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DYEING FIBROUS MATERIALS WITH VAT DYESTUFFS

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This invention relates to dyeing fibrous materials with vat dyestuffs.

It is well known that thorough penetration and levelling of the dyeings with vat dyestuffs on fibrous materials, especially yarns and fabrics, presents great difficulties. Attempts have been made in various ways to overcome the said difficulties and a large number of processes having the object of improving the unequal penetration or levelling power of the dyestuffs have been described.

It has, for example, been proposed to add protective colloids to the dye bath or to the material to be dyed, e g. albuminous substances such as glue and gelatine, sulphite cellulose lye, substances such as the product known under the trade name Peregal O and similar materials. It is assumed that agents of this character retard the absorption of the leuco bases of the vat dyestuffs to such an extent, that a more level dyeing effect is obtained. This method, however, has the drawback that the dyeing operation takes much time and that the baths are only very incompletely exhausted.

The amount of dyestuff remaining in the bath is larger when using protective colloids, than without the same. Moreover the results are not so good that really satisfactory results are obtained, especially when dyeing with light pastel colours.

Another prior process attempts to improve the dyeing by increasing the temperature used in the dyeing operation. In this case it is necessary to bind the hydrosulphite present in the bath by adding aldehydes or ketones, as the hydrosulphite would be decomposed at the temperatures used. However, even in this case the desired thorough penetration and levelling effect is not obtained and the process has the drawback that certain dyestuffs change their colour to some extent at the high dyeing temperature used.

It has also been proposed to meet the difficulties by forcing the dyestuff solution under the pressure of a neutral gas through the material to be dyed, but satisfactory results are not obtained in this way.

It has further been proposed to immerse the material according to the so-called "slop padding process" in a suitable non-reduced suspension of the dyestuffs and to develop the same in a so-called blind vat. In this way satisfactory thorough penetration and levelling results are obtained. However, this process is rather cumbersome and requires very exact working and ideal apparatus conditions, and on the whole it can only be used for the very finely divided dyestuffs. Moreover the same difficulties as indicated above are encountered when dyeing with light pastel colours.

According to the process of this invention an excellent thorough penetration and levelling is obtained by dyeing the fibrous materials with vat dyestuffs by immersing the said materials in an alkaline solution of the leuco base of the dyestuff and producing the dyestuff by oxidation in the fibres using a dye bath containing a substance acting as a water soluble organic solvent for the salts of the leuco base of the dyestuff in an amount which is large with respect to the amount of dyestuff used.

The alkaline solutions referred to above generally contain salts of the leuco bases with inorganic bases, preferably sodium, but they may also contain salts of organic bases.

The effect of the addition of the said solvents is probably due to their increasing the degree of dispersion of the salts of the leuco bases. It is well known that the degree of dispersion of the dyestuffs is a very important factor in the dyeing of fibres. If the degree of dispersion is too high as, for example, in the case of the acid and basic dyestuffs which are dissolved in almost molecular form, the material does not take up an appreciable amount of dyestuff. If the degree of dispersion is too low the adsorption of the dyestuffs is too strong so that they are desposited at the surface of the material in an irregular manner.

In order to obtain satisfactory dyeing conditions the dyestuffs therefore should have a degree of dispersion lying between that of purely colloidal and of molecular dispersions. This condition is generally satisfied by the substantive dyestuffs whereas the soluble salts of the leuco bases of vat dyestuffs are probably in the range of too low degree of dispersion. The favourable effect of the addition of water soluble organic solvents for the salts of the leuco bases of the vat dyestuffs can probably be explained in this way that they increase the degree of dispersion of the dissolved salts of the leuco bases to such an extent that it comes within the range of degrees of dispersions favourable for the dyeing operation. The solutions of the salts of the leuco bases in water have a colloidal character whereas the solutions in certain organic solvents are more or less molecular solutions so that by controlling the relative proportions of water and the or-

ganic solvent the desired degree of dispersion of the dyestuff can be obtained.

The number of organic solvents suitable for the purpose of the invention is rather limited. In the first place they must be soluble, preferably miscible in all proportions with water. Furthermore it is obviously unsuitable to use substances which react with the reduction agents used in the dyeing process so as to form inactive substances. Neither can substances be used which combine with the alkali present in the bath. For practical purposes the cost of the substance to be used will also have to be considered, and it is very important whether this substance can be recovered from the dyeing bath used in an inexpensive way.

I have found that the water soluble lower alcohols are very suitable for the purpose of the invention, and in order to be sufficiently soluble in water they do not in general contain more than five carbon atoms in the molecule. I preferably use alcohols with a boiling point below that of water, as alcohols of this character can be recovered by a simple distillation process. The said alcohols do not react with the hydrosulphite and with caustic soda, and they have a very favourable influence on the thorough penetration and levelling of the dyestuff.

The alcohol which is most suitable for the purpose is ethanol, as this alcohol is very cheap and can be easily recovered; nevertheless the boiling point is such that at the highest temperature usual for the reduction process of the vat dyestuffs (55 to 60° C.) appreciable losses by evaporation do not occur.

The use of dye baths containing alcohol has also the advantage that the wetting power of the same is substantially increased so that the dyestuffs, either in the form of a paste or of a powder, can be incorporated into the dye bath without a previous treatment with a wetting agent. At the same time it is unnecessary in most cases to subject the materials to be dyed to a scouring process or other preliminary treatment prior to the dyeing process.

The process according to the invention can be carried out in various ways for example:

1. The material to be dyed is immersed for some time in the concentrated e. g. aqueous-alcoholic solution of an alkali salt of the leuco base; the solution is now diluted with water to the usual concentration so that the degree of dispersion is reduced, and this solution is used for the dyeing in the usual way.

2. The material to be dyed is immersed for some time in the concentrated, e. g. aqueous-alcoholic solution of an alkali salt of the leuco base, thoroughly squeezed, washed and further treated in the usual way. The bath can be restored to the original volume and the original concentration by adding a concentrated aqueous-alcoholic solution of the leuco base of a suitable concentration, and the bath can then be used again for dyeing fresh material. In this way we can proceed until the amount of impurities remaining in the bath becomes too large.

However, there are also vat dyestuffs which when using the last mentioned method are absorbed after a short immersing period to such an extent, that the bath is practically exhausted. In this case the whole lot to be dyed can be treated simultaneously without appreciable losses of dyestuff.

The process is also suitable for dyeing yarns on cross wound bobbins or on the weaver's beam or by the packing system in which the bobbins are arranged in piles and the dye liquor is caused to circulate through the pile of bobbins. We may also treat yarns in skeins according to the "two bath developing" system known for dyeing with Naphtol A. S. dyestuffs.

Furthermore the process according to the invention has considerable advantages when dyeing in the piece in the jigger or other apparatus.

In all the above mentioned cases a very satisfactory thorough penetration and levelling effect is obtained and generally the time necessary for the process is considerably shortened so that the costs of labour of the dyeing operation proper are materially reduced.

The invention will be illustrated by the following examples in which the fibrous material used is 54/3 mercerised gassed Sakellaridis yarns with 20 turns per inch. The amount of yarn used in the examples is 5.5 kgms. The colors given hereinafter are those found in the work "Schultz Farbstofftabellen" 7th edition, and references will therefore be made in each case to volume and page.

1. A bath of the following composition is prepared:

Distilled water	litres	10
Methylated spirit	do	10
Caustic soda (38° Bé.)	do	1.2
Sodium hydrosulphite	grams	400

To this mixture is added 110 grams of Indanthrene Brilliant violet R. R. Powder (Vol. I, page 1265) and the dyestuff is reduced at a temperature of 55 to 60° C. The yarn which has not been subjected to a preliminary treatment is immersed in the solution for 10 to 15 minutes. The solution is now diluted to a volume of 100 litres with distilled water and 1 kgm. of sodium hydrosulphite is added. The dyeing operation is now continued for 15 minutes in the usual way.

The yarn is subsequently treated in the usual way by washing, oxidizing, acidulating, boiling with soap and washing.

2. A bath of the following composition is prepared:

Distilled water	litres	10
Methylated spirit	do	10
Caustic soda (38° Bé.)	do	0.5
Sodium hydrosulphite	grams	200

To this bath is added 5.5 gms. of Indanthrene Brilliant violet R. R. Powder (Vol. I, page 1265) and the dyestuff is reduced at a temperature of 55 to 60° C. The yarn which has not been subjected to a preliminary treatment is immersed in the solution, thoroughly squeezed and washed, and subsequently treated in the usual way. After the dyeing process the bath is exhausted to a large extent.

3. A bath of the following composition is prepared:

Distilled water	litres	10
Methylated spirit	do	10
Caustic soda (38° Bé.)	do	0.4
Sodium hydrosulphite	grams	400

To this bath is added 110 gms. of Indanthrene Blue R. S. N. Powder (Vol. I, page 1228) and the dyestuff is reduced at a temperature of 55 to 60° C. The yarn which has been scoured or previously wetted is immersed in the dyestuff solution for a period of 30 minutes. The solution is diluted to 100 litres with distilled water having a temperature of 55° C. and 1 kgm. of sodium hydrosulphite and 0.8 litre of a caustic soda solu-

tion of 38° Bé. are added. The yarn is dyed with this dilute bath for some minutes and further treated in the usual way.

4. A bath of the following composition is prepared:

Distilled water	litres	10
Methylated spirit	do	10
Caustic soda (38° Bé.)	do	0.5
Sodium hydrosulphite	grams	400

To this bath is added 110 gms. of Indanthrene Brown G. Powder (Vol. I, page 1219) and the dyestuff is reduced at a temperature of 50° C. The yarn which has not been subjected to a preliminary treatment is immersed in the liquid for a period of 30 minutes, thoroughly squeezed and washed and further treated in the usual way. The bath is exhausted to a large extent.

5. A bath of the following composition is prepared:

Distilled water	litres	10
Methylated spirit	do	10
Caustic soda (38° Bé.)	do	0.5
Sodium hydrosulphite	grams	400

To this bath is added 110 gms. of Indanthrene Brilliantrosa R. Powder (Ciba Red B) (Vol. I, page 1345) and the dyestuff is reduced at a temperature of 55° C. The yarn which has not been subjected to a preliminary treatment is immersed in the liquid for a period of 30 minutes, thoroughly squeezed and washed and further treated in the usual way. The bath is exhausted to a large extent.

6. Two baths of the following composition are prepared:

Distilled water	litres	15
Methylated spirit	do	5
Caustic soda (38° Bé.)	do	1.2
Sodium hydrosulphite	grams	400

To each of the said baths is added 400 gms. of Indanthrene Olive green B. Powder (Vol. II, page 131) and the dyestuff is reduced at a temperature of 55° C. One of the baths is used as "first bath", the other as "after bath".

5.5 kgms. of the yarn which has been previously scoured or wetted out is immersed in the "first" bath for 2 minutes and pressed together. The yarn is subsequently squeezed, washed and further treated in the usual way.

One half of the "after" bath is now added to the "first" bath; the combined bath is used for dyeing 5.5 kgms. of fresh yarn.

The other half of the "after" bath is then added to the "first" bath and the mixture is used for treating again 5.5 kgms. of fresh yarn.

7. A bath of the following composition is prepared:

Distilled water	litres	13
Acetamide	kgms	10
Caustic soda (38° Bé.)	litres	1.2
Hydrosulphite	grams	400

To this bath we add 110 gms. of Indanthrene Brilliant violet R. R. Powder (Vol. I, page 1265) and the dyestuff is reduced at a temperature of 53° C. The yarn which has been previously treated with a wetting agent is immersed in the liquid for a period of 15 minutes. The solution is diluted to a volume of 100 litres with distilled water having a temperature of 55° C. and 1 kgm. of hydrosulphite is added. The yarn is dyed for a period of 25 minutes and further treated in the usual way.

8. A bath of the following composition is prepared:

Distilled water	litres	10
Isopropyl alcohol (propanol-2)	do	10
Caustic soda (38° Bé.)	do	1.2
Sodium hydrosulphite	grams	400

To this bath is added 110 gms. of Brilliant violet R. R. Powder (Vol. I, page 1265) and the dyestuff is reduced at a temperature of 55° C. The yarn which has been previously treated with a wetting agent is immersed in the bath for a period of 15 minutes. The solution is diluted to 100 litres with distilled water having a temperature of 55° C. and 1 kgm. of hydrosulphite is added. The yarn is dyed during 15 minutes and further treated in the usual way.

9. A bath of the following composition is prepared:

Distilled water	litres	10
Acetone	do	10
Caustic soda (38° Bé.)	do	1.2
Sodium hydrosulphite	grams	400

To this bath is added 110 gms. of Brilliant violet RR Powder (Vol. I, page 1265) and the dyestuff is reduced at a temperature of 55° C. The yarn which has been previously treated with a wetting agent is immersed in the bath for a period of 15 minutes. The solution is diluted to 100 litres with distilled water having a temperature of 55° C. and 1 kgm. of hydrosulphite is added. The yarn is dyed during 15 minutes and further treated in the usual way.

10. A bath of the following composition is prepared:

Distilled water	litres	16
Pyridine	do	4
Caustic soda (38° Bé.)	do	1.2
Sodium hydrosulphite	grams	400

To this bath is added 110 gms. of Brilliant violet RR Powder (Vol. I, page 1265) and the dyestuff is reduced at a temperature of 55° C. The yarn which has been previously treated with a wetting agent is immersed in the path for a period of 15 minutes. The solution is diluted to 100 litres with distilled water having a temperature of 55° C. and 1 kgm. of hydrosulphite is added. The yarn is dyed and further treated in the usual way.

For the sake of simplicity the starting material used in the foregoing examples was the same in all cases, viz. cotton. The process can, however, also be used for other fibrous materials.

11. A bath of the following composition is prepared:

Distilled water	litres	20
Methylated spirit	do	20
Caustic soda (38° Bé.)	do	0.5
Sodium hydrosulphite	grams	400

To this bath is added 200 gms. of Indanthrene Marine blue G Powder (Vol. II, page 131) and the dyestuff is reduced at a temperature of 55° C. 10 kgms. of viscose artificial silk bead yarn which has not been subjected to a preliminary treatment is immersed in the liquid for a period of 15 minutes, thoroughly squeezed and washed and further treated in the usual way. The bath is exhausted to a large extent:

By "an amount of water soluble organic solvent which is large with respect to the amount of dyestuff used" I means that the properties of organic solvent in the dyeing liquor is a multiple of the proportion of dyestuff, e. g. not less than 5

and preferably 10 to 100 times as high and the amount of organic solvent, calculated on the aqueous solution is generally not less than 10%.

I claim:

1. A vat process for dyeing fibrous materials with vat dyestuffs comprising immersing the said materials in an alkaline solution of the leuco base of the dyestuff containing a water soluble organic substance acting as a solvent for the salts of the leuco base of the dyestuff in a proportion of at least 20% by weight of the dyeing baths, and producing the dyestuff by oxidation on the fibres.

2. A vat process for dyeing fibrous materials with vat dyestuffs comprising immersing the said materials in an alkaline solution of the leuco base of the dyestuff containing an alcohol having not more than five carbon atoms in the molecule in a proportion of at least 20% by weight of the dyeing baths, and producing the dyestuff by oxidation on the fibres.

3. A vat process for dyeing fibrous materials with vat dyestuffs comprising immersing the said materials in an alkaline solution of the leuco base of the dyestuff containing ethanol in a proportion of at least 20% by weight of the dyeing baths, and producing the dyestuff by oxidation on the fibres.

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