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METHOD OF PRINTING WITH SULFURIC ACID ESTERS OF LEUCO VAT DYES OF THE ANTHRAQUINONE SERIES

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The present invention relates to the printing of textile fibers with sulfuric acid esters of leuco vat dyes, and particularly to such a method involving steam development to yield prints of high wash fastness and high intensity.

It is common practice at the present time to employ vat dyes in the form of their leuco ester salts rather than in the form of the simple leuco compounds. This is attributable to the fact that the leuco ester salts are much more stable than the leuco compounds per se, which facilitates the application of the reduced vat dyes to the fiber.

It is customary in forming prints with the sulfuric acid ester salts of the leuco compounds to print the fabric with a paste containing the ester salts and to develop the dyestuff on the fabrics by steam development. The pastes which are generally employed for this purpose contain a substance which in the steam development liberates an acid and, along with an oxidizing agent and an oxidizing catalyst present in the paste, provides an acid oxidizing medium which causes regeneration of the insoluble parent vat dye. The substances utilized for the purpose of generating acid and which will hereinafter be referred to as "acid splitters" are ammonium salts such as ammonium sulfate, ammonium lactate, ammonium sulfocyanide, and the like, or an ester such as diethyl tartrate (see USP 1,747,107).

The oxidizing agent generally employed is a chlorate of an alkali metal such as sodium chlorate, whereas the oxidizing catalyst almost universally used is ammonium vanadate.

It is known that prints on regenerated cellulose obtained from some of the sulfuric acid esters of leuco vat dyes have very poor wash fastness and low dye intensities. For instance, prints on regenerated cellulose fabrics, while utilizing the aforesaid conventional printing paste containing the leuco sulfuric acid ester of jade green and steam-developing the printed fabric, are practically completely washed off the fiber in soaping. It has been ascertained that these difficulties are in the main caused by the too rapid development or regeneration of the insoluble parent vat dye during steaming. This rapid development prevents full penetration of the soluble dye in the fiber. While the difficulties noticed appear when printing the usual fabrics with printing pastes containing the sulfuric acid esters of leuco anthraquinone dyes, it is most noticeable in the case where the fabrics printed are rayon.

I have ascertained that by completely inhibiting the development reaction by steaming for a period of 1 to 3 minutes and by then inducing an autocatalytic or chain reaction generating an acid-oxidizing state, it is possible to obtain prints even on rayon which have excellent resistance

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to washing and of high density. The inhibition of the development reaction has been effected by replacing the usual acid splitters by an organic sulfur compound incapable of splitting a salt or ester under the conditions which prevail during development.

The particular reactions which occur and their sequence when utilizing such sulfur compounds in lieu of the acid splitters have not been determined. I believe, however, that the oxidizing agent present progressively oxidizes said sulfur compound to sodium bisulfate or in some cases sulfuric acid. At this point, which usually occurs from 1 to 3 minutes after the steam development has been initiated, the desired acid-oxidizing state is created, resulting in a very rapid oxidation within the standard 5 minute steaming period. During the time when the oxidizing agent is effecting its progressive oxidation, the sulfuric acid ester has ample opportunity to completely impregnate the fibers, as a consequence of which the prints obtained are in high yield and tenaciously adhere to the fibers.

It is accordingly an object of the present invention to print textile fibers and fabrics with sulfuric acid esters of leuco vat dyes by the steam development method while obtaining prints of high wash fastness and high density.

It is a further object of the present invention to provide printing pastes of sulfuric acid esters of leuco anthraquinone vat dyes which are to be used to develop prints by steam development, said printing pastes containing an organic sulfur compound incapable of splitting salts or esters in lieu of the usual acid splitters.

It is a further object of the present invention to print textiles by the steam development method with printing pastes containing sulfuric acid esters of leuco anthraquinone vat dyes while inhibiting regeneration of the parent vat dye for a predetermined period.

Other and further important objects of the invention will become apparent as the description proceeds.

As has been stated, the printing pastes which we employ for attaining the aforesaid objects differ from those conventionally used in that the acid splitters, i. e., the salts or esters used to generate an acid medium during steam development are replaced by an organic sulfur compound which is in and of itself incapable of splitting salts or esters. Such organic sulfur compounds are aldehyde sulfites and sulfoxylates and the alkali metal salts thereof. Examples of such compounds are sodium formaldehyde bisulfite, acetaldehyde bisulfite, butyraldehyde bisulfite, glyoxal bisulfite, benzaldehyde bisulfite, and the corresponding sulfoxylates, such as sodium formaldehyde sulfoxylate, and the like. These compounds are well known and hence a description of their

method of preparation is deemed to be unnecessary.

The printing pastes contain, in addition to the aforesaid organic sulfur compounds, the desired sulfuric acid ester of the leuco anthraquinone dye, a stabilizer such as urea and/or an alkali such as sodium carbonate, ammonia, and the like, a thickener, such as starch tragacanth, an oxidizing agent preferably an alkali metal chlorate or bromate, such as sodium chlorate, sodium bromate, or the like, and an oxidizing catalyst, preferably ammonium vanadate. In addition a solvent is usually present, such as thiodiglycol. The remaining ingredient is water to give the desired consistency to the paste.

The components of the composition of the printing pastes other than the organic sulfur compound and the oxidizing agent are employed in the proportions conventional in the art. The quantity of the organic sulfur compound will vary with the particular oxidizing agent and sulfuric acid ester of the leuco vat dye employed, but in general will range from about .03 to about 2 parts for each 100 parts of the printing paste. The amount of oxidizing agent will vary with the organic sulfur compound employed but in general will range from 1 part to about 15 parts per part of organic sulfur compound.

Excellent results are obtained when using a sulfuric acid ester of any leuco anthraquinone vat dye. Examples of vat dyes, the leuco esters of which are contemplated herein, are Jade-Green or bz-2-bz-2'-dimethoxy dibenzanthrone, the vat dyes disclosed in USP 1,809,224, the indanthrene vat dyes disclosed in USP 943,717, 3.4.8.9-dibenzopyrenequinone, the indanthrene disclosed in USP 995,936, dibromated pyranthrone, dibrom-dimethoxy-dibenzanthrone, dichlor-isoviolanthrene and the like. The most noticeable improvement is obtained, however, where the esters of vat dyes of the benzanthrone series.

The paste is applied to the fabric by printing according to conventional practice, and then is steam-developed for 5 minutes, also customary procedure.

The fabrics which may be printed according to our method are the usual hydrophilic textile fabrics such as wool, cotton and the like, but the process has its greatest advantage in the printing of rayon from regenerated cellulose.

The invention is illustrated by the following examples wherein the parts are by weight. It is to be understood, however, that the invention is not restricted to the specific examples.

Example 1

A printing paste is prepared containing the following components:

4 parts of the sulfuric acid ester of leuco Jade Green
4 parts urea 1:1
4 parts thiodiglycol
15 parts warm water
55 parts starch tragacanth paste
3 parts sodium carbonate 1:10
6 parts sodium bromate 1:3
3 parts Rongalite C 1:3
2 parts ammonium vanadate 1:100

Rayon fabric is printed with the composition, after which the fabric is steam-developed in a Mather-Platt for 5 minutes. The prints are then soaped, washed and dried. The prints are far deeper in shade than with standard printing pastes made while employing ammonium salts or diethyl tartrate as an acid splitter.

Example 2

The printing paste of Example 1 is printed on cotton and the cotton processed as in Example 1. The prints obtained have a much greater density and a better wash fastness than those obtained with the conventional printing pastes.

Example 3

The procedure is the same as in Example 1 excepting that the sulfuric acid ester employed is that of dibrom Jade Green. Both cotton and regenerated cellulose when printed with such composition, steamed for 5 minutes, soaped, and rinsed, yield prints much deeper in shade and faster to washing than prints made while employing acid splitters in the composition.

Example 4

A printing paste is made containing the following components:

4 parts of the sulfuric acid ester of leuco Jade Green
4 parts thiodiglycol
14 parts warm water
60 parts starch tragacanth paste
3 parts glyoxal bisulfite 1:100
2 parts ammonia
10 parts sodium chlorate 1:3
3 parts ammonium vanadate 1:100

Rayon printed with this formula develops in 5 minutes to a deep washfast shade.

Similar results are obtained when replacing the above leuco sulfuric acid esters by the sulfuric acid ester of leuco 3.4.8.9-dibenzopyrenequinone.

Example 5

Example 1 is repeated, excepting that the Rongalite C is replaced by an equivalent quantity of sodium acetaldehyde bisulfite.

Various modifications of the invention will occur to persons skilled in the art, and I therefore do not intend to be limited in the patent granted except as necessitated by the prior art and the appended claims.

I claim:

1. A printing paste free from acid splitting agents and capable of yielding when applied to a fiber and steam-developed for 5 minutes prints fast to washing and of high intensity, containing as its essential components a leuco sulfuric acid ester of an anthraquinone vat dye, a thickener, an oxidizing agent, an oxidizing catalyst and an organic sulfur compound selected from the class consisting of aldehyde bisulfites, aldehyde sulfoxylates, and the alkali metal salts thereof.

2. A printing paste as defined in claim 1, wherein the sulfuric acid ester is a sulfuric acid ester of a leuco vat dye of the benzanthrone series.

3. A printing paste free from acid splitting agents and capable of yielding when applied to a fiber and steam-developed for 5 minutes, prints fast to washing and of high intensity, containing as its essential components a thickener, a sulfuric acid ester of a leuco vat dye of the benzanthrone series, an alkali metal bromate, ammonium vanadate, and an aldehyde sulfoxylate, the development of said composition by steaming being inhibited for a predetermined period of time.

4. The printing paste as defined in claim 3 wherein the aldehyde sulfoxylate is sodium formaldehyde sulfoxylate.

5. The process of producing prints on textile fabrics by the steam-development method, said prints being washfast and of high intensity which comprises printing a hydrophilic textile fabric with a printing paste free from acid splitting agents and containing as its essential components a sulfuric acid ester of a leuco vat dye of the anthraquinone series, a thickener, an oxidizing agent, an oxidation catalyst, and an organic sulfur compound incapable of splitting a salt under the steam development conditions and selected from the class consisting of aldehyde bisulfites and aldehyde sulfoxylates, and steam-developing the so printed material for five minutes.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,182,964	Dreyfus	Dec. 12, 1939
2,389,245	Wiazmitinow	Nov. 20, 1945