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3,265,459

DYEING TEXTILE MATERIAL WITH VAT
AND SULFUR DYES

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This invention relates to a process for dyeing textile material with vat dyes and sulfur dyes comprising using as the reducing agent a mixture of sodium dithionite with a sulfinic acid derivative selected from the class consisting of a compound of the general formula:



where x represents a whole number from 0 to 2, y represents a whole number from 1 to 3, $x+y$ being equal to 3, A represents a member selected from the group consisting of hydrogen, low molecular weight alkyl and low molecular weight alkyl substituted by a radical of the general Formula III below, and D represents the radical of a salt of an alkylsulfinic acid with 1 to 4 carbon atoms of the general formula



where each of the radicals R stands for a member selected from the group consisting of hydrogen and alkyl and Z stands for a member selected from the group consisting of an ammonium cation and an alkali metal ion, said substituent of the low molecular weight alkyl designated by A above having the general formula



where H is hydrogen, D has the same meaning as set forth above, p and q each represents a whole number from 0 to 2, $p+q$ being equal to 2, and an alkali metal salt or an ammonium salt of a hydroxyalkylsulfinic acid having 2 to 4 carbon atoms.

Sodium dithionite is normally used as the reducing agent in dyeing cellulosic textile material with vat dyes. The textile material may be dyed in different ways according to how it is made up. Thus hank yarn is dyed on equipment suitable for the purpose, as for example on cheeses and beams, and cloth is dyed according to the "pad-jig" process or by the "pad-steam" process.

Sodium dithionite has the advantage that it effects extremely rapid reduction of the vat dye, particularly at high temperature, and therefore in some dyeing methods it makes possible an extremely short fixing time. This is important in continuous dyeing methods for piece goods, as for example in the pad-steam method and the "stand-fast" method. On the other hand sodium dithionite has the disadvantage that it is very easily oxidized by

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atmospheric oxygen and that its stability in aqueous alkaline solution declines very rapidly with increasing temperature even in the absence of oxygen. In dyeing methods in which the dye liquor comes into contact with air or in which the alkaline dye liquor must be heated to elevated temperature for a long time it is therefore necessary to use an excess of sodium dithionite to compensate for the loss. In some cases the very great reductive power of sodium dithionite may lead to excessive reduction and to destruction of the vat dye. There is a risk of this for example in the so-called high-temperature method in which package dyeing is carried out at temperatures higher than 90° C.

Excessive reduction of the dye can be avoided by decreasing the redox potential of the sodium dithionite by adding aldehydes, particularly formaldehyde (see E. Wilhelm and H. Schlüter, *Textilpraxis*, 8 (1962), 818-823). Since it is possible by adding aldehyde to the pre-vatted dye at temperatures below about 60° C. to decrease the redox potential to below the value for the leuco potential of the dye, so that reoxidation and precipitation of the vat dye may be effected, it is necessary to add the aldehyde only after the dye liquor has reached a temperature of about 60° C. Such an interruption of the dyeing process for the purpose of adding aldehyde has a very disturbing effect on the course of the dyeing. A process has therefore been sought which will permit the dyeing temperature to be raised without interruption to temperatures higher than 90° C. with the object of controlling the dyeing process merely by raising the dyeing temperature.

Dyeing at temperatures higher than 90° C. is known in package dyeing to have the advantage that goods which are difficult to dye, for example those of mercerized cotton or linen, can be dyed satisfactory level shades even when using IN dyes, excellent penetration being achieved. In the high-temperature method it is usual to dye at final temperatures of about 115° C. It is known that when dyeing grey cotton material with the coemployment of ethylenediaminetetracetic acid or nitrilotriacetic acid or the alkali metal salts of these acids and in the presence of sufficiently large amounts of alkali in the dyebath, improved fastness to crocking and a very marked level dyeing and brightening effect can be achieved which in the case of very light and bright shades often renders a separate bleaching process superfluous. Cotton grey cloth may be treated in such a blank vat (i.e. without adding dye) at a temperature of more than 100° C., preferably between 110° and 135° C., merely for bleaching purposes. This advantage of the high-temperature method has not however been fully exploited in practice because of the complicated procedure (interruption of the dyeing process for the purpose of adding aldehyde).

Methods for dyeing with vat dyes are known from German patent specifications Nos. 1,071,653, 1,116,190 and 1,116,628, according to which the reducing agents used are alkali metal or ammonium salts of hydroxyalkylsulfinic acids having two to four carbon atoms or derivatives of ammonia which contain at least once the radical of an alkali metal or ammonium salt of an alkylsulfinic acid having two to four carbon atoms, attached via nitrogen. The use of such dyes in the vat pad method, which is of interest for piece dyeing, offers advantages because the rate of decomposition of these reducing agents in contrast to that of sodium dithionite is so low

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that reduction of the vat dye in the padding liquor is avoided. It is therefore possible to avoid tailing with the said reducing agents by the vat padding method. When dyeing by the pad-steam method, the use of the said reducing agents means that the air passage between the chemical pad and the steamer need not be so short as when using sodium dithionite because the stability of the said reducing agents to atmospheric oxygen is superior to that of sodium dithionite. It has however been found in this case, as in the case of other dyeing methods in which rapid vatting or revatting of the dye is desired, that the rate of decomposition of the said reducing agents at high temperatures is not always satisfactory. Thus for example when dyeing by the pad-steam method it is necessary to use a large amount of the said reducing agents and to effect steaming as far as possible at temperatures of about 110° C. which cannot be reached in many of the continuous steamers used in practice. Another property of the said reducing agents is that re-vatting does not take place sufficiently quickly when they are used. For example when dyeing hank yarn on a yarn or spray dyeing machine, in which it is normally impossible to avoid oxidation of the leuco vat dye occurring on the surface of the liquor by atmospheric oxidation, this leads to non-levelness and in special cases to the formation of spots on the goods. When package dyeing according to the pigmentation graduated temperature process, too slow a reduction may result in dye being filtered off on the packages.

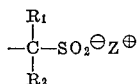
We have now found that the said disadvantages in dyeing textile material with vat dyes and sulfur dyes can be avoided and dyeing may be made considerably more economical by using, as reducing agents, mixtures of sodium dithionite with a sulfinic acid derivative selected from the class consisting of a compound of the general formula

(I)



where x represents a whole number from 0 to 2, y represents a whole number from 1 to 3, $x+y$ being equal to 3, A represents a member selected from the group consisting of hydrogen, low molecular weight alkyl and low molecular weight alkyl substituted by a radical of the general Formula III below, and D represents the radical of a salt of an alkylsulfinic acid with 1 to 4 carbon atoms of the general formula

(II)



where each of the radicals R stands for a member selected from the group consisting of hydrogen and alkyl and Z stands for a member selected from the group consisting of an ammonium cation and an alkali metal ion, said substituent of the low molecular weight alkyl designated by A above having the general formula

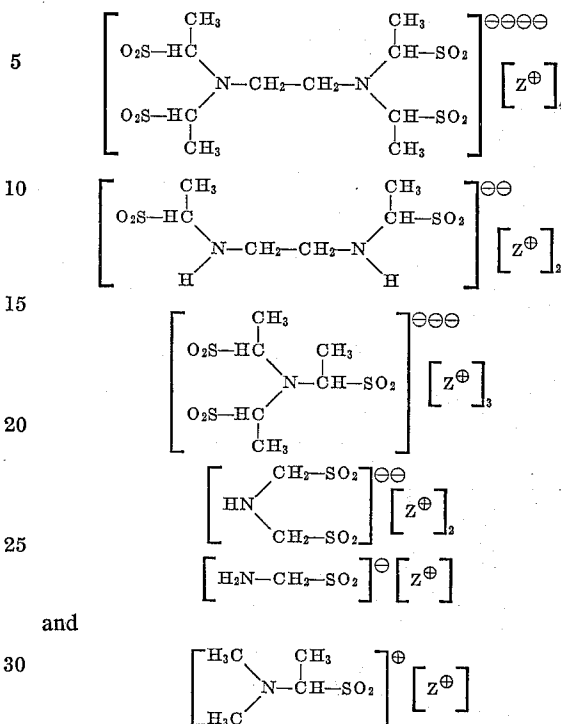
(III)



where H is hydrogen, D has the same meaning as set forth above, p and q each represents a whole number from 0 to 2, $p+q$ being equal to 2, an alkali metal salt of a hydroxyalkylsulfinic acid having two to four carbon atoms and an ammonium salt of a hydroxyalkylsulfinic acid having two to four carbon atoms.

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Suitable compounds of the general Formula I are for example the following:



where each Z stands for a member selected from the group consisting of an ammonium cation and an alkali metal cation. Such compounds are described in German patent specifications Nos. 1,071,042, 1,086,209 and 1,116,190.

Derivatives of ammonia of the said type may be obtained in various ways, for example by allowing to act on ammonia or on derivatives of ammonia bearing at least one hydrogen atom attached via nitrogen, alkali metal salts, such as sodium salts or potassium salts, or ammonium salts, of hydroxyalkylsulfinic acids having one to four carbon atoms which bear the hydroxyl group and the sulfinic acid group on the same carbon atom, for example the sodium salts, potassium salts or ammonium salts of hydroxymethanesulfinic acid, 1-hydroxyethanesulfinic acid-(1), 1-hydroxypropanesulfinic acid-(1), 2-hydroxypropanesulfinic acid-(2) or 1-hydroxy-n-butan-sulfinic acid-(1). This reaction proceeds with elimination of water. Alkali metal salts or ammonium salts of different hydroxyalkylsulfinic acids having one to four carbon atoms may be allowed to act simultaneously or successively in any sequence on ammonia or on derivatives of ammonia of the abovementioned type.

Compounds such as those described for example in German patent specification No. 1,071,653 may be used as alkali metal salts or ammonium salts of a hydroxyalkylsulfinic acid having two to four carbon atoms. For example the sodium salts and potassium salts of hydroxyethanesulfinic acid, hydroxy-n-propanesulfinic acid, hydroxy-isopropanesulfinic acid or hydroxy-n-butan-sulfinic acid may be used.

The advantages of the new process are given in detail in the following description.

The new reducing agent mixtures make possible a substantial decrease in the amount of reducing agent hitherto used. Moreover the new reducing agent mixtures bring about an increased stability of the reducing agent in the liquors which permits achieving readily reproducible results even under unfavorable working conditions. This advantage is particularly evident for example when working by the pad-steam method if the chemical liquor stands for a long period prior to use or if there is a long air passage between the chemical pad and the steamer. Fur-

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thermore the dyeings obtainable according to the new process are distinguished from dyeings developed with sodium dithionite alone by improved levelness, higher brilliance and improved purity of shade. These advantages are particularly evident when the amount of the reducing agent mixture is such that the sodium dithionite concentration in the chemical liquor padded on is just sufficient for vatting the dye. The second component of the reducing agent mixture then maintains the necessary redox potential during the steaming process. Since the sodium dithionite is practically completely used up during the steaming, the leuco compound of the dye is reoxidized in a very short time at the low temperatures prevailing in the rinsing bath. Rinsing out of the leuco compound is thus substantially prevented. A considerably better dye yield is therefore obtained than when dyeing with sodium dithionite alone, particularly when dyes having relatively low affinity are used.

When the new reducing agent mixtures are used for dyeing by the high-temperature method they have the advantage that the dyeing process may be carried out without interruption and that the vat remains more stable at temperatures above 90° C. than when using sodium dithionite and aldehydes. A saving in reducing agents and more reliable operation during prolonged dyeing periods is made possible. Since all the additives may be added to the dye liquor at room temperature, dyeing may be fully automatic. Another advantage is that when using the high-temperature method, dye and reducing agent may be subsequently added in a simple way for the purpose of shading, because the new reducing agent mixture may be easily dosed. When working according to the process known from German patent specification No. 1,025,825 with sodium dithionite and aldehyde as the reducing agent, subsequent addition of reducing agent offers difficulty because the decomposition of the mixtures of sodium dithionite and aldehyde takes place in an indefinable and non-reproducible way.

The reducing agent mixtures to be used according to this invention may be used both for batchwise and continuous dyeing with vat dyes and/or sulfur dyes.

The relative proportions of the components in the reducing agent mixtures may be varied to achieve an optimum effect depending on the method of dyeing.

When dyeing at temperatures up to 90° C., it is advantageous to use reducing agent mixtures which consist of about 40 to 80% by weight of sodium dithionite and about 60 to 20% by weight of a compound of the general Formula I and/or an alkali metal salt or ammonium salt of a hydroxyalkylsulfonic acid having two to four carbon atoms. Within the relative proportions specified, lower proportions of sodium dithionite are usually chosen the higher the dyeing temperature is. When dyeing at temperatures higher than 90° C., it is advantageous to use reducing agent mixtures consisting of about 20 to 80% by weight of sodium dithionite and about 80 to 20% by weight of the said sulfinic acid derivatives, the lower proportions within the said relative proportions being used the longer the periods of dyeing and development required.

For dyeing according to the pad-steam method, it is advantageous to use for example a mixture which consists of about 60% by weight of sodium dithionite and about 40% by weight of a compound of the general Formula I, in which D represents the radical of an alkali metal salt or ammonium salt of an alkylsulfonic acid having two to four carbon atoms. For dyeing by the high-temperature method it is advantageous to use a reducing agent mixture which consists of about 33% by weight of sodium dithionite and about 67% by weight of a compound of the general Formula I, in which D represents the radical of an alkali metal salt or ammonium salt of methanesulfonic acid.

The advantageous effect achieved by the new process is so remarkable that the action of the reducing agent mixtures to be used according to this invention cannot be ex-

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plained simply from the sum of the properties of the components of the mixture. It is evident that adding the said sulfinic acid derivatives to sodium dithionite causes not only increased stability at elevated temperature but also increased stability of the sodium dithionite with respect to oxidative influences of atmospheric oxygen. On the other hand sodium dithionite or its decomposition products effect a marked increase in the rate of decomposition of the said sulfinic acid derivatives at elevated temperature. This mutual diminution and increase in the rate of decomposition in the use according to this invention of the said reducing agent mixtures is naturally the more favorable the higher the temperature at which the dyeing is carried out. For this reason the advantages of the new process are particularly apparent when dyeing at temperatures higher than 90° C., and therefore for example in the pad-steam method, in continuous piece dyeing and in the high-temperature method in package dyeing.

The invention is further illustrated by the following examples. The parts and percentage specified in the examples are units of weight.

Example 1

Precleaned and bleached cotton poplin is padded at 25° C. in a commercial two-roll padding machine with 25 parts of the dye C.I. Vat Blue 6 Colour Index (1956) No. 69825) 975 parts of water

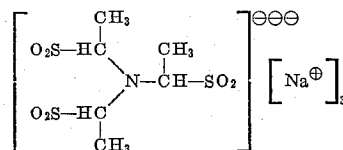
1000 parts.

The impregnated cloth is then given an intermediate drying at 120° C., padded in a commercial two-roll pad at 25° C. with

55 parts of aqueous sodium hydroxide solution (38° Bé.)

9 parts of sodium dithionite

6 parts of the compound having the formula:



930 parts of water

1000 parts

by a continuous method and steamed in a continuous steamer at 103° C. for fifty seconds and finally finished off in the usual way.

A satisfactory dyeing, equally dyed at ends and sides, is obtained which is superior to a dyeing obtained by using sodium dithionite alone as the reducing agent. The said method is also superior to the prior art method (according to which at least 27 parts of sodium dithionite is to be used for the present mixture) in that it requires a considerably smaller amount of reducing agent.

Example 2

Boiled cotton twill is padded at 25° C. in a commercial three-roll pad with

50 parts of the dye C.I. Vat Blue 20 (Colour Index (1956) No. 59800)

950 parts of water

1000 parts

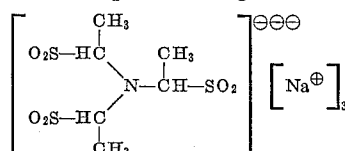
and then steamed for sixty seconds at 103° C. in a commercial steamer provided with a booster for the wet steam method.

The textile material is treated in the booster with a solution having the following composition:

50 parts of aqueous sodium hydroxide solution (38° Bé.)

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- 15 parts of sodium dithionite
10 parts of the compound having the formula:



925 parts of water

1000 parts.

The material is given a conventional aftertreatment. Penetration is very good. The dye yield is higher than when using sodium dithionite alone as the reducing agent in the development.

Example 3

Bleached shirt poplin is impregnated at 85° to 90° C. with

- 10 parts of the dye C.I. Vat Red 10 (Colour Index (1956) No. 67000)
40 parts of aqueous sodium hydroxide solution (38° Bé.)
7.5 parts of sodium dithionite
5 parts of the compound having the formula given in Examples 1 and 2

937.5 parts of water

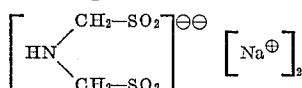
1000 parts.

The dyed material is immediately fixed for seven seconds in a hot liquid metal bath at 90° to 95° C. by the standfast method and then treated in a hot liquor which contains 20 parts of sodium sulfate in 1000 parts of water. A uniformly dyed textile material is obtained having high brilliance of the shade.

Example 4

Uncleansed cotton tricot is treated at a liquor ratio of 10:1 on a commercial beam dyeing machine at 20° C. with a dye liquor having the following composition:

- 2 parts of the dye C.I. Vat Blue 4 Colour Index (1956) No. 69800
20 parts of aqueous sodium hydroxide solution (38° Bé.)
4 parts of the compound having the formula:



- 2 parts of sodium dithionite
3 parts of the sodium salt of ethylenediaminetetraacetic acid
2 parts of glucose
967 parts of water

1000 parts.

The temperature of the liquor is raised from 20° to 115° C. within thirty minutes and dyeing continued at 115° C. for another thirty minutes. The whole is then cooled to 70° C. and the dyeing finished off as usual. A clear blue dyeing is obtained having good levelness.

Example 5

Grey cotton yarn is treated in cross-wound form on a commercial high-temperature dyeing machine at a liquor ratio of 10:1 at 20° C. with a liquor having the following composition:

- 0.5 part of the dye C.I. Vat Green 3 (Colour Index (1956) No. 69500)
20 parts of aqueous sodium hydroxide solution (38° Bé.)
4 parts of the compound having the formula given in Example 4

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- 2 parts of sodium dithionite
3 parts of the sodium salt of ethylenediaminetetraacetic acid
970.5 parts of water

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1000 parts.

The liquor is heated to 115° C. within thirty minutes and dyeing continued for another sixty minutes at this temperature. The liquor is then cooled and the dyeing is finished off as usual. A uniform olive green dyeing fast to crocking is obtained. Penetration is very good.

Example 6

Viscose rayon on cheeses is treated on a commercial high-temperature dyeing machine at a liquid ratio of 15:1 at 40° C. with a liquor having the following composition:

- 1 part of the dye C.I. Vat Black 25 (Colour Index (1956) No. 69525)
18 parts of aqueous sodium hydroxide solution (38° Bé.)
3 parts of the compound having the formula given in Example 5
1.5 parts of sodium dithionite
976.5 parts of water

1000 parts.

The temperature is raised from 40° C. to 115° C. within thirty minutes and dyeing continued for another thirty minutes at 115° C. The material is then cooled and finished off as usual. A very uniformly dyed material is obtained in which the points at which the threads cross are also dyed very uniformly. If dyeing is carried out by the conventional method in which temperatures of up to 80° C. are used, the points where the threads cross remain substantially white.

Example 7

Rayon staple yarn on cross-wound bobbins is dyed in a conventional dyeing machine at a liquor ratio of 10:1 at 85° C. with a liquor having the following composition:

- 4 parts of the dye C.I. Vat Blue 6 (Colour Index (1956) No. 69825)
25 parts of aqueous sodium hydroxide solution (38° Bé.)
4.5 parts of sodium dithionite
1.5 parts of the compound having the formula given in Examples 1 and 2
965 parts of water

1000 parts.

Dyeing is continued for forty-five minutes and the yarn finished off as usual. A dyeing having very good penetration is obtained.

Example 8

Unbleached cotton poplin is padded at room temperature in a commercial three-roll pad with

- 80 parts of aqueous sodium hydroxide solution (38° Bé.)
30 parts of the compound having the formula given in Example 4
10 parts of sodium dithionite
10 parts of the sodium salt of ethylene diaminetetraacetic acid
870 parts of water at 25° C.

1000 parts

and after having been heated up in an infrared zone is wound up into a hank arranged in a reaction chamber. The hank remains for two hours in an atmosphere of

steam of 103° C. while being slowly turned. The poplin is then removed from the chamber, rinsed and neutralized. A white cloth is obtained which cannot be distinguished from a previously bleached cloth as regards degree of whiteness. If this fabric is dyed as described in Example 1, a dyeing is obtained which does not differ from the dyeing obtainable according to Example 1.

Example 9

Prebleached, mercerized cotton poplin is padded in a commercial two-roll pad at 25° C. with a liquor which has the following composition:

35 parts of the dye C.I. Vat Green 5 (Colour Index (1956) No. 69520)
965 parts of water

1000 parts.

The dyeing is then developed on a jigger at 60° C. with a liquor having the following composition (liquor ration 5:1):

35 parts of aqueous sodium hydroxide solution (38° Bé.)

6 parts of sodium dithionite

3 parts of the compound having the formula in Examples 1 and 2

956 parts of water

1000 parts.

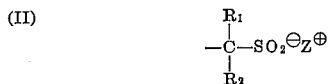
The dyeing is finished off as usual. A cloth dyed uniformly olive green is obtained. If in this case sodium dithionite be used as the sole reducing agent, it is found that at least 15 parts thereof must be used.

We claim:

1. A process for dyeing cellulosic textile material with a dye selected from the class consisting of vat dyes and sulfur dyes comprising using as the reducing agent a mixture which consists of 20 to 80% by weight of sodium dithionite and 80 to 20% by weight of a sulfinic acid derivative selected from the class consisting of a compound of the general formula



where x represents a whole number from 0 to 2, y represents a whole number from 1 to 3, $x+y$ being equal to 3, A represents a member selected from the group consisting of hydrogen, low molecular weight alkyl and low molecular weight alkyl substituted by a radical of the general Formula III below, and D represents the radical of a salt of an alkylsulfinic acid with 1 to 4 carbon atoms of the general formula



where each of the radicals R stands for a member selected from the group consisting of hydrogen and alkyl and Z stands for a member selected from the group consisting of an ammonium cation and an alkali metal ion, said substituent of the low molecular weight alkyl designated by A above having the general formula



where H is hydrogen, D has the same meaning as set forth above, p and q each represents a whole number from 0 to 2, $p+q$ being equal to 2, an alkali metal salt of a hydroxyalkylsulfinic acid having 2 to 4 carbon atoms, and

an ammonium salt of a hydroxyalkylsulfinic acid having 2 to 4 carbon atoms.

2. A process as claimed in claim 1 carried out at a temperature higher than 90° C.

3. A process as claimed in claim 1 carried out continuously.

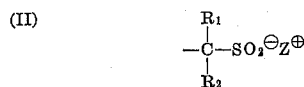
4. A process as claimed in claim 1 carried out batchwise.

5. A process as claimed in claim 1 where dyeing is carried out with an addition of an additive selected from the class consisting of ethylenediaminetetracetic acid and nitrilotriacetic acid and the alkali metal salts of these acids.

6. A process for dyeing cellulosic textile material with a dye selected from the class consisting of vat dyes and sulfur dyes comprising using as the reducing agent a mixture which consists of 40 to 80% by weight of sodium dithionite and 60 to 20% by weight of a sulfinic acid derivative selected from the class consisting of a compound of the general formula



where x represents a whole number from 0 to 2, y represents a whole number from 1 to 3, $x+y$ being equal to 3, A represents a member selected from the group consisting of hydrogen, low molecular weight alkyl and low molecular weight alkyl substituted by a radical of a salt of an alkylsulfinic acid with 1 to 4 carbon atoms of the general formula

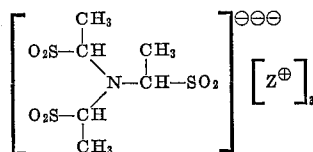


where each of the radicals R stands for a member selected from the group consisting of hydrogen and alkyl and Z stands for a member selected from the group consisting of an ammonium cation and an alkali metal ion, said substituent of the low molecular weight alkyl designated by A above having the general formula



where H is hydrogen, D has the same meaning as set forth above, p and q each represents a whole number from 0 to 2, $p+q$ being equal to 2, an alkali metal salt of a hydroxyalkylsulfinic acid having 2 to 4 carbon atoms and an ammonium salt of a hydroxyalkylsulfinic acid having 2 to 4 carbon atoms.

7. A process for dyeing cellulosic textile material with a dye selected from the class consisting of vat dyes and sulfur dyes comprising using as the reducing agent a mixture which consists of 20 to 80% by weight of sodium dithionite and 80 to 20% by weight of a compound of the formula

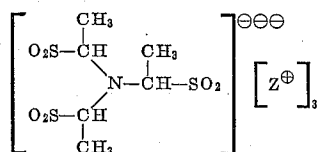


where Z is a member selected from the group consisting of an ammonium cation and an alkali metal ion.

8. A process for dyeing cellulosic textile material with a dye selected from the class consisting of vat dyes and sulfur dyes comprising using as the reducing agent a mixture which consists of 40 to 80% by weight of sodium

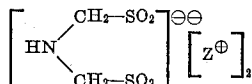
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um dithionite and 60 to 20% by weight of a compound of the formula



where Z is a member selected from the group consisting of an ammonium cation and an alkali metal ion.

9. A process for dyeing cellulosic textile material with a dye selected from the class consisting of vat dyes and sulfur dyes comprising using as the reducing agent a mixture which consists of 20 to 80% by weight of sodium dithionite and 80 to 20% by weight of a compound of the formula



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where Z is a member selected from the group consisting of an ammonium cation and an alkali metal cation.

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