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PRINTING

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This invention relates to the art of printing vat dyes on textiles and more particularly to vat dye printing pastes. Specifically, the invention contemplates vat dye printing pastes containing anthraquinone-sulfonic acids and their equivalents.

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).

While vat dyes lack desirable affinity for textile fiber, dyeing, that is coloring of the entire fabric (as distinguished from printing in which only a portion of the fabric is colored), with such compounds is relatively simple. The process of dyeing comprises suspending the insoluble chemical compound (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 imprinted 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.

Because of the aforementioned and other difficulties it has previously been proposed to add various chemical substances for convenience called "assistants" to the printing paste. One such compound is tri-ethanolamine (U. S. Patent 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 368,910).

It is an object of this invention to provide new and improved assistants for the printing of indigoid dyes. A further object is the production of new and improved indigoid vat dye printing pastes. A more specific object is the production of new and improved thioindigoid vat dye printing pastes. A still further object is the provision of a new and improved printing process. Other objects will appear hereinafter.

These objects are accomplished, according to the present invention, by carrying out the printing of vat dyes of the indigoid type in the presence of an alkali metal anthraquinone-sulfonate. The alkali metal anthraquinone-sulfonate may be introduced into the printing paste as such, either separately or as part of the printing gum, or in another suitable manner, or it may be formed in the printing gum or the printing paste, for example, by reaction of the free sulfonic acid with some of the alkaline reacting agents in the printing gum or printing paste. It may also be added to the dye paste, from which the printing paste is prepared by the addition of the other customary ingredients, such as for example, the reducing agent, alkali and thickening agent. It may also be incorporated into the paste in conjunction with other printing assistants of other types with satisfactory results.

The invention will be further illustrated 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:

	Per cent
Thickener	57.5
Potassium carbonate	16
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:

	Per cent
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 10–25% stronger than those obtained from a similar composition which differed only in the omission of the anthraquinone-2-sodium sulfonate.

In the foregoing procedure, the anthraquinone-2-sodium sulfonate may be substituted by the alkali metal salt of other anthraquinone-sulfonic acids such as, for example, 2:6-anthraquinone-disulfonic acid, 2:5-anthraquinone-disulfonic acid, 2:7-anthraquinone-disulfonic acid, 1:8-anthraquinone-disulfonic acid, 1:5-anthraquinone-disulfonic acid, 1:3:6-anthraquinone-trisulfonic acid, 1:3:7-anthraquinone-trisulfonic acid, 1-hydroxy-anthraquinone-5-sulfonic acid, 1-nitro-anthraquinone-6-sulfonic acid and 1-chloro-anthraquinone-5-sulfonic acid. The free acids may be used, but it will be recognized that a suitable amount of alkali should be used so that an adequate amount is present for printing after neutralization of the free sulfonic acid.

Example II

A printing gum was prepared comprising:

	Per cent
Thickener	57.5
Potassium carbonate	16
Sulfoxite C	11
Glycerine	5
Water	10.5

The thickener consisted of:

	Per cent
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. 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:

	Per cent
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 10–25% stronger than those obtained from the other printing paste.

Instead of silver salt, other anthraquinone-sulfonates may be used such as, for example, potassium and/or sodium salts of 2:6-anthraquinone-disulfonic acid, 2:5-anthraquinone-disulfonic acid, 2:7-anthraquinone-disulfonic acid, 1:8-anthraquinone-disulfonic acid, 1:5-anthraquinone-disulfonic acid, 1:3:6-anthraquinone-trisulfonic acid, 1:3:7-anthraquinone-trisulfonic acid, 1-hydroxy-anthraquinone-5-sulfonic acid, 1-nitro-anthraquinone-5-sulfonic acid and 1-chloro-anthraquinone-5-sulfonic acid.

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:

	Per cent
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:

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

As illustrations of other anthraquinone-sulfonates which may be used to replace all or part of the anthraquinone-2-sodium sulfonate in the above example, may be mentioned the alkali metal salts of 2:6-anthraquinone-disulfonic acid, 2:5-anthraquinone-disulfonic acid, 2:7-anthraquinone-disulfonic acid, 1:8-anthraquinone-disulfonic acid, 1:5-anthraquinone-disulfonic acid 1:3:6-anthraquinone-trisulfonic acid, 1:3:7-anthraquinone-trisulfonic acid, 1-hydroxy-anthraquinone-5-sulfonic acid, 1-nitro-anthraquinone-6-sulfonic acid and 1-chloro-anthraquinone-5-sulfonic acid.

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:

	Per cent
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. 1184, bromination in nitrobenzene) and anthraquinone-2-sodium-sulfonate. After producing a uniform mixture the printing paste, which was composed of:

	Per cent
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.

Further illustrations of anthraquinone-sulfonates which may be used to replace all or part of the anthraquinone-2-sodium sulfonate in the above example are the potassium and/or sodium salts of 2:6-anthraquinone-disulfonic acid, 2:5-anthraquinone-disulfonic acid, 2:7-anthraquinone-disulfonic acid, 1:8-anthraquinone-disulfonic acid, 1:5-anthraquinone-disulfonic acid, 1:3:6-anthraquinone-trisulfonic acid, 1:3:7-anthraquinone-trisulfonic acid, 1-hydroxy-anthraquinone-5-sulfonic acid, 1-nitro-anthraquinone-6-sulfonic acid and 1-chloro-anthraquinone-5-sulfonic acid.

Example V

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

	Per cent
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. 1184), anthraquinone-2-sodium sulfonate. The percentage composition of the printing paste was as follows:

	Per cent
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 10–25% 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:

	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 16% (solids) dye paste of bis-beta-naphthio-naphthene indigo and the sodium salt of anthraquinone-beta-sul-

fonic 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 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.

Variations may be made in the type of printing assistant as described, for instance, in Example IV.

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:

	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 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:

	Per cent
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 conditions from a similar printing paste which omitted the anthraquinone-2-sodium sulfonate showed that the (silver salt) paste gave prints about 15% stronger.

Other anthraquinone-sulfonates may be employed in carrying out the above procedure instead of the anthraquinone-2-sodium sulfonate. The potassium and/or sodium salts of the following anthraquinone-sulfonic acids merit special mention: 2:6-anthraquinone-disulfonic acid, 2:5-anthraquinone-disulfonic acid, 2:7-anthraquinone-disulfonic acid, 1:8-anthraquinone-disulfonic acid, 1:5-anthraquinone-disulfonic acid, 1:3:6-anthraquinone-trisulfonic acid, 1:3:7-anthraquinone-trisulfonic acid, 1-hydroxy-anthraquinone-5-sulfonic acid, 1-nitro-anthraquinone-6-sulfonic acid and 1-chloro-anthraquinone-5-sulfonic acid.

Example VIII

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

	Per cent
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-di-bromisatin chloride with 3-hydroxy-4-methyl-6-chloro-thio-naphthene. The percentage composition of the printing paste was as follows:

	Per cent
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 10–25% 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. 1209)	20
Thickener	55
Glycerine	5
Sodium hydrosulfite	5
Sodium hydroxide (36% strength)	5
Sulfoxite C	6
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:

	Per cent
Of a thickener consisting of:	80
10% wheat starch 30% British gum 60% water	
Water	5
Potassium carbonate	15

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.

In the foregoing example the anthraquinone-2-sodium-sulfonate may be wholly or partly replaced by other alkali metal anthraquinone-sulfonates, such as for example, the alkali metal anthraquinone-sulfonates of 2:6-anthraquinone-disulfonic acid, 2:5-anthraquinone-disulfonic acid, 2:7-anthraquinone-disulfonic acid, 1:8-anthraquinone-disulfonic acid, 1:5-anthraquinone-disulfonic acid, 1:3:6-anthraquinone-trisulfonic acid, 1:3:7-anthraquinone-trisulfonic acid, 1-hydroxy-anthraquinone-5-sulfonic acid, 1-nitro-anthraquinone-6-sulfonic acid and 1-chloro-anthraquinone-5-sulfonic acid.

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, $Na_2S_2O_4$ 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:

	Per cent
Of a composition comprising:	80
10% wheat starch	
30% British gum	
60% water	
Water	5
K_2CO_3	15

The product was printed on textile material. This was aged and developed as usual. The prints were 10–25% 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: Into a composition consisting of 10% wheat starch, 30% British gum and 60% water, there was stirred K_2CO_3 and H_2O 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 10–25% 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′ - di - bromo - indigo (C. I. 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 10–25% 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.

Variations may be made in the type of anthraquinone-sulfonate employed as the printing assistant. Thus, all or a part of the anthraquinone-2-sodium-sulfonate may be replaced by the alkali metal salts of any of the following anthraquinone-sulfonic acids or mixtures thereof: 2:6-anthraquinone-disulfonic acid, 2:5-anthraquinone-disulfonic acid, 2:7 anthraquinone-disulfonic acid, 1:8-anthraquinone-disulfonic acid, 1:5-anthraquinone-disulfonic acid, 1:3:6-anthraquinone-trisulfonic acid, 1:3:7-anthraquinone-trisulfonic acid, 1-hydroxy-anthraquinone-5-sulfonic acid, 1-nitro-anthraquinone-6-sulfonic acid and 1-chloro-anthraquinone-5-sulfonic acid.

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′-di-brom-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 similiar 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 10–25% 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
Of a dye paste of the thioindigo 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 10–25% 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
Of a dye paste of the dye resulting from condensing 5:7-di-brom-isatin chloride with 3-hydroxy-4 - methyl-6 - chloro-thio-naphthalene (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 10–25% 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. 1218) (11.5% solids dye paste)	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 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 10–25% stronger than those obtained from a similar composition which differed only in the omission of the silver salt.

The variations as to the type of printing assistant may be similar to those given in connection with Example XIII.

Example XIX

The printing paste having the following composition:

	Per cent
4:4'-dichlor-5:5-di-brom-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 10–25% 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. 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 10–25% 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.

As further illustrations of alkali metal anthraquinone-sulfonates which may be used to replace all or a part of the sodium salt of anthraquinone-2-sulfonic acid, may be mentioned the potassium and sodium salts of the following anthraquinone-sulfonic acids and mixtures thereof: 2:6-anthraquinone-disulfonic acid, 2:5-anthraquinone-disulfonic acid, 2:7-anthraquinone-disulfonic acid, 1:8-anthraquinone-disulfonic acid, 1:5-anthraquinone-disulfonic acid, 1:3:6-anthraquinone-trisulfonic acid, 1:3:7-anthraquinone-trisulfonic acid, 1-hydroxy-anthraquinone-5-sulfonic acid, 1-nitro-anthraquinone-6-sulfonic acid and 1-chloro-anthraquinone-5-sulfonic acid.

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 10–25% 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 10-25% 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.

The type of anthraquinone-sulfonate may be varied, as for example, according to the variations given in Example XX.

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'-di-bromo-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-di-brom-indol)-2'- anthracene indigo, 2-(5:7-di-brom-indol)-2'-naphthalene indigo, 4:4'-diethyl-thioindigo, 5:5'-dimethyl - bis - thionaphthene indigo, bis-alpha-naphindol indigo, 4:5:6:7:4':5':6':7'-octo-chloro-indigo, dimethyl-indirubin, dibrom-indirubin, dyes prepared by the condensation of reactive 2-isatin derivatives with naphtho-carbazole bodies (e. g. ortho - tolu - 5 - hydroxy - alpha - naphthocarbazole), indol-acenaphthene indigoes, thionaphthene-indol-indigoes, and the like. The specific dyes of U. S. Patents 1,558,252 and 1,792,648 also merit particular mention.

Where a mixture of alkali metal anthraquinone-sulfonates is used, it may be such as is obtainable from a residue resulting from the sulfonation of anthraquinone after the removal of anthraquinone-2-sulfonic acid. The ammonium salts of the various anthraquinone-sulfonic acids are usually considered to be equivalent to the alkali metal salts, insofar as chemical action is concerned, although in some cases the results may not be as satisfactory, particularly where the decomposition of the salt with the liberation of ammonia occurs.

The amount of the assistant is ordinarily varied directly with the amount of solid dyestuff and the paste used based on a 12.5% solids dye paste. The preferred amounts of the printing assistant are about 1 to about 5%. Greater or smaller amounts than this may be used when desired. For example, the use of .5 to 10% of the printing assistant gives good results. Less than .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 process.

As previously indicated, all types of reducing agents are not suitable for printing. This is well recognized by those skilled in the art, and it will be understood, therefore, that the term "reducing agent" as herein used in conjunction with printing pastes, is an agent which is suitable for vat dye printing. 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 importance technically and commercially, since it has been found that the presence of assistants of the types described in indigoid printing pastes, and particularly 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.

So much of this application as relates to printing with unsubstituted anthraquinone sulfonic acid and sulfonates is claimed in our co-pending application Serial No. 504,274 filed December 23, 1930, of which the present application is a continuation-in-part. The specific embodiment of the invention relating to printing with anthraquinone-2-sulfonic acid and salts thereof is claimed in our U. S. application Serial No. 703,156 filed December 19, 1933.

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 vat dye printing paste comprising an alkali metal anthraquinone-sulfonate.

2. An indigoid vat dye printing paste comprising an alkali metal anthraquinone-sulfonate.

3. A printing paste comprising a thioindigoid

dye and an alkali metal anthraquinone sulfonate.

4. A printing paste comprising a thioindigoid dye and an anthraquinone-sodium-sulfonate.

5. A printing paste comprising 4:4'-dimethyl-6:6'-dichloro-thioindigo and an alkali metal anthraquinone-sulfonate.

6. A printing paste comprising 6:6'-diethoxy-thioindigo and an alkali metal anthraquinone-sulfonate.

7. An indigoid printing gum comprising an alkali metal anthraquinone-sulfonate.

8. A thioindigoid printing gum comprising an alkali metal anthraquinone-sulfonate.

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

10. In the process of printing indigoid vat dyes on textiles, the step which comprises incorporating a substance selected from the class consisting of anthraquinone-sulfonic acids and an alkali metal salts thereof into the printing paste.

11. In the process of printing thioindigoid vat dyes on textiles, the step which comprises incorporating a substance selected from the class consisting of anthraquinone-sulfonic acids and an alkali metal salts thereof into the printing paste.

12. In the printing of textile material, the step of printing on the textile material with a printing paste comprising an indigoid vat dye and an alkali metal anthraquinone-sulfonate.

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

14. The process of printing thioindigoid dyes which comprises applying to the fiber a printing paste comprising a thioindigoid dye, an alkali metal salt of an anthraquinone-sulfonic acid, printing gum, potash and sodium formaldehyde-sulfoxylate and thereafter drying, aging and developing the print.

15. 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 an anthraquinone sulfonic acid and an alkali metal carbonate, ageing the same in steam and reoxidizing in a developer.

16. A vat dye printing paste comprising a water-soluble polyhydric alcohol and an alkali metal anthraquinone sulfonate.

17. A printing paste comprising a thioindigoid dye, glycerine, and an alkali metal anthraquinone sulfonate.

18. A thioindigoid printing paste comprising a water-insoluble thioindigoid color, a printing gum and from about 0.1 to about 1.0% of an alkali metal anthraquinone sulfonate.

19. A printing paste comprising a water-insoluble thioindigoid color and an alkali metal hydroxy anthraquinone sulfonate.

20. A printing paste comprising a water-insoluble thioindigoid color and an alkali metal chloro-anthraquinone sulfonate.

21. A printing paste comprising a water-insoluble thioindigoid color and an alkali metal nitro-anthraquinone sulfonate.

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 anthraquinone sulfonate.

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 anthraquinone sulfonate.

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JOHN ELTON COLE.

CERTIFICATE OF CORRECTION.

Patent No. 2,024,974. December 17, 1935.

HERBERT A. LUBS, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 1, strike out the comma after "reducing" and insert the same after "agent" in same line; page 6, second column, line 9, for the syllable "thalene" read thene; 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.

Leslie Frazer

(Seal) Acting Commissioner of Patents.