed by oxidation in a bath of sodium nitrite and sulphuric acid, as for Indigosols.

Other methods of dyeing acetate rayon with vat dyes include:

(1) Acetate rayon is first padded in unreduced vat dye suspensions. It is then given two ends at 60°C. through a bath containing the normal amount of caustic soda which is employed for cotton dyeing. Complete saponification of the cellulose acetate takes place during this treatment. Further additions of caustic soda are then added in order to compensate for that lost in the

process of saponification. Hydrosulphite is then added and dyeing is carried on in the normal manner for cotton dyeing. All vat dyestuffs can be applied by this process, but the acetate rayon loses many of its normal characteristics.

(2) Vat dyestuffs can be successfully applied to acetate rayon by first swelling the material with 2% salicylic acid, drying at a low temperature with elimination of all undue tension, and then applying selected vat dyestuffs by way of the pigment padding process. The dyestuff is subsequently reduced on the jigger using ethylene diamine and ammonia alone or in combination with triethanolamine as the alkali and hydrosulphite as the reducing agent. The surface of the acetate rayon is reported to be only slightly saponified in this way. Butanol may also be employed as a swelling agent in this process.

(3) A continuous process for the production of light shades with vat dyestuffs on acetate rayon and in which the acetate rayon is not saponified can be carried out by padding the reduced vat dye with a minimum amount of caustic soda, hydrosulphite, and 4 oz. butanol for each gallon of dye liquor. The padded fabric is then given a passage through a bath containing soda ash and hydrosulphite and is then rinsed, oxidised, soured and soaped in a neutral bath.

(4) Heavy shades are obtained by pigment padding acetate rayon fabric, drying, and then reducing the vat dyestuff in a solution containing minimum quantities of caustic soda and hydrosulphite. This treatment is immediately followed by a short steaming. The goods are finally rinsed, oxidised, soured and soaped. Choquette (*American Dyestuff Rep.*, 1945, **34**, 213) reports that the acetate rayon in this case is only partially saponified, approximately 2%, based on loss of acetyl groups.

(5) Spun fabrics containing viscose rayon and acetate rayon in the ratio 7:3 can be successfully dyed in light shades with vat dyestuffs by partially saponifying the cellulose acetate fibres. The scoured material is padded at room temperature in a solution containing the vat dyestuff, 20% alcohol, a small amount of gum Karaya, and a wetting agent. The vat dyestuff is subsequently reduced on the jigger with trisodium phosphate and hydrosulphite. Dyestuffs for this purpose must be carefully selected, temperature must be rigidly controlled, and the time factor must be reduced to a minimum.

Superpolyamide Fibres.—Although these fibres, e.g. nylon, can be dyed satisfactorily with many of the vat dyestuffs, it is unlikely that this class of colouring matters will be widely adopted for the purpose. When vat dyestuffs are applied by the normal methods only weak shades of poor fastness to light are obtained. Shades of reasonably high tinctorial strength can be obtained by the use of selected indigoid brands, e.g. Durindone Pink FFS and Durindone Blue 4BCS, or dyestuffs of the dibenzanthrone series. Anthraquinonoid vat dyestuffs of the anthrimide type, however, appear to possess only low affinity for nylon. Solubilised vat dyestuffs also show widely varying affinity.

In *B.P.* 534,085, Imperial Chemical Industries, Ltd., describe a process whereby much fuller shades can be obtained on polyamide fibres. The process entails the use of a higher temperature than that normally used for vat dyeing cotton, e.g. 90°–95°C., and on this account sodium hydrosulphite is replaced by sodium sulphoxylate-formaldehyde, i.e. Formosul, etc. Nylon may also be dyed successfully with vat dyes, using the procedure outlined above for acetate rayon (*B.P.* 517,751).

R. E. Rose (*Amer. Dyestuff Rep.*, 1942, **31,** 204) has stated that: "The effect of nylon on vat dyes is very surprising, most of them show no affinity, but those which do are robbed of their light-fastness to an unbelievable extent; they are hardly more durable than basic dyes. The only possible explanation seems to me to be that the dyes are present in so finely divided a form as to approach a condition of solution and, therefore, to be far more exposed to light than they are in the more or less pigmented form in which they are present in cotton or viscose after soaping" (cf. White, *J.S.D.C.*, 1939, **55,** 412).

Durand & Huguenin A.-G. have recently patented a process (*Dyer*, 1944, **90,** 240) by which it is claimed that Indigosol dyestuffs can be applied to nylon so that the dyeings show a greatly increased fastness to light over those obtained by normal procedures. Nylon is dyed, e.g. with 1% Hydrosulphite NF conc. and 1% Indigosol dyestuff for 10 minutes at 30°C.; 2% acetic acid (80%) is added and the dyeing is allowed to proceed for a further 10 minutes at the same temperature; 2% formic acid (85%) is added, and after a further 10 minutes the bath is raised to 90°C. and dyeing is continued for 1 hour. Development is carried out with 1% potassium bichromate and 2% ammonium sulphocyanide, first for 10 minutes at 30°C., and then, after the addition of 10 ccs. sulphuric acid (168°Tw.) per litre of water, the bath is raised to 90°C. and development continued for 1 hour at this temperature. Neutralisation at 50°–60°C. with soda ash is followed by soaping at 90°C. for 15 minutes. Finally, the goods are steamed for 40 minutes at a pressure of 30 lb. per square inch.

The increase in light-fastness of the steam-treated dyeings is excellent, and it is conjectured that the increase is due to an agglomeration or flocculation of the originally fine dyestuff particles within the nylon fibres (cf. crystallisation theory, page 48).

The following Indigosols show a marked improvement:

Dyestuffs (1% *shade on Nylon*)	*Fastness to Light*	
	Unsteamed	*Steamed*
Indigosol Brilliant Orange IRK	1	7
Indigosol Scarlet IB	3	6
Indigosol Scarlet HB	3–4	6
Indigosol Pink IR extra	3–4	7
Indigosol Red Violet IRH	2	6
Indigosol Purple AR	1	4–5
Indigosol Printing Blue IB	3	6
Indigosol Brown IRRD	2	7
Indigosol Grey IBL	2	6

Improvement is noted in the following Indigosols:

Indigosol Yellow HCG	3	3–4
Indigosol Golden Yellow IGK	1	3
Indigosol Golden Orange I2R	2	3
Indigosol Orange HR	2	4
Indigosol O4B	2–3	4
Indigosol Green AB	3	3
Indigosol Brown IVD	1	3–4
Indigosol Violet ABBF	1	2

Indigosol Brilliant Violet I4R, Indigosol Green IB and Indigosol Green IGG (all dibenzanthrone derivatives) may be applied to nylon from a Glauber's salt bath and then developed as above without steaming treatment. These dyestuffs have light-fastness figures of 6–7, 7 and 7 respectively. Indigosol Brown IBR, Indigosol Blue IBC and Indigosol Olive Green IB, have not yet been successfully applied to nylon.

Casein Fibre and Aralac.—The high alkalinity normally required for the application of the vat dyestuffs precludes their employment on casein and other recently introduced prolons which are very sensitive to alkali. Carmichael (*American Dyestuff Rep.*, 1945, **34**, 173) has shown that Aralac and spun rayon fabrics may be dyed by padding them with vat dyes in the reduced form. Very short contact with the dyebath is necessary if alkali-damage is to be avoided. This writer further suggests that such fabrics may be pigment padded and then reduced on the jigger in a blank vat which has been buffered with sodium bicarbonate. It is possible that the indigoid vat dyestuffs and wool dyeing technique may offer some solution to the problems set by the prolons.

The solubilised vat dyestuffs have been applied to viscose rayon–Aralac mixtures by padding with sodium nitrite and subsequently developing in a sulphuric acid bath. The material is finally neutralised and washed with disodium phosphate and a synthetic detergent.

Jute.—Vat dyes are only employed on jute when exceptional demands are made for fastness to light, washing and cross-dyeing. When dyed jute is to be woven with white mohair or wool for later dyeing with selected acid dyes, it is essential that its cross-dyeing properties should be excellent. Jute may be dyed by the pigment padding process or by the usual reduced vat methods. In any case it is always advisable to cut down the quantity of alkali to a minimum, so as to avoid objectionable swelling and destruction of ligno-cellulose groupings. The use of protective colloids is useful in this respect.

Stripping.—The stripping of vat dyestuffs from textile fibres has always presented a great many difficulties. Shades which are too heavy may often be stripped to a small extent by a treatment in a fresh bath of caustic soda and hydrosulphite at high temperatures. Short treatments remove a little colour, but, if the goods are kept in the bath too long this small amount of reduced dyestuff will commence to dye on to the goods once more. Several treatments in rapid succession, using fresh reducing baths each time, are employed for the removal of more colour. These processes, however, are unsuccessful except for very small lots, and for economic reasons they are not to be recommended.

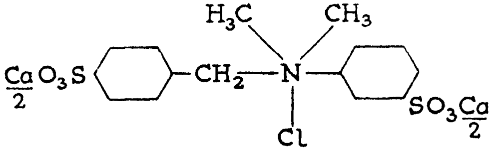
Many vat dyestuffs can be successfully stripped by the use of the sodium or zinc salts of sulphoxylate–formaldehyde compounds of the Erasol, Formosul or Vacolite type. These compounds are best employed as follows. The goods to be stripped are boiled for ½–1 hour in a solution containing 1% soda ash and 5% of the reducing agent, followed by an addition of 2% acetic acid. Objectionable odours are produced, however, and after washing-off the colour is very liable to re-oxidise. The latter defect is much less likely to occur when a magnesium salt is added; magnesium sulphate, chloride or hydroxide can be employed for this purpose.

By boiling vat-dyed cotton goods for 30 minutes in a liquor containing 12 lb. 70°Tw. caustic soda and 4 lb. sodium hydrosulphite per 100 gallons of water, then adding 10 lb. magnesium sulphate and boiling for a further 30 minutes, a very good strip is obtained with most vat dyestuffs. More even strips are obtained when levelling agents of the sulphite cellulose lye type are added to this bath.

The above methods are very difficult to control and very many pieces must have been spoiled in the early days of vat dyeing through the use of such rough stripping treatments. The introduction of new stripping auxiliaries has done much to advance the art of stripping, and the use of compounds such as Peregal O (I.G.), Albatex PO (S.C.I.) and Lissolamine V (I.C.I.) possesses many advantages over the foregoing procedures.

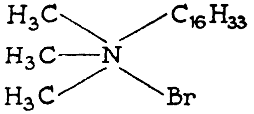
Condensation products of ethylene oxide with oleic, lauric, etc., acids, or the corresponding alcohols, as well as polymerisation products of ethylene oxide, possess high dispersing properties. Peregal O is the chief commercial example of this type of auxiliary agent and is employed in conjunction with hydrosulphite and caustic soda in the stripping bath. Dispersing agents of the benziminazol sulphonate type, e.g. Albatex PO, have also proved very useful under similar conditions. Thus, a liquor containing 4 lb. Albatex PO per 100 gallons, together with the necessary quantities of caustic soda and hydrosulphite, will strip indigo from cotton almost completely, whilst other indigoid and anthraquinonoid vat dyestuffs are stripped to a degree which is usually sufficient to permit a re-dyeing. The polyvinyl alcohols also possess stripping properties and are similarly applied in conjunction with caustic soda and hydrosulphite.

By far the best stripping agents for vat dyestuffs which are at present commercially available are the quaternary ammonium compounds. The Leucotropes (dimethylphenylbenzyl ammonium chlorides), e.g. Leucotrope W (XXXIV), have been employed for stripping and discharging vat dyestuffs for some time. Chemically, these compounds are very similar to the quaternary ammonium compounds represented by the Lissolamines.



(XXXIV)

Lissolamine V and similar commercial products are quaternary ammonium compounds based on the type cetyl pyridinium bromide, cetyl trimethylammonium bromide and octadecyl pyridinium bromide.



Cetyl Trimethyl
Ammonium Bromide

Lissolamine V is marketed as a light grey paste which forms milky solutions with water and possesses a slightly acid reaction. These compounds are not in themselves stripping agents, but are best defined as stripping promoters. For the purpose of stripping they are employed in conjunction with alkaline hydrosulphite. Many vat dyestuffs are stripped so completely that an almost white material is left; in other cases a small amount of colour is retained. In any case it is always possible to re-dye to the required shade.

The Hydron Blues are best stripped at 95°–100°C. in a bath containing 2% Lissolamine A, 4% caustic soda flakes and 5–6% sodium hydrosulphite; 30–45 minutes are usually sufficient to yield an effective stripping. The goods are then rinsed cold, chemicked for 15–30 minutes in cold ¼–½°Tw. sodium hypochlorite and finally rinsed, soured and soaped before re-dyeing.

The remaining vat dyestuffs may be stripped by using a liquor containing 3–5% Lissolamine V, 4–6% caustic soda flakes and 6% sodium hydrosulphite at 85°–90°C. for 30–45 minutes. The goods are then rinsed and chemicked as for Hydron Blues, improved results being obtained by adding ½–1% Lissolamine V to the hypochlorite bleach liquor. A list of Caledon and Durindone dyestuffs follow; they are grouped to show their reactions to stripping with Lissolamine V.

(*a*) *Unaffected:*

Caledon Blacks 2BS, 2BMS, and NBS
Caledon Golden Orange GS

(*b*) *Stripped to a slight degree:*

Caledon Blue 3GS
Caledon Green 2BS
Caledon Violet XBNS
Caledon Golden Orange 3GS
Caledon Red 2GS
Caledon Yellow GS

(*c*) *Stripped to a considerable degree:*

Caledon Direct Black ACS
Caledon Dark Blue BMS
Caledon Brilliant Purples 2RS and 4RS
Caledon Orange 2RTS
Caledon Yellow 5RS
Caledon Brilliant Blue 3GS
Caledon Navy Blue B
Caledon Green BNS
Caledon Brilliant Orange 4RS
Caledon Yellow Brown 3G
Alizanthrene Navy Blue R

(*d*) *Stripped to a very pale Shade:*

Caledon Blues BCD, GCS, GCDS, GCPS, RS, RCS, 2R, and 3GTS
Caledon Browns ER, XRS, BS, HG, HR, EG, GS, RS, 2G, and 5G
Caledon Jade Greens GS, XS, and BS
Caledon Greens RCS, 2G, and G
Caledon Brilliant Violets 2B and RS
Caledon Greys 2RDS and 3R
Caledon Dark Blues 2RDS and 3BS
Caledon Olive RS
Caledon Red X5BS
Caledon Brilliant Blue RS
Caledon Purple RS
Caledon Orange RS
Caledon Yellow 5GS
Durindone Reds BS and 3BS.
Durindone Scarlets 2B, 3B, and YS
Durindone Blue 4BCS
Durindone Pinks FFS and FBS

(*e*) *Stripped practically white:*

Durindone Blue 4BS
Durindone Brown GS
Durindone Orange GS
Durindone Red YS
Caledon Reds BNS, 5GS and FFS
Caledon Red Violet 2RNS
Caledon Yellow 3GS

(I.C.I., *Auxiliary Products*, *Pamphlet No.* 16.)

Lissolamines V and A are unsuitable for stripping vat dyestuffs from natural silk or wool because too much alkali is required, so vat-dyed shades (mainly from indigoid and Helindon dyes) which are either too heavy or uneven are usually difficult to correct. Animal fibres always suffer greatly in any process of stripping and, since alkaline hydrosulphite stripping is the only available method, it is often necessary to dispense with stripping and dye the goods to a deeper shade. Dyeings may be partially stripped by treating them for 30–45 minutes at 60° C. in a vat containing 2–3% dissolved glue (to serve as a protective colloid), 2–3% ammonia (25%), 1½–2% hydrosulphite and 2–4% Monopol Soap. The goods should then be thoroughly squeezed and allowed to oxidise before further treatment. Hawking machines are best employed for wool piece goods.

In the stripping of shoddy and vat-dyed rags it is possible to employ rather stronger alkaline liquors. The bath for this purpose is set at 70° C. with 5–8% soda ash, 2% sulphite cellulose lye agent and either 1% Prestabit Oil V or 2–5% Monopol Soap; 4% hydrosulphite is then sprinkled in and the rags or shoddy entered and treated for 45 minutes. Finally, rinse and sour.

CHAPTER IX

PRINTING AND DISCHARGING

A VERY detailed account of textile printing with the vat dyestuffs cannot be included within the compass of this small volume, and for detailed knowledge it is essential for the interested reader to consult such well-known standard works as *The Principles and Practice of Textile Printing*, by Knecht and Fothergill (Griffin, 3rd Edn., 1936), as well as the publications which appear from time to time in the trade and technical press. In the latter respect, it must be stated at this point that much of the information on the application of the Indigosols is based upon *Indigosols in Textile Printing and Padding* (*Recipes and Processes*, Part 1, 2nd Edn., 1936) by Durand & Huguenin, A.-G., and further details relating to this specialised branch of printing may be found in the original publication.

The total omission of the subject of textile printing would be a serious defect in a book which aims at providing a complete survey of all the uses of vat colouring matters. Indeed, it has often been said that the vat dyes provide the most important series of colours at the command of the textile printer. Only in certain respects are the vat dyestuffs rivalled by another prominent group of colours, viz. the azoic dyestuffs, which in many respects are supplementary to the vat dyestuffs and vice versa.

A brief survey of the methods and principles involved in the printing of vat dyestuffs is set out below. Styles of printing and recipes for the application of all forms of colouring matters are constantly changing. Methods vary widely from factory to factory, whilst local conditions and the demands of fashion and sales requirements call for many modifications in procedure and style. It is therefore impossible to give accurate details of the very latest technique. For these reasons only the broad outlines of the various aspects of vat-colour printing can be dealt with.

Vat dyestuffs can be applied in textile printing by means of a variety of styles, including the dyed, padded, direct printed, reserved, and discharged styles. They may also be employed in the production of coloured discharge effects upon dyed grounds of other dyestuffs, and in special cases upon vat-dyed grounds.

The high cost of vat dyestuffs restricts them to the more expensive fabrics such as are used in shirtings, certain dress materials, and for light and heavy furnishings. In these cases there is always a demand for excellency in resistance to such destructive influences as light and washing, and in this respect the vat dyestuffs and their solubilised derivatives are unsurpassed. There are, of course, many vat dyestuffs which are not of "Indanthrene" fastness, but it is not necessary to use these members of the group since a sufficient number of dyestuffs exhibiting the highest fastness is available.

From the physical point of view, vat dyestuffs for printing must be in a very fine state of division if they are to yield prints which are free from specks. Great care is therefore needed, both in their manufacture and in their preparation for printing. The "paste fine" and "powder fine for printing" types are usually the only ones employed by the fabric printer, although various special brands such as the Suprafix brands (I.G.) are particularly suitable.

It has already been pointed out that, in the application of vat dyestuffs by dyeing methods, it is necessary to convert the insoluble colouring matter into its soluble *leuco*-compound by means of alkaline reduction. After absorption of the *leuco*-compound by the fibre, it is necessary to restore the dyestuff to its insoluble form by means of air-oxidation or chemical oxidation. This principle is adhered to in vat-colour printing, but in this case "local dyeing" is achieved by forming the dyestuff pigment into a paste by means of a thickener, and applying it locally in the presence of an alkali and a reducing agent which only exerts its influence at elevated temperatures. Reduction of the dyestuff is subsequently brought about by passing the printed material through a steaming or ageing device, and the shade is finally developed by oxidation.

Thickening Agents.—The different styles of vat dyestuff printing demand the use of various special thickening agents, and in multi-coloured work different thickeners are often employed side by side to produce the different shades. Dark and light British gums are probably the most important thickeners, but wheat starch, gum tragacanth and crystal gums have their specific uses. For general work it has been shown that the highest colour value is obtained when starch thickeners are employed, but goods so printed exhibit a harsh handle in the areas of the printed design. Uneven results are often obtained with starch, especially when the design or pattern is of large size, but this may be counteracted by small additions of gum tragacanth.

Although the British gums yield rather less colour value than starch, their use is essential for all fine work and their cheapness is a great asset. Individual styles call for mixtures of printing gums, and the choice is mainly dependent upon the fabric and upon the alkali used in making up the print paste.

The reducing agent in general use is sodium sulphoxylate-formaldehyde, which is marketed under a variety of trade names, e.g. Formosul (Bro.) and Erasol (L.B.H.). During steaming, this compound decomposes, with consequent reduction of the vat dyestuff. The alkalis employed are sodium or potassium carbonate, caustic soda and caustic potash. Other compounds are often added to the print paste in order to obtain easy workability, fine dispersion of the colour particles, and brightness and clarity of the finished prints. Such compounds include glycerine, olive oil, cotton-seed oil, sodium benzylsulphanilate (Dissolving Salt (L.B.H.) and Solution Salt (I.C.I.)), phenolates, naphtholates and dihydroxydiethyl sulphide (Glyecine A (I.G.)).

Indigo—Direct Printing Styles for Cotton

The Glucose Process.—In this process the white cotton fabric is first prepared in a padding mangle with a 25% solution of glucose and the goods dried before printing. Thickenings of dark British gum and starch are employed, together with caustic soda, in the preparation of the printing colour. Where pale shades are to be applied it is necessary to reduce the normal print paste in strength, by additions of further quantities of alkaline thickener, gum Senegal and glycerine.

Steaming is carried out in moist steam at 100° C. for ½–1 minute. On leaving the ager the printed portions will be brownish-orange if they are at the correct state of reduction. A yellow colour indicates over-reduction of the indigo, and trouble in the subsequent oxidation of the goods is bound to follow. Steaming should always be carried out immediately after printing, since the caustic soda in the print paste has a strong tendency to absorb carbon dioxide and thus lose its power of reacting with the glucose and the indigo. After ageing, the steamed and printed goods are oxidised by passing them through a cold solution of potassium bichromate and D.O.V. Soaping completes the process.

The Hydrosulphite Process.—In many districts the glucose process has now been entirely replaced by the hydrosulphite process. The former method is said to be cheaper and is still employed to some extent for the production of pure indigo styles.

In preparing print pastes of the hydrosulphite type, the alkaline thickening agent (consisting of British gum and caustic soda) is first mixed with the Formosul type of reducing agent and heated until the latter has dissolved. After this reduction paste has cooled, the indigo paste and a further small quantity of alkaline thickening are added. Steaming of the printed goods is carried out with steam containing varying amounts of moisture (dependent upon the strength of the print) at 102°–104°C. After cooling, the fabric is rinsed in copious amounts of cold running water, and then soured and soaped on the continuous range in open width.

Indigosol O, i.e. the solubilised form of indigo, has replaced ordinary indigo to a large extent on account of its greater simplicity in working. The goods are printed with a starch-tragacanth thickened solution of Indigosol O containing small quantities of soda ash and Turkey Red oil, as well as the sodium nitrite required for oxidation. After printing, the fabric is dried, developed in dilute sulphuric acid, and then finished off in a similar manner to Indigosol dyeings.

Discharge Styles.—There are many processes for discharging dyed or printed indigo grounds. They fall into two classes, viz. oxidation processes and reduction processes, which are briefly described below. Amongst the former, the following are the most important:

(1) *The Chromate Discharge.*—In this process sodium bichromate thickened with British gum is printed on the indigo-dyed fabric, and the goods are then passed through a hot bath containing sulphuric and oxalic acids. Chromic acid is thereby liberated and exerts a strong oxidising action upon the indigo in the printed areas, the isatin dissolving out and leaving the desired white design. Coloured discharge effects are obtained by including suitable mineral pigments or azoic dye components in the discharge paste.

(2) *The Bromate Discharge.*—In this case the indigo-dyed cotton fabric is printed with a discharge paste consisting of sodium bromide, sodium bromate and a thickening agent. The printed goods are then treated in dilute sulphuric acid in order to liberate the bromine. The latter has a very strong oxidising action and, as in the chromate process, isatin is formed, with consequent production of a white discharge.

(3) *The Chlorate Discharge.*—The discharge print paste for this purpose is composed of sodium chlorate and a small amount of an oxygen carrier in the form of a vanadium salt or a ferricyanide, together with China clay, citric acid and British gum, starch or gum Senegal.

Steaming of the printed goods takes place in the rapid ager for 1–3 minutes. Coloured discharges cannot, in general, be produced by this process, although it is possible to produce Chrome Yellow discharges and various other effects of a similar nature. Special methods, however, have now been developed which permit the simultaneous application of anthraquinonoid vat dyestuffs and Naphtol AS combinations in conjunction with chlorate discharges.

(4) *The Prussiate Discharge.*—Medium and light shades of indigo may be discharged by printing the goods with red prussiate of potash and then treating with caustic soda. The process is often used in combination with azoic compounds of the β-naphthol class.

(5) *Nitrate Discharge* (Freiberger Process).—In this process, indigo-dyed goods are discharged by printing first with a thickened paste of sodium nitrate containing a little sodium nitrite. The goods are then dried and passed very rapidly through a bath of 30% sulphuric acid at 90°C, followed immediately by thorough rinsing. The liberated nitric acid, in conjunction with the sulphuric acid, totally destroys the indigo. Coloured discharges are prepared by treating the dyed fabric with a "naphtholate" and including a diazotised amino-compound in the discharge paste.

Reduction Processes for Discharging Indigo.—Reducing agents of the hydrosulphite–formaldehyde class can be employed in the production of white discharges on indigo grounds. Such compounds are applied in the form of a thickened print paste. The printed goods are dried and steamed for 3–5 minutes in air-free steam at 102°C., then given an immediate passage through a hot bath of caustic alkali, and finally soured, washed and soaped. Alternatively, the steamed goods are treated in hot sodium bisulphite solution prior to the alkali bath. There are many disadvantages attached to this process. The purity of the white discharge is very dependent upon the continuity of the process, and if the alkali treatment does not follow immediately after steaming the discharge is not produced. Additions of anthraquinone, acetin and zinc oxide are of great value in preventing such undesirable results.

Leucotrope compounds (tertiary bases with benzyl chloride) are now probably the most widely used discharging agents for indigo. They are used in conjunction with compounds of the hydrosulphite–formaldehyde type, the O brands yielding a bright golden-yellow discharge, whilst the W brands give a white discharge. Anthraquinonoid vat dyestuff discharges may be produced on indigo grounds with the aid of these products. Details of their application may be found in *The Principles and Practice of Textile Printing*, by Knecht and Fothergill (*loc. cit.*).

Other methods of discharging indigo by processes of reduction include the Glucose Discharge Process and the Titanium Discharge Process.

Resists or Reserves under Indigo Grounds.—In contrast to the white or coloured effects produced by discharging the dyed ground, the resist or reserve styles involve treatment of the fabric before dyeing. Discharging agents destroy dyestuffs, whilst resisting agents prevent the dyeing or fixation of dyes on the fabric.

Inorganic salts which possess an acidic and oxidising character, and are capable of being precipitated by the alkali of the dyebath in the form of gelatinous hydroxides, are employed for this purpose, particularly salts of copper, manganese, zinc and lead in the form of their acetates, chlorides, chromates, nitrates and sulphates. They are applied in thickeners which yield an elastic print which is resistant to mechanical damage. The function of the resist salts is to precipitate the dissolved *leuco*-indigo in the printed parts and so prevent dyeing in those areas. The resistance of the coating of thickener, as well as the formation of deposits of hydroxides, also inhibits dyestuff penetration. Both coloured and white resist effects can be obtained in this way, depending on the particular inorganic salts employed. If the cloth is first prepared with Naphtols and subsequently printed with resist pastes containing diazotised bases, it is possible to produce a large range of coloured effects.

Indigoid Vat Dyestuffs.—Derivatives of indigo, represented by the Durindone, Ciba and Helindon ranges, are applied in printing in much the same manner as indigo itself, although individual dyestuffs require modified processes. Much less alkali is required for the derivatives of indigo than for indigo itself, and the alkali carbonates usually replace the caustic alkalis in the printing pastes. The Formosul or Rongalite C type of reducing agent is almost always employed, although a stannic oxide–caustic soda process is suitable for some members of this class. The choice of thickening agents depends upon the style of printing to be used and, in particular, upon the nature of the fabric; in general, a mixture of British gum and gum Senegal yields the best results. Fixation is effected by steaming in the rapid ager at 102°C. and then oxidising in air, and is followed by the usual cold-water rinsing and final soaping.

Indigoid vat dyestuffs are very versatile printing dyestuffs, since they may be dyed, printed, discharged and resisted with equal ease. They can also be applied alongside azoic dyestuffs, steam colours, basic colours, vegetable colours and Aniline Black in the production of multi-coloured designs.

Anthraquinonoid Vat Dyestuffs.—The chief method of applying this class of vat dyestuffs to vegetable fibres is provided by the

Alkali Carbonate–Formosul Process. The print paste is made up as follows:

1–2	gallons Dyestuff Paste
4½	gallons British Gum Thickening
3	pints Glycerine
13½	lb. Potassium Carbonate
6–12	lb. Formosul, and
0–2	lb. Solution Salt BN (I.C.I.)
Bulked to 8	gallons

This print paste is reduced in strength as required by adding a quantity of the following Reduction Paste:

3	pints Glycerine
10	lb. Potassium Carbonate
5	lb. Formosul
0–2	lb. Solution Salt BN (I.C.I.)
7	gallons British Gum Thickening
Bulked to 8	gallons

The goods are printed and dried, and then steamed, either in the rapid ager for 4–7 minutes, or in the Festoon Drier for 20–25 minutes at 101°–102°C. As soon as possible after steaming, the goods are oxidised by passing them in open width through a solution of bichromate. The prints are then soaped at the boil.

The alkali carbonate–Formosul process is also very suitable for printing indigoid vat dyestuffs, and it is probably the most widely used method of printing vat dyestuffs, although other methods such as the pre-reduction process, the caustic alkali process and the non-ageing process may also be employed.

In the *Pre-Reduction Process* sodium hydrosulphite is used as the preliminary reducing agent. For this purpose, 1–2 gallons dyestuff paste are incorporated with 4 gallons thickening, 3 pints glycerine and 13½ lb. sodium carbonate or potassium carbonate; 2–3 lb. hydrosulphite are then worked well into the paste and the whole is heated in a steam-jacketed pan to 50°C. until reduction of the dyestuff is complete. The print paste is then allowed to cool down, 5–10 lb. Formosul are added and the volume is adjusted to 8 gallons.

Caustic soda may be employed in the initial reduction of the dyestuff, in conjunction with hydrosulphite, but it must be converted into sodium carbonate before printing by adding sodium bicarbonate. Thus, 1–2 gallons dyestuff paste are incorporated with 1 gallon thickening and 3 pints glycerine; 2 pints 90°Tw. caustic soda and 2–3 lb. hydrosulphite are then added and the mixture is worked well for 10–15 minutes while heating to 60°C. The reduced vat dyestuff paste is then allowed to cool and 5–7½ lb. sodium bicarbonate or potassium bicarbonate, as well as 3½ lb. potassium carbonate, are added. Finally, 5–10 lb. Formosul and a further 3 gallons of thickening are added and the whole bulked to 8 gallons.

By employing the pre-reduction process the ageing time may be shortened. Further, the print pastes may be applied immediately after preparation, whereas those of the alkali carbonate–Formosul type are only suitable for use after standing for several hours. The likelihood of uneven prints, however, is increased by the use of the pre-reduction technique, on account of the formation of a scum of oxidised colour on the surface of the paste in the colour box.

The *Caustic Alkali Process* is now almost entirely restricted to individual dyestuffs, e.g. the Blue RS types and the browns of the anthrimide class (Browns R and G, etc.). A thickening consisting of British gum, caustic soda and Formosul is employed. The greater the proportion of caustic alkali employed in the print paste, the greater is the colour yield on the printed goods. However, too much caustic alkali results in many working difficulties, and 4 gallons 90°Tw. caustic soda per 8 gallons of print paste (containing 4 gallons British gum thickening and 8 lb. Formosul) is about the quantity required for good working conditions. Fabrics of viscose rayon or other types of regenerated cellulose should not be printed by this process.

The *Non-Ageing Process*, or Ferrous Sulphate–Stannous Chloride Process, may be adopted for a large number of anthraquinonoid vat dyestuffs; indeed it is to be recommended for such dyestuffs as Caledon Direct Black ACS (as grey), Caledon Olive RS, Caledon Red FFS and Caledon Yellow 3GS.

The printing paste for this purpose is made up of the dyestuff, ferrous sulphate and a little stannous chloride. The printed and dried goods are then passed through warm 30°Tw. caustic soda, which reduces the dyestuff. Depending on the amount of dyestuff, from 2 to 12 lb. ferrous sulphate and up to 1% stannous chloride, based on the weight of the print paste, are employed.

The printed and dried fabric is treated in open width in the 30°Tw. caustic soda solution for ½–¾ minute at about 85°C., and then, after cooling, it is immersed in a second bath containing cold 15°Tw. caustic soda. After thorough rinsing to remove excess alkali, the goods are finally steeped for 1 hour in 4°Tw. sulphuric acid, rinsed again and soaped at the boil.

In order to prevent migration of the reduced dyestuff during the caustic soda treatments, additions of up to 10% Glauber's salt are made. Alternatively, aqueous manganese dioxide (1–10 gallons per 10–100 gallons caustic soda solution), prepared from 1 gallon of 72°Tw. manganese chloride solution and 3½ gallons water, may be used. This solution is then stirred into 1 gallon of 52°Tw. caustic soda and 3½ gallons of 12°Tw. bleaching powder solution.

Colloresine Process.—Colloresine DK is a methyl cellulose thickener which is insoluble in hot water and concentrated alkalis, but soluble in cold water. Prints in which methyl cellulose has been used do not mark off during steaming or boiling after-treatments. The prints may be dried after printing and stored for a considerable time without any fear of deterioration.

Colloresine DK is pasted with water at 70°C., containing a little ammonium thiocyanate. After cooling to 50°C., the solution is thickened with starch paste. A suitable paste may be made up as follows:

250 parts Dyestuff Paste
80 parts Water
20 parts Solution Salt B
350 parts Starch Thickening
50 parts Glycerine, and
250 parts Colloresine Solution

The printed and dried fabric is padded in a cold bath prepared from 70 parts Formosul, 33 parts soda ash, 50 parts glycerine, 33 parts Glauber's salt and 310 parts of water. A rapid steaming follows, and the goods are then rinsed, first in cold water (which removes the Colloresine) and then in hot water, and finally soaped at the boil. The Colloresine process is particularly suitable for screen printing.

Discharge Styles and Discharging Vat-Dyed Grounds.—The anthraquinonoid and indigoid ranges of vat dyestuffs, when applied to direct- or azoic-dyed grounds by the alkali carbonate–Formosul process, are suitable for obtaining coloured discharge effects. On account of their brilliance of shade and their excellent fastness properties, these dyestuffs, in particular the indigoid range, are ideal for the purpose of "illumination." With certain direct cotton dyestuffs which are difficult to destroy, it is often necessary to make additions of anthraquinone, which aids the discharging effect of the Formosul by acting as a catalyst.

In order to prevent the transference of small amounts of print paste on to the ground shades, which would result in a general dulling of the undischarged areas, it is advisable to prepare the goods prior to printing, by padding them in solutions of Resist Salt L (sodium *m*-nitrobenzene sulphonate). If the ground shade has been obtained by the use of dyestuffs which are sensitive to alkali, a pre-treatment with a solution of a weak acid, e.g. citric acid, will counteract any undesirable large change in shade. The glycerine content of the print paste is usually regarded as the deciding factor to be regulated in the event of the formation of white rings or "halos" round the vat-printed portions.

The actual discharging of vat-dyed grounds is probably one of the calico printer's most difficult problems. With only a few exceptions, chlorate or Leucotrope pastes have little effect and, consequently, special methods have to be employed. Rongalite–Leucotrope discharge processes are the only ones capable of providing any degree of success at present, and their success depends upon the method employed in the production of the vat-dyed grounds.

Goods for this purpose are probably best dyed by the continuous process, with an immersion period of not more than 20 seconds. This method of dyeing is particularly suitable for dyeings of the anthraquinoneazine blues (RS and GCD) and for the Jade Greens. However, ordinary jigger dyeings, as well as those produced by pigment dyeing methods, will, in the majority of cases, yield good discharge effects. With many vat dyestuffs, pre-treatment of the goods with a solution of Leucotrope W Conc. is necessary before they are discharged; other vat dyestuffs, however, can be discharged satisfactorily without any preliminary treatment.

Many vat dyestuffs may be discharged to a degree described as "good to very good" by the use of the following strongly alkaline white discharge paste, without any pre-treatment:

20	parts British Gum
80–130	parts Water
50	parts Glycerine or Glyecine A
100	parts Zinc Oxide (1:1)
300	parts Rongalite CL (or equivalent)
75–125	parts Leucotrope W Conc. (or equivalent), and
375–275	parts 91°Tw. Caustic Soda
1,000	parts

(page 186), besides resisting vat dyestuffs, acts as an oxidising agent for the Indigosols.

Battik Dyeing.—This is an ancient Oriental process of ornamentation originally used for the production of resisted pattern effects upon sarongs, etc., use being made of the water-repellent nature of waxes and resins in the preparation of designs. Penetration of dyestuffs into the prepared areas is thus prevented, and, after dyeing, the resist is removed either by soaping or by solvent extraction, and the undyed portions are left in the form of a white design upon a dyed ground.

There are many modern modifications of this ancient process, and the cold-dyeing vat dyestuffs play an important part in the production of durable fabrics printed in this style; β-naphthol is often employed to prevent saponification of the wax resists during dyeing.

The Sulphurised Vat Dyestuffs.—Hydron Blues, Hydron Black C, and the Indo Carbon Blacks are widely used in the printing of cellulosic fabrics. They are applied in a manner similar to that used for anthraquinonoid vat dyestuffs, using print pastes thickened with starch–tragacanth, gum Arabic or British gum, and including an alkali-metal carbonate, glucose, and a reducing agent of the sulphoxylate–formaldehyde class. The following examples will serve to illustrate the formulation of print pastes for this class of colouring matters:

150 parts Hydron Printing Blue 3R Paste, stirred into
30 parts Glycerine
30 parts Glyecine A
150 parts Water
500 parts Starch–Tragacanth Thickening
70 parts Potassium Carbonate
70 parts Rongalite C (I.G.)

1,000 parts

120 parts Hydron Black C Suprafix Powder, stirred (cold) into
750 parts Special Thickener
130 parts Water are then added

1,000 parts

The Special Thickener for this purpose consists of:

550 parts Starch–Tragacanth Thickening, stirred with
40 parts Glycerine
40 parts Glyecine A
65 parts Soda Ash
200 parts Glucose (1:1)
40 parts Rongalite C
45 parts Water. This is heated slightly, and then
20 parts Depanol J (I.G.) are added

1,000 parts

The above print pastes are allowed to stand overnight before use. The printed goods are dried and then steamed in the rapid ager for 3–5 minutes. They are then oxidised with either sodium perborate or sodium bichromate and acetic acid. Finally, the prints are rinsed and soaped at the boil.

Printing with Indigosol and Soledon Dyestuffs.—The solubilised vat dyestuffs possess excellent printing properties and can be printed by a large variety of processes. Each process possesses specific advantages for particular purposes, and some of these advantages will be enumerated along with the descriptions of the more important processes which are given below.

For the purpose of direct printing, the following processes come into consideration:

(1) Bichromate Process
(2) Nitrite Process
(3) Sulphocyanide Steaming Process
(4) Developer Steaming Process
(5) Ammonium Chlorate Steaming Process
(6) Urea–Durit Process
(7) Aluminium Chlorate Hanging Process
(8) Persulphate Hanging Process

Apart from individual members, e.g. Indigosol Brown IVD, dyestuffs in the solubilised ranges are not suitable for application by all the above processes. Most Indigosol and Soledon dyestuffs, however, can be applied by at least four of them, and outstanding exceptions will be noted in the following descriptive outlines.

(1) *The Bichromate Process.*—Examples of print pastes for this process are as follows:

(*a*) 50 parts Indigosol Golden Yellow IGK
100 parts Dehapan O (D.H.)[1]
350 parts Water
500 parts Neutral Starch–Tragacanth

1,000 parts

Heat up to dissolve; cool before use.

(*b*) 60 parts Indigosol Golden Yellow IRK
60 parts Glyecine A
30 parts Indigosol Developer D (D.H.)
250 parts Water
600 parts Neutral Starch–Tragacanth

1,000 parts

Heat up to dissolve; cool before use.

(*c*) 80 parts Indigosol Printing Violet IBBF
50 parts Dehapan O
360 parts Water
500 parts Neutral Starch–Tragacanth
Heat up to dissolve, and then add
10 parts Oxalic Acid Crystals

1,000 parts

(*d*) 60 parts Indigosol Red HR
410 parts Water
500 parts Neutral Starch–Tragacanth
Heat up to dissolve, and then add
30 parts Ammonium Oxalate Crystals

1,000 parts

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[1] Dehapan O has been stated to be a preparation of urea and cresylic acid.

(*e*) 60 parts Indigosol Brilliant Pink I3B
100 parts Dehapan O
90 parts Water
500 parts Neutral Starch–Tragacanth
Heat up to dissolve, and then add
50 parts Soda Ash (10%)
200 parts Bichrome (10%)

1,000 parts

(*f*) 50 parts Soledon Green GS
50 parts Solaval B (I.C.I.)
50 parts Solafix F (I.C.I.)
350 parts Water
500 parts Neutral Starch–Tragacanth

1,000 parts

Heat up to dissolve, and then cool down before use.

All the above starch–tragacanth thickenings should be neutralised with soda ash.

The dyestuff is first pasted with the prescribed quantity of the auxiliary solvent preparation, e.g. Dehapan O or Solaval B. Water at 90°C. is then poured on, and when the dyestuff is dissolved, the thickening is added. Heating is continued in a water-bath or steam-jacketed pan until the colour paste is smooth and free from specks of undissolved dye. The paste is then cooled and strained and any other compounds which may be required are dissolved and added.

The printed fabrics are dried and then immersed for 2 seconds in a bath containing 3 oz. bichromate and ¼ pint D.O.V. per gallon of water at 35°C. An even squeeze between bowls precedes a short air-run before the goods are finally washed off, neutralised, and soaped at the boil. Indigosol Brilliant Pink I3B can be considerably improved in respect of yield by steaming before developing. Certain other brands show slight improvement. Indigosol Blue IBC, Indigosol Olive Green IB and Indigosol Printing Black IB, cannot be applied by the Bichromate Process.

The Neutral Chromate Process is described on page 176.

(2) *The Nitrite Process.*—Print pastes for this process are made up according to the examples given below:

(*a*) 100 parts Indigosol Blue IBC
360 parts Water
500 parts Neutral Starch–Tragacanth
Heat to dissolve, and then add
20 parts Soda Ash (10%)
20 parts Sodium Nitrite (30%)

1,000 parts

(*b*) 60 parts Indigosol Olive Green IB
100 parts Dehapan O
275 parts Water
500 parts Neutral Starch–Tragacanth
Heat to dissolve, and then add
20 parts Soda Ash (10%)
45 parts Sodium Nitrite (30%)

1,000 parts

(*c*) Reduction Paste for Nitrite Printing Pastes
978 parts Neutral Tragacanth (80:1,000)
20 parts Sodium Nitrite (30%)
2 parts Soda Ash

1,000 parts

All thickenings for this purpose should be neutralised with soda ash.

The printed and dried goods are passed for 8 seconds through a 2% solution of sulphuric acid at 70°C. A short air passage then precedes the usual rinsing, neutralising and boiling soap treatments.

In preparing the print pastes, the dyestuff is first pasted with Dehapan O, if this is required, and then diluted with water at 70°–90°C. whilst stirring thoroughly. The thickening is then added and the whole is heated on the water-bath until the paste is smooth and free from specks. Whilst dissolving and mixing, the temperature of the print paste should be 60°–70°C. The sodium nitrite should only be added when the paste has cooled to 40°C. and is best added just prior to use. The pastes prepared in the above manner are almost of unlimited stability, provided that they are protected against the action of direct sunlight and acid fumes.

Indigosol Brilliant Pink I3B, Indigosol Red Violet IRH, and Indigosol Golden Yellow IRK are not applied by the normal Nitrite Process. The first two dyestuffs mentioned are only partially developed; the Golden Yellow is precipitated despite the addition of solvents. For the latter reason it is usual to employ the *Special Nitrite Process* for Indigosol Golden Yellow IRK. By this method, sodium nitrite additions to the print paste are omitted, but in other respects the formulation is the same as for the normal procedure. After the goods have been printed and dried they are padded in a bath containing 50 parts neutral thickening per litre of 4% sodium nitrite solution. The fabric then passes into the usual sulphuric acid developing bath and is finished off as usual.

Certain dyestuffs give an improved yield if a short steaming treatment is included prior to development. Especially worthy of note in this respect are Indigosol Green IB, Indigosol Brown IBR, Indigosol Brown IRRD, and Indigosol Yellow HCG. When printing viscose rayon crêpe, steaming before development will be found to give a greatly increased yield when using Indigosol Scarlet HB, Indigosol Pink IR extra, Indigosol Green IB, Indigosol Brown IBR, Indigosol Brown IRRD, and Indigosol Printing Black IB.

(3) *The Sulphocyanide Steaming Process.*—This is the oldest of the existing steaming processes (cf. (4) and (5) below) and may be carried out by (i) the *Short Steaming Method*, and (ii) the *Long Steaming Method.*

Examples of print paste formulation for (i) are:

(*a*) 60 parts Indigosol Printing Blue IB
383 parts Water
500 parts Neutral Starch–Tragacanth

Heat to dissolve, then add, hot

20 parts Sodium Chlorate (1:3)
30 parts Ammonium Sulphocyanide (1:1)

Cool and add

7 parts Ammonium Vanadate (1%)

1,000 parts

(*b*) 30 parts Indigosol Pink IR extra
200 parts Dehapan O
170 parts Water
500 parts Neutral Starch–Tragacanth
Heat to dissolve, then add, hot
40 parts Sodium Chlorate (1:3)
40 parts Ammonium Sulphocyanide (1:1).
Cool and add
20 parts Ammonium Vanadate (1%)

1,000 parts

(*c*) Reduction Paste for the Short Steaming Process:

205 parts Water
750 parts Neutral Tragacanth (80:1,000)
10 parts Sodium Chlorate (1:3)
15 parts Ammonium Sulphocyanide (1:1)
10 parts Ammonium Vanadate (1%)
10 parts Ammonia (25%)

1,000 parts

The goods are printed, dried, steamed for 8–15 minutes, rinsed, and soaped at the boil. Indigosol Pink IR extra and Indigosol Scarlet HB must not be steamed for less than 10 minutes. Indigosol Brown IRRD is not printed by the Sulphocyanide Process whilst Indigosol Green AB, is best applied by the Developer Process (4).

Examples of print paste formulation for (ii) are:

(*a*) 60 parts Indigosol Printing Blue IGG
50 parts Dehapan O
236 parts Water
600 parts Neutral Starch–Tragacanth
24 parts Sodium Chlorate (1:3)
20 parts Ammonium Sulphocyanide (1:1)
10 parts Ammonium Vanadate (1%)

1,000 parts

(*b*) 50 parts Indigosol O4B
304 parts Water
600 parts Neutral Starch–Tragacanth
16 parts Sodium Chlorate (1:3)
20 parts Ammonium Sulphocyanide (1:1)
10 parts Ammonium Vanadate (1%)

1,000 parts

(*c*) Reduction Paste for the Long Steaming Process:

226 parts Water
750 parts Neutral Tragacanth (80:1,000)
8 parts Ammonium Sulphocyanide (1:1)
6 parts Sodium Chlorate (1:3)
10 parts Ammonium Vanadate (1%)

1,000 parts

All the thickenings used in the above steaming processes must be first neutralised with ammonia.

The goods are printed, dried, steamed for 1–2 hours, and finally washed and soaped at the boil.

(4) *Developer Steaming Process.*—This is another steam-developed style in which use is made of Soledon Developer T (I.C.I.) or Indigosol Developer D (D.H.); the latter product has been stated to be diethyl tartrate, and in addition to being a solvent for the solubilised vat dyestuff, it will liberate acid during steaming operations. This method of printing is rather more expensive than the Sulphocyanide Process and it is therefore usually employed for those dyestuffs which do not work well (or not at all) with the Sulphocyanide Process.

Almost all of the dyestuffs in the solubilised ranges can be applied by the Developer Process, but those dyes for which this method is most recommended are:

Indigosol Golden Yellow IGK
Indigosol Pink IR extra
Indigosol Green AB
Indigosol Golden Yellow IRK
Indigosol Scarlet HB
Indigosol Brown IRRD.

Examples of print pastes suitable for this process are set out below:

(*a*)	40 parts	Indigosol Brown IRRD
	60 parts	Indigosol Developer D (D.H.)
	50 parts	Dehapan O
	270 parts	Water
	500 parts	Neutral Starch–Tragacanth
		Mix cold and then add
	40 parts	Sodium Chlorate (1 : 3)
	10 parts	Ammonium Vanadate (1 %)
	30 parts	Ammonia (25 %)
	1,000 parts	

(*b*)	60 parts	Soledon Dark Brown 3RS
	80 parts	Soledon Developer T (I.C.I.)
	140 parts	Hot Water
	600 parts	Neutral Starch–Tragacanth
		Heat to dissolve, and then add
	100 parts	Sodium Chlorate (10 %)
	20 parts	Ammonium Vanadate (1 %)
	1,000 parts	

The printed goods are dried, steamed for 10–15 minutes and, finally, rinsed and soaped at the boil.

When printing solubilised vat dyestuffs alongside the chrome dyes (i.e. where longer steaming is required), it is necessary in many cases to reduce the quantity of developer employed, so that steaming can proceed with safety for periods of up to 1 hour. This precaution also applies to the Sulphocyanide Steaming Process.

(5) *Ammonium Chlorate Steaming Process.*—This is the most recent and also the shortest of the steaming processes; oxidation is obtained with only 2 minutes steaming. The majority of print pastes prepared according to the examples given below are very stable and keep perfectly well for periods extending from 8–15 days.

Certain viscose rayon fabrics, e.g. crêpes, require an extended steaming time of 4–8 minutes in order to obtain complete development of the dyestuff.

Examples:

(*a*) 120 parts Indigosol Printing Black IB
270 parts Hot Water
550 parts Neutral Starch–Tragacanth
50 parts Ammonium Chlorate (23°Tw.)
Cool and then add
10 parts Ammonium Vanadate (1%)

1,000 parts

(*b*) 40 parts Indigosol Red Violet IRH
200 parts Dehapan O
10 parts Hot Water
550 parts Neutral Starch–Tragacanth
150 parts Ammonium Chlorate (23°Tw.)
Cool and then add
50 parts Ammonium Vanadate (1%)

1,000 parts

Ammonium Chlorate Solution of 23°Tw. is prepared by pouring a solution of 133 g. ammonium sulphate dissolved in 450 ccs. water into a solution of 323 g. barium chlorate dissolved at the boil in 400 ccs. water. After settling, the solution is filtered and adjusted to 23°Tw.

(6) *The Urea–Durit Process.*—The print paste for this process is made up in accordance with the following example:

70 parts Indigosol Yellow V
140 parts Urea
70 parts Durit ADF (D.H.)
115 parts Water
500 parts Neutral Starch–Tragacanth
70 parts Neutral Chromate Solution (1:2)
35 parts Ammonium Sulphocyanide (1:1)

1,000 parts

The printed and dried fabric is steamed for 4 minutes in the presence of acetic or formic acid vapour, and is then fully developed by a passage of 6 seconds at 40°C. though a 2% sulphuric acid solution containing ½% bichrome on the weight of the bath. Finally, the fabric is rinsed and soaped as usual.

With the Indigosol Golden Yellows IGK and IRK, Indigosol Greens AB and IB, and Indigosol Brown IRRD, ammonium sulphocyanide is omitted from the print pastes. In the case of Indigosol Blue IBC, the addition of neutral chromate solution yields green and dull prints, and it is therefore omitted. An addition of furfuryl alcohol (equal to the weight of dyestuff) is found to improve prints of the Indigosol Golden Yellows IGK and IRK. Furfuryl alcohol (twice the weight of dyestuff) has a similar effect upon Indigosol Brown IRRD.

The Urea-Durit Process is especially suitable for use alongside the Rapidogen dyestuffs, and to some extent it has replaced the *Ferric Nitrate Process.* Printing pastes for the latter contain neutral sodium chromate powder and Durit O (Carbic Chem. Co.), and after printing and drying the goods are developed by a short treatment at 65°–80°C. in a bath containing 40 ccs. sulphuric acid (168°Tw.) and 40 ccs. ferric nitrate mordant (97°Tw.) per litre of water. Iron is then removed (after a short air-run and rinse) by treatment with oxalic acid and sodium acetate. Finally, the goods are soaped at the boil as usual. The Ferric Nitrate Process is still practised in the United States.

(7) *The Aluminium Chlorate Hanging Process.*—This is a very simple process in which the solubilised vat dyestuffs are developed without steaming or without passing the material through a developing bath.

The material is first padded in a solution containing 0·1% ammonium vanadate and 0·5% tartaric acid and dried without rinsing. After printing and drying completely, the goods are allowed to hang for about 24 hours until the dyestuffs are fully developed. Washing and soaping are then carried out as usual.

Examples of print pastes:

(*a*) 80 parts Indigosol O
60 parts Glyecine A
260 parts Water
550 parts Starch–Tragacanth
20 parts Tartaric Acid (10%)
30 parts Aluminium Chlorate (32°Tw.)

1,000 parts

(*b*)
60 parts Indigosol Orange HR
50 parts Dehapan O
60 parts Glyecine A
280 parts Water
500 parts Starch–Tragacanth
20 parts Tartaric Acid (10%)
30 parts Aluminium Chlorate (32°Tw.)

1,000 parts

(*c*) Reduction Paste for the Aluminium Chlorate Process:

900 parts Tragacanth Thickening (80:1,000)
50 parts Glyecine A
20 parts Water
10 parts Tartaric Acid (10%)
20 parts Aluminium Chlorate (42°Tw.)

1,000 parts

Aluminium Chlorate Solution 42°Tw. is prepared by adding a solution of 790 g. barium chlorate dissolved in 800 ccs. boiling water to a solution of 528 g. aluminium sulphate dissolved in 550 ccs. boiling water. The precipitated barium sulphate is allowed to settle, and the decanted liquor is filtered and adjusted to 42°Tw. by evaporation on the water-bath at 60°C.

In making up the printing pastes it is advisable to dissolve the dyestuff in water, add the solution to the thickener, and heat in a jacketed pan whilst stirring. When the colour paste is smooth and transparent, cool down to 30°–40°C., add the tartaric acid and follow with the aluminium chlorate. Finally, cool to room temperature and strain. The Glyecine A, besides acting as a solvent for the dyes, also accelerates the development.

The Aluminium Chlorate Process is suitable for machine work, but it is of particular interest for screen, block, and aerograph or spray printing; it is also employed in the printing of yarns.

(8) *The Persulphate Hanging Process.*—This is a modified hanging process similar in principle to the last. The oxidising element in the print pastes in this case is ammonium persulphate.

An example of a printing paste for this purpose is given below.

60 parts	Indigosol Brown IVD
60 parts	Dehapan GB (D.H.)
50 parts	Dehapan O
170 parts	Water
550 parts	Starch–Tragacanth
60 parts	Ammonium Chlorate (23°Tw.)
40 parts	Ammonium Persulphate (1:3)
10 parts	Ammonium Vanadate (1%)
1,000 parts	

The printed fabrics are allowed to develop by hanging them for 24 hours, as in the Aluminium Chlorate Process mentioned above.

Direct Printing with Indigosol and Chrome Dyestuffs.—The Indigosol dyestuffs may be employed for the purpose of complementing the chrome dyestuff range. Where fast-to-light, pale and medium shades of violet, blue or green are required in a multi-coloured chrome dyestuff print, the solubilised vat dyestuffs can be employed to advantage. Amongst the dyestuffs used for this purpose, the following are especially worthy of mention:

Indigosol Green IB
Indigosol Blue IBC
Indigosol O4B
Indigosol Pink IR extra
Indigosol Printing Blue IGG
Indigosol Printing Violet IBBF
Indigosol Red Violet IRH

In certain cases it is also possible to mix Indigosol and chrome dyes in the same print paste, e.g. a bright yellowish-green is given with a combination of Indigosol Green IB and a yellow chrome dye of the Chromotartrine or Chromocitronine type.

In making Indigosol prints it is often necessary to produce such expensive shades as nigger browns, chestnuts, navy blues and blacks, and for economic reasons it is permissible to use the chrome dyestuffs. By the use of Fixer CDH (D.H.) and chromium acetate, it is possible to cut down the steaming time of most chrome dyes to 8 minutes when one of the short steaming recipes is employed. If necessary, however, it is of course possible to develop chrome and Indigosol prints by steaming them for 1 hour.

Direct Printing with Indigosol and Azoic Dyestuffs.—Here, the following groups must be discussed.

(*a*) Indigosols printed with Rapidogen and Rapid Fast dyestuffs.
(*b*) Indigosols and Azoic Colours printed on Naphtol Prepare.
(*c*) Indigosols and "naphtolates" printed on white fabric and then developed with diazotised Fast Colour Bases.

(*a*) The *Rapidogen and Rapid Fast* dyestuffs only exhibit good fastness properties in deep shades, and for this reason it often becomes necessary to supplement them with Indigosols, particularly when fast styles are required. Furthermore, many of the shades which can be obtained with the following solubilised vat dyestuffs cannot be obtained with the present ranges of stabilised azoic dyestuffs.

Indigosol Green IB
Indigosol Blue IBC
Indigosol O4B
Indigosol Grey IBL
Indigosol Printing Blue IGG
Indigosol Printing Violet IBBF
Indigosol O6B

There are four main methods of carrying out this class of work, viz.:

Steaming Processes.—These may be used for side-by-side prints of Rapidogens or Rapid Fast Colours and Indigosols, but not for mixtures of these dyes. Short steaming processes are preferred; the Ammonium Chlorate Process is recommended, but tragacanth thickening and Turkey Red oil should be used. Steaming should be carried out in acid vapours, or, if this is undesirable, development in an acid bath containing acetic acid, formic acid and Glauber's salt may be employed.

Nitrite Process.—By this process, Indigosols and Rapid Fast colours may (after separate preparation) be mixed and applied from a single print paste. The Nitrite Process may also be used for side-by-side printing of the Indigosol, Rapidogen, and Rapid Fast classes. After printing, a short acid steaming is given, and then the goods are padded with sodium nitrite in tragacanth thickening and developed immediately in a 2% solution of sulphuric acid at 70°C.

Bichromate Process.—This process may be used for either side-by-side or for mixed prints. (*a*) *Without Steaming*: either the Bichromate or the Neutral Chromate Process (page 176) may be employed. When the Rapidogen or Rapid Fast dyes are to be mixed with Indigosols, then Dehapan O is replaced by Fixer CDH. After printing and drying, the goods are padded in an acetic–formic acid bath, dried over drums and developed in the usual bichrome-acid bath, or, if the Chromate method is employed, in a bath containing sulphuric acid, oxalic acid, and Glauber's salt. (*b*) *With Short Acid Steam and Acid Bath Development*: development of the Rapidogen and Rapid Fast dyestuffs is accomplished by an acid steaming, and the Indigosols are subsequently developed in the acid oxidising bath.

Aluminium Chlorate Process.—(*a*) *Without Steaming:* the goods are prepared with ammonium vanadate and tartaric acid (page 170). and the printing pastes are prepared as for the ordinary Aluminium Chlorate Process. Rapid Fast colours are prepared in the usual manner with the addition of a little caustic soda and neutral chromate. Rapidogens require special preparation. The printed and dried goods are allowed to lie in a warm room for 24 hours in order to allow the Indigosols to develop. The Rapid Fast colours and Rapidogens are then developed by a short hot passage through a mixed acid bath containing acetic acid, formic acid and Glauber's salt. (*b*) *With Short Acid Steaming*: a short acid steaming develops all three classes of dyestuff simultaneously.

(*b*) *Indigosols and Azoic Colours Printed on Naphtol Prepare.*—It is often necessary to employ the azoic colours alongside the solubilised vat dyestuffs in order to fill the shade gaps present in either of the ranges. Furthermore, weak (or reduced) prints of azoic dyestuffs are not generally of very high fastness. For the latter reason it is usual to employ Indigosols when pale shades are required.

In combination styles of this kind the brightest results are obtained by the steaming processes. The processes usually employed are:

(i) The Nitrite–Oxalic Acid Process.
(ii) The Nitrite–Sulphuric Acid Process.
(iii) The Lead Chromate Process.
(iv) The Neutral Chromate Process.
(v) The Aluminium Chlorate Process.
(vi) The Ammonium Oxalate Steaming Process.

Briefly, these processes are carried out as follows:

(i) *Nitrite–Oxalic Acid Process.*—The Indigosol print pastes prepared according to the following example are applied to Naphtol-prepared cloth alongside the Fast Colour Bases or Fast Salts.

80 parts Indigosol O
2 parts Soda Ash
268 parts Hot Water
600 parts Starch-Tragacanth (faintly alkaline with ammonia).
Heat until dissolved, cool down, and then add
50 parts Sodium Nitrite (1:2).
1,000 parts

Reduction Paste:
600 parts Tragacanth Thickener (80:1,000)
380 parts Water
20 parts Sodium Nitrite (1:2)
1,000 parts

After printing and drying, the fabric is passed through a bath containing 30 g. oxalic acid crystals per litre of water at 20°C. The fabric is then squeezed and given a brief air passage, and finally rinsed and soaped at the boil.

White grounds become yellowed during the acid development, but they may be cleared again by passing the fabric through boiling caustic soda (1·4°Tw.), rinsing well, and then soaping at the boil.

(ii) *Nitrite-Sulphuric Acid Process.*—The printing pastes are prepared as for the ordinary Nitrite Process (page 163) and are applied to Naphtol-prepared goods alongside Fast Bases or Fast Salts. After printing and drying, the goods are passed in open width at 20°–60°C. through a bath containing 20 ccs. sulphuric acid (168°Tw.) and 10 ccs. formic acid (90%) per litre of water. The formic acid has a favourable influence upon the white reserves and also retards the evolution of nitrous fumes during development. Discoloured whites may be cleared by a dilute caustic soda treatment. The printed fabric is then finished as usual.

(iii) *Lead Chromate Process.*—This process is only employed in print-works where the Reserve Style Under Variamine Blue is practised, the advantage being that the print pastes used in the latter operation may also be applied to Naphtol-prepared goods with lead chromate. Paste formulation is described under Variamine Blue (page 184); after printing and drying, the goods are treated for 30 seconds at 80°C. in a bath containing 30 ccs. hydrochloric acid (30°Tw.) per litre of water. Finally, they are washed, soaped at the boil, rinsed and dried.

The density of the prints and brilliance of shade produced by this process are usually inferior to the results obtained by the use of processes (i) and (ii) described above.

(iv) *Neutral Chromate Process.*—The Bichromate Process of direct printing cannot be employed for printing the Indigosols upon Naphtol-prepared goods; the main reason for this is that the whites are very much soiled by the developing bath. The Neutral Chromate Process, however, is quite suitable for this purpose; printing colours are made up according to the following example and then applied to Naphtol-prepared fabrics alongside Fast Bases or Fast Salts.

40–100	parts Dyestuff
20–150	parts Dehapan O
363–165	parts Hot Water
500	parts Starch-Tragacanth Thickening (neutralised with soda ash)
75–120	parts Neutral Chromate Solution (1:2)
2	parts Soda Ash
1,000	parts

Reduction Paste for the Neutral Chromate Process:

700	parts Neutral Tragacanth (80:1,000)
10	parts Dehapan O
14	parts Neutral Chromate Solution (1:2)
276	parts Water
1,000	parts

The Neutral Chromate Solution (1:2) may be prepared as follows: 100 g. sodium bichromate crystals are dissolved in 350 ccs. cold water. Whilst stirring, 61 ccs. caustic soda (71°Tw.) are added; this yields 450 ccs. of a 1:2 solution of neutral sodium chromate in water.

The printed goods are dried and developed by an 8-seconds passage at 35°C. through a bath containing 25 ccs. sulphuric acid (168°Tw.), 30 g. oxalic acid, and 50 g. calcined Glauber's salt per litre of water. Finally, the developed prints are rinsed, neutralised, and soaped at the boil.

(v) *Aluminium Chlorate Process.*—Preparation of the fabric with Naphtol AS is carried out by the following special procedure.

17·5 parts Naphtol AS
20 parts Caustic Soda (62°Tw.)
16 parts Monopol Brilliant Oil
832 parts Boiling Water
Dissolve and add whilst hot—
5 parts Acid-resisting Wetting Agent (10 %)
100 parts Ammonium Vanadate (1 %)

1,000 parts

Padding is done at 80°C.

Indigosols and Fast Bases or Fast Salts are then printed on the dried goods. The Indigosol print colours are prepared as below:

80 parts Indigosol Printing Violet IBBF
100 parts Glyecine A
160 parts Water
500 parts Starch-Tragacanth Thickening
40 parts Aluminium Sulphate (1:1)
120 parts Aluminium Chlorate (42°Tw.)

1,000 parts

The printed material is then allowed to lie overnight (viscose rayon being given a preliminary short steaming) so that the Indigosols become fully developed. The Aluminium Chlorate Process can also be employed for the production of reserves under Variamine Blue (page 185).

(vi) *Ammonium Oxalate Steaming Process.*—Naphtol-prepared cloth is printed with Indigosol pastes made according to the following example. The goods are then dried and steamed for 8 minutes, and finally washed and soaped at the boil. Whites may be cleared by the caustic soda treatment described above.

60 parts Indigosol Yellow HCG
50 parts Dehapan O
185 parts Water
600 parts Tragacanth Thickening (80:1,000)
Heat to dissolve, and then add:
35 parts Ammonium Oxalate (or Ammonium Sulphocyanide)
Cool, and then add
60 parts Sodium Chlorate (1:3)
10 parts Ammonium Vanadate (1 %)

1,000 parts

Such colour pastes may also be employed for the production of resists under Variamine Blue (page 183).

(*c*) *Printing Indigosols* and "*Naphtholates*" *and then Coupling the latter with Azoic Bases.*—Fabrics are printed with pastes containing Naphtols and with pastes containing Indigosols made up as for the ordinary Nitrite Process. Afterwards, the goods are padded through solutions of the diazotised Fast Bases or through solutions of stabilised Fast Salts. The Indigosols are developed by passing the printed fabric at 65°C. for 8 seconds through a bath containing 20 ccs. sulphuric acid (168°Tw.) and 5 g. urea per litre of water. The goods are then rinsed and treated for a few seconds at 80°C. in a bath containing 15 ccs. sodium bisulphite (69°Tw.) per litre of water. Finally, they are rinsed and soaped at the boil. Indigosols are somewhat dulled by passage through the diazo solution.

Aniline Black.—Since Aniline Black is an oxidation colour it may be applied alongside the soluble ester salts of vat dyestuffs without difficulty. On account of its low cost and good fastness, it is doubtful whether Aniline Black will ever be replaced by the more costly solubilised black vat dyestuffs.

The process most recommended for the simultaneous application of Aniline Blacks and Indigosols is the Ammonium Chlorate Process (page 168); this allows full development of the Indigosols by a very short steaming. Aniline Black and Indigosol prints may also be obtained by the wet development processes, in which, prior to development of the Indigosols, the Aniline Black is developed by a short passage through the ager (Steam Black Style).

Indigosols made up according to the recipes given for the Aluminium Chlorate Process (page 170) can also be printed with Aniline Black. The following special method has been developed so that the black can be oxidised without steaming:

Aniline Salt	100
Hot Water	260
Starch-Tragacanth Thickening .	500
Aluminium Chlorate (42°Tw.) .	120
Sodium Acetate Crystals . .	20
	1,000

The *prepared* goods (see page 170) are printed and dried. They are then allowed to lie overnight, passed through a bath containing 5 g. bichrome and 5 g. soda ash per litre of water, and finally rinsed and soaped at the boil.

Reserve Styles and Discharge Styles with Solubilised Vat Dyestuffs.—The extent to which the *leuco*-esters of vat dyestuffs may be employed in the production of resist or reserve and discharge effects is almost limitless. It has been necessary to develop a large number of processes to fulfil all demands, but the results obtained are so brilliant, durable, and pleasing in their effect as to be a monument to the energies of the dyestuff manufacturers (in particular Durand & Huguenin A.-G.) and the textile printers who have developed them.

Cover Styles.—The Indigosols may be applied along with vat dyestuffs, azoic dyestuffs (including stabilised types), and chrome dyestuffs, for the production of the type of print known generally as the "cover style." This is really a combination of direct printing and reserve printing in which the white fabric is first printed with a colour containing an alkali or a reducing agent (or both, depending upon the size of the design, etc.). The goods are then over-printed with a cover-roller engraved in herringbone, pin, or a similar all-over design. The over-printing is done with Indigosols thickened with tragacanth, and the print pastes are prepared after the manner of those for the steaming processes. Print and cover may often be carried out at one operation, but the type of engraving or design very often demands that there shall be an intermediate drying between each operation. When the printed goods are dry they are aged for several minutes so as to develop the Indigosols and the coloured reserves. The actual final treatment, however, is dependent upon the type of reserve which has been employed.

The great advantage of the cover style is that it enables the production of a full range of different colour patterns by the employment of a single engraved roller.

When vat dyestuffs are to be covered with Indigosols, they are first printed by the ordinary recipes and then covered with solubilised vat colour pastes made up according to the recipe given for the steaming process. When dry, the prints are steamed for 5–8 minutes in moist steam, and finally the goods are finished off in the usual manner for vat dyestuffs. In this way an all-vat dyestuff print can be obtained. The process may also be reversed, i.e. the white cloth is first printed with thickened Indigosols containing Ludigol, then over-printed with vat dyestuffs for cover, and finally dried, steamed and finished as usual. White reserves under Indigosols in this printing style can be obtained by the use of sodium acetate.

Rapid Fast dyestuffs are applied by the usual reserve method and then covered by Indigosols in a steaming process. The Rapidogens are applied from a fairly alkaline printing paste so that they will resist the over-printed Indigosols. Chrome mordant dyes are printed by the usual recipe for the reserve style under padded Indigosol grounds, and then covered with Indigosols.

Indigosol Reserves under Aniline Black.—These may be obtained either by printing the reserves on white cloth and then padding with Aniline Black liquor and steaming, or by first padding Aniline Black liquor, drying and then printing the reserves before steam development. The first-mentioned process is not generally recommended for very fine patterns, but has the advantage that the reserve-printed fabrics can be left indefinitely before application of the black. The second process can be employed without difficulty for all types of designs, and for this reason it is usually preferred to the first-mentioned process. The Rapidogen dyestuffs can be simultaneously applied by the second process.

When reserves are to be printed on white cloth, either the Bichromate Process or the Sodium Citrate Process may be used.

Bichromate Process.—Indigosol and Rapidogen or Rapid Fast reserves are prepared according to the following examples:

Rapidogen Red G—
80 parts Dyestuff
30 parts Caustic Soda (71°Tw.)
30 parts Alcohol
150 parts Hot Water
} pasted and stirred together until dissolved. Then added to
400 parts Neutral Starch–Tragacanth. Then add
150 parts Zinc oxide (1:1) and
160 parts Cold Water

1,000 parts

Allow to stand overnight before use.

Indigosol Brown IBR—
20 parts Dyestuff
50 parts Dehapan O
350 parts Hot Water
400 parts Neutral Starch–Tragacanth
150 parts Zinc Oxide (1:1)
30 parts Caustic Soda (71°Tw.)

1,000 parts

White Reserve—

80 parts	Caustic Soda (71°Tw.)
500 parts	Neutral Starch–Tragacanth
250 parts	Zinc Oxide (1:1)
80 parts	Sodium Thiosulphate
90 parts	Water
1,000 parts	

Pastes similar to the above are printed, dried strongly, and then padded in a thickened Aniline Black liquor which contains 40 g. acetic acid (50%) and 10 g. formic acid (90%) per litre. The goods are then immediately dried on drums. The drying develops the Rapidogen and Rapid Fast colours and leaves the rest of the cloth a faint greenish-yellow shade. The prints are then steamed for 2 minutes at 98°–100°C. in a Mather & Platt ager in order to develop the Aniline Black. Finally, the Indigosols are developed by a short passage (30 seconds) through a bath containing 2–3 g. potassium bichromate, 20 ccs. sulphuric acid (168°Tw.) and 30 ccs. ammonium vanadate (0·1%) per litre of water. The goods are then washed, neutralised with soda ash, rinsed, and then soaped at the boil.

Zinc acetate may be used in place of the caustic soda and zinc oxide; this alteration results in a better yield of Indigosol, especially if the goods are aged for 4 minutes before padding on the Aniline Black liquor.

Sodium Citrate Process.—In this case, the Indigosol reserves are applied from pastes such as the following:

50 parts	Indigosol Grey IBL
80 parts	Glyecine A
50 parts	Dehapan O
80 parts	Water
500 parts	Starch–Tragacanth (neutralised with ammonia)
100 parts	Sodium Citrate
40 parts	Sodium Acetate (1:1)
100 parts	Aluminium Chlorate (42°Tw.)
1,000 parts	

This is printed (alongside Rapidogens, if required), dried, and then padded in Aniline Black liquor and developed as for the Bichromate Process just described.

When Aniline Black liquor is padded on to white goods, Indigosol and Rapidogen reserved are over-printed by either the Bichromate Process or the Sodium Citrate Process. Examples of reserve pastes are given:

Bichromate Process—

80 parts	Rapidogen Red G
30 parts	Caustic Soda (71°Tw.)
30 parts	Monopol Brilliant Oil (or Alcohol)
120 parts	Tepid Water
400 parts	Neutral Starch–Tragacanth
200 parts	Zinc Oxide (1:1)
60 parts	Sodium Nitrite (20%)
50 parts	Glyecine A
30 parts	Potassium Sulphocyanide
1,000 parts	

100 parts	Indigosol Brown IBR
50 parts	Dehapan O
150 parts	Hot Water
500 parts	Neutral Starch–Tragacanth. Heat to dissolve, and at 60°C., add
140 parts	Sodium Acetate
60 parts	Soda Ash
1,000 parts	

The goods are printed, dried, steamed for 2 minutes, and then given a short passage at 30°C. through a bath containing bichrome, vanadate, and sulphuric acid as previously described.

Sodium Citrate Process—

50 parts	Indigosol Grey IBL
50 parts	Dehapan O
80 parts	Glyecine A
140 parts	Water. Heat to dissolve, and then add
500 parts	Neutral Starch–tragacanth (neutralised with ammonia) and add without cooling
100 parts	Sodium Citrate
40 parts	Sodium Acetate (1:1)
40 parts	Aluminium Chlorate (42°Tw.)
1,000 parts	

Print, dry, steam for 2 minutes in the Mather & Platt ager, and then develop in a bichrome bath as before.

Indigosol Reserves under Variamine Blue.—While there are a great many processes for this purpose, only four of the more important ones will be described. These are:

(i) Steaming Process
(ii) Lead Chromate Process
(iii) Copper Sulphate Process
(iv) Aluminium Chlorate Process

Process (i) is the only process calling for the agency of steam. The latter is generally considered to be unfavourable to the brightness of the ground shade and also to the azoic colour reserves which may be printed simultaneously. Reserving agents for this purpose are usually acids or compounds which are capable of liberating acid during development treatments. Easily dissociable acid-salts, e.g. aluminium sulphate, may also be employed. Such acid compounds inhibit the coupling power of the Variamine Blue. In several of the processes to be outlined, use is also made of sulphites and hydrosulphites for the purpose of destroying the diazo solutions in the regions where reserves are printed.

(i) *The Steaming Process.*—Here the Naphtol AS-prepared[1] fabric is dried and printed with Indigosol colour pastes which contain Dehapan O, gum tragacanth, ammonium oxalate, sodium chlorate, and ammonium vanadate. In some cases, ammonium oxalate is replaced by a similar quantity of ammonium sulphocyanide or aluminium sulphate. An example of a suitable print paste containing Indigosol Yellow HCG has been given on page 177. After printing and steaming for 8 minutes in fairly dry steam, the ground shade is developed by a passage through a solution of Variamine Blue Salt B (e.g. 40 g. Salt B per litre cold water) on a two-bowl mangle. An air-run of 20–30 seconds or a very short steaming in a conveniently placed apparatus is then given. Brief steaming at this stage will give more intense ground shades than a simple air-run. The goods are then given a short passage in open width at 60°C. through a bath containing 10 ccs. hydrochloric acid (32°Tw.) per litre of water. The purpose of this acid treatment is to remove any excess Variamine Blue solution which would otherwise couple with the Naphtol present below the

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[1] The Naphtol-prepare for the steaming process contains 20 g. urea per litre of naphtholate solution.

reserves. The hydrochloric acid is removed by a hot followed by a cold rinse. The fabric is finally soaped in the presence of soda ash in a short run at the boil. Soaping should not be carried out until a test sample has shown that the reserves are perfectly clear and bright.

In the Steaming Process (and also in the Aluminium Chlorate Process (iv)) the hydrochloric acid treatment may be replaced by a short passage through a boiling bath containing 15 ccs. sodium bisulphite (71°Tw.) per litre of water. Sodium bisulphite destroys any uncoupled Variamine Blue in an analogous manner to the hydrochloric acid. When bisulphite has been employed, soaping is carried out at the boil with the addition of a little caustic soda.

(ii) *The Lead Chromate Process* is reputedly quicker and simpler than the foregoing steaming process. The Naphtol AS-padded fabric is dried and printed with Indigosol reserves prepared according to the following examples which illustrate the use of sodium bisulphite, potassium sulphite and zinc sulphate. The last of these agents gives more stable pastes and brighter prints.

40 parts Indigosol Brown IRRD
60 parts Dehapan O
350 parts Hot Water
400 parts Neutral Starch-Tragacanth.
Cool and add
20 parts Sodium Bisulphite (71°Tw.)
10 parts Ammonium Sulphocyanide
120 parts Chrome Yellow Paste (60%)

1,000 parts

50 parts Indigosol Pink IR extra
110 parts Dehapan O
235 parts Hot Water
400 parts Neutral Starch-Tragacanth.
Cool and add
70 parts Potassium Sulphite (91°Tw.)
15 parts Ammonium Sulphocyanide
120 parts Chrome Yellow Paste (60%)

1,000 parts

30 parts	Indigosol Printing Blue IGG
50 parts	Glyecine A
335 parts	Hot Water
470 parts	Neutral Starch-Tragacanth
60 parts	Chrome Yellow Paste (60%)
50 parts	Zinc Sulphate Crystals
5 parts	Ammonia (25%)
1,000 parts	

The above pastes are allowed to stand overnight before printing. The Indigosol reserves may be printed alongside Fast Salt reserves. A white reserve may be prepared from aluminium sulphate 1:1 (200 parts), water (300 parts), and neutral starch-tragacanth thickening (500 parts). After printing, the goods are padded immediately in 45 g. Variamine Blue Salt B per litre of water. They are then dried lightly and finished in a dilute hydrochloric acid bath as described on page 183.

(iii) *The Copper Sulphate Process* employs Indigosol print colours which consist of Glyecine A, starch-tragacanth thickening, and zinc sulphate. In some cases, e.g. Indigosol Printing Blue IGG, it is also necessary to make additions of bichrome and ammonia. The printed reserves do not require steaming; after drying, they are padded in the Variamine Blue Salt B bath and then given a short air-run and dried (on the cans). Development is then carried out by passing the goods for 2 seconds at 70°–80°C. through a bath containing 40 g. copper sulphate crystals and 40 ccs. sulphuric acid (168°Tw.) per litre of water. A second and shorter air-run is then given. Finally, the goods are given a 5-minutes warm treatment in a dilute sulphuric acid bath (5 ccs. per litre), rinsed thoroughly and then soaped at the boil. White reserves and azoic reserves are unaffected by the copper sulphate treatment.

(iv) *The Aluminium Chlorate Process* is perhaps the simplest of the methods used for the production of Indigosol reserves under Variamine Blue. The preliminary Naphtol-prepare liquor contains additions of acid-resisting wetting agents (e.g. Nekal BX) and ammonium vanadate; a recipe for this purpose is given on page 177, together with details of the preparation of the Indigosol reserve pastes. The printed fabric is dried strongly and then allowed to lie for about 24 hours before padding in the Variamine Blue bath. Subsequent treatments are identical with those given for the steaming process described above.

All-Vat Dyestuff Prints.—For the purpose of producing all-vat dyestuff multi-coloured prints, several processes are possible. These are listed below, and will be described in the pages which follow.

(i) The fabric is printed with Indigosol reserves and subsequently vat dyed.

(ii) Indigosol discharges are printed on dischargeable vat-dyed grounds.

(iii) Indigosols are padded on to material which has been printed with Indigosol resists.

(iv) Indigosols are padded on to white fabric, which is then printed with vat dyestuff reserves. The Indigosol ground is then developed.

(v) Vat dyestuffs or Indigosols are printed in the normal direct manner and then over-padded with Indigosols.

(i) *Indigosol Reserves under Vat Dyestuffs*

Ludigol–Manganese Resist Process.—This process has already been described in detail on pages 111, 159, where dyeing details and general principles have been described. Manganese Ludigolate is prepared by dissolving 200 g. manganese chloride in 250 ccs. hot water and pouring this solution into a solution of 200 g. Ludigol in 300 ccs. hot water. When cold, crystals of Manganese Ludigolate are formed; these are filtered off and the filter-cake is adjusted to a weight of about 375 g. (approx. 65–70 % dry content). Reserve pastes are prepared according to the following examples:

80 parts	Indigosol Green AB
90 parts	Dehapan O
100 parts	Water
520 parts	Gum (1:1)
30 parts	Sodium Chlorate (1:3)
30 parts	Ammonium Vanadate (1 %)
150 parts	Manganese Ludigolate (65–70 %)
1,000 parts	

60 parts Indigosol Orange HR
40 parts Dehapan O
100 parts Water
540 parts Gum (1:1)
30 parts Sodium Chlorate (1:3)
10 parts Ammonium Vanadate (1%)
20 parts Ammonium Lactate
200 parts Manganese Ludigolate (65–70%)

1,000 parts

The printed goods are dried completely and aged for 5–10 minutes. They are then allowed to lie overnight and are dyed with vat dyestuffs in the continuous dyeing machine (page 111). After dyeing, the goods are given an air-run, washed, and then soured and developed in a bath containing 10 g. hydrochloric acid (32°Tw.) and 1–2 g. potassium sulphocyanide per litre of water. Finally, the prints are washed and soaped at the boil.

A method described as the *Metallic Salt Process* or *Copper-Lead Salt Process* may similarly be employed in order to produce Indigosol reserves under vat-dyed grounds. The reserving agents are made up from the following constituents:

(i)	(ii)	
100	—	Copper Sulphate
60	150	Lead Sulphate (60% paste)
160	—	Lead Nitrate
120	—	Copper Acetate
—	50	Ludigol
—	25	Zinc Oxide
200	—	China Clay: Gum Senegal (1:1)
560	425	Gum Senegal (1:1)
—	350	British Gum (1:1)
1,200	1,000	

Various other assistants such as Dehapan O, Rongalite, Indigosol Developer D, and sodium chlorate are often required in the Indigosol print paste. Dyeing, developing, and finishing treatments are then similar to the Ludigol–Manganese Resist Process.

Another process for producing an all-vat colour print usually known as the *Double Roller* or *Fall-On Process* consists of first printing the Indigosols by one of the steaming recipes and then over-printing the pattern exactly (by a second roller) so that a vat colour resisting substance "falls on" the Indigosols. The developed prints are then dyed in the continuous vat.

Indanthrene Blue RS and equivalent products appear to be the only vat dyestuffs which are of real importance for the continuous dyeing of resisted fabrics.

(ii) *Vat-dyed Grounds Discharged with Indigosol Discharge Pastes*

Dischargeable vat-dyed grounds may be illuminated by printing a thickened mixture of Indigosol dyestuffs, sodium hydrosulphite, and Leucotrope W. The prints are then dried and aged for 8 minutes. During steaming, discharging is completed; development of the Indigosol illuminants is then accomplished by passing the goods through an acid-bichrome oxidising bath. Finally, the goods are washed, neutralised, and soaped at the boil.

In addition to the compounds already mentioned, discharge pastes of this type usually contain zinc oxide, soda ash, and a solvent for the dyestuff, e.g. Dehapan O. The pastes are thickened either with dextrine, tragacanth or gum. Print pastes of this type should be thoroughly ground in a mill before application.

A white discharge for this purpose is made up from Rongalite CL, Leucotrope W, British Gum, zinc white, precipitated chalk, and caustic soda (page 193).

(iii) *Indigosol Pads on Fabric Reserved with Indigosols*

Durand & Huguenin A.-G. (1936) first suggested this process, claiming that excellent results had been obtained on a small scale. The advantage of the process lies in the fact that Indigosol-dyed grounds can be illuminated with Indigosols without resort to steaming treatments. Furthermore, dyestuffs such as Indigosol Olive Green IB, Indigosol Green IB, and Indigosol Blue IBC (which cannot ordinarily be reserved) may be employed in this process. Reserve X (D.H.) is used in the production of white reserve pastes.

The reserves (prepared from an Indigosol dyestuff and a solvent, thickened with gum Arabic and containing zinc white and sodium nitrite) are printed on to white cloth, dried, and then padded in an Indigosol padding liquor prepared according to the Nitrite Process. The padded fabric is then oxidised (without intermediate drying) in the usual sulphuric acid bath at 70°C. Certain Rapidogen colour reserves may be applied alongside the Indigosol reserves, and when these are present the final oxidation bath consists of oxalic acid, formic acid, and Glauber's salt. Indigosols suitable for printing alongside Rapidogens in this manner are:

Indigosol Golden Yellow IGK
Indigosol Blue IBC
Indigosol Green IB
Indigosol Brown IRRD
Indigosol Grey IBL
Indigosol Printing Black IB

In addition to these, the following dyestuffs can be employed for the general process outlined above (i.e. in the absence of Rapidogens):

Indigosol Orange HR
Indigosol Scarlet IB
Indigosol O4B
Indigosol Printing Blue IGG
Indigosol Pink IR extra

(iv) *Indigosol Pads on Fabrics Reserved with Vat Dyestuffs*

In this process, the material is first padded with the solubilised vat dyestuffs, either by the Nitrite Process, the Neutral Chromate Process, or the Steaming Process. The padded goods are dried in the hot flue or on cylinders and then printed immediately with vat dyestuff reserves. The latter are prepared with potassium carbonate and should contain a minimum of reducing agent and glycerine. When dry, the padded and printed fabric is steamed for 8 minutes in damp steam at 101°–102°C. The ground is then developed in an acid bath, rinsed, neutralised, and finally soaped in the usual manner.

Only the fastest of the Indigosol dyestuffs can be employed for this style of printing, and furthermore the cost of the Indigosols usually restricts their use in anything but light shades. Before soaping it is often necessary to give the goods a passage through a dilute hydrosulphite bath in order to counteract any over-oxidation of the vat dyestuff reserves; this is especially important when the anthraquinoneazine blues have been employed.

Vat dyestuff reserves may also be printed on the white cloth. These are then fixed by steaming and the goods are afterwards padded in thickened Indigosol solutions and developed in the usual acid oxidising bath. For this purpose, the padding liquor should be well thickened and development should be carried out very quickly so as to prevent any bleeding of the vat dye reserves.

(v) *Vat Prints on Vat Grounds*

This style is often produced by printing the white material with Indigosol dyestuffs, drying, and then padding with Indigosols, drying again and then simultaneously developing both the print and the pad in an acid oxidising bath. An alternative process consists of printing ordinary vat dyestuffs in the normal manner and then over-padding with Indigosols. The Steaming Process is recommended for this purpose since the Nitrite Process and the Bichromate Process are apt to cause an over-oxidation of the vat prints.

Chrome Dyestuff Reserves.—Indigosol padded grounds may be printed with fast chrome dyestuff reserves and then developed by steaming. There are two general processes for this style. The first consists in padding the Indigosols by the Steam Process, drying, and then over-printing with chrome dyestuff reserves containing sodium acetate or sodium thiosulphate. The prints are dried and steamed for 8 minutes, and then washed and soaped at the boil. The second process permits the chrome reserves to be first applied to the white cloth in the usual manner; the Indigosols are then padded and steamed for development. This process thus involves a double steaming treatment, the first steaming being of long duration (e.g. 1 hour), and the second of short duration (e.g. 8 minutes). The chrome colour reserves for this purpose contain zinc white, lithopone and chromium acetate in addition to the chrome dyestuff and gum tragacanth thickening.

Rapid Fast Dyestuff Reserves.—Bright reserve effects under Indigosol-padded grounds may be obtained by using the Rapid Fast dyestuffs in conjunction with reserving agents such as sodium acetate or sodium thiosulphate. Neutral ammonium oxalate is an acid liberator which is usually employed in the Indigosol padding liquor. The goods are padded with Indigosol dyestuffs, dried in the hot flue and then printed immediately with the Rapid Fast colour reserves. The goods are then dried at a fairly low temperature and steamed for 8 minutes. Finally, the goods are worked in boiling water and then treated for a short time in a boiling soap bath containing a small addition of caustic soda. A short treatment at 75°C. in dilute acetic acid prior to washing and soaping will brighten the reserves. When both vat colour and Rapid Fast colour reserves are being printed, a small addition of sodium perborate should be made to the dilute acetic acid bath, and in this case the treatment is carried out at 25°C.

Rapidogen Dyestuff Reserves.—Since Rapidogen printing pastes are strongly alkaline they are very suitable for printing reserve effects under padded Indigosol grounds. Working according to the Nitrite Process, the Indigosol is padded and then dried. The fabric is then over-printed with Rapidogen reserves containing zinc oxide and sodium thiosulphate. The latter agents prevent the Rapidogen dyestuffs from being affected by the acid employed to develop the ground shade of Indigosol dyestuff. Reserves and ground shades are simultaneously developed by padding in dilute acid and drying on cylinders; a simple passage through the usual acid bath may also be employed for development.

The Steam Process may also be employed for the production of Rapidogen reserves under padded Indigosol grounds. By this method the goods are padded by the Developer Process, dried, and over-printed with Rapidogens, and then finally steamed to oxidise the ground shades. The reserves are subsequently developed by a passage through an acid bath. Simultaneous development of both ground and reserve may be effected by adding an excess of acid-liberating salts to the padding bath. In this way, sufficient acid is liberated during steaming to develop the stabilised diazo compounds. Acid-steam ageing may also be employed.

Special Rapidogen reserve recipes containing Reserve X (D.H.) must be employed when the Indigosol ground has been produced with either Indigosol Blue IBC, Indigosol Green IB, Indigosol Olive Green IB, or Indigosol Brown IBR.

Azoic Reserves.—The azoic colours are generally employed for the production of very bright yellows, oranges and reds upon Indigosol grounds. The goods are padded with Indigosols by the Steam Process, dried, and then over-printed with an alkaline Naphtol AS type of reserve. The ground shade is next developed by steaming for 8 minutes and the reserves are then developed by a passage through a diazo solution.

The easily oxidised Indigosols such as Indigosol Golden Yellow IGK, Indigosol Green IB, Indigosol O, Indigosol Blue IBC, Indigosol Printing Blue IGG, and Indigosol Printing Black IB, may be employed for shading the azoic colours which require a weakly acid diazo bath. The Indigosol is applied in the Naphtol padding liquor along with sodium nitrite. The padded goods are dried and then passed through a weakly acid diazo bath containing the coupling component. A short air-run is given before the goods are finally washed and soaped.

White Reserves.—These may be produced under padded Indigosol grounds by the use of sodium acetate, sodium thiosulphate, and Hydrosulphite NF conc. Reserve X (D.H.) is an agent which has been specially prepared for reserving the more difficult Indigosols such as Green IB and Olive Green IB. When steaming processes are being employed, it is necessary to avoid the use of hydrosulphite compounds, since these may have a reducing action upon the ground shade, which is not normally reserved. For the latter reason, sodium acetate or sodium thiosulphate is always used in processes requiring steam development. Reserve X or Hydrosulphite NF must be used for the production of white reserves when the Indigosols are applied by either the Nitrite Process or the Bichromate Process.

Soledon Resist A (I.C.I.) appears to have similar properties to Reserve X. A typical recipe illustrating the formulation of a white resist comprises:

6 pints British Gum Solution
8 oz.–1 lb. Soledon Resist A (I.C.I.)
3 oz.–1 lb. Sodium Carbonate or Potassium Carbonate, and
1½ oz.–8 oz. Formosul, bulked to 1 gallon with Water

Coloured Discharges on Azoic Grounds.—The process employed for the production of Indigosol-coloured discharges on vat-dyed grounds (page 188) can also be employed to produce similar effects on azoic-dyed grounds. Many Naphtol combinations suffer an alteration in shade during development of the Indigosols in the acid-bichrome bath and careful selection of the least-affected dyes is necessary. Discharge pastes may consist of Dehapan O, soda ash, hydrosulphite, zinc white and anthraquinone paste, in addition to the dyestuff solution and starch–tragacanth thickening.

Dischargeable Indigosol Dyestuffs.—Rongalite CL and equivalent products such as Erasol CL may be employed for discharging light shades of the following dyestuffs:

Indigosol Golden Yellow IGK
Indigosol Pink IR extra
Indigosol Scarlet IB
Indigosol Red Violet IRH
Indigosol Printing Violet IBBF
Indigosol Printing Blue IGG
Indigosol Brown IBR
Indigosol Grey IBL
Indigosol Orange HR
Indigosol Brilliant Pink I3B
Indigosol Scarlet HB
Indigosol Printing Violet IRR
Indigosol Green AB
Indigosol Printing Blue IB
Indigosol Brown IRRD

Dark shades of the following dyes may be discharged white by the same treatment:

Indigosol O4B
Indigosol O
Indigosol O6B
Indigosol OR
Indigosol AZG

The example on the next page of a white discharge paste (recommended by Durand & Huguenin A.-G.) is suitable for either Indigosol dyeings or Indigosol pads.

170 parts	Rongalite CL
170 parts	Leucotrope W
100 parts	Caustic Soda (71°Tw.)
60 parts	Zinc White (1:1)
50 parts	Precipitated Chalk
450 parts	Industrial Gum
1,000 parts	

Viscose Rayon.—Apart from extra caution in handling and the selection of suitable plant, the recipes described for cotton are, in general, quite suitable for application to viscose rayon. Slight modifications of the processes, together with additional notes, are given in the following paragraphs.

Rayon and mixed fabrics of rayon and cotton (particularly crêpe fabrics) are very difficult to print in a level manner, but careful choice of thickening agents is of great assistance in giving better results when this problem arises. Combinations of dextrine and Blandola are very effective thickeners for the more difficult fabrics. Thickenings consisting of British gum; dextrine and certain proprietary gums have also been found excellent in this respect. This type of mixed thickener is to be particularly recommended when "push through" styles are required. Solvitex ST and Solvitex BG are specially prepared thickeners of Dutch origin (Scholten) and are reported to be of exceptional value for viscose rayon fabric printing.

Nitrite Process.—The remarks which have already been made (page 165) regarding the steaming of prints applied by this process are of particular interest when handling viscose rayon crêpes and similar difficult fabrics.

Ammonium Chlorate Process.—With this process it becomes necessary to extend the steaming period of 2 minutes given for cotton to 6–8 minutes for viscose rayon fabrics in order to obtain complete fixation of the Indigosol dyestuff.

Steaming Processes.—The yield of dyestuffs obtained upon viscose rayon and cuprammonium rayon fabrics depends upon the precise physical nature of the goods. In many cases it will be found that the steaming processes described for cotton are quite suitable for rayon fabrics. The chief point to note about printing rayons by these methods is that the fabric must be carefully freed from all impurities and finishing compounds. This may necessitate a scouring treatment with either ammonia, Igepon T, soda ash, or Laventine KB (I.G.) or a combination of these. When linseed oil sizes are known to be present, the use of such agents as Cycloran M (I.G.) is to be recommended. Desizing agents of the enzyme type are generally quite suitable for the removal of starch, glue, and gelatine finishes.

When printing by the Sulphocyanide Process, it may be necessary to increase the period of steaming from 8 minutes up to 16 minutes. Steaming processes involving the use of acid vapours offer little trouble with rayons.

Aluminium Chlorate Process.—The preliminary padding liquor for this process, i.e. containing ammonium vanadate and tartaric acid (page 170), requires double the quantity of tartaric acid given for cotton. Furthermore, it is recommended that an addition of 50 g. Glyecine A per litre should be added to this bath. Glyecine A accelerates development of the dyestuff on viscose rayon.

A new process for printing the Indigosols on spun rayons has been recently developed by Durand & Huguenin A.-G. Many dyestuffs, e.g. Indigosol Green IB and Indigosol Olive Green IB are insufficiently fixed upon certain qualities of spun rayon fabric. Prints of good yield and fixation can be obtained with such dyestuffs by the use of this new process, which is known as the *Ferrocyanide Process*. Indigosol Blue IBC cannot be applied by this method. Examples of print pastes for printing spun viscose fabrics by this process are:

(*a*) 60 parts Indigosol Olive Green IB
80 parts Dehapan GB
80 parts Fixer CDH
170 parts Water
400 parts Starch–Tragacanth
80 parts Ammonium Chlorate (23°Tw.)
130 parts Sodium Ferrocyanide (1:3)

1,000 parts

(*b*) Reduction Paste for Recipe (*a*)—
500 parts Starch–Tragacanth
400 parts Water
50 parts Ammonium Chlorate (23°Tw.)
50 parts Sodium Ferrocyanide (1:3)

1,000 parts

(*c*) 60 parts Indigosol Brilliant Pink I5B
20 parts Dehapan GB
295 parts Water
500 parts Starch-Tragacanth
30 parts Ammonium Sulphate (1:3)
70 parts Sodium Chlorate (1:3)
5 parts Ammonia (20%)
20 parts Sodium Ferrocyanide (1:3)

1,000 parts

(*d*) Reduction Paste for Recipe (*c*)—
700 parts Neutral Tragacanth (80:1,000)
30 parts Ammonium Sulphate (1:2)
50 parts Sodium Chlorate (1:3)
5 parts Ammonia (20%)
20 parts Sodium Ferrocyanide (1:3)
195 parts Water

1,000 parts

After printing, the dried goods are steamed for 5–10 minutes in the rapid ager, and finally soaped at the boil in the usual manner. Incidentally, sodium ferrocyanide or sodium ferricyanide provides a good substitute for ammonium vanadate for use in other processes.

Acetate Rayon.—Recipes and processes described for the production of Indigosol prints on cotton are quite unsuitable for use upon acetate rayon materials. Short steaming is insufficient to allow full penetration of the dyestuffs into the cellulose ester, and the prints show poor fastness to rubbing and washing since most of the colour stays on the surface of the fibre. For these reasons it is necessary to modify the usual processes, in the manner briefly outlined below. The processes more nearly resemble those employed for natural silk than those for cotton.

For the Nitrite Process, the printing colour is prepared as follows:
5–80 parts Dyestuff are dissolved in
475–385 parts Hot Water, to which may be added a little Dehapan O. This solution is then thickened with
500 parts Tragacanth (80:1,000). Finally, add
15–30 parts Sodium Nitrite, and
5 parts Ammonia (25%)

1,000 parts

The prints are dried and steamed for 10–20 minutes. The dyestuff is then developed by a passage at 75°–80°C. through a bath containing 20 ccs. sulphuric acid (168°Tw.) per litre of water. Soaping is carried out at *60°–70°C. Solid shades upon mixed* fabrics containing acetate rayon and cotton or viscose rayon can be obtained by this process.

In the Bichromate Process, the printing colour is simply a tragacanth-thickened solution of the Indigosol dyestuff. The printed goods are dried and steamed for 20–30 minutes, and then developed for 4 minutes at 75°C. in a bath containing 10 ccs. sulphuric acid (168°Tw.) and 2·5 g. bichrome per litre. Soaping is carried out at 50°–60°C.

Special processes have been developed for printing acetate rayon with combinations of Rapidogen dyestuffs and Indigosols.

Acetate rayon may be successfully printed with the ordinary vat dyestuffs by the alkali carbonate–Formosul process. Slight modifications are often required to suit local conditions and particular care must be paid to manipulative detail.

Natural Silk.—Almost all the anthraquinonoid and indigoid vat dyestuffs can be printed on natural silk by means of the alkali carbonate–Formosul process. It is often found necessary, however, to apply the anthraquinonoid vat dyestuffs by the pre-reduction process (page 154), using caustic soda and converting this to carbonate before use. The alkali content of all natural silk print pastes should be reduced to a minimum in order to avoid any deleterious effect upon the fibre.

A thickening composed of either British gum, gum Senegal, or gum Arabic is usually employed, and the paste is made up as follows:

560 parts Gum Senegal (1 : 1)
80 parts Glyecine A
30 parts Potassium Carbonate
80 parts Sulphoxylate Formaldehyde (e.g. Erasol C)

750 parts

This thickening is heated until all is dissolved, and then cooled. The print paste is then prepared from:

60 parts Dyestuff
190 parts Water
750 parts Thickener (prepared as above)

1,000 parts

The above paste is heated to 65°C. and then allowed to cool for several hours before use. Additions of Solution Salt, urea, or other auxiliary compounds are reported to yield increased colour value when applying the anthraquinonoid vat dyestuffs.

After printing, the fabric is steamed for 5 minutes in air-free steam and finally developed in a bath containing oxidising agents, e.g. sodium perborate and acetic acid, or sodium bichromate.

For the direct printing of natural silks with Indigosol the Bichromate Process is usually employed. By this method the Indigosols and Rapidogens may be printed side by side on unweighted silk. When handling weighted silk it is only possible to apply the Indigosols: Rapidogens must be avoided. The steaming processes described for the application of Indigosols to cotton may also be employed for direct printing on unweighted silk. A short steaming is insufficient for correct development and fixation, and it is usual to steam natural silk for 20–30 minutes.

Printing paste recipes for the Bichromate Process are based upon the use of neutral gum thickenings, Dehapan O, soda ash, and sodium chromate. After printing and drying, the fabrics are steamed for 30 minutes and then given a passage (2–5 minutes) at 80°C. in a bath containing 10 ccs. sulphuric acid (168°Tw.), 10 ccs. formic acid (90%), 10 g. Glauber's salt, and 5 g. oxalic acid crystals per litre of water. Rinsing and a short soaping is carried out in the usual manner.

Coloured discharges may be obtained with Indigosols upon many dyed grounds produced from selected direct cotton dyestuffs or acid wool dyestuffs. The print colours are slightly alkaline and contain Glyecine A and Hydrosulphite NF. The Indigosol discharges are developed in a nitrite–sulphuric acid bath.

Unweighted silk may be padded either by the Steam Process or by the Bichromate Process; weighted silk may only be padded by the Bichromate Process. The recipe already given for the Steam Process of Padding (page 126) may be employed, but it is advisable to make a small addition of Glyecine A. Padding should be carried out at 30°–40°C., and steaming for 30 minutes is necessary for correct development. The recipe given for the Bichromate Process of Padding (page 125) may be used, but it is advisable to make small additions of Dehapan O; padding is done at 30°–40°C., and the goods are then dried and steamed for 20 minutes before development in a bath containing 0·2 g. bichrome and 5 ccs. sulphuric acid per litre of water at 60°C.

Wool.—In this country the vat printing of wool does not appear to have been developed very far, and only in exceptional circumstances where almost perfect fastness to soaping is required are these dyestuffs used. The use of caustic alkalis in wool printing is obviously impossible, and the alkali carbonate methods alone are suitable. It is possible, however, to employ caustic soda in the pre-reduction process, but it must always be converted to sodium carbonate before the print paste is applied to the fabric. This process results in superior yields from the viewpoint of colour value. Procedures closely resemble those employed in natural silk printing.

The use of the soluble *leuco*-esters of vat dyestuffs makes possible the production of fast prints upon chlorinated wool fabrics. The shades obtained are not of the same order of brightness as those obtained by the use of basic and acid dyestuffs. The fabrics are first chlorinated by one of the well-known "wet" methods which employ sodium hypochlorite or bleaching powder and acid. Chlorination must be thorough, as inferior results are obtained on fabrics which are under-chlorinated.

Steam Process.—The print pastes contain sodium chlorate, ammonium sulphocyanide and ammonium vanadate. Additions of Indigosol Developer D, Indigosol Developer GA,[1] Dehapan O, glycerine and ammonia are also necessary for some dyestuffs. The solutions are thickened with neutral starch–tragacanth paste.

The printed goods are dried lightly and passed through a damping machine. The pieces are then rolled in damped cotton greys and steamed for 1 hour with a steam pressure below 3 lb. per sq. in. The latter precaution prevents yellowing of the unprinted portions. The goods are then rinsed and soaped lightly. Finally, a treatment with Indigosol Soap SP (D.H.) in dilute sulphuric acid is given to improve the fastness to rubbing. Incidentally, the rubbing fastness of Indigosols printed on chlorinated wool is only of the order 3 in the usual fastness rating figures.

Lead Chromate Process.—The Indigosol dyestuff is pasted with glycerine and then brought into solution by heating with water. The solution is then thickened with a paste containing lead chromate paste, Igepon T, gum tragacanth, British gum, sodium acetate and turpentine. Additions of ammonium sulphocyanide and urea are then made in the case of certain dyestuffs.

The dry prints are steamed for 10 minutes and then the vat dyestuffs are regenerated by a passage at 85°–90°C. through a bath containing hydrochloric acid and oxalic acid. The developed

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[1] Indigosol Developer GA has been stated to be ethylene glycol.

pieces are after-treated in dilute sodium bisulphite solution, and then rinsed and washed in a bath containing a synthetic detergent of the Igepon T type.

Nylon.—Ordinary vat dyestuffs may be printed on nylon by employing the usual technique. Pastes are made up from British gum thickening, glycerine, potassium carbonate and hydrosulphite-formaldehyde. Many of the vat dyestuffs which exhibit very high fastness properties upon cotton and other cellulosic fibres are found to yield fugitive results on the superpolyamide fibres which have hitherto been commercialised. The affinity of most of the dyestuffs is only mediocre and varies from "fair to good" (cf. page 141).

It is probable that the vat dyestuffs, as well as their solubilised *leuco*-esters, will never be of great interest for the direct printing of this type of fibre; several individual dyes, however, will no doubt find use for illumination purposes in mixed and multi-coloured styles.

CHAPTER X

MACHINERY

HITHERTO, only scanty reference to dyeing and printing machinery has been made. In the present chapter the more salient features of suitable machinery are described, and illustrated by drawings and photographs.

Raw Stock Dyeing.—Julius Otto Obermaier, in 1882, was probably the first patentee to cover the manufacture of apparatus suitable for the dyeing of loose fibres and yarns. The principle of his early machine lay in the fact that the material to be dyed was kept in a stationary position while the dye liquor was forced through it by means of a pump. This original Obermaier machine was the forerunner and prototype of the many circulating-liquor and package-dyeing machines which have since been developed. Based on the simple principle of circulating dye liquor through a stationary mass of fibres, machines for dyeing not only raw stock, but also sliver, cops, cheeses and beams, are now in general use throughout the industry.

Machines of this type had just become established in general use when the demand for vat-dyed materials became more common, and such a demand could never have been met by the old process of hand-poling of open vats.

The two main types of raw stock dyeing equipment are (i) the oscillatory type, and (ii) the circulatory type. The former is not suitable for use with vat dyestuffs, since it is difficult to maintain a thoroughly reduced solution throughout the dyeing operation without the expenditure of large quantities of costly reducing agents. Such a machine can be employed for the application of the solubilised ranges, but this practice does not appear to be very popular.

This machine consists of a perforated metal cylinder which contains the raw stock. The cylinder is caused to revolve or oscillate horizontally and is partially or totally submerged in a vessel containing the dye liquor. The opened raw stock is charged into the perforated cylinder by hand. The comparatively vigorous oscillation during the subsequent long dyeing process twists up the loose fibres severely into what are known as "rat-tails."

The circulating-liquor type of machine is far more suitable for the application of vat dyestuffs. This type of machine consists essentially of a cylindrical tank with a removable perforated false bottom. The cylindrical tank is evenly packed by hand with the opened raw stock, and a perforated metal cover is placed on top. A second tank containing the dye liquor is arranged so that its contents flow on to the top of the packed cylinder. The dye liquor is drawn through the goods by means of a pump and then returned to the dye tank, thus forming a continuous cycle. Dyeing machines of this type may either be open, or closed by a lid fixed on the top of the dyeing compartment. In the latter case, the dye liquor completely fills the dyeing vessel and is circulated through the goods under pressure. The different makes of circulating-liquor machines vary widely in details of construction.

Goods dyed in these machines, if proper attention to load and packing has been given, are usually free from mechanical defects and are in good condition for subsequent spinning operations.

Package Machines for Cheeses, Yarn and Warp Beams

By dyeing yarn in the form of cheeses, cones and cops, it is possible to eliminate the operations of winding the yarn into hanks and then, after dyeing, re-winding into cops or cheeses before weaving or warping. This saving is made possible by using the package-dyeing principle and circulating dye liquor through the more or less solid bodies of the cheeses. The materials are thus kept in a good physical condition with a minimum of labour and handling, and the good results obtained as regards penetration and level dyeing have now been brought to a state almost approaching perfection.

Before a description of the simple procedure involved in package dyeing is given, it is desirable to review briefly the materials of construction. Wooden vessels were employed in the early days, but stainless steel has now almost completely replaced all other types of material. Formerly, pumps and piping were made from bronze and phosphor-bronze, but these metals, as well as the copper often used in the construction of the containers and vessels, were found to be unsuitable for vat dyeing. Nickel and Monel metal have also proved to be satisfactory materials for constructing all types of circulating-liquor machines for use with all classes of dyestuffs. Perforated spindles and tubes of nickel and of Monel metal are widely used, and complete machines, including pumps, have been constructed entirely of the latter metal. Stainless steels of the Staybrite (Firth-Vickers) type have been found to be almost *sine qua non* for this purpose. Other steels, used for the same purpose and bearing the nomenclature of British firms, are

Evershyne, Weldshyne, Anka, Weldanka and BB4K. The Krupp V2A and V4A steels are the German counterparts of Staybrite FST and Staybrite FMB. Stainless steel was first discovered by Brearley, while working in Firth-Brown's Research Laboratories, in 1913, and at the outset it was employed for the production of cutlery. Staybrite FST (Krupp V2A is similar) is said to contain about 8% nickel and 18% chromium in admixture with the steel. Staybrite FMB (Krupp V4A is similar) contains similar amounts of nickel and chromium, supplemented by 2–3% molybdenum to prevent weld-decay. Staybrite FDP contains a small proportion of titanium, which is added to prevent inter-crystalline corrosion and makes the steel more suitable for welding. Machines constructed of such steels are found to be almost completely resistant to all chemicals used in dyeing; they are rustless and free from deleterious effects upon the shades of dyestuffs, and, furthermore, they are easily cleaned.

The yarns are wound upon hollow perforated spools, tubes, or on a coiled-spring core, and then placed over perforated spindles connected to a frame. The latter is mounted in a cylindrical dye vessel and the whole machine can be closed by means of a bolted lid. The dye liquor is contained in a separate tank and is circulated by a pump through the perforated spindles, with a periodic reversal of the direction of flow. Modern machines are fitted with hydro-extracting or vacuum devices, and compressed air or hot-air drying systems.

As with raw stock dyeing machines, yarn package equipment varies greatly in constructional style and detail, but the Obermaier principle is common to all types.

The Longclose Engineering Company (Leeds) manufacture a variety of circulating liquor machines, and especially worthy of note is their totally enclosed yarn dyeing machine which is made completely of stainless steel. This machine consists of a totally enclosed pressure dyeing chamber, from the base of which run two pipes which lead to a reversing mechanism and thence to a pump. Within the circuit of the system is an expansion tank through which all the dye liquor circulates during the dyeing cycle.

The machine is designed so that various inner containers can be introduced into the dyeing vessel, thus making possible the dyeing of all forms of fibres, e.g. warps, hanks, cheeses, cones and rayon cakes. Warps and hanks may be packed into a cage or container (consisting of two concentric cylinders) which is screwed into the machine. Modifications of the machine are available that carry a specially strong inner cage which, when dyeing is complete, can be lifted out completely and hydro-extracted in a suitable apparatus.

An open machine is made to work in conjunction with the above machine. Here, the final soaping-off of the vat-dyed cheeses and cones takes place, thus leaving the dyeing machine itself free to be employed straight away for dyeing the next batch of goods without waiting for the completion of the first batch. (See Figs. 1, 2, 3 and 7.)

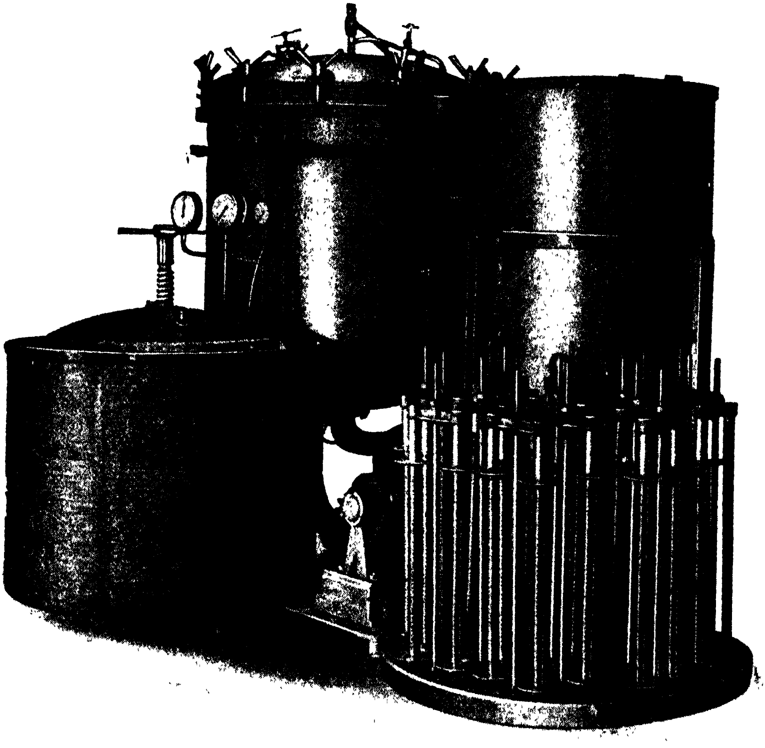

FIG. 1.—Illustration of a 200-lb. Machine complete with Warp and Hank Container and also Cheese Frame

(By kind permission of the Longclose Engineering Co., Ltd., Leeds)

Franklin Process Package Dyeing Machines are very similar in principle to the ones just described. Instead of using rigid perforated spindles for the package dyeing of cheeses, however, this machine makes use of the Franklin Tube, which consists of a spiral spring covered with a knitted fabric to prevent the yarn from falling between the coils of the spring. Such a tube is compressible lengthwise, and when cheeses wound on the Franklin

Tube are arranged in columns on the perforated spindles in the machine they can be compressed so that the packages acquire practically the same density. (See Figs. 4, 5 and 6.)

The winding of the yarn and its preparation are the processes which chiefly govern the results obtained in package dyeing.

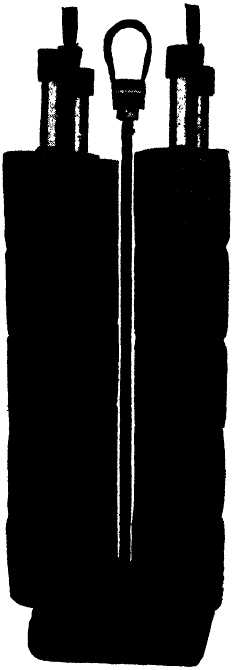

FIG. 2.—Cheeses mounted on Dyeing Unit

(By kind permission of the Longclose Engineering Co., Ltd., Leeds)

FIG. 3.—Cone Frame

(By kind permission of the Longclose Engineering Co., Ltd., Leeds)

Details relating to these important factors have been given by Hardman (*Amer. Dyestuff Rep.*, 1942, **31,** 345), who considers that the five important details which have a direct bearing on the dyeing result are (1) the weight of the pack, (2) the dimension, (3) the yarn count, (4) the angle of wind, and (5) the density or compactness of wind. Great attention must be paid to all these factors if a high standard of work is to be achieved.

Warp yarns are dyed in machines which are very similar to those used in dyeing cones and cheeses, the main difference lying in the greatly increased size of the perforated spools employed.

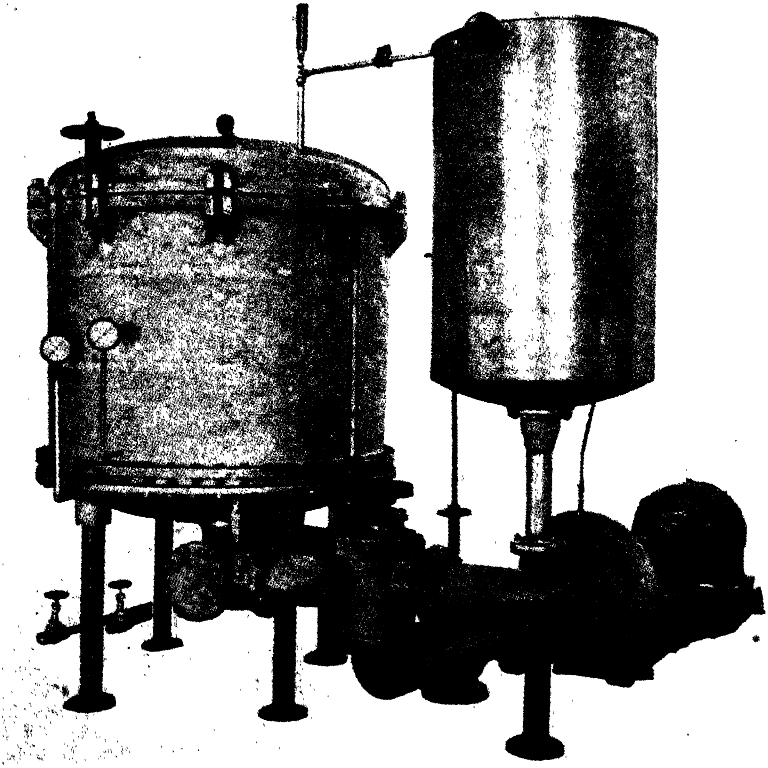

FIG. 4.—Exterior of 500-lb. Franklin Process Yarn Dyeing Machine
(By kind permission of the Franklin Process Company, U.S.A.)

Entire warps are dyed at one operation, thus eliminating the defect of "ending," which is often prevalent on ordinary dyed warps.

Hank Dyeing Machines.—Although the simple method of dyeing on sticks in open becks is still very widely employed for the vat dyeing of hanks, the high labour costs and the variables introduced by manual operation are distinct disadvantages. These disadvantages can very often be removed by the employment of special equipment. There are several types of machine designed for skein dyeing, but few of them are suitable for vat dyestuffs. Thus, the Klauder-Weldon machine, which consists of a wheel-like hank-frame rotating in a dyevat, is totally unsuitable for dyeing vat dyestuffs, on account of the excessive agitation and carriage of the goods through the air. A second machine which is also found to be unsuitable for dyeing reduced vat dyestuffs works on

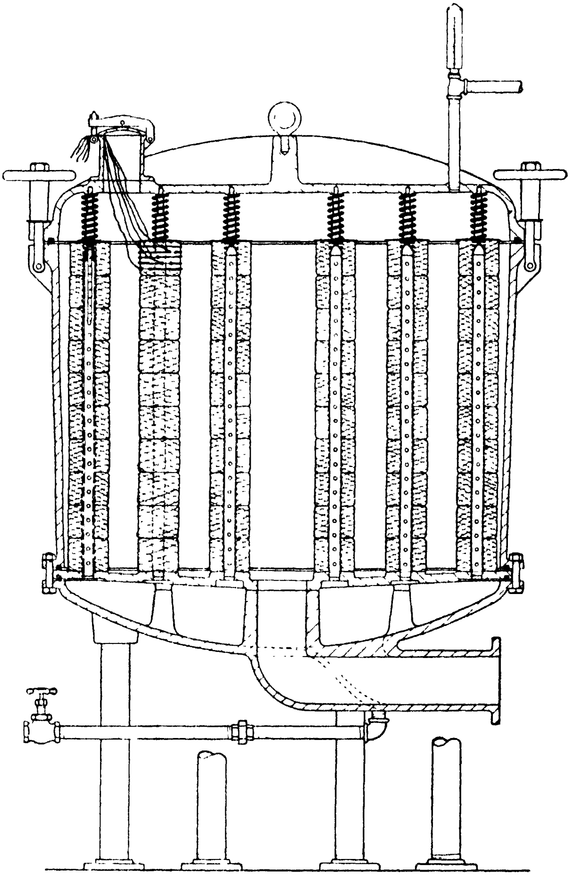

FIG. 5.—Cross Section of Franklin Process Package Dyeing Machine for Cotton Yarn showing sampling arrangement
(By kind permission of the Franklin Process Company, U.S.A.)

the following lines. The hanks of yarn are suspended from sticks which are mounted on the cover of the dyebath, the lower ends of the material hanging free. Agitation is effected by means of a propeller; difficulties in loading and unloading are encountered.

A machine formerly known as the *Spencer Skein Dyeing Machine* (Hall, *Textile Bleaching, Dyeing, Printing and Finishing Machinery*, 1926) is suitable for the application of the vat dyestuffs, since the skeins can be totally immersed in the liquor. The machine consists of a framework carrying a number of vertical reels which are capable of being raised or lowered as desired. An electric motor rotates the reels and periodically reverses the direction of circulation. The reels are loaded with skeins and the framework is lowered into a rectangular wooden vat containing the dye liquor. During the dyeing of vat dyestuffs, the skeins are completely submerged in the vat. On completion of the dyeing process the framework carrying the dyed skeins is raised and the dye liquor is replaced by water or other after-treating liquor. The raising and lowering of the frame is effected hydraulically.

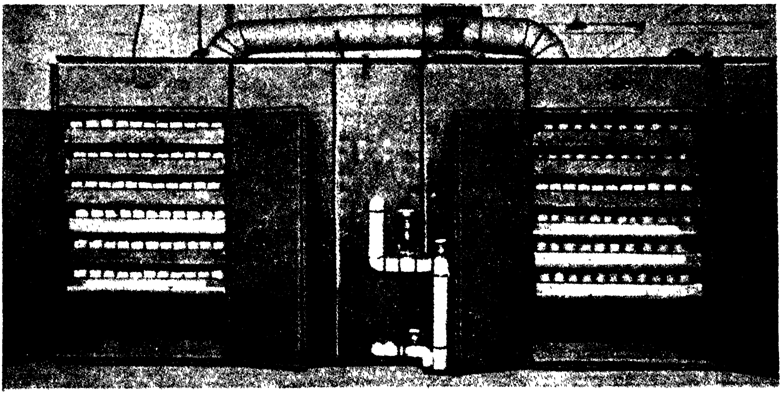

FIG. 6.—Franklin Packages in Proctor and Schwartz Tray Dryer
(By kind permission of the Franklin Process Company, U.S.A.)

Another type of machine suitable for vat dyeing is exemplified by the *Mayoux* and the *Swindells* skein dyeing machines. This type of machine comprises two or more rectangular wooden vats which may be lined with Monel metal or stainless steel. A framework bearing dye-sticks is suspended over the vat and is capable of being raised or lowered, or it may be transferred to another vat. The skeins are suspended from the frame dye-sticks and kept taut by means of a second series of dye-sticks in the lower ends of the skeins. During dyeing, i.e. after the skeins have been lowered into the prepared dyevat, a rocking device (eccentric) is set in motion. The framework is moved upwards and downwards and backwards and forwards, and the submerged skeins are consequently moved gently during the whole of the dyeing period. On completion of dyeing, the framework is raised and then lowered into an adjacent vat prepared with water for oxidation. Rinsing, souring and soaping, or any other treatment necessary, can be carried out in similar vessels.

Pegg Hank Dyeing Machines are reported by the makers to be suitable for the application of vat dyestuffs. These machines are built in a range of capacities for dyeing from 2 lb. to 2,000 lb. yarn. They are constructed of stainless steel and are supported in Columbian pine cradles. Dye liquor circulation is effected by stainless propellers worked by a horizontal motor. (See Fig. 8.)

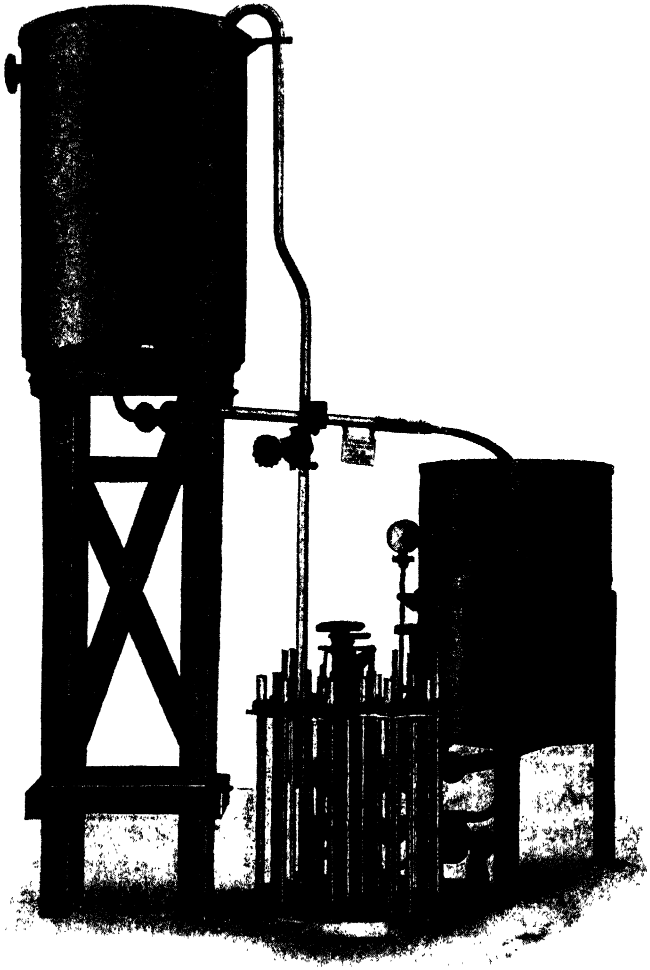

FIG. 7.—Open Machine for Final Soaping-off
(By kind permission of the Longclose Engineering Co., Ltd., Leeds)

Piece Dyeing.—The vat dyeing of piece goods consists chiefly of dyeing on winch machines, jiggers, padding mangles and continuous ranges. As regards the materials of construction it may be said that wood has been almost completely replaced by stainless steels. Wood is unsatisfactory because (*a*) it absorbs large quantities of dyestuffs and chemicals and is therefore difficult to clean, besides being costly in dyeing materials; (*b*) it has a marked tendency to rot in places of difficult access, thus making the life of the machine comparatively short; (*c*) it offers poor resistance to abrasion, and rough places which cause damage to the cloth are difficult to avoid. Stainless steel vessels with welded joints and corners are non-absorbent and easy to clean. Welding technique has now become highly developed, and joints capable of standing up to the stress of temperature changes and vibratory strain give the machine long life.

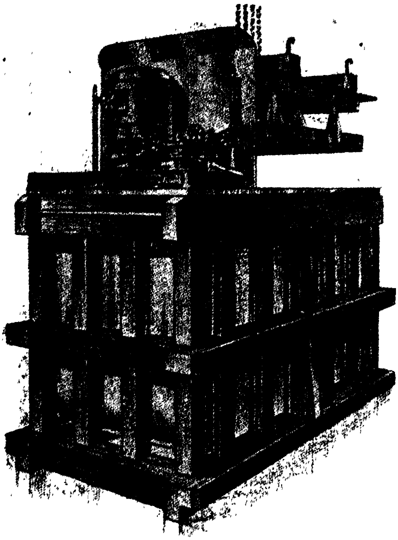

FIG. 8.—Small Hank Dyeing Machine for 90-120 lb. Yarn
(By kind permission of Samuel Pegg & Sons, Leicester)

Winch Machines.—The up-to-date wince or winch machine consists of a stainless steel vessel supported in a mild steel or wooden frame. The reel or wince is mounted on shafting driven at a constant speed and is fixed above the dyeing vessel. The shape and construction of both the vessel and the reel vary somewhat from maker to maker. Reels of an oval shape have lately become popular, since they result in lower tension or strain being put on the goods. Oval reels are formed from about eight stainless spars which are bolted to oval end-plates. Back rollers are fitted for the purpose of lifting the cloth on to the reel, whilst a rail bearing adjustable pegs is fitted to keep the individual pieces separate and free from entanglement.

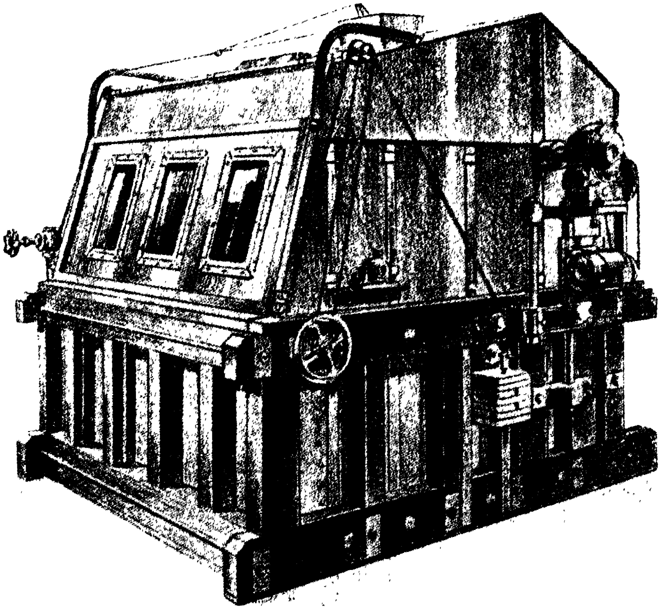

FIG. 9.—Enclosed Piece Dyeing Machine
(By kind permission of Samuel Pegg & Sons, Leicester)

A so-called "stuffing box" is constructed at the back of the machine by means of a perforated division plate, and it is here that additions of dyestuffs, chemicals and auxiliary compounds are made. The dye liquor is heated by means of a steam-pipe which lies in the bottom of this compartment.

Pieces for winch dyeing are fed into the machine, first over the wince and then down into the vessel. They are then led up through the peg rail and over the back roller; at this point the ends of the pieces are sewn together so as to form endless belts. The machine is set in motion and the oval shape of the reel causes the fabric to fall in even folds which slide down the sloping front of the dye vessel.

Only delicate fabrics are vat-dyed on this machine, and the wince should be set as low as possible so as to give a minimum period of air exposure to the fabric during dyeing. Indigosols are widely applied on this machine.

The firms of Samuel Pegg & Son and John Dalglish & Sons make stainless hoods fitted with balance doors and adequate lighting. These hoods fit over the machine and thus conserve heat and retard oxidation. (See Figs. 9 and 10.)

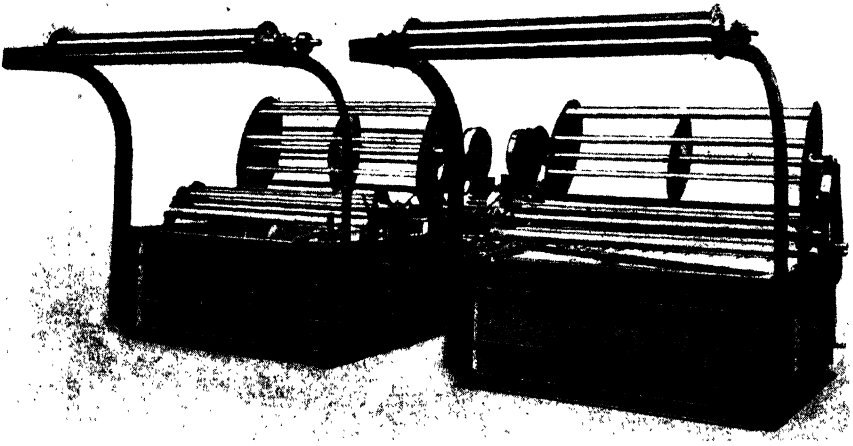

FIG. 10.—Stainless Steel Dye Boxes

By kind permission of Messrs. John Dalglish & Sons, Glasgow

Jiggers.—The detailed designs of jig dyeing machines vary widely and many patented fittings such as special drives, tensionless equipment and automatic reversing devices have been introduced. In principle, however, the jigger is made on the following lines.

It consists of a narrow, deep dye tank over which two rollers are mounted. The small capacity of the tank enables short liquors to be employed for comparatively large quantities of fabric, whilst the small surface of the liquor prevents undue oxidation by the air. The rollers are driven and fitted with a braking device. Various methods of drive are employed, but the bevel-gear drive appears to be the most popular.

Before dyeing is commenced, the fabric is wound open width on to one roller and the loose end of the material is threaded through the dye tank round a number of idle guide rollers in the tank. The fabric is then attached to the second roller above the liquor, and this roller is set in motion. The cloth is thus made to travel through the dye liquor and wound from the first roller to the second. This process is repeated by reversing the direction of travel, and the reversals are continued until the dyeing operation is complete. Tension on the fabric is controlled by means of the brake on the unwinding roller. Further notes concerning jiggers are given on pages 108 and 117; see also Figs. 11 and 12.

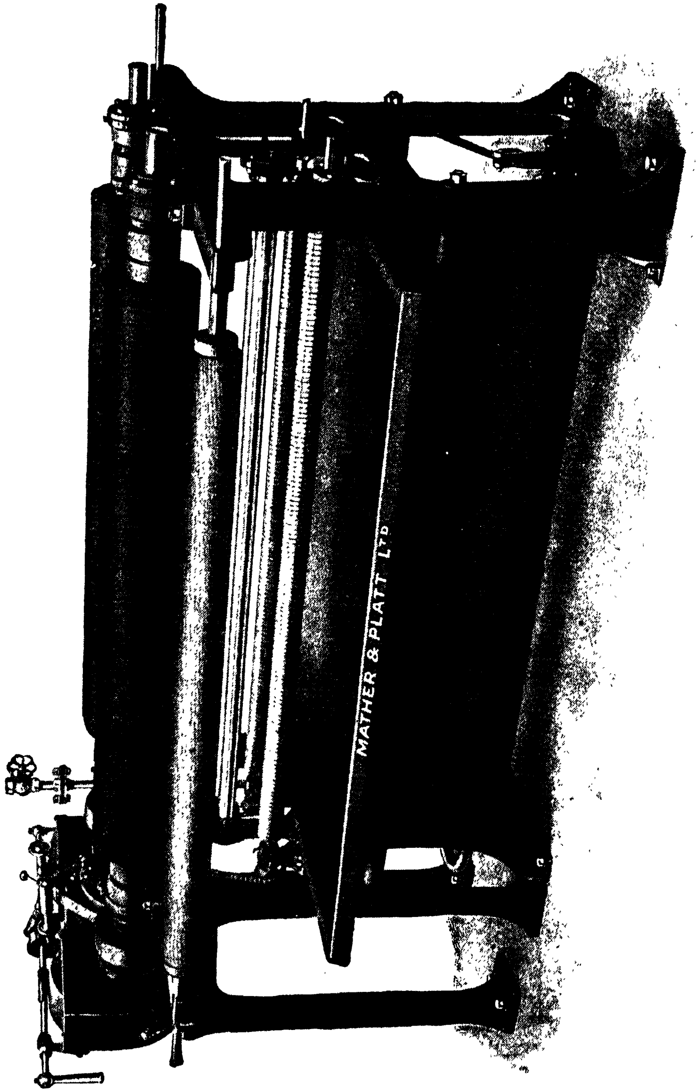

FIG. 11.—Dye Jigger for Delicate Fabrics with Tension Control and Constant Speed

(By kind permission of Mather & Platt, Ltd., Manchester)

"Fibe" Dyeing Machine (Benninger, Uzwil, Switzerland) (G.P. 464,714).—This machine is exceptionally suitable for the dyeing

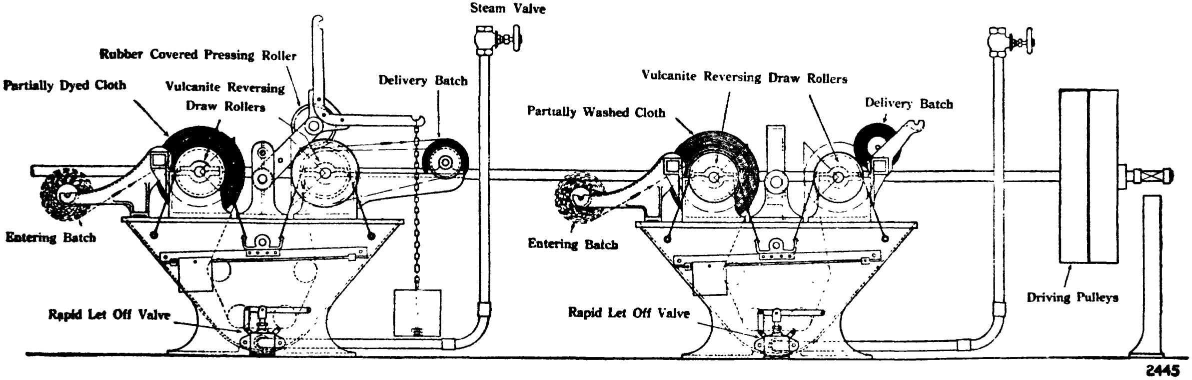

FIG. 12.—Cast Iron Dye and Wash-off Jiggers
(*By kind permission of Mather & Platt, Ltd., Manchester*

and impregnation of fabrics in full width with all classes of vat dyestuffs and their solubilised derivatives. It differs in many respects from the ordinary jiggers and the padding machines described below. The excellent results of its novel principle are well worthy of note, and by its employment fabrics are dyed by one passage through the machine. Delicate and fine fabrics of the crêpe and velvet class, for instance, can be treated without the slightest damage, since dyeing on this machine is carried out with little or no tension. Both light and heavy cellulosic fabrics of all types of weave can be dyed satisfactorily, whilst it is claimed that weaving faults are scarcely visible in the finished dyeings.

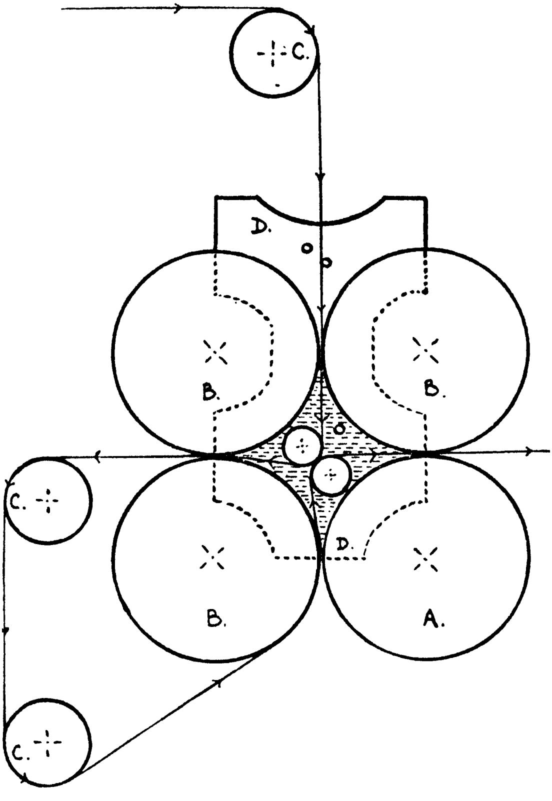

FIG. 13.—Diagram of "Fibe" Machine

The machine consists of a cast-iron frame which supports the bearings of a driving bowl (*A*) (see Fig. 13). Three more bowls (*B*) are mounted in levers so that they are pressed against the driving bowl (*A*) and against each other; the pressure on these bowls is adjustable. The space between the four bowls constitutes the dyebath, which is consequently of very small capacity, viz. about 2 gallons for a machine of 36 in. width.

The fabric is passed through this central dyebath around guide rollers (*C*) and air is pressed out of the fabric by the pressure of the two upper bowls. The expression of air from all fabrics to be dyed is of prime importance and, furthermore, the fabric is then in a state to absorb the dye liquor to its full extent. The fabric next passes out of the dyebath through the side bowls and is led back by means of more guide rollers (*C*) between the lower bowl and the driving bowl (*A*). After the second entry into the dye liquor, the fabric once more travels outwards through the opposite side-bowls, air and liquor being expressed at each passage between the adjusted bowls.

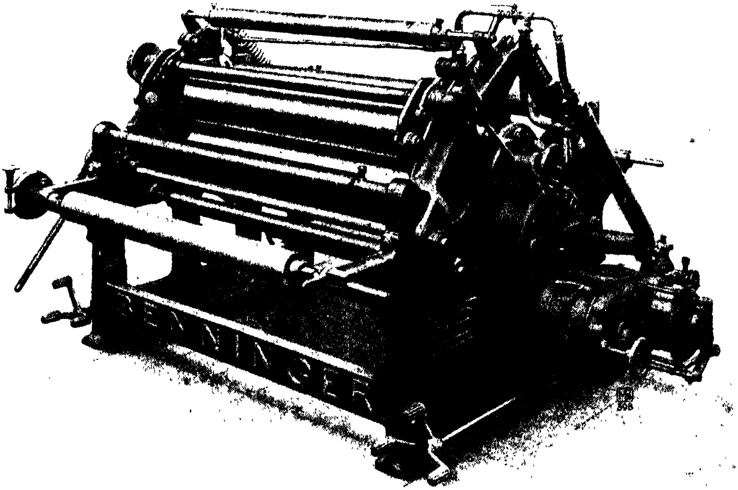

FIG. 14.—Full-width Dyeing and Impregnating Machine ("Fibe")
(By kind permission of Benninger, S.A., Uzwil, Switzerland)

It is obvious that such a machine is very economical as regards consumption of dye liquor; it is stated that 6 to 10 gallons of dye liquor only are required for 100 lb. dry cloth.

In order to form a seal for the dyebath, machine-ground tightening plates (*D*) are allowed to press lightly against soft rubber rings placed on the side-faces of the bowls. The liquor is introduced into the machine by means of a centrifugal pump, and is circulated through the dyebath and into a tank, thus travelling in an endless cycle. Suitable arrangements for temperature control and heating are also fitted. (See Figs. 13 and 14.)

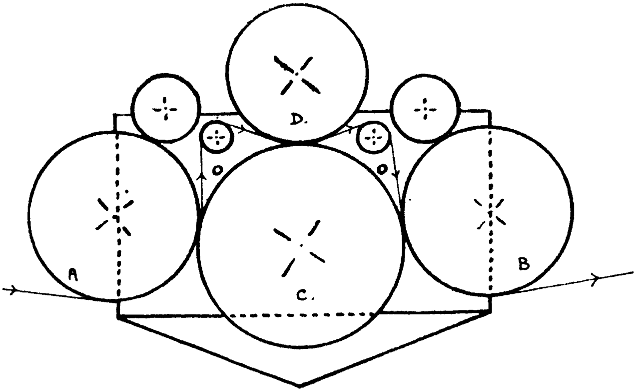

FIG. 15.—Principle of the Haubold Fz Dyeing Machine

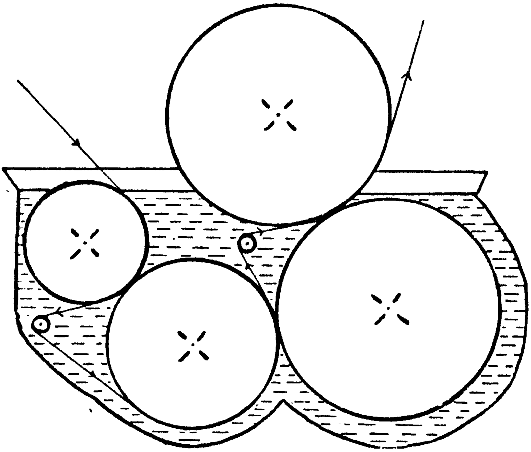

FIG. 16.—Principle of the Zittau KZ Dyeing Machine

Haubold Fz Machine (Haubold A.-G., Chemnitz).—This machine, which is illustrated in Fig. 15, is very similar to the "Fibe" machine just described. It consists of two lateral rollers (*A* and *B*) covered with soft rubber which are pressed by levers against a larger roller (*C*) covered with hard rubber. A lighter and smaller cylinder (*D*), which is also covered with soft rubber, rests upon the large central roller.

FIG. 17.—Hawking Machine
(*By kind permission of the "Textile Recorder," Manchester*)

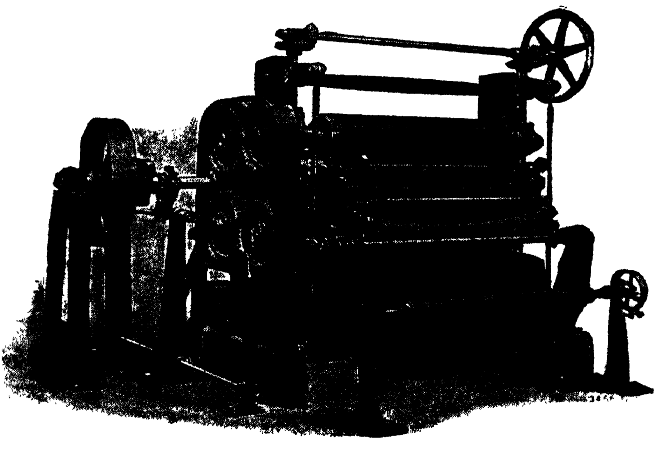

FIG. 18.—Three-bowl Padding Mangle
(*By kind permission of Mather & Platt, Ltd., Manchester*)

The fabric to be dyed follows the direction of the arrow in the diagram, i.e. it enters the machine beneath roller (*A*) and then passes between rollers (*A*) and (*C*), the fabric being freed from air by their pressure. The fabric next passes through the liquor on an inner guide roller and is lightly pressed on to the large central bowl, after which it passes through the dye liquor once more by way of a second guide roller and then leaves the machine *via* rollers (*C*) and (*B*). Heating arrangements, as well as sealing devices based on rubber rings and nickel plates, as in the "Fibe" machine, are also fitted. (See Fig. 15.)

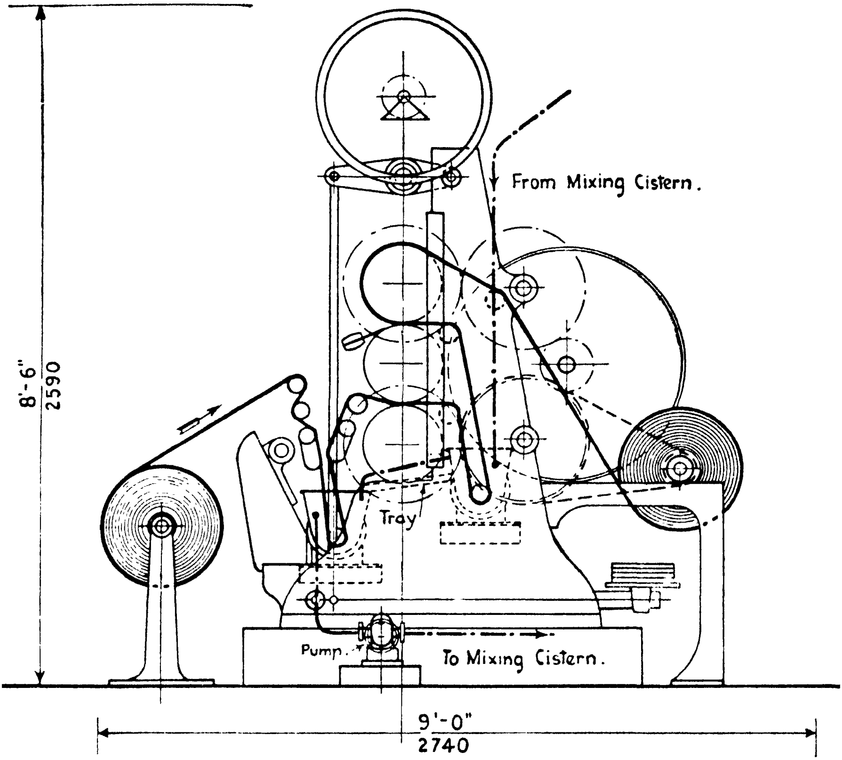

FIG. 19.—Side Elevation of Padding Mangle, cf. Fig. 18.
(By kind permission of Mather & Platt, Ltd., Manchester)

Zittau KZ Machine (Zittauer Maschinenfabrik A.-G.).—As in the two preceding machines, the entering fabric is freed from air by means of pressure bowls. A second pair of rollers enables the goods to be squeezed while in the dye liquor, whilst a third pair provides a final squeezing as the cloth emerges. The volume of liquor in this machine is controlled by the shape of the vessel, as well as by the large amount of space occupied by the large squeezing rollers. (See Fig. 16.)

Hawking Machine.—This machine is the standard machine for the dyeing of wool piece goods with indigo. The name is derived from the hook-shaped tools or "hawks" which were formerly employed to assist the fabric in its passage through the vat (Stansfield, *Jubilee Issue*, *J.S.D.C.*, 1934, 139). The machine consists of a rectangular wooden vat which is approximately 7 ft. square and 5½ ft. deep and let into the floor. A pair of greenheart wooden draw-rollers is situated just below the liquor level and towards one end of the vat. The rollers are about 6 in. diameter and are balanced by a weight which is attached to the shaft. This arrangement allows the rollers to be raised out of the liquor. Lying horizontally and in front of the draw-rollers (and also below the level of the liquor) is a flat wooden scray. There is a similar short scray behind the draw-rollers. The latter are positively driven from overhead shafting.

The machine is loaded by raising the hawking arrangement clear of the vat, and the pieces are then threaded through the draw rollers and the ends are stitched together. The loaded hawking arrangement is then lowered into the prepared vat so that the pieces fall into folds at the bottom of the vessel. The pieces are dyed in open width and are drawn along the front scray just below the surface of the liquor. After passing through the draw-rollers, the nipped fabric continues its cycle round the vat until dyeing is complete.

Two hawking machines are illustrated in Fig. 17 (page 217); the machine in the foreground is working and the machine in the rear is being unloaded at the end of the dyeing process. The squeezing rollers through which the piece is emerging are fixed on overhead rails so that they can be transported easily from one vat to another. Bird has given an excellent description of this machine (*Textile Recorder*, 1943, **60**, 42).

Padding Mangles and Ranges.—A large number of machines have been designed for the padding processes used in the application of the vat dyestuffs to piece goods. The processes are (*i*) the padding of reduced dyestuffs; (*ii*) the padding of unreduced dyestuffs, i.e. pigment padding; and (*iii*) the padding of Indigosol dyestuffs. Reduced dyestuff padding is usually carried out on the jigger.

Some details regarding the machines employed for these purposes have already been given on pages 110–111, 124, and

131–135, and the illustrations and diagrams (Figs. 18–22) will provide a clearer picture.

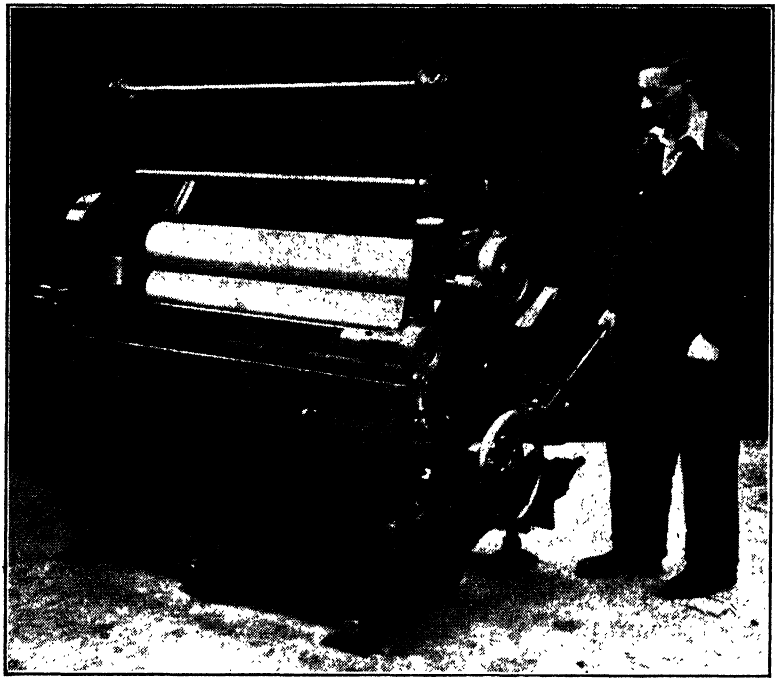

FIG. 20.—Portable Mangle
(By kind permission of John Dalglish & Sons, Glasgow)

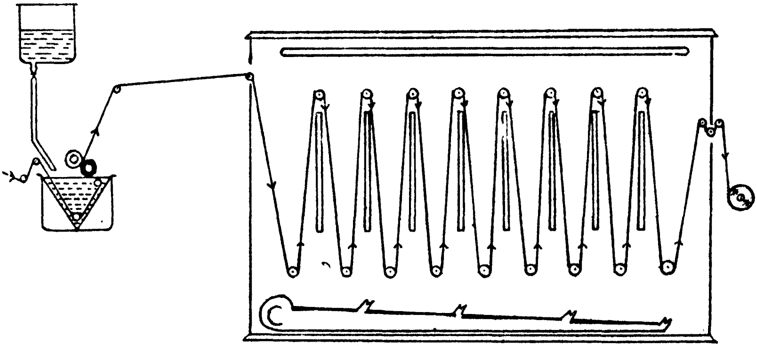

FIG. 21.—Padding and Hot-Flue Drying System

Fig. 18 shows the Mather and Platt three-bowl padding mangle for vat dyestuffs. This machine is designed for the continuous treatment of cloth with vat dyestuffs in the unreduced condition. The frame is constructed to withstand the heavy pressures applied by means of weights and levers, whilst the padding bowls themselves are mounted in ring-oiled bearings, the upper and lower bowls being composed of vulcanite and the centre bowl of india-rubber. The upper and lower bowls are driven by machine-cut spur wheels which are instrumental in avoiding any slippage. The machine can be employed for one or two immersions by the

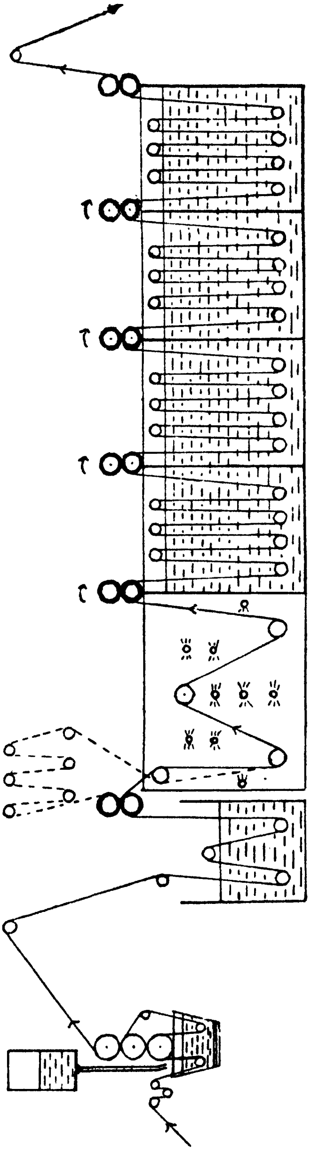

FIG. 22.—Continuous Padding and Developing Range

use of the two stainless-steel troughs provided. An overhead tank where the dye liquor is prepared is fitted with an agitator and a feed pipe to the steam-heated troughs through which the liquor is circulated. Four-bowl padding mangles of similar construction and provided with three troughs are available; these machines are designed to give improved output and increased penetration. (See Figs. 18–19.)

Fig. 21 shows a padding range for the production of deep shades. The goods are dried before developing by a passage through a hot-flue unit heated either by a steam-chest or by means of hot-air circulation.

Fig. 22 shows a continuous padding and developing range suitable for pigment padding, as well as for the dyeing of Indigosols. A three-bowl padding mangle works in conjunction with a developing bath, a skying arrangement, a spirt-pipe washing tank and a series of open vessels for souring or neutralisation, washing and soaping.

Continuous Ranges.—The continuous piece-dyeing machine for vat dyestuffs comprises four cisterns fitted with the necessary guide rollers and squeezing devices for each vessel. The cisterns are constructed from cast-iron plates with machined joints and are provided with overflow pipes, let-off valves and closed-coil steam-heating pipes. The separate vessels are inter-connected with pipes and valves so that, if required, the same liquor level can be maintained throughout the machine.

The squeezing device consists of a cast-iron bowl and an india-rubber bowl mounted in frames with single levers and weights for the application of even pressure. The guide rollers are made from steel tubes fitted in bearings at the sides of the vessel, and arrangements are made so that the top row of rollers can be carried well above the liquor to permit oxidation to take place when necessary. In front of each set of squeezing bowls is a series of opening rollers which facilitates the removal of creases from the fabric being processed.

A special continuous dyeing range (Fig. 23) is necessary for dyeing cotton piece goods with indigo. The cloth is passed through the first vessel containing the reduced indigo and then through the nip to the overhead winces, which are designed to give the goods an air passage sufficient to promote oxidation. The cloth then falls from the winces on to slowly moving endless creepers or aprons to complete the oxidation of the indigo before passing into the next dyeing vessel. The process is continuous, and the necessary number of immersions are given before the

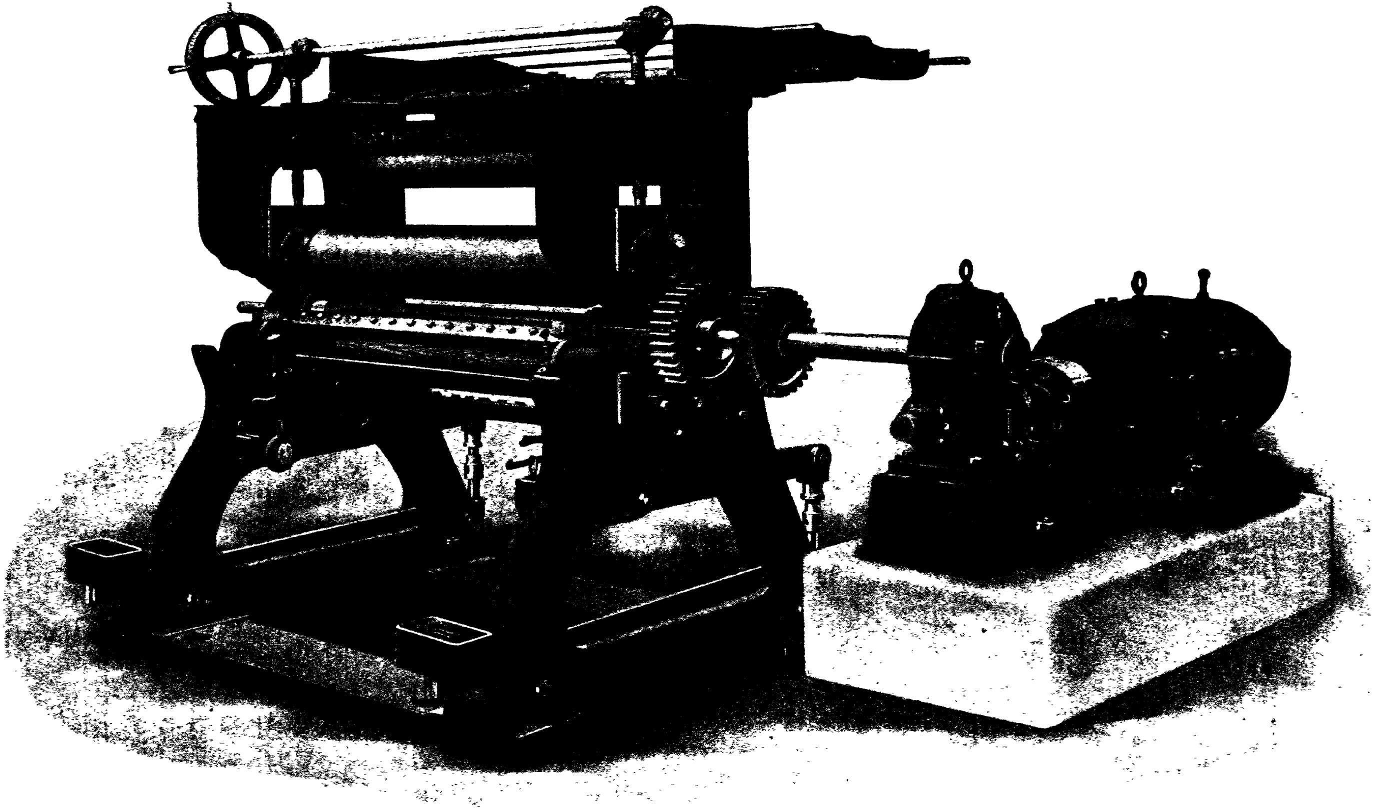

FIG. 24.—Single-Colour Printing Machine with Roller Bearings

By kind permission of Mather & Platt, Ltd., Manchester) goods are piled down ready for subsequent souring and washing.

In the machine illustrated (Fig. 23) there are four dyeing vessels composed of cast-iron plates with machined joints. Each cistern contains a series of pine rollers which run in bronze-bushed filbores, and these are contained in a steel cage. The latter is arranged so that its complete removal is possible when cleaning or inspection is necessary. Blocks fitted to the joists or the roof of the dyehouse enable easy removal of the cages. Automatic agitators are fitted in each vessel.

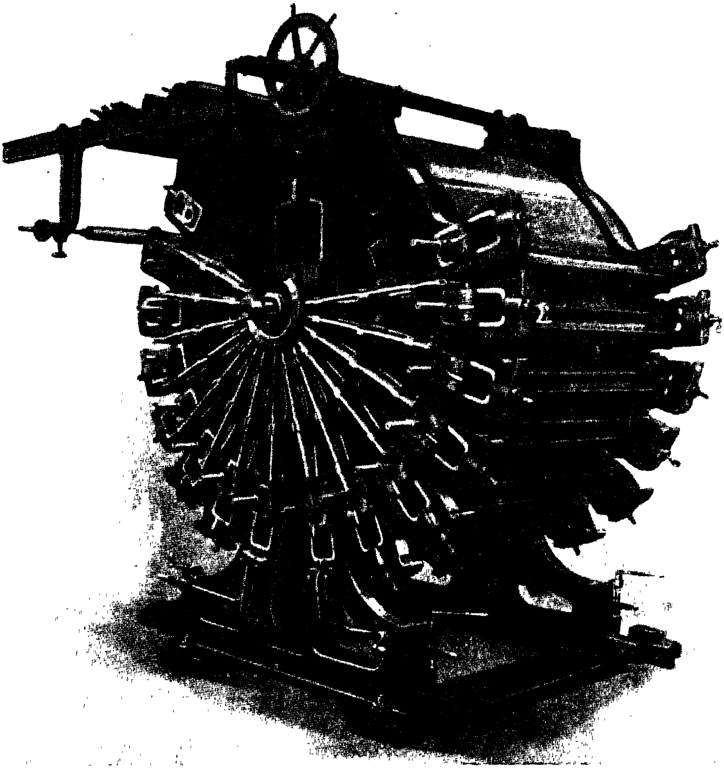

FIG. 25.—Fourteen-Colour Garment Printing Machine
(By kind permission of Mather & Platt, Ltd., Manchester)

The squeezing nip at the delivery end of each cistern is provided, in the first three cases, by a bowl of cast iron and one of sycamore or india-rubber. The final squeezing bowls are both constructed from cast iron.

sequent souring and

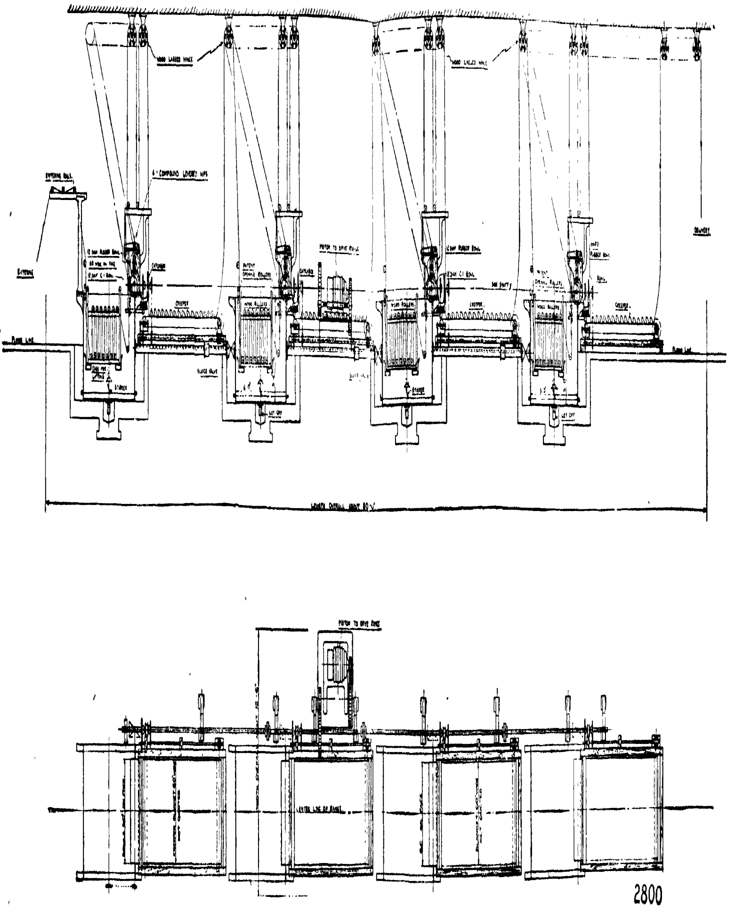

FIG. 23.—Continuous Indigo Piece-Dyeing Range with Creepers arranged for Oxidising

(By kind permission of Mather & Platt, Ltd., Manchester)

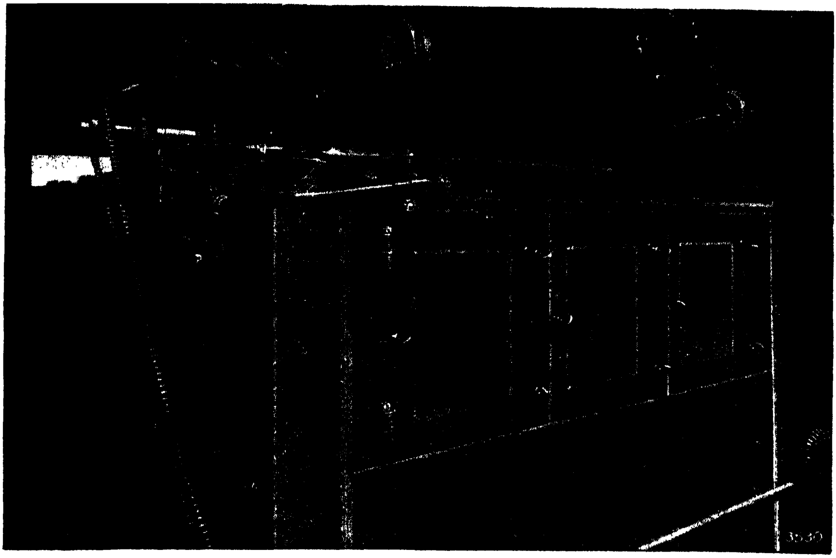

Fig. 26.—Continuous Steamer and Ager
(*By kind permission of Mather & Platt, Ltd., Manchester*)

Fig. 27.—Continuous Steamer and Ager
By kind permission of Mather & Platt, Ltd., Manchester)

Printing Machinery.—Machines for the printing of textiles are very complicated and are not described in this book, but a single-colour and a fourteen-colour printing machine are illustrated in Figs. 24 and 25.

Continuous Steaming and Ageing Machinery.—The world-famous Mather & Platt machine illustrated in Figs. 26 and 27 is used for developing prints of vat dyestuffs, as well as for discharges and prints of basic, chrome, and alizarine dyestuffs. With this machine it is possible to obtain and control accurately the atmospheres of different humidity and temperature required by different steaming and ageing treatments. It consists of an all-metal chamber with a roof fitted with steam-chests of cast iron which work at a pressure of 5 lb. per square inch. With this arrangement there is little risk of condensation difficulties. The requisite conditions of temperature and humidity are obtained by means of closed heating coils and perforated steam pipes at the bottom of the chamber. The pieces enter the chamber *via* a pair of steam-heated brass draw-rollers, and the cloth then automatically falls into a series of folds. The latter travel forward on poles which are fixed to travelling chains and move along rails situated at the sides of the machine. Finally, the cloth leaves the machine through apertures and is plaited down by means of guide rollers.

The Hydrosulphite and Aniline Ageing Machine.—This machine is employed for the fixation of vat colour prints and in the production of discharges. It consists of a chamber made from cast-iron plates and is fitted with steam-heated chests on the roof and at each end. A series of guide rollers inside the chamber allow the cloth to travel in a number of long folds through the machine. The cloth enters and emerges from the machine at the same end by way of a steam-heated mouthpiece fitted with a self-closing device for the exclusion of air. (See Fig. 28.)

Other machines of interest in vat dyeing and printing, such as hydro-extractors, suction extractors, can-drying ranges, stenters and other auxiliary and miscellaneous machines, have been described in the following publications:

A. J. Hall, *Textile Bleaching, Dyeing, Printing and Finishing Machinery*, Benn, 1926.

K. S. Laurie, "Modern Textile Finishing Machinery," *J.S.D.C.*, 1940, **56**, 289.

K. S. Laurie, "Some Textile Finishing Machines," Institution of Mechanical Engineers. Lecture delivered on 19th February 1943 and published by the Institution.

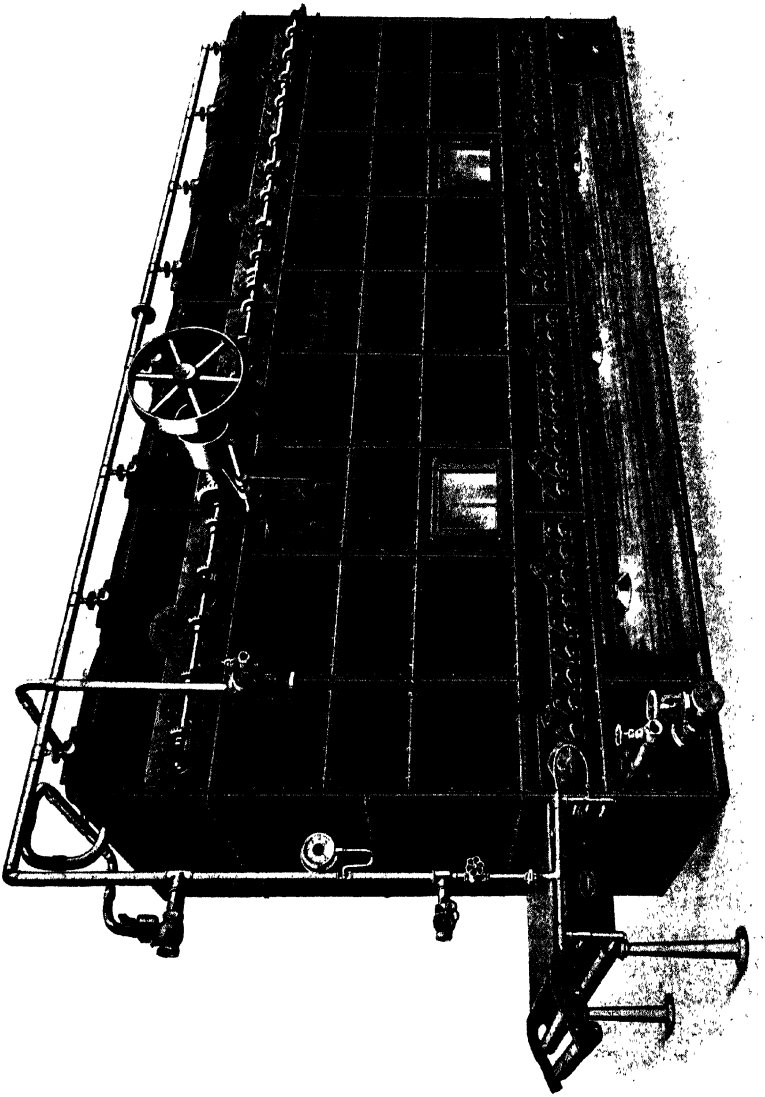

FIG. 28.—Hydrosulphite and Aniline Ageing Machine

(By kind permission of Mather & Platt, Ltd., Manchester)

CHAPTER XI

NON-TEXTILE USES OF VAT DYESTUFFS

QUITE apart from the great many uses to which vat dyestuffs are put in the dyeing and printing of textiles, there are other departments of industry which employ them in the form of pigments.

Both the indigoid and anthraquinonoid classes of vat dyestuffs are employed in the paint industry and allied trades. The expense is somewhat prohibitive, however, and their relatively low tinctorial value as pigments prevents their use in certain fields. Hitherto, the vat dyestuffs have been chiefly employed in pale and pastel shades on account of expense. Disadvantages of this kind, however, are outweighed by the excellent properties which the vat dyestuffs possess in respect of fastness to light, weathering, solvents and heat. Duller shades than are obtained on textile fibres result from the use of these colours in the form of pigments, and even if the dyestuff is first reduced and then oxidised before application only small increases in brightness and colour value are obtained. Vat dyestuffs therefore require special preparation for the pigment-consuming industries, the aim being to accentuate the brightness and tinctorial value of the dyestuff to the utmost, rather than to improve its solubility or speed of vatting, as is demanded by the textile trade. Particular attention is paid to the texture, fineness, shape and size of the pigment particles. Such specially prepared vat dyestuffs exhibit an excellent standard of workability, a high standard of texture and good resistance to bronzing.

Their fastness to outdoor conditions outweighs any of their disadvantages. In lithographic ink preparations the vat dyestuffs show no "breaking down" tendency, and they are able to resist severe buffing. Paints and lacquers for outdoor use make high demands upon the fastness to light and weathering of the pigment. Vat dyestuffs, therefore, are eminently suitable for this purpose and find extensive use in the production of lacquers and enamels for use on coachwork and automobiles. The phthalocyanine dyestuffs are perhaps the only rivals of the vat dyestuffs, and the two classes may be mixed without any reduction in fastness properties.

Vat dyestuffs may be employed in the coloration of distempers, size and lime mixes, oil paints, enamels, lacquers, poster colours, pastel crayons and coloured pencils.

The beater dyeing of paper pulp may be accomplished by the use of the vat dyestuffs. For this purpose it is essential that the dyestuff should possess a high degree of dispersion, an extremely fine form being necessary in order to avoid the appearance of specks in the dyeings. The dyestuff particles are retained mechanically by the fibres, and good sizing with resin size assists the retention. The precipitating properties of aluminium sulphate also promote fixation. High-class papers free from mechanical wood pulp, for which very exacting demands are made as regards fastness to acids, alkalis, chlorine, water and light, are dyed almost exclusively with vat dyes.

When paper wrapping materials, such as are required for soap packages, are dyed or printed with vat dyestuffs, a high degree of resistance to alkali is necessary. Fastness to alkali, e.g. lime, is also very important in printed wallpapers and sanitary papers, as well as in the newer washable paints of the distemper type.

The most popular dyestuffs for these purposes are probably the anthraquinoneazine Blues and *iso*-dibenzanthrone Violets and the Jade Greens. The I.G. Farbenindustrie A.-G. market a number of "P" brand vat dyestuffs which are specially prepared for pulp coloration. They include Indanthrene Blues GGSP, 3GP, RSP; Indanthrene Brilliant Violet RRP; Indanthrene Red Violets RHP and RRKP; Indanthrene Brilliant Pinks BP and RP; Indanthrene Pink BP; Eglantine BBP; Indanthrene Red RKP; Indanthrene Yellow GP; Indanthrene Golden Orange G and Indanthrene Brilliant Orange RK.

A process of paper dyeing with vat dyestuffs which closely imitates cotton dyeing technique has been described by Lips (*Paper Trade Journal*, 1944, **118**, TAPPI, 105). A solution of the reduced dye is added to the pulp in the beater at 60°C. Amounts of caustic soda and hydrosulphite are only sufficient to prevent the oxidation of the dye for about 10 minutes. The pulp is dyed during this short span of time and the dye begins to oxidise without the employment of chemical oxidants. When oxidation is complete, sufficient acid, alum, or nitre-cake is added to neutralise the excess alkali and the pulp is then sized in the normal manner.

The author has made small tests which indicate that paper pulp can be dyed in all depths of shade using cotton dyeing technique with a minimum of caustic alkali. After a short dyeing time at a temperature which suits the particular dye in use, sufficient of the sodium salt of *m*-nitro-benzene sulphonic acid is added to fully oxidise the dye *in situ*. In this way, any dye which has not been absorbed by the cellulose is precipitated in a very fine form which is readily taken up by the pulp after neutralisation and sizing. Dyeings carried out in this manner are bright, free from visible specks and excellent in respect of colour yield.

For the manufacture of printing inks and oil paints, Indigo Pure BASF; Brilliant Indigos B, 4B and 4G; Indanthrene Blues GGSL, GGSNL and RL; Helio Fast Pink RL and Helio Fast Yellow 6GL are recommended. ("L"=for use as a lake.)

Helio Fast Yellow 6GL is a condensation product of *a*-aminoanthraquinone and salicylic acid, and, although it is of no use for textiles, its structure and properties show it to be essentially a vat dyestuff. The thio-indigoid reds and pinks, indigo, and various other indigoid derivatives, show slightly inferior fastness properties compared with the anthraquinonoid derivatives, particularly as regards fastness to light.

Opaque or almost transparent spirit- and nitro-lacquers may be coloured with Indanthrene Red Violet RH for Lakes and Indanthrene Blue GGSL, which show good resistance to weathering and over-varnishing. Helio Fast Pink RL shows less resistance to over-varnishing, but has good fastness to weather and light.

Special brands of Indanthrene Blues are employed for producing "whites" on bleached cotton materials, as well as in the production of white papers and for whitening bleached sugar.

In recent years, several patents have been granted for the preparation of special vat dyestuffs of the benzanthrone and dibenzanthrone classes for colouring plastics, oils and rubber (cf. *B.P.* 487,705, and 480,162). Vat dyestuffs from the ordinary textile ranges, when specially prepared from the physical standpoint, are also highly suitable for colouring plastics, synthetic resins, moulding powders and rubber, on account of their resistance to heat and other agencies encountered in processing. Allied to this type of coloration is that employed in the production of oilcloth, linoleum and lincrusta. Here, the vat dyestuffs fill the demands for fastness to heat, insolubility in oil, insolubility in water and freedom from lead.

Vat dyestuffs are very suitable for colouring rubber since they are resistant to all types of curing treatments, e.g. they withstand treatment with sulphur chloride and mild alkali, which are used in the cold-cure process of vulcanisation. They are insoluble in rubber, and therefore cause no trouble through bleeding into adjacent rubber patterns, etc., during vulcanisation. The stability and fastness to light of the Jade Greens and indanthrone Blues make them very useful for this purpose.

CHAPTER XII

IDENTIFICATION OF VAT DYESTUFFS

THIS chapter provides a review of the methods employed in the identification of vat dyestuffs under the following general scheme:

(i) Identification of Single Dyestuffs. (*a*) In substance. (*b*) In dyed or printed patterns.

(ii) Identification of the Components of Vat Dyestuff Mixtures. (*a*) In substance. (*b*) In dyed or printed patterns.

A number of methods and tables have been published for the purpose of such investigation, and the following is a brief résumé of the more important methods.

(1) **Holden** (*J.S.D.C.*, 1909, **25**, 47).

Holden examined approximately two dozen dyestuffs available at the time of the investigation, and gave lists of distinguishing reactions based upon (*a*) the use of chloroform as a solvent, (*b*) the use of titanous chloride as a reducing agent, and (*c*) the reactions of the dyed patterns towards bleaching powder solutions.

(2) **Green and Frank** (*J.S.D.C.*, 1910, **26**, 83).

These workers gave identification reactions for some 60 vat dyestuffs of the period, using (*a*) reduction with Hydrosulphite X; (*b*) a dry-heat test, with observation of the vapours evolved; and (*c*) treatment of the dyed fibre with concentrated sulphuric acid, with observation of the colour change. Hydrosulphite X is a solution of hydrosulphite–formaldehyde activated by the addition of a little anthraquinone.

(3) **Jones and Kilby** (*J.S.D.C.*, 1925, **41**, 217).

These authors examined about 250 vat dyestuffs with the aid of eight tests. The tests comprised examination of: (*a*) The colour of the *leuco*-vat dye in alkaline hydrosulphite solution. (*b*) The reduced sample from (*a*) after acidification with dilute sulphuric acid. (*c*) A solution of the dye in concentrated sulphuric acid. (*d*) Colour and bleeding in concentrated nitric acid. (*e*) The pattern from (*d*), after pressing between white filter papers and then immersing in acid stannous chloride solution (prepared from 100 g. stannous chloride, 100 g. hydrochloric acid, sp. gr. 1·16, and 50 ccs. water). (*f*) A fresh pattern after immersion in a 5°Tw. sodium hypochlorite solution containing a drop of acetic acid;

any colour change was noted. (*g*) The pattern and solution from (*f*) after boiling together; a note was made of any further shade change. (*h*) A fresh pattern after boiling in benzene; the colour of the solution and any fluorescence were noted.

(4) **Schultz** (*Farbstofftabellen*, 1931, and subsequent supplementary volumes).

In this work, which is the German equivalent of the British *Colour Index* (Rowe), tabulated lists of synonymous dyestuffs are given, together with details of their spectrum analyses. The colour of the vat dyestuffs in certain solvents and sulphuric acid, as well as the colour of the *leuco*-compounds and the fastness properties, are given in concise form.

(5) **Herzog** (*Reactionstabelle der Küpenfarbstoffe*, 1933, Wepf et Cie, Basle).

In this booklet by Dr. E. Herzog (printed in French and German), colour reactions of individual vat dyestuffs on the fibre are described, including (*a*) the colour of the dyeing in concentrated sulphuric acid, (*b*) the colour of the *leuco*-compound in alkaline hydrosulphite solution, and (*c*) the colour of the dyeing in acid hydrosulphite solution. The colours shown by the pattern under the various tests are tabulated in the order (*c*), (*b*) and (*a*), and numbers are allotted to each shade for the purpose of consulting the tables which Herzog has provided. Thus, there are ten denominations of colour given, viz. 0=unchanged, 1=yellow, 2=orange, 3=red, 4=carmine, 5=violet, 6=blue, 7=green, 8=brown, and 9=grey or black.

Further, this system places the dyestuffs in their constitutional classes, viz.:

I Derivatives of 3-Indole-2′-thionaphthenindigo
II Indigoid and Thioindigoid Dyestuffs
III Acenaphthene Dyestuffs
IV Carbazole, Sulphurised Dyestuffs
V Anthraquinone Dyestuffs
VI Benzanthrone Dyestuffs

Special detailed attention is given to the identification of closely allied dyestuffs such as indigo and its halogenated derivatives, the indigoid Violets, the carbazole-indophenol group, e.g. Hydron Blues; the dibenzanthrone Dark Blues, Violets and Blacks; and the anthraquinoneazine Blues (indanthrone and its derivatives). In all, over 500 dyestuffs are mentioned by name.

The general procedure recommended by Herzog is as follows:

Concentrated Sulphuric Acid.—A small pattern is immersed in about 1 cc. of pure sulphuric acid. If the colour of the dyestuff is not evident within about 1 minute, it is permissible to warm the solution slightly, but care must be taken to ensure that the sulphuric acid is not browned by heat. The number corresponding to the resulting shade is then allotted and set down in the report.

Alkaline Hydrosulphite.—In this case the pattern is immersed in a warm 2% solution of caustic soda containing a little hydrosulphite. The colour of the *leuco*-compound is noted and recorded numerically.

Acid Hydrosulphite.—To the above alkaline test-solution is added a little hydrochloric acid, until a shade change in the pattern becomes apparent; the shade number is then recorded.

The results of the three tests are recorded (from left to right) in the order—Acid Hydrosulphite Number, Alkaline Hydrosulphite Number, Sulphuric Acid Number:

e.g. 1 (yellow) 9 (grey) 8 (brown)

The three-figure number thus obtained is then located in the table; in the case of the example, 198, Indanthrene Yellow GK or a corresponding product is indicated. In Herzog's tables, the Schultz numbers are given as an additional guide.

(6) **Green** (*Analysis of Dyestuffs*, 1920, Griffin & Co.).

Green gives details for identifying various classes of vat dyestuffs by the employment of different test-solutions.

(7) **Bradley and Derrett-Smith** (*J.S.D.C.*, 1940, **56**, 97–121).

This is the most recently published work on the identification of individual vat dyestuffs, and probably the most concise and most complete yet issued. Bradley and Derrett-Smith make use of four colour reactions, and have tabulated the properties of 813 vat dyestuffs.

The tests employed are as follows:

(i) *Alkaline Hydrosulphite.*—A small sample of the dyed or printed material is immersed in 5 ccs. of a reagent made up from 25 g. sodium hydrosulphite dissolved in 500 ccs. cold 2% caustic soda solution. The pattern and reagent are boiled in a test-tube for 2–3 seconds and the colour of the sample noted.

(ii) *Acid Hydrosulphite.*—For this test two reagents are required, viz. (*a*) 2 ccs. glacial acetic acid diluted to 500 ccs. with water, and (*b*) 50 g. Formosul dissolved in 500 ccs. warm water. Equal parts of these two solutions are employed and a pattern is boiled in 10 ccs. of the mixture for 2–10 seconds. The resultant shade is noted.

(iii) *Nitric Acid.*—A pattern of the coloured material is immersed in about 10 ccs. concentrated nitric acid (sp. gr. 1·42) in a dry white porcelain dish. After immersion for 15–30 seconds the colour of the pattern and any bleeding are noted.

(iv) *Sulphuric Acid.*—The colour of the pattern and "bleed" are noted during an immersion for 15–30 seconds in pure sulphuric acid (sp. gr. 1·84) in a white porcelain dish.

The tables of Bradley and Derrett-Smith provide a useful work of reference. In addition the investigator should, if possible, always be able to compare the pattern under analysis with actual patterns of the dyestuff indicated by the tables, i.e. for the purpose of confirmation.

The first essential in the identification of a vat dyestuff is, of course, to prove that the pattern or dyestuff sample under examination is actually a vat dyestuff. Simple tests for distinguishing vat dyestuffs from other groups of colouring matters have been developed by Green (*loc. cit.*) and by Clayton ("Identification of Dyes on Textile Fibres," *J.S.D.C.*, 1937, **53**, 178; and in book form, published by the Society of Dyers and Colourists, 1937). In Clayton's Tables, for instance, the procedure for cotton fabrics is as follows: (*i*) Boil a sample of the dyeing or print in dilute ammonia solution for 1–2 minutes; with vat dyestuffs the solution does not become coloured. (*ii*) A pattern is boiled for a few seconds in a solution consisting of 1 cc. of 5% caustic soda solution; 4 ccs. of 5% ammonium chloride solution are then added and boiling continued for a further short period. Tests are then described for the identification of basic dyestuffs. (*iii*) A pattern is boiled in 5% caustic soda solution for 2 minutes; if no dyestuff (or only a trace) is removed the test indicates that either an azoic or a vat dyestuff is present. (*iv*) To distinguish between these two classes of dyestuffs, a fresh pattern is boiled vigorously for 2 minutes in Formosul "G" solution containing a few drops of 70°Tw. caustic soda. Formosul G solution is prepared by dissolving 20 g. Formosul in 75 ccs. hot water, diluting with 75 ccs. cold water and adding 50 g. commercial ethylene glycol. By this treatment, the azoic dyeings are partially or completely stripped and any changes are permanent, i.e. there is no return to the original shade on exposure to air or treatment with oxidants. The vat dyestuffs, on the other hand, are either decolorised or altered in shade, but upon exposure to air or on being treated with Vat Dye Developer the original colour returns, although not always in its original depth. (*v*) The inference—"vat dyestuff"—is finally confirmed by boiling a pattern in ethylene diamine containing a little solid glucose. The shade of the *leuco*-compound is immediately evident, and the original colour may then be re-developed by treating the reduced pattern with Vat Dye Developer. The latter consists of 1 g. ammonium persulphate and 0·5 g. ammonium dihydrogen phosphate in 100 ccs. of cold water.

(1) Identification of Single Dyestuffs

(*a*) *In Substance.*—For many years it has been the present author's practice to test all samples of vat dyestuffs which come his way and to keep a list of the results for ready reference. The preliminary tests generally applied consist merely of determining the colour of the dyestuff in sulphuric acid and of noting the colour of its *leuco*-compound. Where similarities between dyestuff types have been observed, such dyestuffs have been tested side by side using a greater number of tests of the type already described in the above text. In this way it has been possible to build up a valuable list of synonymous products. Such a list serves as a personal Colour Index, and its value is inestimable in investigations of this type.

Occasionally it has been found that the presence of large amounts of dispersing agents and diluents have altered the apparent colour of the dyestuff to a marked degree, e.g. in sulphuric acid. On this account it has been found advisable to begin by boiling up a small sample of the dyestuff in water in order to dissolve out any water-soluble compounds which may be present. The dyestuff is then filtered off, washed several times on the filter with boiling water and allowed to dry thoroughly. The "spot" tests may then be carried out, either in test-tubes or on a white porcelain spotting-tile.

In general, it will be found that a few preliminary tests will indicate the class of vat dyestuffs to which the unknown sample belongs. For example, the derivatives of indigo and thioindigo, and indeed all the indigoid vat dyestuffs, are almost without exception found to yield almost colourless, pale yellow, golden yellow, or yellow-brown *leuco*-compounds when treated with caustic soda–hydrosulphite solution. Further, these dyestuffs are volatile when subjected to dry heating, and several of them give characteristic coloured fumes during sublimation, e.g. indigo and its halogenated derivatives yield violet fumes on being heated in a dry test-tube. The indigoid vat dyestuffs are usually soluble in boiling pyridine, benzene and glacial acetic acid.

The anthraquinonoid vat dyestuffs are usually distinguishable by their great shade change when converted to the *leuco*-state, and with a little practice it is soon possible to narrow down the possibilities to one or two likely dyestuffs. The anthraquinonoid vat dyestuffs, in contrast to the indigoid vat dyestuffs, are non-volatile and dry heat rarely results in sublimation, but much oftener in charring followed by complete destruction. The solubility of these dyestuffs in such solvents as boiling pyridine, benzene and glacial acetic acid varies widely; in general, they are only partially soluble or remain totally undissolved.

Dyestuffs of the sulphurised type, i.e. Hydron Blues, etc., do not sublime on heating, but give characteristic yellow to yellow-brown vats and are insoluble in pyridine.

A great many dyestuffs may be recognised immediately, once the investigator has had some practice. The dyeing properties alone may at once indicate the dyeing class to which the dyestuff belongs. For this purpose it is best to carry out the following series of dyeings with 5-g. cotton skeins, using the same weight of dyestuff in each case and dyeing for 40 minutes:

(1) Dye cold. Use the IK Method + salt.
(2) Dye at 40°–50°C. IW Method + salt.
(3) Dye at 60°C. IN Method.
(4) Dye by the hydrosulphite–sulphide process, as for Hydron Blues.
(5) Dye at 60°–70°C. using only small amounts of alkali, as for the indigoid dyestuffs.

The dyeing process which yields the best colour value and proceeds most evenly should indicate the dyeing class; dyeings carried out in the exhaust-liquors will show the method which gives the best degree of exhaustion. A search can then be made for the particular dyestuff in the specific class thus indicated.

Several dyestuffs with characteristic *leuco*-compounds can be identified almost at once, and simple confirmatory spotting tests will then help in the final decision. The Indanthrene Blues, for instance, all give blue vats and blue dyeings. *leuco*-Indanthrene Brilliant Orange GR is green with a red fluorescence; Indanthrene Yellow G reduces at once to the characteristic cornflower blue; Indanthrene Scarlet GG is olive-green in the dye bath—and so on. Caledon Jade Green may be readily recognised by heating a small pattern of the dyeing in a Formosul solution containing a little anthraquinone (or use Clayton's Formosul G). After boiling for a few seconds, Jade Green patterns acquire a characteristic cherry-red shade.

(*b*) *In Dyed or Printed Patterns.*—When it is necessary to identify the homogeneous dyestuff which has been used to produce a print or a dyeing it is best to employ the methods of Herzog or of Bradley and Derrett-Smith. For this purpose it is essential that the actual tables published by these authors should be in the hands of the investigator. Self-prepared tables are also useful, and may be prepared from patterns taken from the dyestuff manufacturers' pattern cards. The investigator must also take into account the effect of the human factor in describing shades and deciding, for instance, whether a brown shade is "yellow-brown," "brown," or "red-brown." In consulting tables, allowance must necessarily be made for such differences in colour conception. For this reason alone it is always safest to compile one's own lists, or at least to compare the unknown pattern side by side with known standards indicated by the tables.

Slight differences in shade may occur with spot tests, even when the same dyestuffs are being tested. Such differences occur, for instance, if the dyed or printed colour has been carelessly applied or insufficiently soaped after dyeing. Deviations are also likely to occur when the pattern has become damp or affected by destructive chemical agencies, or when small quantities of other dyestuffs (e.g. vat dyes or direct cotton dyes) have been added in order to obtain some specific shade. In the latter event, the different procedures mentioned under Section (2), below, should be carried out. With regard to mixture shades, Bradley and Derrett-Smith state that if the results of the spot tests do not correspond with, or cannot be regarded as being similar to, those of any dyestuff in their tables, then the pattern must have been dyed with a mixture of vat dyestuffs. This evidence in itself is hardly sufficient to prove that the pattern has been coloured by the use of more than one dyestuff, and more careful testing is recommended, in accordance with the procedures described in Section (2), below.

The nature of the fibres which compose the dyed or printed material also has some slight influence upon colour tests, particularly in the case of the sulphuric acid test. Coloration differences between the fibres themselves can be observed, for example, between bleached and unbleached cotton, bleached and unbleached mercerised cotton, bleached and unbleached linen, and dull and bright viscose rayon. The depth of shade of a dyeing or print

Indigo and its Halogenated Derivatives

		Sulphuric Acid		leuco-*Colour*		*Acid Hydrosulphite*		*Nitric Acid*	
1. Indigo BASF (or equivalent)	Increasing amounts of halogen present	Blue-green	Very slight increase in blueness	Green-yellow	Slight increase in redness	Grey-blue	Slight increase in blueness	Red-yellow	Increasing order of resistance to oxidation
2. Indigo BASF/R (or equivalent)		Blue-green		Green-yellow		Grey-blue		Red-yellow	
3. Indigo BASF/RR (or equivalent)		Blue-green		Green-yellow		Grey-blue		Red-yellow	
4. Indigo BASF/RB (or equivalent)		Blue-green		Green-yellow		Green-blue		Red-yellow	
5. Indigo MLB/4B (or equivalent)		Blue-green		Red-yellow		Green-blue		Black-blue, then through Brown to Red-yellow	
6. Indigo MLB/6B (or equivalent)		Blue-green		Red-yellow		Blue-green		Blue-green	

is also liable to cause misleading results when comparing personal observations with published lists. This is particularly noticeable when heavy shades are being tested, and it is always advisable to compare such dyeings side by side with the standard dyed to a similar strength.

Difficult dyestuffs to identify are those belonging to families such as the halogenated derivatives of indigo, and indanthrone and its halogenated derivatives. With care, however, it is possible to indicate the particular brand in the majority of cases.

Only by comparing a range of definite standards of the different indigoid derivatives in similar depths of shade, side by side with the unknown, is it possible to distinguish individual brands. Control of the strength and quantity of the reagent used is also very important if contradictory results are to be avoided.

Indanthrone and its Derivatives.—This large class of dyestuffs presents similar difficulties to the indigo group and modified analytical procedure is necessary.

By assuming that the dyeings have been carried out strictly under the correct conditions of temperature, i.e. 50°C. for chlorine-fast Blues, and 60°C. for the non-chlorine-fast Blues, it is possible to narrow the field down into these two classes by treating the unknown pattern side by side with a standard range in cold ½°Tw. sodium hypochlorite solution for 20 minutes. The chlorine-fast Blues, represented by Caledon Blue RCS, Paradone Blue GCD, Paradone Blue FC and Indanthrene Blue BC, will show only a very slight greening by this treatment. On the other hand, the unsubstituted indanthrones, e.g. Indanthrene Blue RS and the dyestuffs containing smaller amounts of halogen or non-halogen groups, will show a very marked greening.

Bradley and Derrett-Smith similarly make distinction between the two groups by treatment with solutions of nitric acid, which, in a similar manner to the hypochlorite, shows up the greening or oxidising effect. These workers make use of two solutions, viz. (*i*) equal parts by volume of nitric acid (sp. gr. 1·42) and water, and (*ii*) 3 parts by volume of nitric acid (sp. gr. 1·42) and 1 part of water. By immersing patterns in these solutions for 15 seconds, it is possible to classify the indanthrone derivatives into four groups designated (*A*), (*B*), (*C*) and (*D*).

Dyestuffs falling into Groups (*C*) and (*D*) exhibit good bleaching fastness, whilst those falling into (*A*) and (*B*) are of poor resistance to bleaching.

Groups (*A*) and (*B*) are differentiated from groups (*C*) and (*D*) by the use of the acid-hydrosulphite test. Thus, in Group (*A*),

Group	*Solution (i)*		*Solution (ii)*
	Pale Shades	*Medium and Deep Shades*	*All Shades*
(*A*)	Yellow-green	Green	Yellow
(*B*)	Green	Blue-green	Yellow
(*C*)	Blue-green	Blue	Green-yellow
(*D*)	Blue-green	Blue	Green-yellow

comprising Indanthrene Blue 3G, Blue 3GF and Brilliant Blue 3G; and in Group (*B*), comprising Indanthrene Blues RS, RSN, KRS, GCD, GCDN, etc., violet colorations are given in all cases. In Group (*C*), comprising Indanthrene Blue 3GT, Caledon Blue GCS; and in Group (*D*), comprising Caledon Blue RCS, Indanthrene Blue BC, etc., the patterns all remain blue in acid hydrosulphite solution.

Again, whenever possible, it is desirable to examine the pattern for degree of resistance to oxidation side by side with as many standard dyeings of the same depth as are available.

The difference between "*direct*" *blacks* and "*oxidised*" *blacks* may be rapidly shown by treatment with caustic soda–hydrosulphite solution. The reduced dyeing is pressed on to bleached cotton cloth or white filter paper and the colour of the oxidised bleed noted. In the case of the "oxidised" blacks, the green diamino-compound is re-formed, and this may be reconverted to the black by treatment with hypochlorite solution.

(2) Mixtures of Vat Dyestuffs

During the preliminary attempts to classify and identify an unknown dyestuff it may be evident that the dyestuff possesses the character of a mixture. It may appear more logical to treat all dyeings and prints as potential mixtures and to carry out the following tests before attempting the series of tests described in Section (1), above. Even when the dyestuff is known to be a mixture, however, the tests carried out in the foregoing section should always be made, since much valuable information can be derived by careful observation of the results obtained.

(*a*) *Dyestuffs in Substance.*—Preliminary note should be taken of the dispersion, solubility, colour of the *leuco*-compound and colour in sulphuric acid, and the best conditions for dyeing should be ascertained by the tests described in Section (1) on page 236. A solution of the dyestuff is then made up and fractional dyeings carried out. For this purpose, six or eight skeins of bleached cotton yarn of approximately equal weight are prepared by wetting-out and squeezing uniformly. The first skein is then entered into the prepared dyebath, worked for 30 seconds, lifted, and all excess dye liquor squeezed from it back into the dyeing vessel. A second skein is then immersed and dyed for 1 minute. This procedure is repeated until all the dyestuff has been removed from the dyebath, doubling the period of immersion at each change of skein, i.e. dyeing for 30 secs., 1 min., 2 min., 4 min., 8 min., 16 min., etc. The dyed skeins are kept in the right order (number with knotted strings) and examined after being oxidised, soured, soaped and dried in the usual manner.

With mixtures of dyestuffs which possess dissimilar dyeing properties, the fractional dyeing test is very useful for effecting a separation. The rapid-dyeing dyestuffs in the mixture are exhausted on to the first few skeins, whilst the more sluggish dyestuffs are found on the last few skeins and usually tail-off gradually. Quite distinct shades may often be seen from skein to skein in this type of mixture, but when dyes with similar dyeing properties have been employed in the preparation of the mixture the problem of separation becomes very difficult and, indeed, fractional dyeing is often valueless. Even when dyestuffs possessing almost equal rates of exhaustion are present, however, it is often possible to effect a separation, although not as well as with mixtures of dissimilar dyes. For finer separations of this kind it is necessary to shorten the periods of immersion and dye a larger number of skeins, each for the same period, e.g. for 10 seconds. More than twenty skeins may be required, but gradual changes will often be noticeable and will be of assistance in reaching a final decision.

When the range of skeins obtained from the fractional dyeing trials has been dried, spotting reactions are carried out on samples from every skein. The alkaline hydrosulphite, acid hydrosulphite and concentrated sulphuric acid tests are usually sufficient to give preliminary indications, and the results from the full range of dyeings should be tabulated and studied.

The disadvantages of fractional dyeing are (*a*) that it is difficult to separate dyestuffs possessing similar properties, and (*b*) that it is possible to mistake homogeneous dichroic dyestuffs, e.g. Ciba Brown G, for mixtures.

The usual procedure of "blowing out" dyestuffs on to wet filter paper, as used for detecting mixtures of acid dyestuffs, direct cotton colours, etc., is unsuitable for use with insoluble dyestuffs. Sulphur dyestuff mixtures can usually be detected by blowing out on to filter paper which has been saturated in sodium sulphide solution. The dispersed dyestuffs used for cellulose acetate rayon can be blown on to filter paper wetted with acetone and methylated spirits. Vat dyestuffs, however, when blown on to filter paper which has been dipped into hot caustic soda–hydrosulphite solution, usually reduce and oxidise so quickly that even mechanical mixtures rarely show up. Furthermore, many commercial vat dyestuff mixtures are vatted together and precipitated together by air-blowing or salting-out, so that particles of the individual dyestuffs can seldom be detected. In rare cases of dispersed mechanical mixtures it is possible to see and isolate particles of the individual dyestuffs by blowing on to water-wetted or spirits-wetted filter paper, or by merely allowing a small sample to fall on to a column of water in a measuring cylinder.

Blowing out on to a flat dish containing sulphuric acid is perhaps the best method of determining the homogeneity of a vat dyestuff, but only the mechanically mixed vat dyestuffs respond to this test.

Another method for dealing with mixtures of vat dyestuffs which are difficult to identify is based on the fact that the oxonium salts of the various dyestuffs are precipitated in varying strengths of sulphuric acid. Large samples of dyestuff powder are necessary, and it is essential that all diluents and dispersing agents should be removed and the sample thoroughly dried.

The purified dyestuff (e.g. 20 g.) is carefully dissolved in twenty times its weight of sulphuric acid monohydrate at a low temperature, ice and salt baths being placed round the beaker containing the agitated acid. The temperature should not be allowed to rise above 5°C. The solution is then filtered through a Syntex-type glass filter funnel, any insoluble matter remaining on the filter being washed well with monohydrate and then isolated and freed from acid. Very few vat dyestuffs are insoluble in sulphuric acid, and care should be taken to ensure that the insoluble matter is not undissolved original material. The filtrate is next diluted[1] with water (from a burette) to 95% sulphuric acid, taking care to maintain a low temperature and thorough agitation during dilution. Any precipitated dyestuff removed by the filter is isolated by pasting up with water and washing free from acid on an ordinary Buchner funnel, with suction. The filtrate from this test is then further diluted to 90% sulphuric acid, and the procedure repeated a number of times until no more dyestuff is present in

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[1] During dilution of the sulphuric acid ample precautions against splashing must be taken. The eyes should be protected by goggles.

the filtrate. It may be necessary to reduce the strength of the acid to 40%; this should be done gradually in stages.

By this time, a number of separately precipitated portions of the original vat dyestuff will have been collected and dried. Dyeings of each portion will then yield varying shades, which can be examined by means of the usual spot tests and the components of the mixture identified. This procedure is a long one, but it will often be found to work when other methods of separation fail.

Chromatographic Analysis.—This method of analysis has not been employed to any great extent for identifying vat dyestuffs, and nothing of importance appears to have been published in this connexion, although it provides a suitable topic for research, and its development would be equally valuable to both dyestuff chemists and textile chemists.

Chromatographic adsorption analysis is the simultaneous adsorption and separation of mixtures of organic compounds in solution. The method was first used in 1906 by Tswett, who succeeded in isolating various pigments from the leaves of plants. The apparatus employed consists essentially of a glass tube containing an adsorbent paste or powder through which the solution being analysed is passed. Many modified forms of this apparatus have been designed to suit special purposes, e.g. for use in micro-analysis and for certain large-scale industrial applications. The apparatus found suitable for vat dyestuff separation is very simple and cheap (Fig. 29). It consists of a stop-cock funnel to contain the solution of vat dyestuffs, and this is inserted into the upper end of the adsorption column, which consists of a glass tube carefully packed with the adsorption material. The lower end of the tube is partially closed and is plugged loosely with a small wad of glass-wool to prevent escape of the adsorbent paste or powder. This apparatus is fitted by means of a rubber bung into a Buchner-funnel, which in turn is placed in a filter flask and connected to the vacuum line or pump.

The adsorption column may vary in width between 0·5 and 6 cms., and in length between 5 and 35 cms.; a tube about 1·5 cms. wide and 10 cms. long is perhaps the most suitable for use in preliminary trials. The packing of the tube must be carried out very carefully, since the separation of the components of the mixture depends upon the even percolation of the solution through the uniform mass. The adsorbent may be converted to a thick even slurry by mixing it in a mortar with a little of the solvent; but the author has found it best to employ the dry adsorbent, on account of the difficulty of preparing pastes of the correct consistency. The powder should be added to the tube little by little, and each addition should be carefully "tamped" down as evenly as possible. The tube should be filled to within ½ cm. from the top.

A number of adsorbents give very good separations, e.g. magnesia, starch, precipitated chalk and sucrose, but alumina gives the best separations. Aluminium Oxide "Special for Adsorbent Purposes," as prepared by British Drug Houses, Ltd., is very suitable for use in the following procedure.

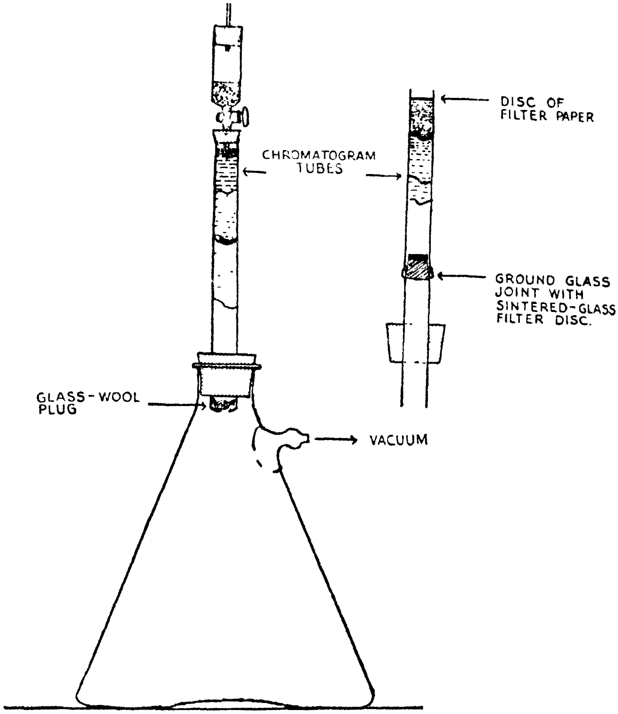

FIG. 29.—Apparatus for Chromatographic Analysis

The choice of solvents is very limited in the case of vat dyestuffs, since so few of the organic solvents at present available are capable of completely dissolving these dyestuffs. Many solvents will dissolve vat dyestuffs at the boil, but during the adsorption the solutions cool very rapidly and the dyestuff tends to precipitate. It is difficult to maintain a high temperature in the chromatograph tube. Thermostatically controlled water jackets can be fitted, but, in general, these are too cumbersome for use on small test apparatus. Elevated temperatures may adversely affect separation and 60°C. should be considered as a maximum for ordinary purposes. Benzene, chloroform and pyridine solutions of certain vat dyestuffs, e.g. indigoid derivatives, are often found to be satisfactory.

It may not be in accordance with correct technique to employ alkaline reducing agents in conjunction with aluminium oxide adsorbents, but in practice it will be found that strongly alkaline solutions containing a minimum amount of sodium hydrosulphite work quite well. The vat dyestuff under examination is dissolved carefully and thoroughly with the use of ample caustic soda and a small amount of sodium hydrosulphite at about 70°C. This solution is then poured into the funnel and is drawn through the separation tube by means of vacuum. With many mixtures, separation of the various *leuco*-compounds begins immediately, and when the adsorbent column is approximately one-third coloured by the solution the entry of fresh solution into the tube must be arrested. The various dyestuffs will then be seen in close narrow bands or strata in the column of alumina. These bands may be widened by allowing a little hot water to run through the tube. At this stage, a note is made of the order of the bands of the adsorbed dyestuff, and the colour of the various *leuco*-compounds is observed. An experienced worker can then predict the dyestuffs present, but it is always necessary to make confirmatory tests.

Air is next drawn through the column by means of the vacuum, until the *leuco*-compounds are completely oxidised. Oxidising solutions containing hydrogen peroxide may be found useful if difficulties are experienced with air oxidation. A note is next made of the colours and order of the oxidised bands. The apparatus is then dismantled and the damp column of alumina pushed out from the bottom of the tube in one piece on to a glass plate. The extruded column is then dissected carefully with a razor blade, separating the small sections of the individual colours. The separated dyestuffs can then be examined by the usual procedures of spot testing.

Several trials are always necessary, especially where narrow bands of shading matter are obtained. When sufficient of each band has been collected it is possible to make small dyeings of the individual colours upon small amounts of viscose rayon or mercerised cotton. Further tests can then be carried out on the dyeings.

Although further purification of the individual dyestuffs can be carried out by collecting the bands from a number of chromatograms, vatting and filtering-off the adsorbent, and then subjecting the filtrate once more to chromatographic adsorption, the procedure is somewhat lengthy for ordinary working, although clearer separations and more precise information can be gained.

It will be found that mixtures separable by fractional dyeing will separate quickly on the chromatogram, whilst mixtures of dyestuffs possessing similar affinities and exhaustion properties are more difficult to separate, although chromatographic analysis will result in better separations than can be effected by fractional dyeing. Dyestuffs containing isomers, e.g. Indanthrene Scarlet 2G (cf. page 24), can be separated into their component parts with little difficulty. Non-dyeing impurities may also be detected in vat dyestuffs; these are often misleading and should be collected in as large a quantity as possible and examined carefully. Non-vattable impurities can be removed and examined before the adsorption test by vatting large quantities of the dyestuff and filtering the reduced solution under vacuum; the use of filter-aids such as Filter Cel will be found useful in speeding up this operation.

No published work (apart from a brief reference in the *Dyer*, 1941, **86**, 311) has appeared concerning the chromatographic analysis of vat dyestuffs, but Ruggli and Jensen (*Helv. Chim. Acta*, 1935, **18**, 624; 1936, **19**, 64) have examined certain water-soluble dyestuffs, e.g. azo dyes, indolene dyes, fluorescein dyes, and basic dyes. Ruggli and Staüble (*Helv. Chim. Acta*, 1940, **23**, 689–717) have shown that the affinity of Indigosols for textile fibres is related to their adsorption on aluminium oxide. The value of chromatographic analysis is thus evident, and the future will probably see a wider use of this comparatively new tool.

(*b*) *In Dyed or Printed Patterns.*—Dyeings and prints containing mixtures of vat dyestuffs should be examined by the usual spot tests described earlier. Bleaching tests and the common solvents may also be tried, as well as tests for fastness to soda-boiling. The latter, in themselves, often indicate the predominant dyestuff in the mixture. If a piece of the vat dyeing or print is enclosed in a tightly rolled sandwich of bleached mercerised cotton and boiled for some time in 5% caustic soda, with or without sodium hydrosulphite as used for vatting, individual bleeds or uneven stains on the white will often result. Marking-off conditions can be controlled by using different strengths of solutions and different temperatures. Several experiments are usually necessary before maximum separation of the components of the mixture is effected.

Direct cotton and basic dyestuff "toppings" on vat-dyed grounds can be identified by following the routine tests of Green or Clayton.

When some idea as to the nature of the components has been formed, it is advisable to endeavour to match the shade by employing "possible" dyestuffs. Tests may then be carried out side by side on the known and unknown dyeings. Components used and found to give dissimilar reactions to those in the unknown must then be discarded and other "possibles" tried in their places.

Fractional stripping tests often yield valuable information. These are effected by first immersing a pattern in a hot bath (70° C.) of vatting solution for 5 minutes. A small pattern is then cut from the stripped piece and the procedure repeated in a fresh reducing solution for a similar period. This operation is repeated until no more dyestuff can be removed, when the range of partially stripped patterns can be examined by the usual routine. It is often necessary to shorten (or even lengthen) the time of immersion to suit different dyeings, and frequently small additions of anthraquinone or Lissolamine V will be found to increase the stripping effect. Like fractional dyeing, fractional stripping is of much less value when dyestuffs of similar desorption rates are present in the mixture.

The use of organic solvents in fractional stripping may be found of great value. A table of respective solubilities of the vat dyestuffs under different conditions of temperature could be prepared, using such solvents as chloroform, benzene, pyridine, glacial acetic acid, ethylene diamine, ethylene glycol, diethylene glycol, monoethanolamine, cresylic acid and quinoline.

Solutions of solvent-extracted dyestuffs or dyeings may be examined with the aid of the chromatogram. Very large patterns are required for solvent extraction tests; in fact, patterns (or samples) submitted for investigation should always be as large as possible.

The author has examined about one dozen homogeneous vat dyestuffs in order to obtain sufficient information to serve as the basis for a solvents table. Six tests have been devised, using the above-mentioned solvents, and the results obtained have proved very useful. Pieces of the pattern are immersed in portions of each of the solvents under the following conditions:

(1) Cold for 10 minutes.
(2) Raise to the boil, cool during 3 minutes.
(3) Boil for 3 minutes.
(4) Cold for 10 minutes, plus a little caustic soda.

(5) Add caustic soda and raise to the boil, then cool during 3 minutes.
(6) Add caustic soda and boil for 3 minutes.

The patterns are then washed off and compared with the original dyeing for the extent of stripping. Several of the solvents, e.g. pyridine and ethylene diamine, reduce the dyestuff to its *leuco*-compound; caustic soda assists this reaction.

By this means it was possible to separate the individual dyestuffs from dyeings made with mixtures of up to three components. In all cases the composition of the mixture was known, but it was nearly always possible to effect a good separation and isolate the individual components.

CHAPTER XIII

ANALOGOUS DYESTUFFS

THE following list of analogous vat dyestuffs is as complete as possible. Dyestuffs grouped together are very similar in dyeing and fastness properties, as well as in chemical composition. A great many dyestuffs are listed which have no present countertypes to the best of the author's knowledge. A list of some of the American vat dyestuffs has been included at the end in most of the sections. It is probable that these American types have European equivalents, but, as they have not been tested, they have been grouped separately.

Neither Japanese (Nihonthrene, Teisenthrene, etc.), Italian (Romantrene, Solindene, etc.), nor Russian vat dyestuffs have been included, on account of the scanty information available at the present time.

Many obsolete dyestuffs have been purposely included, since these will probably be of interest to students and research workers. All German vat dyestuffs have been listed as products of the I.G., Farbenindustrie A.-G., including those dyestuffs marketed at an earlier date by M.L.B., B.A.S.F., Gr.E., etc., with names other than Indanthrene or Algol.

For the sake of convenience, the following subdivision has been made:

(I) The Black group—including blacks, greys and black-browns.
(II) The Brown group—including dark browns, red-browns, yellow-browns, coppers, etc.
(III) The Orange group.
(IV) The Yellow group.
(V) The Green group.
(VI) The Olive group—including olive-greens and khakis.
(VII) The Blue group—including indigos, dark blues, navy blues, blue-greens and turquoise blues.
(VIII) The Violet group—including purples, red-violets and heliotropes.
(IX) The Red group—including pinks, corinths, maroons, scarlets, magentas, bordeaux, rubines, etc.

Key to Manufacturers' Abbreviated Names

AAP	American Aniline Products Inc., New York.
BA	Bates Chemical Co., Inc., Lansdowne, Pa.
CCC	Calco Chemical Co., New Jersey.
Ciba	Society of Chemical Industry in Basle. American branch.
DH	Durand & Huguenin A.-G., Basle.
DuP	E. I. du Pont de Nemours & Co., Wilmington.
G	General Dyestuffs Corp., New York.
Gy	J. R. Geigy A.-G., Basle, Switzerland.
HCW	Harmon Color Works, New Jersey.
HM	Heller & Merz Dpt., Calco Chemical Division, N.Y.
ICI	Imperial Chemical Industries, Ltd., Dyestuffs Division.
IG	Interessen Gemeinschaft für Farbenindustrie A.-G., Frankfurt-am-Main. This abbreviation has been used to cover all obsolete German firms.
K	Kuhlmann, France (now Francolor).
LBH	L. B. Holliday & Co., Ltd., Huddersfield.
NAC	National Aniline & Chemical Co., Inc., New York.
Nova	Nova Chemical Co., Canada.
PCC	Peerless Color Co., Inc., New Jersey.
PhC	Pharma Chemical Corp., New York.
S	Chemische Fabrikvorm Sandoz & Co., Basle, Switzerland.
SAm	Sandoz Chemical Works, New York.
SCI	Society of Chemical Industry, Basle, Switzerland.
St Cl	Saint Clair du Rhône, France.
St D	Saint Denis, France.

Group I

Calcosol Black BB		CCC.
Caledon Black BS	Chemically similar; shades and purity differ slightly	ICI.
Caledon Black 2BS		
Caledon Black 2BMS		
Caledon Black NBS		
Carbanthrene Black B		NAC.
Carbanthrene Black BS		
Cibanone Black 2B		SCI.
Cibanone Black 2BA		
Hydroform Black G		PCC.
Hydroform Black GB		
Hydroform Black G2B		
Indanthrene Black BBA		G.
Indanthrene Black BBF		
Indanthrene Black BBN		

Continued on p. 251.

Indanthrene Black BGA	IG.
Indanthrene Black 2B	
Paradone Black AB	LBH.
Paradone Black 2B	
Ponsol Black BA	DuP.
Ponsol Black BN	
Ponsol Black BNS	
Ponsol Green B	
Sandothrene Black N2B	S.
Sandothrene Black N2BA	
Solanthrene Black N2B	K.
Solanthrene Black N2BA	
Tinon Chlorine Black 2B	Gy.
Tinon Chlorine Black 2BA	

The above are "oxidised" blacks

Helindon Black B	Schultz No. 1304. Mixtures based on Indigo. Obsolete	IG.
Helindon Black 2B		
Helindon Black 3B		
Helindon Black R		
Helindon Black T		

Cibanone Grey 2B	SCI.
Indanthrene Grey 3B	IG.
Paradone Grey 3B	LBH.
Sandothrene Grey N2B	S.

Indanthrene Printing Black BL	IG.
Indigosol Grey IBL	DH.
Soledon Grey BS	ICI.
Tinon Printing Black BL	Gy.

Algol Black B	IG.
Algol Printing Black BB	
Alizarine Indigo Black B	

Ciba Grey B, G	SCI.
Tetra Grey G	S.
Tinon Grey B, G	Gy.

Indanthrene Printing Black B	IG.
Indanthrene Printing Black BA	G.
Indigosol Printing Black IB	DH.

Cibanone Black 2G	SCI.
Sandothrene Black N2G	S.
Tinon Chlorine Black 2G	Gy.

Cibanone Black BA	SCI.
Sandothrene Black NBA	S.
Tinon Black BA	Gy.
Cibanone Grey BN	SCI.
Tetra Grey NBN	S.
Tinon Grey BN	Gy.
Cibanone Grey GN	SCI.
Tetra Grey NGN	S.
Tinon Grey GN	Gy.
Cibanone Grey RN	SCI.
Tetra Grey NRN	S.
Tinon Grey RN	Gy.
Cibanone Grey RA	SCI.
Tetra Grey NRA	S.
Tinon Grey RA	Gy.
Cibanone Black BF	SCI.
Sandothrene Black NBF	S.
Tinon Chlorine Black BF	Gy.
Cibanone Black 4BA	SCI.
Tinon Chlorine Black 4BA	Gy.
Cibanone Grey G	SCI.
Tinon Grey GG	Gy.
Indanthrene Direct Black RB	IG.
Indanthrene Direct Black RBA	G.
Indanthrene Grey B	IG.
Amanthrene Grey 2BG	AAP.
Tinon Chlorine Black EA	Gy.
Sandothrene Black NEA	S.
Caledon Black ACS	ICI.
Tinon Chlorine Black CAC	Gy.

Tinon Black B	Gy.
Tetra Black NB	S.

Indanthrene Printing Black TL	IG.
Indanthrene Printing Black TLA	G.

Vat Printing Deep Black BD	SCI.
Tinon Printing Deep Black BD	Gy.

Algol Deep Black BD	IG.
Algol Deep Black BDA	G.

Caledon Grey 3R	ICI.
Tinon Chlorine Grey CR	Gy.

Algol Grey R	IG.
Anthra Grey B (obsolete name)	IG.

Algol Grey BG	IG.
Alizarine Indigo Grey B (obsolete name)	IG.

Algol Grey GG	IG.
Helindon Grey GG	IG.

{Algol Printing Black R	IG.

{Caledon Grey 2RDS	ICI.

{Caledon Grey 2RHS	ICI.

{Caledon Grey KT	ICI.

{Caledon Direct Black GS	ICI.

{Caledon Direct Black RS	ICI.

{Caledon Printing Black R	ICI.

{Cibanone Black BN	SCI.
{Ciba Printing Black BDN	SCI.
{Durindone Black A	ICI.
{Helindon Grey BR	IG.
{Hydron Black B	IG.
{Indanthrene Grey RRH	IG.
{Indanthrene Printing Black D	IG.
{Indanthrene Direct Black R	IG.
{Indanthrene Direct Black B	IG.
{Indanthrene Black Brown R	IG.
{Indanthrene Grey BTR	IG.
{Indanthrene Printing Black BR	IG.
{Indanthrene Grey M	IG.
{Indanthrene Grey MG	IG.
{Indanthrene Printing Black BGL	IG.
{Indanthrene Printing Black RL	IG.
{Indanthrene Direct Black G	IG.
{Indanthrene Direct Black RR	IG.

{Indanthrene Grey K	IG.
{Indanthrene Grey BG	IG.
{Indanthrene Grey 6B	IG.
{Paradone Grey R	LBH.
{Paradone Grey B	LBH.
{Paradone Direct Black R New	LBH.
{Paradone Direct Black BG	LBH.
{Paradone Direct Black RS New Conc	LBH.
{Solanthrene Grey N2B	K.
{Solanthrene Grey N4BI	K.
{Soledon Black 2B	ICI.
{Tinon Chlorine Black EF	Gy.
{Tinon Printing Black GL	Gy.
{Vat Printing Black BL	SCI.
{Vat Printing Black GL	SCI.
{Vat Printing Black New	SCI.

American Types Unplaced

Algol Deep Black RDA	G.
Amanthrene Black NM	AAP.
Calcoloid Black AD	CCC.
Calcoloid Direct Black JD	CCC.
Calcoloid Grey BD	CCC.
Calcoloid Grey GD	CCC.
Calcoloid Grey RD	CCC.
Calcosol Black DDB	CCC.
Calcosol Black 2GP	CCC.
Calcosol Printing Black G	CCC.
Calcosol Printing Black 3G	CCC.
Calcosol Printing Black R	CCC.
Carbanthrene Black BD	NAC.
Carbanthrene Direct Black DR	NAC.
Carbanthrene Direct Black RB	NAC.
Carbanthrene Printing Black J	NAC.
Carbanthrene Printing Black JB	NAC.
Ciba Printing Black A	Ciba.
Indanthrene Black BF	G.
Indanthrene Black Brown VA	G.
Indanthrene Grey M3G	G.
Indanthrene Printing Black BBA	G.
Midland Vat Printing Black Extra	Ciba.
Ponsol Black RP	DuP.
Ponsol Direct Black 3G	DuP.
Ponsol Direct Black 3GS	DuP.
Sulfanthrene Black PG	DuP.
Sulfanthrene Black PGN	DuP.
Vat Printing Black G.	Ciba.
Vat Printing Black RL	NAC.

Group II

Calcoloid Brown RRD	CCC.
Calcoloid Brown RRP	CCC.
Calcosol Brown RRD	CCC.
Ciba Brown G	SCI.
Ciba Brown G	Ciba.
Durindone Brown GS	ICI.
Indanthrene Brown RRA	G.
Indanthrene Brown RRD	IG.
Indigosol Brown IRRD	DH.
Luxiane Brown RRD	St. Cl.
Nova Vat Printing Brown GGN	Nova.
Pharmanthrene Brown CR	PhC.
Sandothrene Brown G	S.
Sandothrene Brown G	SAm.
Solanthrene Brown N2RI	K.
Soledon Brown GS	ICI.
Sulfanthrene Brown G	DuP.
Sulfanthrene Brown GN	DuP.
Tinon Chlorine Brown G	Gy.

Calcosol Brown G	CCC.
Caledon Brown EG	ICI.
Caledon Brown GS	ICI.
Carbanthrene Brown AG	NAC.
Cibanone Brown BG	SCI.
Cibanone Brown BG	Ciba.
Indanthrene Brown G	IG.
Indanthrene Brown GA	G.
Indanthrene Brown GAF	G.
Indanthrene Brown GAP	G.
Indanthrene Brown GWF	G.
Indanthrene Brown GWP	G.
Paradone Brown G	LBH.
Sandothrene Brown EG	S.
Solanthrene Brown NJ	K.
Tinon Chlorine Brown BG	Gy.
Tinon Chlorine Brown CG	Gy.

Caledon Brown RS	ICI.
Caledon Brown XRS	ICI.
Caledon Brown ER	ICI.
Caledon Brown HR	ICI.
Cibanone Brown GR	SCI.
Cibanone Brown GRF	SCI.
Indanthrene Brown R	IG.
Indanthrene Brown FFR	IG.
Indanthrene Printing Brown RS	IG.
Paradone Brown R	LBH.
Sandothrene Brown ER	S.
Solanthrene Brown NR	K.
Solanthrene Brown NRF	K.
Tinon Chlorine Brown GR	Gy.

Calcosol Brown 2G	CCC.
Caledon Brown 2GS	ICI.
Cibanone Brown 2G	SCI.
Indanthrene Brown GG	IG.
Indanthrene Brown GGA	G.
Indanthrene Brown GGF	G.
Indanthrene Brown GGWP	G.
Paradone Brown 2G	LBH.
Ponsol Brown 2G	DuP.
Ponsol Brown 2GN	DuP.
Sandothrene Brown N2G	S.
Solanthrene Brown N2J	K.
Tinon Chlorine Brown N2G	Gy.

Indanthrene Brown BR	IG.
Indanthrene Brown BRA	G.
Indanthrene Brown BRF	G.
Indanthrene Brown BRWF	G.
Indanthrene Brown BRWP	G.
Indigosol Brown IBR	DH.
Paradone Red Brown 2RD	LBH.
Solanthrene Brown NBR	K.
Soledon Dark Brown 3RS	ICI.

Algol Brown BT	IG.
Anthra Brown B (obsolete name)	IG.
Caledon Brown BS	ICI.
Carbanthrene Brown BB	NAC.
Indanthrene Brown B	IG.
Ponsol Brown BB	DuP.

Algol Brown FFR	IG.
Ciba Brown 2R	SCI.
Indanthrene Printing Brown 3R	IG.
Sandothrene Brown 2R	S.
Tinon Chlorine Brown 2R	Gy.

Algol Brown RN	IG.
Alizarine Indigo Brown R (obsolete)	IG.
Helindon Brown GGR	IG.
Indanthrene Printing Brown R	IG.
Thioindone Brown GT (obsolete)	IG.

Caledon Yellow Brown 3GS	ICI.
Indanthrene Yellow Brown 3G	IG.
Indanthrene Yellow Brown 3GA	G.
Indanthrene Yellow Brown 3GWP	G.
Solanthrene Yellow Brown N3J	K.

Cibanone Brown G	SCI.
Tinon Chlorine Brown BR	Gy.
Sandothrene Brown NG	S.

Cibanone Brown B, V	SCI.
Tetra Brown NB, NV	S.
Tinon Brown B, V	Gy.

Algol Brown 3R	IG.
Helindon Brown 2R (obsolete)	IG.
Thioindigo Brown R (obsolete)	IG.

Algol Brown 5R		IG.
Helindon Brown 5R (obsolete)		IG.
Thioindigo Brown 3R (obsolete)		IG.
Ciba Brown 3G		SCI.
Tinon Brown 3GD		Gy.
Ciba Brown FF		SCI.
Tinon Brown FFD		Gy.
Indigosol Brown IVB		DH.
Soledon Red Brown BS		ICI.
Ciba Red Brown R		SCI.
Tinon Red Brown SD		Gy.
Ciba Brown ST		SCI.
Tinon Chlorine Brown STD		Gy.
Algol Brown GN		IG.
Indanthrene Printing Brown GN		IG.
Ciba Brown 5G		SCI.
Tinon Brown 5GD		Gy.
Cibanone Brown RN		SCI.
Tinon Chlorine Brown RN		Gy.
Indanthrene Brown TM	chemically similar	IG.
Indanthrene Brown TMR		IG.
Caledon Brown 5GS		ICI.
Tinon Chlorine Brown C5G		Gy.
Indanthrene Brown RT		IG.
Indanthrene Brown RTA		G.
Indanthrene Copper R. (obsolete)		IG.
Paradone Brilliant Copper R, D (obsolete)		LBH.

{Helindon Brown G (obsolete) Thioindigo Brown G (obsolete)	IG. IG.
{Indanthrene Red Brown R	IG.
{Indanthrene Brown 3R	IG.
{Indanthrene Red Brown G	IG.
{Indanthrene Printing Brown 5R	IG.
{Indanthrene Printing Brown B	IG.
{Indanthrene Brown NG	IG.
{Indanthrene Red Brown GR	IG.
{Indanthrene Red Brown 5RF	IG.
{Indanthrene Brown 3GT	IG.
{Indanthrene Red Brown 2R	IG.
{Indanthrene Brown GR	IG.
{Algol Brown B (obsolete)	IG.
{Caledon Brown HG	ICI.
{Caledon Brown KT	ICI.
{Caledon Dark Brown A	ICI.
{Caledon Dark Brown 4RBS	ICI.
{Caledon Dark Brown 6RS	ICI.

{Ciba Brown BB	SCI.
{Ciba Brown R	SCI.

American Types Unplaced

Calcosol Brown R	CCC.
Carbanthrene Brown NR	NAC.
Carbanthrene Red Brown R	NAC.
Duraval Brown OY	DuP.
Hydroform Brown A	PCC.
Hydroform Brown G.	PCC.
Indanthrene Brown RAR	G.
Indanthrene Brown RARWP	G.
Indanthrene Brown RRV	G.
Indanthrene Brown RTW	G.
Indanthrene Dark Brown RG	G.
Indanthrene Dark Brown RGF	G.
Indanthrene Dark Brown RT	G.
Indanthrene Printing Brown D	G.
Indanthrene Printing Brown RD	G.
Indanthrene Printing Brown TMA	G.
Ponsol Brown AG	DuP.
Ponsol Brown AGG	DuP.
Ponsol Brown AGS	DuP.
Ponsol Brown VR	DuP.
Ponsol Brown VRS	DuP.
Ponsol Dark Brown R	DuP.
Vat Brown 2RD	NAC.
Vat Printing Brown G	NAC.

Group III

Algol Orange RF	IG.
Algol Orange RFA	G.
Algol Orange RFP	G.
Algol Orange RV	G.
Anthra Orange RH (obsolete name)	IG.
Calcoloid Orange RD	CCC.
Calcoloid Orange RP	CCC.
Calcosol Printing Orange RY	CCC.
Ciba Orange R	SCI.
Ciba Orange R	Ciba.
Ciba Orange RDL	Ciba.
Ciba Orange RP	Ciba.
Durindone Orange RS	ICI.
Heliane Orange SC	St. Cl.
Helindon Orange R (obsolete name)	IG.
Hydron Orange R (obsolete name)	IG.
Indigosol Orange HR	DH.

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Nova Vat Orange R	Nova.
Sandothrene Orange R	S.
Solane Orange NR	K.
Soledon Orange RS	ICI.
Sulfanthrene Orange R	DuP.
Sulfanthrene Orange RC	DuP.
Sulfanthrene Orange RS	DuP.
Sulfanthrene Orange RN	DuP.
Thioindigo Orange R (obsolete name)	IG.
Tinon Orange R	Gy.
Vat Orange R	NAC.
Vat Printing Orange R	NAC.

Amanthrene Golden Orange G	AAP.
Calcoloid Golden Orange GD	CCC.
Calcosol Golden Orange G	CCC.
Caledon Golden Orange GS	ICI.
Caledon Paper Orange GS	ICI.
Carbanthrene Golden Orange G	NAC.
Carbanthrene Printing Golden Orange G	NAC.
Cibanone Golden Orange GN	SCI.
Indanthrene Gold Orange G	IG.
Indanthrene Gold Orange GA	G.
Indanthrene Gold Orange GWF	G.
Indanthrene Gold Orange GWP	G.
Indanthrene Printing Orange GO	IG.
Paradone Golden Orange G	LBH.
Ponsol Golden Orange G	DuP.
Ponsol Golden Orange GS	DuP.
Sandothrene Golden Orange NG	S.
Solanthrene Orange NJ	K.
Tinon Golden Orange GN	Gy.

Calcoloid Golden Orange RRTD	CCC.
Calcosol Golden Orange RRTD	CCC.
Calcosol Golden Orange RRTP	CCC.
Caledon Orange 2RTS	ICI.
Carbanthrene Golden Orange RRT	NAC.
Carbanthrene Printing Golden Orange RRT	NAC.
Cibanone Golden Orange 2R	SCI.
Cibanone Golden Orange 2R	Ciba.
Indanthrene Orange RRT	IG.
Indanthrene Orange RRTA	G.
Indanthrene Orange RRTF	G.
Indanthrene Orange RRTP	G.
Indanthrene Orange RRTW	G.
Ponsol Golden Orange RRT	DuP.
Ponsol Golden Orange RRTS	DuP.
Sandothrene Red Orange NG	S.
Tinon Chlorine Orange 2RT	Gy.

Caledon Orange 4RS	ICI.
Caledon Brilliant Orange 4RS[1]	ICI.
Cibanone Orange 8R	SCI.
Indanthrene Orange 4R	IG.
Indanthrene Orange 4RA	G.
Sandothrene Red Orange NR	S.
Soledon Orange 4RS	ICI.
Tinon Chlorine Orange 8R	Gy.
Tinon Chlorine Brilliant Orange C4R[1]	Gy.

[1] Purer types.

Caledon Brilliant Orange 6RS	ICI.
Indanthrene Brilliant Orange RK	IG.
Indanthrene Brilliant Orange RKA	G.
Indanthrene Brilliant Orange RKF	G.
Indanthrene Brilliant Orange RKN	IG.
Indanthrene Brilliant Orange RKS	IG.
Indigosol Brilliant Orange IRK	DH.
Soledon Brilliant Orange 6RS	ICI.

Caledon Golden Orange 3GS	ICI.
Indanthrene Gold Orange 3G	IG.
Paradone Brilliant Orange 2G	LBH.
Sandothrene Golden Orange E3G	S.
Solanthrene Orange N3J	K.

Cibanone Orange R	SCI.
Ponsol Orange RC	DuP.
Sandothrene Orange NR	S.
Solanthrene Orange N4J	K.
Tinon Chlorine Orange R	Gy.

Calcosol Flaming Orange 2R	CCC.
Indanthrene Scarlet G	IG.
Ponsol Golden Orange 4R	DuP.
Ponsol Golden Orange 4RS	DuP.

Ciba Orange G	SCI.
Tetra Orange G	S.
Tinon Orange G	Gy.

Cibanone Orange 6R	SCI.
Sandothrene Orange N6R	S.
Tinon Chlorine Orange 6R	Gy.

Cibanone Orange 2R	SCI.
Tinon Chlorine Orange 2R	Gy.

Indanthrene Orange RRK	IG.
Algol Brilliant Orange FR	IG.
Indanthrene Orange 6RTK	IG.
Grelanone Orange RB (obsolete)	IG.
Indanthrene Orange RT (obsolete)	IG.
Paradone Orange R (obsolete)	LBH.
Indanthrene Brilliant Orange GR	IG.
Indanthrene Brilliant Orange GRA	G.
Cibanone Golden Orange 2G	SCI.
Tinon Chlorine Golden Orange 2G	Gy.
Algol Orange GR	IG.
Helindon Orange D (obsolete)	IG.
Indanthrene Orange 2R	IG.
Indanthrene Orange GG	IG.
Indanthrene Gold Orange GN	IG.
Indanthrene Brilliant Orange GK	IG.
Indanthrene Orange F3R	IG.
Indanthrene Orange 7RK	IG.
Sandothrene Golden Orange N2G	S.
Sandothrene Orange L3R	S.
Solanthrene Orange N5J	K.

American Types Unplaced

Calcoloid Flaming Orange 6R	CCC.
Calcoloid Flaming Orange 6RD	CCC.
Carbanthrene Golden Orange 4R	NAC.
Duraval Orange R	DuP.
Indanthrene Gold Orange 3GF	G.
Ponsol Golden Orange 4G	DuP.
Ponsol Golden Orange RRG	DuP.
Ponsol Golden Orange YL	DuP.

Group IV

Algol Yellow GC	IG.
Algol Yellow GCA	G.
Algol Yellow GCF	G.
Algol Yellow GCN	IG.
Algol Yellow GCWF	G.
Algol Yellow GCWP	G.
Algol Printing Yellow GCA	G.
Anthra Yellow GC	IG.
Benzadone Yellow GC	YDC.
Calcoloid Printing Yellow GC	CCC.
Caledon Yellow 5GS	ICI.
Carbanthrene Flavine GC	NAC.
Carbanthrene Printing Flavine GC	NAC.
Carbanthrene Printing Flavine GCL	NAC.
Cibanone Yellow GC	SCI.
Helindone Yellow AGC (obsolete)	IG.
Helindone Yellow DAGC (obsolete)	IG.
Paradone Yellow GC	LBH.
Paradone Yellow GCX	LBH.
Ponsol Flavone GC	DuP.
Ponsol Flavone GCS	DuP.
Sandothrene Yellow NGC	S.
Solane Yellow NJ	K.
Tinon Yellow 3GF	Gy.

Amanthrene Yellow G	AAP.
Benzadone Yellow G	YDC.
Calcosol Yellow G	CCC.
Caledon Yellow GS	ICI.
Caledon Yellow GNS	ICI.
Carbanthrene Yellow G	NAC.
Carbanthrene Printing Yellow G	NAC.
Cibanone Yellow G	SCI.
Cibanone Yellow GN	SCI.
Cibanone Yellow GN	Ciba.
Indanthrene Yellow G	IG.
Indanthrene Yellow GA	G.

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Indanthrene Yellow GD	G.
Paradone Yellow G New	LBH.
Ponsol Yellow G	DuP.
Ponsol Yellow GS	DuP.
Sandothrene Yellow NG	S.
Sandothrene Yellow NGN	S.
Soledon Yellow GS	ICI.
Solanthrene Yellow NJ	K.
Tinon Chlorine Yellow RG	Gy.
Tinon Chlorine Yellow RGN	Gy.
Vat Yellow J	St. D.

Calcoloid Yellow 5GD	CCC.
Calcosol Printing Yellow 5G	CCC.
Cibanone Yellow R	SCI.
Cibanone Yellow RBN	Ciba.
Hydroform Bright Yellow 3G	PCC.
Nova Vat Yellow 5GN	Nova.
Sandothrene Yellow NR	S.
Solane Yellow NR	K.
Sulfanthrene Yellow R	DuP.
Tinon Chlorine Yellow G	Gy.

Benzadone Yellow 5GK	YDC.
Caledon Yellow 5GKS	ICI.
Indanthrene Printing Yellow 5GK	IG.
Indanthrene Yellow 5GK	IG.
Paradone Yellow 5GK	LBH.
Solanthrene Brilliant Yellow N5J	K.
Soledon Yellow 5GS	ICI.

Amanthrene Yellow GK	AAP.
Benzadone Yellow 3G	YDC.
Caledon Yellow 3GS	ICI.
Cibanone Yellow GK	SCI.
Indanthrene Yellow GK	IG.
Ponsol Yellow AR	DuP.
Sandothrene Yellow NGK	S.
Solanthrene Yellow N2J	K.
Tinon Chlorine Yellow GK	Gy.

Indanthrene Golden Yellow GK	IG.
Indanthrene Golden Yellow GKA	G.
Indanthrene Printing Yellow GOK	IG.
Indigosol Golden Yellow IGK	DH.
Solanthrene Brilliant Yellow NJ	K.
Soledon Golden Yellow GKS	ICI.

Cibanone Yellow 3R		SCI.
Indanthrene Yellow 3R	(purer than 3RT)	IG.
Indanthrene Yellow 3RT		IG.
Sandothrene Yellow N3R		S.
Tinon Chlorine Yellow 3R		Gy.

Hydron Yellow GF		IG.
Hydron Yellow NF		IG.
Luxiane Yellow GF		St. Cl.
Indanthrene Yellow GF		IG.
Indanthrene Yellow GFS		IG.

Indanthrene Golden Yellow RK		IG.
Indigosol Golden Yellow IRK		DH.
Solanthrene Brilliant Yellow NR		K.
Soledon Golden Yellow RKS		ICI.

Ciba Yellow G		SCI.
Sandothrene Yellow G		S.
Tinon Chlorine Yellow 3G		Gy.

Algol Yellow 4GK		IG.
Helindon Yellow 3GN	(obsolete)	IG.
Thioindone Yellow 3G	(obsolete)	IG.

Indanthrene Yellow 3GF	(chemically similar)	IG.
Indanthrene Yellow 3G		IG.
Paradone Yellow 2G		LBH.

Indigosol Yellow HCG		DH.
Helindon Yellow CG		IG.
Thioindigo Yellow GW	(obsolete)	IG.
Helindon Brown CM	are thionated derivatives of this yellow dyestuff (Kranzlein, through Schultz *Farbstofftabellen*, 7. Auflage, Erg. Band II, No. 1284)	IG.
Helindon Brown CR		IG.

Cibanone Yellow 2GR		SCI.
Sandothrene Yellow N2GR		S.
Tinon Chlorine Yellow 3GR		Gy.

Anthraflavone GC, 2R (obsolete)	IG.
Calcoloid Yellow GCD	CCC.
Algol Yellow GR	IG.
Hydron Yellow GG (obsolete)	IG.
Sandothrene Yellow N2R	S.
Tinon Chlorine Yellow 2R	Gy.
Algol Yellow 3G (obsolete)	IG.
Algol Yellow 3GK	IG.
Ciba Yellow 2R (obsolete)	SCI.
Ciba Yellow 5R (obsolete)	SCI.
Indanthrene Printing Yellow GOW	IG.
Indanthrene Printing Yellow GOW	G.
Sandothrene Yellow N3G	S.
Tinon Chlorine Yellow 2G	Gy.
Sandothrene Yellow N2G	S.
Tinon Chlorine Yellow 2GR	Gy.
Sandothrene Orange 4GS	S.
Tinon Chlorine Yellow 6R	Gy.
Algol Yellow WG	IG.
Caledon Yellow R	ICI.
Caledon Yellow 5RS	ICI.
Hydron Yellow G (obsolete)	IG.
Indanthrene Yellow 6G	IG.
Indanthrene Yellow 6GD	IG.

{Indanthrene Yellow GN	IG.
{Indanthrene Yellow 4GK	IG.
{Indanthrene Yellow 7GK	IG.
{Indanthrene Yellow FFRK	IG.
{Indigo Yellow 3G (obsolete)	IG.

American Types Unplaced

Algol Yellow 4GF	G.
Amanthrene Yellow A2G	AAP.
Anthra Yellow GDA	G.
Duraval Yellow R	DuP.
Indanthrene Yellow PGF	G.
Indanthrene Yellow PGWP	G.
Ponsol Brilliant Yellow 4G	DuP.
Ponsol Yellow GGK	DuP.
Ponsol Yellow FG	DuP.

Group V

Algosol Green IBW	G.
Calcosol Jade Green N	CCC.
Calcosol Jade Green NP	CCC.
Caledon Jade Green BS, BNS	ICI.
Caledon Jade Green XS, XNS	ICI.
Carbanthrene Brilliant Green	NAC.
Cibanone Brilliant Green BF	SCI.
Indanthrene Brilliant Green B	IG.
Indanthrene Brilliant Green FFB	IG.
Indigosol Green IBA	DH.
Indigosol Green IEB	DH.
Paradone Jade Green B	LBH.
Paradone Jade Green XS	LBH.
Ponsol Jade Green	DuP.
Ponsol Jade Green S	DuP.
Ponsol Jade Green Soluble	DuP.
Ponsol Jade Green Supra	DuP.
Sandothrene Green EX	S.
Solanthrene Brilliant Green NB	K.
Solanthrene Brilliant Green N2F	K.
Soledon Jade Green XS	ICI.
Tinon Chlorine Brilliant Green B	Gy.

Caledon Jade Green 2GS	ICI.
Cibanone Brilliant Green 2G	SCI.
Indanthrene Brilliant Green 2G.	IG.
Indigosol Green IE2G	DH.
Paradone Jade Green 2G	LBH.
Ponsol Brilliant Green 2G	DuP.
Soledon Jade Green 2GS	ICI.

Algol Brilliant Green 5G	IG.
Algol Brilliant Green 5GA	G.
Anthra Brilliant Green 5G (obsolete name)	IG.
Cibanone Green 5G	SCI.
Helindon Brilliant Green D5G, 5G (obsolete names)	IG.
Tinon Chlorine Green 5G	Gy.

Caledon Jade Green 4GS	ICI.
Indanthrene Brilliant Green 4G	IG.
Paradone Jade Green 4G	LBH.
Ponsol Brilliant Green 4G	DuP.
Cibanone Brilliant Green 4G (this is slightly different in acid hydrosulphite to above)	Gy.

Algol Green B (obsolete)	IG.
Caledon Green 2BS	ICI.
Hydron Green B	IG.
Indanthrene Green BB (obsolete name)	IG.

Caledon Jade Green 3BS	ICI.
Cibanone Brilliant Green 2B	SCI.
Indigosol Green IE3B	DH.
Soledon Jade Green 3BS	ICI.

Cibanone Green 2G	SCI.
Paradone Green 2G	LBH.
Tinon Chlorine Green 2G	Gy.
Sandothrene Green N2G	S.

Cibanone Green GN	SCI.
Paradone Green G	LBH.
Sandothrene Green NGN	S.
Tinon Chlorine Green GN	Gy.

Cibanone Green B	SCI.
Tetra Green NB	S.
Tinon Chlorine Green B	Gy.

Cibanone Green 4G . . . . SCI.
Tinon Chlorine Green 4G . . . . Gy.

Hydron Green G . . . . IG.
Indanthrene Green GT . . . . . . IG.

Indigosol Green I3G . . . . DH.
Soledon Brilliant Green 5GS . . . . . ICI.

Algol Brilliant Green BK . . . . IG.
Indigosol Green AB . . . . DH.

Indanthrene Green G . . . . IG.
Indanthrene Green GA . . . . . . G.

Indanthrene Green 2G . . . . . IG.
Indanthrene Green 2GA . . . . . . G.

Sandothrene Green NGC . . . . S.
Tinon Green GC . . . . Gy.
Caledon Green BNS . . . . ICI.
Sandothrene Green EB . . . . S.

{Caledon Green GS . . . . ICI.

{Caledon Green 2GS . . . . ICI.

{Caledon Jade Green GS . . . . . . ICI.

{Caledon Green RCS . . . . ICI.

{Ciba Green G (obsolete) . . . . . . SCI.

{Cibanone Brilliant Green 2GF . . . . . SCI.

{Helindon Green G (obsolete) . . . . . IG.

{Indanthrene Green 4G . . . . . . IG.

American Types Unplaced

Calcosol Green 6G	CCC.
Indanthrene Brilliant Green BNWP	G.
Indanthrene Green GGF	G.
Indanthrene Printing Green B	G.
Indanthrene Printing Green BG	G.
Ponsol Green 2BL	DuP.
Ponsol Green 2BX	DuP.
Ponsol Green RC	DuP.
Ponsol Jade Green 4GW	DuP.
Vat Green 2G	DuP.

Group VI

Amanthrene Olive R	AAP.
Benzadone Olive R	YDC.
Calcosol Olive R	CCC.
Caledon Olive RS	ICI.
Carbanthrene Olive R	NAC.
Cibanone Olive R	SCI.
Cibanone Olive 2R	Ciba.
Indanthrene Olive R	IG.
Indanthrene Olive RA	G.
Indanthrene Olive RAP	G.
Indanthrene Olive RW	G.
Indanthrene Olive RWF	G.
Indanthrene Olive RWP	G.
Paradone Olive R	LBH.
Ponsol Olive AR	DuP.
Ponsol Olive ARS	DuP.
Sandothrene Olive N2R	S.
Solanthrene Olive NR	K.
Tinon Chlorine Olive 2R	Gy.

Algol Olive G (obsolete name)	IG.
Anthra Olive G (obsolete name)	IG.
Cibanone Olive 2G	SCI.
Hydron Olive B, G, GX (obsolete names)	IG.
Indanthrene Olive G	IG.
Paradone Olive G	LBH.
Ponsol Olive G	DuP.
Solane Olive NJ	K.
Tetra Olive N2G	S.
Tinon Olive 2G	Gy.
Vat Olive G	St. Cl.
Vat Olive GN	DuP.

Amanthrene Khaki 2G	AAP.
Calcosol Khaki G	CCC.
Caledon Khaki 2GS	ICI
Carbanthrene Khaki 2G	NAC.
Indanthrene Khaki 2G	IG.
Indanthrene Khaki 2GA	G.
Indanthrene Khaki 2GF	G.
Indanthrene Khaki 2GP	G.
Indanthrene Khaki 2GWP	G.
Paradone Khaki 2G	LBH.
Ponsol Khaki 2G	DuP.
Ponsol Khaki 2GS	DuP.

Cibanone Olive 2B	SCI.
Indanthrene Olive Green B	IG.
Indanthrene Olive Green BA	G.
Indanthrene Olive Green BAF	G.
Indanthrene Olive Green BWP	G.
Indigosol Olive Green IB	DH.
Sandothrene Olive N2B	S.
Soledon Green GS	ICI.
Solanthrene Dark Green NJ	K.
Tinon Chlorine Olive 2B	Gy.

Cibanone Olive BG	SCI.
Sandothrene Olive NBG	S.
Tinon Chlorine Olive BG	Gy.

Cibanone Olive B	SCI.
Sandothrene Olive NB	S.
Tinon Chlorine Olive B	Gy.

Indanthrene Olive T	IG.
Indanthrene Olive TA	G.

Cibanone Olive GN	SCI.
Sandothrene Olive NG	S.
Tinon Chlorine Olive G (similar, but acid hydrosulphite spot greener)	Gy.

{Caledon Khaki M	ICI.

{Caledon Khaki RS	ICI.

{Indanthrene Olive 3G	IG.

{Indanthrene Olive GB	IG.

{Indanthrene Olive GN	IG.

{Indanthrene Olive Green GG	IG.

American Types Unplaced

Calcosol Olive Green BN	CCC.
Calcosol Olive Green BP	CCC.
Ponsol Olive GGL	DuP.
Vat Khaki OG	CCC.

Group VII

Amanthrene Dark Blue BO	AAP.
Benzadone Dark Blue BO	YDC.
Calcoloid Dark Blue BOD	CCC.
Calcosol Dark Blue BO	CCC.
Calcosol Dark Blue BOP	CCC.
Calcosol Navy Blue BP	CCC.
Caledon Dark Blue B	ICI.
Caledon Dark Blue BMS	ICI.
Caledon Navy Blue B	ICI.
Carbanthrene Dark Blue DR	NAC.
Carbanthrene Printing Dark Blue DR	NAC.
Cibanone Dark Blue BO	SCI.
Cibanone Dark Blue BOA	SCI.
Cibanone Dark Blue MB	SCI.
Cibanone Dark Blue MBA	SCI.
Hydroform Deep Blue BOA	PCC.
Indanthrene Dark Blue BGA	IG.
Indanthrene Dark Blue BO	IG.
Indanthrene Dark Blue BOA	IG.
Indanthrene Dark Blue BOD	G.
Indanthrene Dark Blue BOF	G.
Indanthrene Dark Blue BOW	G.
Indanthrene Dark Blue BOWF	G.
Paradone Dark Blue	LBH.
Ponsol Dark Blue BOA	DuP.
Ponsol Dark Blue BR	DuP.
Ponsol Dark Blue BRS	DuP.
Sandothrene Dark Blue NBO	S.
Sandothrene Dark Blue NBOA	S.
Sandothrene Dark Blue NMB	S.
Sandothrene Dark Blue NMBA	S.
Solanthrene Dark Blue NB	K.
Solanthrene Dark Blue NBA	K.
Soledon Dark Blue 2RS	ICI.
Tinon Chlorine Dark Blue B	Gy.
Tinon Chlorine Dark Blue BO	Gy.
Tinon Chlorine Dark Blue MB	Gy.
Vat Dark Blue B	St. D.
Vat Dark Blue BA	St. D.

(The above show slightly different shades and degrees of purity but are chemically dibenzanthrone.)

Hydron Blue Types Collectively Grouped

Ciba Blue BH	SCI.
Ciba Blue GBH	SCI.
Ciba Blue RH	SCI.
Ciba Blue 3RH	SCI.
Hydron Blue B	IG.
Hydron Blue BDD	G.
Hydron Blue BG	G.
Hydron Blue FB	IG.
Hydron Blue G	IG.
Hydron Blue GA	G.
Hydron Blue GT	IG.
Hydron Blue R	IG.
Hydron Blue RA	G.
Hydron Blue 2R	IG.
Hydron Blue RB	IG.
Hydron New Blue GC	IG.
Hydron New Blue RC	IG.
Hydron Printing Blue 3R	IG.
Sandone Blue G	S.
Sandone Blue R	S.
Sandone Blue 2R	S.
Sandone Blue RG	S.
Solane Blue NB	K.
Solane Blue NJB	K.
Solane Blue NR	K.
Solane Blue N2R	K.
Solane Blue NRB	K.
Sulfanthrene Blue G	DuP.
Sulfanthrene Blue GR	DuP.
Sulfanthrene Blue RNN	DuP.
Thiotinon Blue GB	Gy.
Thiotinon Blue R	Gy.
Thiotinon Blue 2R	Gy.
Thiotinon Blue 3R	Gy.

(The above show slightly different shades, but are chemically similar.)

Benzadone Blue RS	YDC.
Calcosol Blue RS	CCC.
Caledon Blue RSN	ICI.
Caledon Brilliant Blue RNS[1]	ICI.
Cibanone Blue RS	SCI.
Cibanone Blue RSN	SCI.
Indanthrene Blue KRS	IG.
Indanthrene Blue RS	IG.
Indanthrene Blue RSA	G.
Indanthrene Blue RSN	IG.

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[1] Purer Type.

Indanthrene Blue RSP	G.
Indanthrene Brilliant Blue R[1]	IG.
Indanthrene Brilliant Blue RA[1]	G.
Indanthrene Printing Blue FRS	IG.
Paradone Blue RS	LBH.
Ponsol Blue GZ	DuP.
Ponsol Blue RP	DuP.
Ponsol Blue RPC	DuP.
Ponsol Blue RS	DuP.
Ponsol Blue RSS	DuP.
Ponsol Brilliant Blue R[1]	DuP.
Sandothrene Blue NRS	S.
Sandothrene Blue NRSN	S.
Solanthrene Blue NRS	K.
Solanthrene Blue NRSN	K.
Tinon Chlorine Blue RS	Gy.
Tinon Chlorine Blue RSN	Gy.
Vat Blue RSN	St. D.

[1] Purer Types.

Algosol Blue IBC	G.
Amanthrene Blue RCL	AAP.
Calcoloid Blue BCS	CCC.
Calcoloid Blue BCSD	CCC.
Calcoloid Blue BLD	CCC.
Calcoloid Blue BLP	CCC.
Calcosol Blue BCS	CCC.
Caledon Blue BCD	ICI.
Carbanthrene Blue BCF	NAC.
Carbanthrene Blue BCS	NAC.
Cibanone Blue BCS	Ciba.
Cibanone Blue GCXL	Ciba.
Dowanone Blue BCS	Ciba.
Indanthrene Blue BC	IG.
Indanthrene Blue BCD	IG.
Indanthrene Blue BCFN	G.
Indanthrene Blue BCRWF	G.
Indanthrene Blue BCS	IG.
Indanthrene Blue BCSA	G.
Indanthrene Blue BCSN	G.
Indanthrene Blue BCSW	G.
Indanthrene Blue BCSWP	G.
Indanthrene Blue BCX	G.
Indanthrene Brilliant Blue RCLN	G.
Indanthrene Brilliant Blue RCLWP	G.
Indigosol Blue IBC	DH.
Ponsol Blue BCS	DuP.
Solanthrene Blue NB	K.
Solanthrene Blue NSB	K.

The following dyestuffs are very similar to the above products

Alizanthrene Blue RC	ICI.
Benzadone Blue RC	YDC.
Caledon Blue RCS	ICI.
Indanthrene Blue RC	IG.
Paradone Blue FC	LBH.
Paradone Blue RC	LBH.
Sandothrene Blue ERC	S.
Soledon Blue 2RCS	ICI.
Tinon Chlorine Blue RC	Gy.

The following have similar properties to the above but give slightly greener shades

Benzadone Blue GCD	YDC.
Caledon Blue GCDS	ICI.
Paradone Blue GCD	LBH.
Sandothrene Blue EGCD	S.
Tinon Chlorine Blue GCD	Gy.

The next group of dyestuffs belongs to a similar chemical class, but its members exhibit lower fastness to chlorine

Amanthrene Blue GCD	AAP.
Calcoloid Blue GCD	CCC.
Calcosol Blue GCP	CCC.
Caledon Blue GCPS	ICI.
Carbanthrene Blue GCD	NAC.
Carbanthrene Blue GCDRN	NAC.
Carbanthrene Printing Blue GCD	NAC.
Cibanone Blue GCD	Ciba.
Cibanone Blue GCDN	SCI.
Dowanone Blue GCD	Ciba.
Indanthrene Blue GCD	IG.
Indanthrene Blue GCDA	G.
Indanthrene Blue GCDN	IG.
Indanthrene Blue GCDS	G.
Indanthrene Blue GCDW	G.
Indanthrene Blue GD	G.
Paradone Blue GCP	LBH.
Ponsol Blue GD	DuP.
Ponsol Blue GDS	DuP.
Ponsol Blue GDP	DuP.
Sandothrene Blue NGCDN	S.
Solanthrene Blue NJI	K.
Tinon Chlorine Blue GCDN	Gy.
Vat Blue JIN	St.D.

Algosol Blue O4B	G.
Brilliant Indigo 4B	IG.
Brilliant Indigo 4B	NAC.
Brilliant Indigo 4BA	G.
Brilliant Indigo BASF/4B	IG.
Brilliant Indigo 4BR	NAC.
Brom Indigo FBD	IG.
Calcosol Blue 2BD	CCC.
Calcosol Blue 2BP	CCC.
Ciba Blue 2B	SCI.
Ciba Blue 2B	Ciba.
Ciba Blue 2BD	Ciba.
Ciba Blue 2BDG	Ciba.
Ciba Brilliant Blue BS	Ciba.
Durindone Blue 4BS	ICI.
Indigo 4B	IG.
Indigo MLB/4BD	IG.
Indigo N4B	K.
Indigosol O4B	DH.
Sulfanthrene Blue 2BD	DuP.
Sulfanthrene Blue 2BDN	DuP.
Tetra Blue 2B	S.
Tinon Blue 2B	Gy.

Calcosol Blue Green FFB	CCC.
Calcosol Blue Green FFBP	CCC.
Cibanone Blue 3G	SCI.
Cibanone Blue 3G	Ciba.
Cibanone Blue 3GF	Ciba.
Hydroform Bright Blue 4G	PCC.
Indanthrene Blue Green FFB	IG.
Indanthrene Blue Green FFBA	G.
Indanthrene Blue Green FFBN	G.
Indanthrene Blue Green FFBW	G.
Indanthrene Blue Green FFBWP	G.
Ponsol Blue Green FFB	DuP.
Sandothrene Blue N3G	S.
Sandothrene Blue N3GF	S.
Tinon Chlorine Blue 3G	Gy.
Tinon Chlorine Blue 3GF	Gy.

(The above show very slight differences dependent upon their route of manufacture.)

Indigo Ciba R	SCI.
Indigo Ciba RR	SCI.
Indigo MLB/R	IG.
Indigo MLB/2R	IG.
Indigo MLB/5B	IG.
Indigo NR	K.

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Indigo N2R	K.
Indigo Pure BASF/R	IG.
Indigo Pure BASF/2R	IG.
Indigo RRN	IG.
Indigosol OR	DH.
Tinon Indigo R	Gy.
Tinon Indigo RR	Gy.

Synthetic Indigo

Algosol Blue O	G.
Indigo	DuP.
Indigo BASF	IG.
Indigo Ciba	SCI.
Indigo LL	ICI.
Indigo MLB	IG.
Indigo NAC	NAC.
Indigo NACCO	NAC.
Indigo Synthetic	Ciba.
Indigo Synthetique	K.
Indigo W Synthetic	Ciba.
Indigosol O	DH.
Lithosol Deep Blue B	DuP.
Soledon Indigo LL	ICI.

Brilliant Indigo KMR	NAC.
Calcosol Blue R	CCC.
Calcosol Blue RP	CCC.
Indigo BASF/RB	IG.
Indigo MLB/BB	IG.
Indigo N2B	K.
Indigo RBN	IG.
Midland Vat Blue R	Ciba.
Midland Vat Blue RG	Ciba.
Sulfanthrene Navy Blue MR	DuP.

Indigotine

FD & C Blue No. 2 (Indigotine 692)	BA.
FD & C Blue No. 2 (Indigotine Certified)	NAC.
Gendarme Blue Conc.	HM.
Indigo Carmine	IG.
Indigotine	NAC.
Indigotine Conc.	DuP.
Indigotine O	DuP.
Indigotine Synthetic	Ciba.

(These are water-soluble acid dyes)

Calcosol Blue 3G	CCC.
Caledon Blue 3GS	ICI.
Indanthrene Blue 3G	IG.
Ponsol Blue 3G	DuP.
Solanthrene Blue N3J	K.
Caledon Brilliant Blue 3GS	ICI.
Indanthrene Brilliant Blue 3G	IG.

Brilliant Indigo BR	IG.
Ciba Blue BR	SCI.
Ciba Blue BR	Ciba.
Indigo NBR	K.
Tetra Blue BR	S.
Tinon Blue BR	Gy.

Brilliant Indigo BASF/4BC	IG.
Durindone Blue 4BCS	ICI.
Indigo N4BR	K.
Soledon Blue 4BCS	ICI.

Alizanthrene Navy Blue R	ICI.
Cibanone Navy Blue RA	SCI.
Sandothrene Navy Blue NR	S.
Tinon Chlorine Navy Blue RA	Gy.

Cibanone Blue B2G	SCI.
Indanthrene Blue 5G	IG.
Tetra Blue N2BG	S.
Tinon Blue B2G	Gy.

Caledon Blue GCS	ICI.
Indanthrene Blue GC	IG.
Sandothrene Blue EGC	S.
Tinon Chlorine Blue GC	Gy.

Ciba Blue G	SCI.
Durindone Blue 5B	ICI.
Tetra Blue G	S.
Tinon Blue G	Gy.

Algol Blue 4R	IG.
Alizarine Indigo 3R (obsolete name)	IG.
Thioindone Sky Blue R (obsolete name)	IG.
Vat Blue JR (obsolete name)	IG.

Indanthrene Printing Blue GG	IG.
Indigosol Blue AGG	DH.
Indigosol Printing Blue IGG	DH.

Indigo MLB/6B	IG.
Indigosol Blue O6B	DH.
Midland Vat Blue 5B	Ciba.

Algol Blue 3GN	IG.
Helindon Blue 3G, 3GN (obsolete)	IG.
Thioindigo Blue 2G, GGD (obsolete)	IG.

Brilliant Indigo BASF/4G	IG.
Brilliant Indigo N4J	K.
Sulfanthrene Brilliant Blue 4G	DuP.

Indanthrene Printing Blue B	IG.
Indigosol Blue AB	DH.
Indigosol Printing Blue IB	DH.

Indanthrene Brilliant Blue RCL	IG.
Sandothrene Blue NRSC	S.
Tinon Chlorine Blue 2R	Gy.

Cibanone Blue G	SCI.
Sandothrene Blue NG	S.
Tinon Chlorine Blue B	Gy.

Cibanone Blue GL, GLN	SCI.
Sandothrene Blue NGL	S.
Tinon Chlorine Blue BL, BLN	Gy.

Caledon Dark Blue 2RDS	ICI.
Indanthrene Navy Blue RRDE	IG.
Indanthrene Printing Navy Blue 2R	IG.

Cibanone Navy Blue GA	SCI.
Sandothrene Dark Blue NG	S.
Tinon Chlorine Navy Blue GA	Gy.

Caledon Dark Blue 3BS	ICI.
Sandothrene Navy Blue EBS	S.
Tinon Chlorine Navy Blue	Gy.

Ciba Blue 2G	SCI.
Tetra Blue 2G	S.
Tinon Blue 2G	Gy.
Algol Blue B	IG.
Helindon Blue B	IG.
Indigosol Blue HB	DH.
Alizarine Indigo 5R (obsolete name)	IG.
Algol Blue 5R	IG.
Vat Blue JRR (obsolete name)	IG.
Indanthrene Blue GT	IG.
Hydron Blue BBF	IG.
Brilliant Indigo 2B	NAC.
Brilliant Indigo BASF/2B	IG.
Indigosol Blue 4GS	DH.
Soledon Blue 4GS	ICI.
Brilliant Indigo B	NAC.
Brilliant Indigo BASF/B	IG.
Sandothrene Blue N2G	S.
Tinon Chlorine Blue 2G	Gy.
Cibanone Blue GF	SCI.
Tinon Chlorine Blue BN	Gy.
Caledon Brilliant Blue 2RS	ICI.
Cibanone Blue 2R	SCI.
Caledon Dark Blue GS	ICI.
Indanthrene Navy Blue G	IG.
Algol Blue K	IG.
Indanthrene Blue RK	IG.
Cyananthrone (obsolete name)	IG.
Indanthrene Dark Blue BT (obsolete)	IG.

Indanthrene Blue 3BCS	IG.
Indanthrene Blue 3BCSA	G.
Indigo MLB/T (obsolete name)	IG.
Indigo Pure BASF/G	IG.
Indigo MLB/N (obsolete)	IG.
Reduced Indigo (obsolete)	IG.
Algol Blue 7G	IG.
Alizarine Indigo 7G (obsolete)	IG.
Algol Blue FFK	IG.
Hydron Sky Blue FK	IG.
Alizarine Indigo G (obsolete name)	IG.
Algol Blue G	IG.
{Alizarine Indigo B (obsolete)	IG.
{Brilliant Indigo BASF/G (obsolete)	IG.
{Caledon Blue 2R	ICI.
{Caledon Ming Blue XS	ICI.
{Caledon Navy Blue R	ICI.
{Caledon Navy Blue 2RS	ICI.
{Hydron Dark Blue G	IG.
{Hydron Dark Blue 2G	IG.
{Hydron Navy Blue CN	IG.
{Indanthrene Blue CE	IG.

{Indanthrene Blue CLG	IG.
{Indanthrene Blue 2GS	IG.
{Indanthrene Blue 3GF	IG.
{Indanthrene Dark Blue BG	IG.
{Indanthrene Navy Blue BF	IG.
{Indanthrene Navy Blue R	IG.
{Indanthrene Printing Blue R	IG.
{Indanthrene Turquoise Blue GK	IG.
{Indanthrene Turquoise Blue 3GK	IG.
{Indigotine P (acid dyestuff)	IG.
{Methyl Indigo R (obsolete)	IG.
{Solanthrene Blue N3JF	K.
{Solanthrene Blue NJN	K.
{Solanthrene Navy Blue NJ	K.
{Solanthrene Navy Blue NR	K.

American Types Unplaced

Amanthrene Navy Blue BN	AAP.
Calcoloid Navy Blue NTD	CCC.
Calcosol Blue BCL	CCC.
Calcosol Blue BCLP	CCC.
Calcosol Navy Blue EP	CCC.

Calcosol Navy Blue GP	CCC.
Calcosol Navy Blue MP	CCC.
Calcosol Navy Blue NTP	CCC.
Calcosol Navy Blue 2RP	CCC.
Calcosol Navy Blue 4RP	CCC.
Carbanthrene Blue RCS	NAC.
Carbanthrene Blue FFB	NAC.
Carbanthrene Blue RBCF	NAC.
Carbanthrene Printing Blue GR	NAC.
Carbanthrene Blue Green FFB	NAC.
Carbanthrene Printing Navy Blue B	NAC.
Carbanthrene Printing Navy Blue R	NAC.
Duraval Blue G	DuP.
Hydroform Navy Blue	PCC.
Indanthrene Blue BD	G.
Indanthrene Blue GCDWP	G.
Indanthrene Blue GPZA	G.
Indanthrene Blue RPZA	G.
Indanthrene Navy Blue BRP	G.
Indanthrene Navy Blue BRWP	G.
Indanthrene Navy Blue 3GA	G.
Indo Blue Paste B-41	HCW.
Ponsol Blue BCL	DuP.
Ponsol Blue BF	DuP.
Ponsol Blue BFS	DuP.
Ponsol Blue BF Soluble	DuP.
Ponsol Blue CLX	DuP.
Ponsol Blue GCL	DuP.
Ponsol Blue RBF	DuP.
Ponsol Blue RCX	DuP.
Ponsol Blue Green Y	DuP.
Ponsol Navy Blue	DuP.
Ponsol Navy Blue RA	DuP.
Vat Printing Navy RB	Ciba.

Group VIII

Amanthrene Brilliant Violet RR	AAP.
Benzadone Brilliant Purple 2R	YDC.
Calcoloid Violet RRD	CCC.
Calcosol Violet RR	CCC.
Caledon Brilliant Purple 2RS	ICI.
Carbanthrene Printing Violet 2R	NAC.
Cibanone Violet 2R	Ciba.
Cibanone Violet 2RB	SCI.
Indanthrene Brilliant Violet 2R	IG.
Indanthrene Brilliant Violet 2RA	G.
Indanthrene Brilliant Violet 2RAP	G.
Indanthrene Brilliant Violet RRWP	G.
Indanthrene Printing Violet 2R	G.

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Paradone Brilliant Violet 2R	LBH.
Ponsol Violet RR	DuP.
Ponsol Violet RRD	DuP.
Ponsol Violet RRP	DuP.
Sandothrene Violet N2R	S.
Solanthrene Brilliant Violet N2R	K.
Soledon Brilliant Purple 2RS	ICI.
Tinon Chlorine Violet B2R	Gy.
Tinon Chlorine Violet B2RB	Gy.

Calcosol Red 3B	CCC.
Calcosol Red 3BP	CCC.
Ciba Red 3B	Ciba.
Ciba Red 3BN	SCI.
Durindone Red 3BS	ICI.
Indanthrene Red Violet RH	IG.
Indanthrene Red Violet RHA	G.
Indanthrene Red Violet RHA for Lakes	G.
Indanthrene Red Violet RHF	G.
Indanthrene Printing Violet RH	IG.
Indigosol Red Violet IRH	DH.
Sandothrene Red 3B	S.
Solanthrene Heliotrope N	K.
Soledon Red 3BS	ICI.
Sulfanthrene Red 3B	DuP.
Tinon Chlorine Red 3B	Gy.
Vat Printing Red Violet RH	NAC.
Vat Red Violet RH	NAC.

Caledon Brilliant Violet 4RS	ICI.
Cibanone Violet 4R	SCI.
Indanthrene Brilliant Violet 4R	IG.
Indanthrene Brilliant Violet 4RA	G.
Indanthrene Brilliant Violet 4RWP	G.
Indanthrene Printing Violet 4RN	G.
Indigosol Brilliant Violet IE4R	DH.
Ponsol Brilliant Violet 4RN	DuP.
Ponsol Brilliant Violet 4RNS	DuP.
Sandothrene Violet N4R	S.
Solanthrene Brilliant Violet N4R	K.
Tinon Chlorine Violet B4R	Gy.

Algol Purple R	IG.
Ciba Violet 6R	SCI.
Indanthrene Printing Purple R	IG.
Indigosol Purple AR	DH.
Tetra Violet 6R	S.
Tinon Chlorine Violet 6R	Gy.

Indanthrene Brilliant Violet 3B	IG.
Indanthrene Brilliant Violet 3BA	G.
Indanthrene Brilliant Violet 3BWP	G.
Indanthrene Printing Violet F3B	IG.
Ponsol Brilliant Violet 3B	DuP.
Sandothrene Violet N3B	S.
Tinon Chlorine Violet 4B	Gy.

Indanthrene Red Violet RRN	IG.
Indanthrene Red Violet RRNA	G.
Indanthrene Red Violet RRNAP	G.
Indanthrene Red Violet RRNWP	G.
Indanthrene Printing Red Violet RRN	IG.
Ponsol Red Violet RRNX	DuP.

Algol Brilliant Violet RK (obsolete name)	IG.
Caledon Brilliant Violet RS	ICI.
Indanthrene Brilliant Violet RK	IG.
Ponsol Violet AR	DuP.
Sandothrene Brilliant Violet ER	S.
Solanthrene Brilliant Violet NR	K.

Caledon Violet XBNS	ICI.
Indanthrene Violet FFBN	IG.
Indanthrene Violet FFBNA	G.
Indanthrene Violet FFBNF	G.
Indanthrene Violet FFBNFW	G.

Algol Violet BBN (replaced Hydron Violet BBF)	IG.
Indanthrene Printing Violet BBF	IG.
Indigosol Printing Violet IBBF	DH.
Indigosol Violet ABBF	DH.
Soledon Violet BS	ICI.

Caledon Purple RS	ICI.
Indanthrene Violet B (Indanthrene Printing Violet BF ?)	IG.
Paradone Violet B	LBH.
Sandothrene Violet NR	S.
Tinon Chlorine Violet BR	Gy.

(The above show slightly different shades and degrees of purity, but are chemically similar.)

Calcosol Violet BN	CCC.
Ponsol Violet BN	DuP.
Ponsol Violet BNX	DuP.
Ponsol Violet BNXS	DuP.

Ciba Violet B	SCI.
Ciba Violet B, R	Ciba.
Tetra Violet B	S.
Tinon Chlorine Violet B	Gy.

Algol Violet BB	IG.
Anthra Violet B (obsolete name)	IG.
Helindon Violet B (obsolete name)	IG.
Thioindigo Violet B (obsolete name)	IG.

Caledon Red Violet 2RNS	ICI.
Indanthrene Red Violet 2RK	IG.
Sandothrene Red Violet E2RN	S.
Tinon Chlorine Red Violet 2RN	Gy.

Ciba Violet RN	SCI.
Tetra Violet RN	S.
Tinon Chlorine Violet RN	Gy.

Ciba Violet 2R	SCI.
Tetra Violet 2R	S.
Tinon Chlorine Violet 2R	Gy.

Cibanone Violet 2BW	SCI.
Sandothrene Violet N2BW	S.
Tinon Chlorine Violet 2BW	Gy.

Caledon Brilliant Violet 2BS	ICI.
Indanthrene Brilliant Violet BBK	IG.
Solanthrene Brilliant Violet N2B	K.

Algol Violet 2R	IG.
Helindon Violet R (obsolete name)	IG.
Thioindigo Violet 2R (obsolete name)	IG.

Caledon Violet RN	ICI.
Indanthrene Violet BN, RN	IG.

Algol Violet R	IG.
Hydron Violet R (obsolete name)	IG.

Indigosol Printing Violet IRR	DH.
Indigosol Violet ARR	DH.

Cibanone Violet 6B	SCI.
Tinon Chlorine Violet 6B	Gy.
Cibanone Violet BW	SCI.
Tinon Chlorine Violet BW	Gy.
Algol Violet 3B	IG.
Hydron Violet B	IG.
Algol Violet AZB	IG.
Alizarine Indigo Violet B (obsolete)	IG.
Helindon Violet BBN	IG.
Hydron Violet BBF	IG.
Helindon Violet 2B (obsolete)	IG.
Thioindigo Violet 2B (obsolete)	IG.
{Algol Violet B	IG.
{Algol Violet RFN (replaced Hydron Violet RF)	IG.
{Ciba Heliotrope B (obsolete)	SCI.
{Ciba Violet 3B (obsolete)	SCI.
{Ciba Violet 4B	SCI.
{Helindon Violet D (obsolete)	IG.
{Indanthrene Printing Violet F4R	IG.
{Indanthrene Printing Violet RF	IG.
{Indanthrene Violet RT	IG.
{Paradone Violet BR	LBH.
{Solanthrene Brilliant Violet N3R	K.

American Types Unplaced

Calcoloid Violet 6RD	CCC.
Calcosol Violet 6RD, 6RP	CCC.
Calcosol Violet 4RD	CCC.
Indanthrene Brilliant Violet RAF	G.
Indanthrene Printing Violet 6R Extra	G.
Indanthrene Red Violet 2RM	G.
Indanthrene Violet MV—1	HCW.
Ponsol Violet ABB	DuP.
Sulfanthrene Red Violet 2RN	DuP.

Group IX

Calcoloid Pink FFD	CCC.
Calcosol Pink FF	CCC.
Calcosol Pink FFP	CCC.
Ciba Brilliant Pink R	SCI.
Ciba Brilliant Pink RDL	Ciba.
Ciba Pink FF	Ciba.
Durindone Pink FFS	ICI.
Helindon Pink R (obsolete)	IG.
Hydron Pink FF	IG.
Indanthrene Brilliant Pink R	IG.
Indanthrene Brilliant Pink RA	G.
Indanthrene Brilliant Pink RAM	G.
Indanthrene Brilliant Pink RAP	G.
Indanthrene Brilliant Pink RWP	G.
Indanthrene Printing Pink FFRS	IG.
Indigosol Pink IR	DH.
Luxiane Brilliant Pink SCR	St. Cl.
Nova Vat Pink 100%	Nova.
Sandothrene Brilliant Pink R	S.
Solanthrene Brilliant Pink NR	K.
Soledon Pink FFS	ICI.
Sulfanthrene Pink FF	DuP.
Sulfanthrene Pink FFN	DuP.
Sulfanthrene Pink FFS	DuP.
Tinon Brilliant Pink CR	Gy.
Vat Pink FF	NAC.

Algol Scarlet 3B	IG.
Algol Scarlet 3BA	G.
Anthra Scarlet B (obsolete name)	IG.
Calcosol Printing Scarlet 2B	CCC.
Calcosol Printing Scarlet 3B	CCC.
Calcosol Scarlet B	CCC.
Ciba Scarlet 2B	SCI.
Durindone Scarlet 3BS	ICI.

Continued on p. 291.

Heliane Scarlet 3B	St. Cl.
Helindon Fast Scarlet B (obsolete name)	IG.
Hydron Scarlet 3B (obsolete name)	IG.
Nova Vat Scarlet B	Nova.
Solane Scarlet N3B	K.
Soledon Scarlet BS	ICI.
Thioindone Scarlet BB (obsolete name)	IG.
Tinon Scarlet 2B	Gy.

Algol Scarlet GG	IG.
Anthra Scarlet GG (obsolete name)	IG.
Ciba Scarlet G	SCI.
Ciba Scarlet G	Ciba.
Durindone Scarlet YS	ICI.
Helindon Fast Scarlet C (obsolete name)	IG.
Helindon Scarlet GG	IG.
Sulfanthrene Scarlet Y	DuP.
Tetra Scarlet G	S.
Thioindigo Scarlet GG (obsolete name)	IG.
Tinon Scarlet G	Gy.

Calcosol Pink FB	CCC.
Calcosol Pink FBP	CCC.
Ciba Brilliant Pink B	SCI.
Durindone Pink FBS	ICI.
Helindon Pink B (obsolete name)	IG.
Hydron Pink FB	IG.
Indanthrene Brilliant Pink B	IG.
Indanthrene Brilliant Pink BA	G.
Indanthrene Brilliant Pink BY	G.
Sandothrene Brilliant Pink B	S.
Solanthrene Brilliant Pink NB	K.
Tinon Brilliant Pink CB*	Gy.

*See p. 293.

Algol Scarlet RB	IG.
Ciba Scarlet BG	SCI.
Durindone Scarlet 2BS	ICI.
Helindon Fast Scarlet BG (obsolete name)	IG.
Hydron Scarlet BB	IG.
Indigosol Scarlet HB	DH.
Solane Scarlet NRB	K.
Sulfanthrene Scarlet 2BN	DuP.
Tetra Scarlet BG	S.
Thioindone Scarlet BBR (obsolete name)	IG.
Tinon Scarlet BG	Gy.

Thioindigo—

Algol Red 5B	IG.
Anthra Red B (obsolete name)	IG.
Calcosol Pink 2BP	CCC.
Ciba Pink B	SCI.
Durindone Red BS	ICI.
Helindon Red BB (obsolete name)	IG.
Indanthrene Printing Red 5B	IG.
Tetra Pink B	S.
Thioindigo Red B (obsolete name)	IG.
Tinon Pink B	Gy.

Algol Scarlet GGN	IG.
Algol Scarlet GGNA	G.
Algol Scarlet GGNV	G.
Anthra Scarlet G (obsolete name)	IG.
Calcoloid Scarlet 2GHN	CCC.
Calcosol Printing Scarlet 2GHN	CCC.
Helindon Fast Scarlet G (obsolete name)	IG.
Solane Scarlet N2J	K.
Thioindone Scarlet B (obsolete name)	IG.

Algol Brilliant Red 2B	IG.
Algol Pink BBK (obsolete name)	IG.
Algol Red BK (obsolete name)	IG.
Algol Red FF (obsolete name)	IG.
Algol Red R Extra (obsolete name)	IG.
Caledon Red FFS	ICI.
Ponsol Red AFF	DuP.
Vat Red 3B (obsolete name)	IG.

Calcosol Red BN	CCC.
Caledon Red BNS	ICI.
Carbanthrene Red BN	NAC.
Cibanone Red RK	SCI.
Indanthrene Red RK	IG.
Ponsol Red BN, BNS	DuP.
Sandothrene Red N2R	S.
Tinon Red RK	Gy.

Algol Bordeaux B	IG.
Anthra Bordeaux B (obsolete name)	IG.
Cibanone Bordeaux 2B	SCI.
Helindon Bordeaux B (obsolete name)	IG.
Sandothrene Bordeaux N2B	S.
Tinon Chlorine Bordeaux BG	Gy.

Ciba Red G	SCI.
Durindone Red YS	ICI.
Tetra Red G	S.
Tinon Chlorine Red G	Gy.

Ciba Red 2B	SCI.
Indanthrene Magenta B	IG.
Indanthrene Printing Magenta B	IG.
Sandothrene Red 2B	S.
Tinon Chlorine Red 2B	Gy.

Algol Pink B	IG.
Helindon Pink BN (obsolete name)	IG.
Sulfanthrene Pink FB, FBS	DuP.
Thioindigo Pink BN (obsolete name)	IG.

(See p. 291—probably analogous to the group marked*)

Ciba Red R	SCI.
Ciba Red R	Ciba.
Sandothrene Red R	S.
Tinon Chlorine Red R	Gy.

Algol Pink BG	IG.
Anthra Pink AN (obsolete name)	IG.
Helindon Pink AN (obsolete name)	IG.
Thioindigo Pink AN (obsolete name)	IG.

Algol Scarlet GGR	IG.
Heliane Scarlet SC	St. Cl.
Helindon Fast Scarlet R (obsolete name)	IG.
Solane Scarlet NR	K.

Indanthrene Red FBB	IG.
Indigosol Red IFBB	DH.
Soledon Red 2BS	ICI.

Cibanone Red 4B	SCI.
Sandothrene Red N4B	S.
Tinon Chlorine Red B2R	Gy.

Cibanone Red B	SCI.
Sandothrene Red NB	S.
Tinon Chlorine Red BC	Gy.

Cibanone Red 3G	SCI.
Sandothrene Red N3G	S.
Tinon Chlorine Red 3G	Gy.

Cibanone Red G	SCI.
Sandothrene Red NG	S.
Tinon Chlorine Red BG	Gy.

Ciba Pink BG	SCI.
Sandothrene Pink BG	S.
Tinon Chlorine Pink 2B	Gy.

Calcosol Pink B	CCC.
Indanthrene Pink B	IG.
Ponsol Pink B	DuP.

Caledon Red 2GS	ICI.
Indanthrene Red 2G	IG.
Sandothrene Red L2G	S.

Grelanone Red 2B	IG.
Indanthrene Rubine R	IG.
Ponsol Red G2B, G2BS	DuP.

Benzadone Red 5G	YDC.
Caledon Red 5G	ICI.
Indanthrene Red 5GK	IG.

Algol Bordeaux RT	IG.
Anthra Bordeaux R (obsolete name)	IG.
Indanthrene Bordeaux R	IG.

Algol Red BB	IG.
Helindon Red R (obsolete name)	IG.
Indigosol Red HR	DH.

Algol Rubine B	IG.
Helindon Red B (obsolete name)	IG.
Thioindigo Red BG (obsolete name)	IG.

Durindone Scarlet R (obsolete)	ICI.
Thioindigo Scarlet R (obsolete)	IG.

Helindon Scarlet S (obsolete)	IG.
Thioindigo Scarlet S (obsolete)	IG.

Algol Scarlet G	IG.
Algol Printing Scarlet GRN	IG.

Amandone Bordeaux B	AAP.
Ciba Bordeaux B	SCI.

Indanthrene Printing Red B	IG.
Indanthrene Printing Red BA	G.

Ciba Bordeaux 2RN	SCI.
Tetra Bordeaux 2RN	S.

Indanthrene Scarlet B	IG.
Indigosol Scarlet IB	DH.

Indanthrene Pink 3BF	IG.
Indigosol Brilliant Pink I3B	DH.

Ciba Brilliant Pink 2B	SCI.
Tinon Brilliant Pink 2B	Gy.

Ciba Scarlet 3G	SCI.
Tetra Scarlet 3G	S.

Algol Red B (obsolete name)	IG.
Algol Red BTK	IG.

Algol Red GT	IG.
Anthra Red RT (obsolete name)	IG.

Algol Scarlet RT	IG.
Thioindigo Scarlet G (obsolete name)	IG.

{Ciba Red B	SCI.

{Algol Scarlet B	IG.

{Indanthrene Bordeaux B	IG.
{Indanthrene Scarlet F3G	IG.
{Indanthrene Rubine B	IG.
{Indanthrene Brilliant Scarlet FR	IG.
{Indanthrene Brilliant Scarlet RK	IG.
{Indanthrene Red BK	IG.
{Indanthrene Scarlet 4G	IG.
{Indanthrene Printing Pink FFB	IG.
{Indanthrene Printing Red 3B	IG.
{Tinon Pink G	Gy.
{Indanthrene Scarlet R	IG.
{Indanthrene Pink FBBL	IG.
{Tinon Chlorine Bordeaux B	Gy.
{Indanthrene Scarlet 2G	IG.
{Indanthrene Scarlet GK	IG.
{Indanthrene Maroon R	IG.
{Ciba Lake Red B	SCI.
{Caledon Red X5BS	ICI.
{Caledon Red 5BS	ICI.
{Algol Pink R (obsolete)	IG.
{Indanthrene Red G	IG.
{Algol Bordeaux 3B (obsolete)	IG.
{Indanthrene Red R	IG.
{Indanthrene Corinth RK	IG.

American Dyestuffs Unplaced

Algol Scarlet GGM	G.
Calcosol Brilliant Pink RB	CCC.
Calcosol Red 7RP	CCC.
Calcosol Scarlet G	CCC.
Ciba Bordeaux RB	Ciba.
Ciba Brilliant Red G	Ciba.
Duraval Pink B	DuP.
Indanthrene Rubine RD	G.
Indanthrene Rubine RW	G.
Indanthrene Scarlet BBN	G.
Ponsol Brilliant Red B	DuP.
Sulfanthrene Scarlet G	DuP.
Sulfanthrene Scarlet GN	DuP.
Sulfanthrene Scarlet 2G	DuP.
Vat Pink FB	NAC.
Vat Printing Pink FF	NAC.
Vat Printing Scarlet GGN	NAC.

The Tinosol (Gy.) and Cibantine (S.C.I.) ranges of solubilised vat dyestuffs have been omitted owing to lack of information at the present time; they represent new ranges of products equivalent to the Indigosols and Soledons.

The following sources have been used in compiling the list of equivalents:

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An index of all the dyestuffs listed in the foregoing pages is given in Appendix I.

APPENDIX I

INDEX TO DYESTUFFS LISTED IN CHAPTER XIII

APPENDIX II

CURRENT LITERATURE

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APPENDIX III

INDEX TO FORMULAE

INDEX