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VAT DYE COMPOSITIONS AND APPLICATION THEREOF

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This invention relates to the art of applying vat dyes to textiles, and more particularly to the art of textile printing. It also relates to new vat dye compositions.

This application is a continuation of our co-pending application, Serial No. 504,274 filed December 23, 1930. It also contains subject matter disclosed in our co-pending application Serial No. 703,155 filed December 19, 1933.

Except for indigo, vat dyes (which are unlike all other types of dyes both in properties and mode of application to the fiber) were not known prior to the beginning of the present century.

"By the term vat dye is meant a colouring matter insoluble in water, but which can be converted on reduction into a so-called leuco compound, which is soluble in alkalis, and in such a solution, termed a vat, the actual dyeing process is effected; on removing the material from the bath and exposing to the air oxidation takes place, the dye being precipitated on the fibre in insoluble form; . . ."

From page 423 of "A Textbook of Dye Chemistry" by Georgievics and Grandmougin (1920).

In the application of vat dyes to textile fibers, a distinction is to be made between dyeing (that is, coloring of the entire fabric) and printing, in which only a portion of the fabric is colored. The mode of applying the dye in each case is different.

The process of dyeing comprises suspending the insoluble vat dye in an alkaline solution and thereafter adding a reducing agent to change the vat dye to its hydro derivative (the reducing agent may also be added before or simultaneously with the dye). The fiber is then steeped in the solution of the hydro derivative (referred to above as leuco compound) and is removed as soon as a sufficient amount of the leuco body solution has been absorbed. Exposing the soaked fabric to an oxidizing influence, usually the oxygen of the atmosphere, regenerates the vat dye on the fiber producing a dyed material.

There is an alternative process known as "padding" which is used to some extent at present. According to this process the fiber is immersed in a suspension of a vat dye until a sufficient quantity of the dye has adhered mechanically to the fiber (this adherence is analogous to wet sand clinging to stick used for stirring a sand and water mixture). Thereafter the fiber, with the dye particles mechanically held thereon, is immersed in an alkaline solution containing a reducing agent whereby the dye particles are reduced to the soluble hydro derivative, penetrate the fiber and, upon removal from the solution followed by oxidation, are regenerated, resulting in a dyeing taking place as in the general process first described. As will be obvious, some of the dye is lost from the fiber by reason of going into solution in the vat. If this process is continued long enough, sufficient dye would be removed from the fiber to render the reducing solution a dye vat of ordinary concentration. Inasmuch as a reduction to the hydro derivative is necessary both in dyeing from a solution and by the padding method, the solution-dyeing process is the one most widely used where space and equipment permit.

While various reducing agents may be used in the dyeing (as differentiated from printing) of vat dyes, the one most commonly utilized is a hydrosulfite.

"For some years past solid hydrosulphite of soda, containing amounts of $Na_2S_2O_4$ varying from 60 to 95 per cent., has been in the market in the form of a dry, almost white, powder. It is largely used in the dyeing of indigo and other vat dyes, but, owing to the rapidity with which its solutions oxidize in contact with the air, it is not suitable for textile printing."

From page 250 of the "Principles and Practice of Textile Printing" by Knecht & Fothergill (1924). As indicated in the above quotation, the ordinary reducing agent utilized in the dyeing of vat dyes cannot be used practically in the printing of vat dyes on textile. This is a serious disadvantage because vat dye printing is, for other reasons, much more complicated than vat dyeing. This particular difficulty has been partially overcome by the discovery and commercial production of the compound sodium formaldehyde sulfoxylate which only exerts its reducing influence at elevated temperatures. By use of this and equivalent compounds the vat dye can be printed on a fabric in the desired design and thereafter reduced and fixed to the fiber.

At the present time, the most extensive textile printing is done with cylinder or roll printing machines. The fundamental principles in this process are simple and comprise passing the cloth to be printed under some tension and pressure over an intaglio metal roll, the engraving of which is filled with a printing paste. After leaving the printing machine, the printed cloth is quickly passed into a drier. This dries the printing paste on the cloth in its proper place and prevents the dye from spreading to other portions of the fabric with consequent ruination of the design (in dyeing with vat dyes, spreading of the color solution over

the entire cloth is earnestly sought for, but in the printing of vat dyes, the slightest spreading of the color destroys the value of the printed cloth to such an extent that the same is not salable).

The printing paste applied to the cloth from the roller is a material thickened to such an extent that it does not run readily. It varies with different fabrics and manufacturers, but usually consists of a mixture of unreduced vat dye, a strong reducing agent such as sodium formaldehyde sulfoxylate, an alkali and a thickening agent. The thickening agent is usually a gum (for instance, British gum), starch, or both. The printing paste is usually prepared by mixing a dye paste or pastes with the other ingredients enumerated, said other ingredients being in the form of a gummy mixture hereinafter called "printing gum". The dye pastes are essentially finely divided suspensions of dye with or without a dispersing agent. These dye pastes (hereinafter referred to as "dye pastes", "dyestuff pastes" or "color pastes") usually have the dye suspended in water.

In order to complete the printing, the cloth, after leaving the drier, is passed into an ager (usually a steam ager) for a period of a few minutes, during which time the vat color undergoes reduction (the sodium formaldehyde sulfoxylate in the printing paste producing its reducing action because of the elevated temperature in the ager) and passes to the fiber. The fabric is then subjected to oxidizing conditions which may include passing it into a steeping bath, usually of water or water containing an oxidizing agent. Any excess color is washed off in a soap solution with which the textile material is treated following the steeping.

Vat dyes at the time of printing are not in true solution. For this reason, the effecting of complete reduction of the dye and the transfer of the color to the fabric in the brief time which the goods are steamed is a process accompanied by great difficulties, as previously stated. In order to make sure that satisfactory results are obtained, it is important that the dye paste be of special fineness, but even then a great deal of color is lost because of its failure to dye the cotton. This excess color is washed off during the soaping which follows the steaming.

In both dyeing and printing it has been proposed to assist the process by the addition of various substances, for convenience called "assistants". The purpose for which such assistants are added and the functions which they perform may vary widely. Thus, in dyeing, some assistants are added to speed up reduction of the dye, others to retard oxidation of the vat. It does not follow, however, that more brilliant and brighter dyeings are obtained. The same is true of printing.

To illustrate this distinction, attention is called to British Patent No. 3241 of 1911, in which it is stated that: ". . . the preparation and the working of vats of indigoid dyestuffs (that is to say dyestuffs, except indigo, which, like indigo, contain the chromophorous group —CO—C= C—CO—) can be greatly facilitated by adding anthraquinone or a derivative thereof, such, for example, as (alpha-) or (beta)-oxyanthraquinone, a dioxyanthraquinone or a sulphonic acid of one of these, to the stock-vats and to the dye-vats. The action of the anthraquinone and its derivatives in the vat is due to the ease with which they are reduced and to their power of acting as hydrogen carriers. This latter property enables them themselves to exert a reducing action upon the vat-dyestuff used; this enhancement of the reducing power of the vats is also favourable for the setting and working of the vats, because on the one hand the dyestuff is reduced more quickly and on the other hand the oxidation of the vats is better checked. . . ."

This patent indicates that substances such as anthraquinone act as assistants in reducing the dye and in checking oxidation, thereby effecting a better utilization of the dye, but it does not indicate that better dyeings are obtained. Similarly, Remlein, U. S. Patent No. 1,750,942, discloses a padding process (defined above) in which anthraquinone is used, although its use is not claimed nor is its function given.

The following tests indicate that anthraquinone does not in fact give stronger dyeings:

A cotton skein was introduced into a vat whose volume in cubic centimeters was approximately twenty times the weight of the skein in grams. The vat was maintained at a temperature of about 160° F. and contained 5% of a color paste comprising approximately 12% 6:6'-diethoxy thioindigo, about 4% caustic soda and about 7.5% sodium hydrosulfite (all percentages based on the weight of the skein). The reduction took place at about 180° F. The skein was then oxidized and soaped in the well known manner.

A similar dyeing, except that the vat contained one gram of anthraquinone per liter of solution, was judged to be only about 33% as strong as the dyeing made from the vat in which no anthraquinone was present.

On account of the greater complexities, it is much more difficult to obtain suitable assistants for printing than for dyeing. However, a number of such assistants have been proposed. One such compound is tri-ethanolamine (U. S. Patent No. 1,790,950) and with it markedly improved results have been produced. Another compound which has been proposed for this use is beta:beta'-dihydroxy-diethyl ether (British Patent No. 368,910). Further examples might be given without adding anything to the discussion of the prior art.

Practical experience has shown those skilled in the art the utter futility of attempting to predict what substances will or will not be good assistants in dyeing and/or printing; or that assistants in dyeing produce stronger and brighter printings; or that assistants in printing produce stronger and brighter dyeings. It is well recognized by those skilled in the art, and is therefore worthy of note, that assistants in dyeing and printing other types of dyes cannot be expected to be assistants in dyeing and printing vat dyes because the mechanisms of the reactions involved are different.

It is an object of this invention to produce new and improved dye compositions of the indigoid type. A further object is to provide new and improved dye compositions of the indigoid type which are suitable for use in printing pastes and when printed on the textile fiber yield prints of unusual strength and brilliancy. A more specific object is to provide new and improved thioindigoid dye compositions. Other objects are to produce improved printing pastes, improved printing gums, improved dye pastes and to provide new and improved results in textile printing. Still further objects will appear hereinafter.

These objects are accomplished by the production of dye compositions comprising an indigoid dye, or mixture of indigoid dyes, containing as an

assistant an alkali metal or ammonium salt of anthraquinone-2-sulfonic acid, or a mixture of said salts, and by the application of such compositions to textile fibers and fabrics. The new printing assistants may be used alone or in conjunction with other assistants. They may be incorporated into the dye paste, printing gum, or printing paste either as such or in the form of the free sulfonic acid. It will be recognized that the free sulfonic acid may be converted to the alkali metal salt by reaction with alkalis such as are present in the printing gum or printing paste. Strong alkalis also tend to replace weak alkalis such as ammonia.

The invention will be further understood, but is not limited, by the following examples.

Example I

A thickener was prepared containing 10% wheat starch, 30% British gum and 60% water. From this thickener a printing gum consisting of:

	Percent
Thickener	57.5
Potassium carbonate	16.0
Sulfoxite C (sodium formaldehyde-sulfoxylate)	11
Glycerine	5
Water	10.5

was prepared. This printing gum was made into a printing paste by incorporating therein a dye paste of 4:4'-dimethyl-6:6'-dichloro-thioindigo and anthraquinone-2-sodium sulfonate. The percentage composition of the printing paste was as follows:

	Percent
Printing gum	79.9
Dye paste (12.5% dye)	20
Anthraquinone-2-sodium sulfonate	0.1

This product was printed on textile material which was then aged and developed in the usual and well known way. The prints obtained were from 10 to 25% stronger than those obtained from a similar composition which differed only in the omission of the anthraquinone-2-sodium sulfonate.

Example II

A printing gum was prepared comprising:

	Percent
Thickener	57.5
Potassium-carbonate	16
Sulfoxite C	11
Glycerine	5
Water	10.5

The thickener consisted of:

	Percent
Wheat starch	10
British gum	30
Water	60

This printing gum was made into a printing paste by mixing it with a 6:6'-diethoxy-thioindigo (C. I. No. 1218) dye paste containing 11.5% solids. To this mixture there was added silver salt (the sodium salt of anthraquinone-2-sulfonic acid). The percentage composition of the resulting printing paste was as follows:

	Percent
Printing gum	79
Dye paste	20
Silver salt	1

Another paste, similar in all respects except that the silver salt was omitted, was prepared and prints made from the two pastes under similar conditions. The prints obtained from the printing paste containing silver salt were 10 to 25% stronger than those obtained from the other printing paste.

Example III

A thickener consisting of 10% wheat starch, 30% British gum and 60% water was prepared and made into a printing gum having the following composition:

	Percent
Thickener	67.5
Potassium carbonate	8
Sulfoxite C	4
Glycerine	5
Water	15.5

A dye paste containing 12% of 6:6'-dimethoxy-thioindigo and the sodium salt of anthraquinone-2-sulfonic acid were incorporated into the printing gum to produce a printing paste having the following composition:

	Percent
Printing gum	79.5
Dye paste	20
Anthraquinone-2-sodium sulfonate	.5

Example IV

A thickener containing 10% wheat starch, 60% water and 30% British gum was prepared and made into a printing paste having the following percentage composition:

	Percent
Thickener	67.5
Potassium carbonate	8
Sulfoxite C	4
Glycerine	5
Water	15.5

This printing gum was made into a printing paste by stirring the same with a 20% dye paste of 5:5':7:7'-tetra-brom-indigo (C. I. No. 1184, bromination in nitrobenzene) and anthraquinone-2-sodium sulfonate. After producing a uniform mixture the printing paste, which was composed of:

	Percent
Printing gum	79.5
Dye paste	20
Silver salt	0.5

was printed on cotton, dried, aged and developed in the usual way. The prints obtained were more than 10% stronger than those obtained from a paste printed under similar conditions which was similar in every respect except that the anthraquinone-2-sodium sulfonate had been omitted.

Example V

A thickener was prepared including 10% wheat starch, 30% British gum and 60% water. From this thickener a printing gum consisting of:

	Percent
Thickener	57.5
Potassium carbonate	16
Sodium formaldehyde-sulfoxylate	11
Glycerine	5
Water	10.5

was prepared. This printing gum was made into a printing paste by incorporating therein a dye paste of 5:5':7:7'-tetra-brom-indigo containing 20% solids (C. I. No. 1184), anthraquinone-2-

sodium sulfonate. The percentage composition of the printing paste was as follows:

	Percent
Printing gum	79.9
Dye paste (20% dye)	20
Anthraquinone-2-sodium sulfonate	0.1

This product was printed on textile material which was then aged and developed in the usual way. The prints obtained were from 10 to 25% stronger than those obtained from a similar composition which differed only in the omission of the anthraquinone-2-sodium sulfonate.

Example VI

A thickener was prepared consisting of 10% wheat starch, 30% British gum and the remainder water. This thickener was incorporated in a printing gum having the following composition:

	Percent
Thickener	56.5
Potassium carbonate	10
Sodium hydroxide	1
Commercial glucose	15
Glycerine	5
Water	12.5

This printing gum was mixed with a 16% (solids) dye paste of bis-beta-naphthio-naphthene indigo and the sodium salt of anthraquinone-beta-sulfonic acid to produce a printing paste. This printing paste, being composed of:

	Percent
Printing gum	79
Dye paste	20
Anthraquinone-2-sodium sulfonate	1

was printed on cotton textile material in the well known way. Comparison of these prints with prints obtained under similar conditions from a similar printing paste which omitted the anthraquinone-2-sodium sulfonate showed them to be about 15% stronger.

Example VII

A thickener was prepared consisting of 10% wheat starch, 30% British gum and the remainder water. This thickener was incorporated in a printing gum having the following composition:

	Percent
Thickener	56.5
Potassium carbonate	10
Sodium hydroxide	1
Commercial glucose	15
Glycerine	5
Water	12.5

This printing gum was mixed with a 16% solids dye paste of 6:6'-difluoro-thioindigo and sodium salt of anthraquinone-beta-sulfonic acid to produce a printing paste. This printing paste, being composed of:

	Percent
Printing gum	79.1
Dye paste	20
Anthraquinone-2-sodium sulfonate	0.9

was printed on cotton textile material in the well known way. Comparison with prints obtained under similar condition from a similar printing paste which omitted the anthraquinone-2-sodium sulfonate showed that the (silver salt) paste gave prints about 15% stronger.

Example VIII

A thickener was prepared containing 10% wheat starch, 30% British gum and 60% water. From this thickener a printing gum consisting of:

	Percent
Thickener	57.5
Potassium carbonate	16
Sodium formaldehyde-sulfoxylate (Rongalite)	11
Glycerine	5
Water	10.5

was prepared. This printing gum was made into a printing paste by incorporating therein anthraquinone-2-sodium sulfonate and a dye paste of the dye resulting from condensing 5:7-dibromisatin chloride with 3-hydroxy-4-methyl-6-chloro-thionaphthene. The percentage composition of the printing paste was as follows:

	Percent
Printing gum	79.9
Dye paste (10% dye)	20
Anthraquinone-2-sodium sulfonate	0.1

This product was printed on textile material which was then aged and developed in the usual way. The prints obtained were from 10 to 25% stronger than those obtained from a similar composition which differed only in the omission of the anthraquinone-2-sodium sulfonate.

Example IX

The printing paste having the following composition:

	Per cent
5:5'-dichloro-7:7'-dimethyl-thioindigo (20% dye paste) (C. I. No. 1209)	20
Thickener	55
Glycerine	5
Sodium hydrosulfite	5
Sodium hydroxide (36% strength)	5
Sulfoxite C	5
Water	3
Anthraquinone-beta-sodium sulfonate	1

was prepared. In the preparation of this composition all of the ingredients except the last three mentioned (namely, the sulfoxite C, water and silver salt, were brought together, uniformly mixed and heated until reduction was complete, whereupon the remaining ingredients were added and the product stirred to uniformity. The thickener in this case consisted of:

80% of a thickener consisting of:
- 10% wheat starch
- 30% British gum
- 60% water

5% water
15% potassium carbonate

This product was printed on textile material which was then aged and developed in the usual way. The prints obtained were stronger than those obtained from a similar composition which differed only in the omission of the anthraquinone-2-sodium sulfonate.

Example X

A printing paste was made from the following ingredients:

	Per cent
6:6'-dichloro-thioindigo dye paste (10% solids)	20
Thickener	55
Glycerine	5
$Na_2S_2O_4$	5
NaOH (36% strength)	5
Sodium formaldehyde-sulfoxylate (Rongalite)	6
Water	3
Anthraquinone-2-sodium sulfonate	1

The method of preparation was as follows: The dye paste, thickener, glycerine, Na_2S_2O. and NaOH were uniformly mixed and heated until reduction was complete. The Rongalite, water and anthraquinone-2-sodium sulfonate were thereafter added. The product was stirred to uniformity. The thickener used was:

80% of a composition comprising:
10%---wheat starch
30%---British gum
60%---water
5%---water
15%---K_2CO_3

The product was printed on textile material. This was aged and developed in the usual way. The prints were 10 to 25% stronger than those made with a similar composition from which the anthraquinone-2-sodium sulfonate had been omitted.

Example XI

The following ingredients were incorporated into a printing paste:

	Per cent
5:5'-difluoro-thioindigo dye paste (10% solids)	20
Thickener	55
Glycerine	5
$Na_2S_2O_4$	5
NaOH (36% strength)	5
Sodium formaldehyde-sulfoxylate (Rongalite)	6
Water	3
Anthraquinone-2-sodium sulfonate	1

The dye, thickener, glycerine, $Na_2S_2O_4$ and NaOH were brought together and uniformly mixed. Heat was applied until reduction was complete. Then the Rongalite, water and anthraquinone-2-sodium sulfonate were added. The product was stirred to uniformity.

The thickener used was prepared as follows: In a composition consisting of 10% wheat starch, 30% British gum and 60% water, there were stirred K_2CO_3 and water until the resultant material was as follows:

	Per cent
Composition	80
Water	5
K_2CO_3	15

The printing paste obtained was printed on a textile material and aged and developed as usual. These prints were from 10 to 25% stronger than a corresponding paste without the silver salt.

Example XII

A printing paste of the following composition was prepared:

	Per cent
4:4'-dichloro-5:5'-dibromo-indigo (C. I. No. 1189) (20% solid dye paste)	20
Thickener	55
Glycerine	5
$Na_2S_2O_4$	5
NaOH (36% strength)	5
Sodium formaldehyde-sulfoxylate	6
Water	3
Anthraquinone-2-sodium sulfonate	1

The method used in preparation was this: The dye paste, thickener, glycerine, $Na_2S_2O_4$ and NaOH were uniformly mixed and heated to complete reduction. The sulfoxylate, water and anthraquinone sulfonate were added. This product was stirred to uniformity. The thickener used was made by mixing 10% wheat starch, 30% British gum and 60% water and to 80% of such composition adding 5% water and 15% potassium carbonate. When the product was printed on a textile material, aged and developed, the prints were found to be 10 to 25% stronger than those made without any anthraquinone-2-sodium sulfonate.

Example XIII

A thickener was prepared containing 10% wheat starch, 30% British gum and the remainder water. This thickener was incorporated in a printing gum having the following composition:

	Per cent
Thickener	56.5
Potassium carbonate	10
Sodium hydroxide	1
Preserver's syrup	20
Water	7.5
Glycerine	5

This printing gum was mixed with a 12.5% color paste of 4:4'-dimethyl-6:6'-dichloro-thioindigo and sodium salt of anthraquinone-beta-sulfonic acid to produce a printing paste. This printing paste, being composed of:

	Per cent
Printing gum	79
Dye paste	20
Anthraquinone-2-sodium sulfonate	1

was printed on cotton textile material in the well known way. Comparison with prints obtained under similar conditions from a similar printing paste which omitted the silver salt showed about 20% greater strength in the print from the printing paste of this invention.

Example XIV

A thickener was prepared containing 10% wheat starch, 30% British gum and the remainder water. This thickener was incorporated in a printing gum having the following composition:

	Per cent
Thickener	56.5
Potassium carbonate	10
Sodium hydroxide	1
Commercial glucose	15
Glycerine	5
Water	12.5

This printing gum was mixed with a 20% solids dye paste of 5:5'-dibrom-7:7'-dimethyl-thioindigo and anthraquinone-beta-sulfonic acid to produce a printing paste. This printing paste, being composed of:

	Per cent
Printing gum	79
Dye paste	20
Anthraquinone-2-sulfonic acid	1

was printed on cotton textile material in the well known way. The prints obtained under similar conditions from a similar printing paste which omitted the anthraquinone-2-sodium sulfonate were about 15% weaker.

Example XV

The printing paste having the following composition:

	Per cent
4:4'-dimethyl-thioindigo (10% dye)	20
Thickener	55
Glycerine	5
Sodium hydrosulfite	5
Sodium hydroxide (36% strength)	5
Commercial glucose	9
Silver salt	1

was prepared. In the preparation of this composition all of the ingredients except the commercial glucose, water and silver salt were added, uniformly mixed and heated until reduction was complete, whereupon the remaining ingredients listed were added and the product stirred to uniformity. The thickener in this case consisted of:

	Per cent
Water	53
Wheat starch	8
Potassium carbonate	15
British gum	24

This product was printed on textile material which was then aged and developed in the usual way. The prints obtained were from 10 to 25% stronger than those obtained from a similar composition which differed only in the omission of the silver salt.

Example XVI

The printing paste having the following composition:

	Per cent
Dye paste of the thionindigo dye prepared by well known methods from 2-thioglycol naphthalene (14% solids)	20
Thickener	55
Glycerine	5
Sodium hydrosulfite	5
Sodium hydroxide (36% strength)	5
Commercial glucose	9
Anthraquinone-beta-sodium sulfonate	1

was prepared. In the preparation of this composition all of the ingredients except the commercial glucose, water and anthraquinone-beta-sodium sulfonate were added, uniformly mixed and heated until reduction was complete, whereupon the remaining ingredients were added and the product stirred to uniformity. The thickener in this case consisted of:

	Per cent
Water	53
Wheat starch	8
Potassium carbonate	15
British gum	24

This product was printed on textile material which was then aged and developed in the usual way. The prints obtained were from 10 to 25% stronger than those obtained from a similar composition which differed only in the omission of the anthraquinone-2-sodium sulfonate.

Example XVII

The printing paste having the following composition:

	Per cent
Dye paste of the dye resulting from condensing 5:7-dibrom-isatin chloride with 3-hydroxy-4-methyl-6-chloro-thionaphthene (10% solids)	20
Thickener	55
Glycerine	5
Sodium hydrosulfite	5
Sodium hydroxide (36% strength)	5
Commercial glucose	9
Anthraquinone-2-sodium sulfonate	1

was prepared. In the preparation of this composition all of the ingredients except the glucose, water and silver salt were added, uniformly mixed and heated until reduction was complete, whereupon the remaining ingredients were added and the product stirred to uniformity. The thickener in this case consisted of:

	Per cent
Water	53
Wheat starch	8
Potassium carbonate	15
British gum	24

This product was printed on textile material which was then aged and developed in the usual way. The prints obtained were from 10 to 25% stronger than those obtained from a similar composition which differed only in the omission of the silver salt.

Example XVIII

The printing paste having the following composition:

	Per cent
6:6'-diethoxy-thioindigo (C. I. No. 1218) (11.5% solids dye paste)	20
Thickener	55
Sodium hydrosulfite	5
Glycerine	5
Sodium hydroxide (36% strength)	5
Commercial glucose	9
Silver salt	1

was prepared. In the preparation of this composition all of the ingredients except the commercial glucose, water and silver salt were added, uniformly mixed and heated until reduction was complete, whereupon the remaining ingredients were added and the product stirred to uniformity. The thickener in this case consisted of:

	Per cent
Water	53
Wheat starch	8
Potassium carbonate	15
British gum	24

This product was printed on textile material which was then aged and developed in the usual way. The prints obtained were from 10 to 25% stronger than those obtained from a similar composition which differed only in the omission of the silver salt.

Example XIX

The printing paste having the following composition:

	Per cent
4:4'-dichlor-5:5'-dibrom-indigo (20% solids dye paste)	20
Thickener	55
Glycerine	5
Sodium hydrosulfite	5
Sodium hydroxide (36% strength)	5
Commercial glucose	9
Anthraquinone-beta-sodium sulfonate	1

was prepared. In the preparation of this composition all of the ingredients except the glucose, water and anthraquinone-beta-sodium sulfonate were added, uniformly mixed and heated until reduction was complete, whereupon the remaining ingredients were added and the product stirred to uniformity. The thickener in this case consisted of:

	Per cent
Water	53
Wheat starch	8
Potassium carbonate	15
British gum	24

This product was printed on textile material which was then aged and developed in the usual way. The prints obtained were from 10 to 25% stronger than those obtained from a similar composition which differed only in the omission of the anthraquinone-beta-sodium sulfonate.

Example XX

A printing gum was prepared from:

	Per cent
Thickener	57.5
K_2CO_3	16
Sulfoxite C	11
Glycerine	5
Water	10

The thickener contained 10% wheat starch, 30% British gum and 60% water. A printing paste was made from the printing gum by adding 6:6'-diethoxy-thioindigo (C. I. No. 1218) dye paste containing 11.5% solids. To this mixture was added milled silver salt (sodium salt of anthraquinone-2-sulfonic acid). The resulting printing paste had the following composition:

	Per cent
Printing gum	79.9
Dye paste	20
Milled silver salt	0.1

Two other pastes were prepared, similar in all respects except that in one the silver salt was not milled and in the other the silver salt was omitted. Prints were made from the three pastes under similar conditions. The prints made from the two printing pastes containing the silver salt were 10 to 25% stronger than those made from the paste from which silver salt was omitted. But it is also worthy of notice that those prints made from the paste containing the milled silver salt were noticeably stronger than those printed with the paste containing silver salt which had not been milled.

Example XXI

A printing gum was made from:

	Per cent
Thickener	67.5
K_2CO_3	8
Sulfoxite C	4
Glycerine	5
Water	15.5

The thickener contained 10% wheat starch, 30% British gum and 60% water. This printing gum was used to make a printing paste by mixing uniformly with a dye paste containing 12.5% of 4:4'-dimethyl-6:6'-dichloro-thioindigo and a small amount of milled silver salt. The following proportions were present in the finished composition:

	Per cent
Printing gum	79.9
Dye paste	20
Milled silver salt	0.1

Prints made from this printing paste were 10 to 25% stronger than those made from a similar paste in which silver salt was absent, and noticeably stronger than those made from a similar paste which contained silver salt which had not undergone the milling process.

Example XXII

A printing gum was made from:

	Per cent
Thickener	56.5
K_2CO_3	10
NaOH	1
Preserver's syrup (mainly glucose and fructose)	20
Glycerine	5
H_2O	7.5

The thickener contained 10% wheat starch, 30% British gum and 60% water. A printing paste was made from this gum by mixing uniformly with a 16% solids dye paste of bis-beta-naphthio-naphthene indigo, and the milled sodium salt of anthraquinone-beta-sulfonic acid in the following proportions:

	Per cent
Printing gum	79
Dye paste	20
Milled anthraquinone-beta-sodium sulfonate	1

Prints were made from this paste. These prints were compared with prints made from a similar paste which lacked the presence of the milled assistant. The prints from the paste with the milled silver salt assistant were 10 to 25% stronger than the others. They were also noticeably stronger than prints made from a similar paste in which the silver salt assistant used was not milled.

Example XXIII

A printing gum was prepared containing:

	Per cent
Thickener	56.5
Potassium carbonate	10
Sodium hydroxide	1
Commercial glucose	15
Glycerine	5
Water	12.5

The composition of the thickener herein utilized was 10% wheat starch, 30% British gum and 60% water. This printing gum was made into a printing paste with a 5:5'-dichloro-6:6'-dimethyl-thioindigo dye paste containing anthraquinone-2-sulfonic acid. The composition of the printing paste was:

	Per cent
Printing gum	79
Color paste (12.5% dye solids)	20
Anthraquinone-2-sulfonic acid	1

This paste gave prints several percent stronger than a similar paste not containing anthraquinone-2-sulfonic acid when printed, dried, aged and developed in the usual way.

Example XXIV

A thickener whose composition was 10% wheat starch, 30% British gum and 60% water, was incorporated into a printing gum whose composition was:

	Per cent
Thickener	57.5
Sodium formaldehyde-sulfoxylate	11
Glycerine	5
Water	10.5

This printing gum was made into a printing paste by mixing the same with appropriate quantities of a 20% dye paste of 5:5'-dichloro-7:7'-dibrom-

indigo and a water suspension of anthraquinone-2-sodium sulfonate which had been milled in water. The composition of the resulting printing paste was as follows:

	Per cent
Printing gum	79.9
Color paste	20
Anthraquinone-2-sodium sulfonate	0.1

It is to be understood that the invention is not limited to the specific dyes listed in the above examples. Other indigoid dyes are well known to those skilled in the art and are disclosed in such publications as:

1. Technologie Der Textilefasern Künstliche Organische Fabstoffe H. E. Fierz-David, 1926.

2. Color Index (1924), Supplement (1928), Society of Dyers and Colourists.

3. Fortschritte der Teerfarben—Fabrikation P. Friedlaender.

4. Farbstofftabellen Gustav Schultz (1931).

5. Enzyklopädie der Küpenfabstoffe Truttwin (1920).

Specific mention may be made of such other compounds as 2:3:2':3'-di-anthraquinone indigo, bromo-2-beta-naphthindol-2-indol indigo, indigo, thioindigo 2 - (5:7-dibrom-indol)-2'-anthracene indigo, 2-(5:7-dibrom-indol)-2'-naphthalene indigo 4:4'-diethyl-thioindigo, 5:5'-dimethyl-bis-thionaphthene indigo, bis-alphanaphthindol indigo, 4:5:6:7:4':5':6':7'-octo-chloroindigo, dimethyl-indirubin, dibrom-indirubin, dyes prepared by the condensation of reactive 2-isatin derivatives with naphthocarbazole bodies (e. g., ortho-tolu-5 -hydroxy-alpha-naphthocarbazole), indolacenaphthene indigos, thionaphthene-indol-indigos, and the like. The specific dyes of U. S. Patents Nos. 1,558,252 and 1,792,648 also merit particular mention.

The amount of the assistant is ordinarily varied directly with the amount of solid dye and the paste used, based on a 12.5% solids dye paste. In printing, the preferred amounts are about 1 to about 5%. Greater or smaller amounts than this may be used when desired. For example, the use of 0.5 to 10% of the assistant in printing gives good results. Less than 0.5% may be used if desired, although the result is not as noticeable as that produced by using an amount falling within the preferred range. Generally, more than 10% may be used without detriment to the printing process.

It will be recognized that the type of reducing agent is to be chosen according to the method to be used in applying the dye to the fiber. Sodium formaldehyde-sulfoxylate is a material well adapted for printing vat dyes, inasmuch as it is not oxidized at ordinary temperatures and exercises its reducing action at elevated temperatures.

This invention is of great technical and commercial importance since it has been found that the presence of assistants of the type described in indigoid printing pastes, and especially in the printing of thioindigoid dyes, makes possible the production of prints of superior strength and brightness to those obtained from a similar printing paste from which the assistant has been omitted. The prints are also much stronger and brighter than printing pastes in which the assistant is a substance such as anthraquinone.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments thereof except as defined in the following claims.

We claim:

1. A dye composition comprising a vat printing and a substance selected from the group consisting of anthraquinone-2-sulfonic acid, the ammonium salt of anthraquinone-2-sulfonic acid and alkali metal salts of anthraquinone-2-sulfonic acid.

2. A dye paste comprising an indigoid printing and a substance selected from the group consisting of anthraquinone-2-sulfonic acid, the ammonium salt of anthraquinone-2-sulfonic acid and alkali metal salts of anthraquinone-2-sulfonic acid.

3. A dye paste comprising a thioindigoid printing and a substance selected from the group consisting of anthraquinone-2-sulfonic acid, the ammonium salt of anthraquinone-2-sulfonic acid and alkali metal salts of anthraquinone-2-sulfonic acid.

4. A dye paste comprising a thioindigoid printing and the sodium salt of anthraquinone-2-sulfonic acid.

5. A printing paste comprising an indigoid dye and an alkali metal salt of anthraquinone-2-sulfonic acid.

6. A printing paste comprising a thioindigoid dye and an alkali metal salt of anthraquinone-2-sulfonic acid.

7. A printing paste comprising 4:4'-dimethyl-6:6'-dichloro-thioindigo and an alkali metal salt of anthraquinone-2-sulfonic acid.

8. A printing paste comprising 6:6'-diethoxy-thioindigo and an alkali metal salt of anthraquinone-2-sulfonic acid.

9. An indigoid printing gum comprising an alkali metal salt of anthraquinone-2-sulfonic acid.

10. A thionindigoid printing gum comprising an alkali metal salt of anthraquinone-2-sulfonic acid.

11. The process of printing indigoid dyes which comprises applying to the fiber a printing paste comprising the indigoid dye, an alkali metal salt of anthraquinone-2-sulfonic acid, printing gum, alkali and a reducing agent suitable for printing, and thereafter drying, aging and developing the print.

12. In the process of printing indigoid dyes on textiles, the step which comprises incorporating a substance from the group consisting of anthraquinone-2-sulfonic acid and an alkali metal salt thereof into the printing paste.

13. In the process of printing thionindigoid dyes on textiles, the step which comprises incorporating a substance from the group consisting of anthraquinone-2-sulfonic acid and an alkali metal salt thereof into the printing paste.

14. In the printing of textile material, the step of printing on the textile material with a printing paste comprising an indigoid dye and an alkali metal salt of anthraquinone-2-sulfonic acid.

15. In the printing of textile material, the step of printing on the textile material with a printing paste comprising an indigoid dye and milled sodium anthraquinone-2-sulfonate.

16. The process of printing thioindigoid dyes which comprises applying to the fiber a printing paste comprising the thioindigoid dye, an alkali metal salt of anthraquinone-2-sulfonic acid, printing gum, alkali and a reducing agent suitable for printing, and thereafter drying, aging and developing the print.

17. The process of printing thioindigoid dyes which comprises applying to the fiber a printing

paste comprising a thioindigoid dye, an alkali metal salt of anthraquinone-2-sulfonic acid, printing gum, potash and sodium formaldehyde-sulfoxylate, and thereafter drying, aging and developing the print.

18. The method of printing with vat dyes of the indigoid type which comprises applying to the goods a composition containing the indigoid dye, a reducing agent suitable for printing, an alkali metal salt of anthraquinone-2-sulfonic acid and an alkali metal carbonate, aging the same in steam, and re-oxidizing in a developer.

19. A vat dye printing paste comprising a water-soluble polyhydric alcohol and a substance from the group consisting of anthraquinone-2-sulfonic acid, the ammonium salt of anthraquinone-2-sulfonic acid and alkali metal salts of anthraquinone-2-sulfonic acid.

20. A printing paste comprising a thioindigoid dye, glycerin and a substance from the group consisting of anthraquinone-2-sulfonic acid and alkali metal salts thereof.

21. The process of preparing printed textile materials which comprises printing on a textile material with a printing paste containing a water-insoluble thioindigoid color, a printing gum and from about 0.1 to about 1.0% of an alkali metal salt of anthraquinone-2-sulfonic acid.

22. The process of preparing printed materials which comprises printing on a textile material with 4:4'-dimethyl-6:6'-dichloro thioindigo in the presence of an alkali metal salt of anthraquinone-2-sulfonic acid.

23. The process of preparing printed materials which comprises printing on a textile material with 6:6'-diethoxy thioindigo in the presence of an alkali metal salt of anthraquinone-2-sulfonic acid.

HERBERT A. LUBS.
JOHN ELTON COLE.

Certificate of Correction

Patent No. 2,024,975 December 17, 1935

HERBERT A. LUBS ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Page 4, second column, line 39, for "Sulfoxite C___5" read *Sulfoxite C___6*; page 5, first column, line 2, for "Na_2S_2O" read $Na_2S_2O_4$; page 8, second column, lines 4, 10, 16, and 22, claims 1, 2, 3, and 4, respectively, for "dye" read *printing*; and lines 4, 10–11, 16–17, and 22–23, claims 1, 2, 3, and 4, respectively, for "printing" read *dye*; same page and column, line 39, claim 10, for "thionindigoid" read *thioindigoid*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 11th day of February, A. D. 1936.

[SEAL]

LESLIE FRAZER,
Acting Commissioner of Patents.