

UNITED STATES PATENT OFFICE

2,434,173

PROCESS FOR DYEING WOOL WITH AZO
DYE CHROME COMPLEXES AND CHROMIC
SALTS

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6 Claims. (Cl. 8—43)

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This invention relates to a new method of dyeing with chromium complexes of azo dyestuffs.

An extensive new field in dyeing is with metallized complexes of azo dyes having certain groups ortho to the azo group capable of uniting with certain metals to form metallized complexes. Among the metallized dyes, those metallized with chromium have achieved great importance for dyeing wool and the present invention is particularly concerned with improvements in the dyeing by means of certain of these chromium complexes of azo dyestuffs.

A number of types of fixing metallized azo dyes on the fiber have been in general use. In some of these processes such as the metachrome and top chrome processes, the azo dyestuff and a suitable metal salt are used separately. Another type of dyeing is with preformed metal complexes of azo dyes and it is with this last dyeing method alone that the present invention is concerned, and it should not be confused with metachrome, top chrome and similar processes.

In the past the dyeing of many basic nitrogenous fibers such as wool and the like with chromium complexes of certain azo dyes described below has been open to serious disadvantages. It has been difficult when dyeing from the customary sulfuric acid bath to reproduce the same shade, and the shade obtained is very sensitive to changes in dyeing conditions such as time, temperature, acid concentration and the like. As a result undesirable changes and particularly dull shades have often been produced, and this has been a known serious disadvantage in the dyeing with chromium complexes of these azo dyes particularly in the case of some green shades.

The present invention is directed to a method of dyeing with chromium complexes of certain particular classes of monoazo dyes having the formula $X-R-N=N-R_1-Z$ where R and R_1 are radicals included in the group consisting of benzene and naphthalene radicals; X is a radical included in the group consisting of hydroxyl and carboxyl radicals and is situated in the ortho position to the azo bridge; Z is an amino group situated in the ortho position to the azo bridge; and where the dyestuff contains at least one radical included in the group consisting of sulfonic and sulfonamide radicals.

In accordance with the present invention it is found that brighter and fuller shades are obtained when the chromium complexes of the azo dyes above referred to are dyed from a bath containing a salt of trivalent chromium. Shades are not only brighter and fuller, but are more easily re-

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produced, and are less sensitive to reaction conditions.

The mechanism of the dyeing reaction according to the present invention is not fully known, and it is not intended to limit the present invention to any theory of action. It is, however, clear that the process is in no sense the same as metachrome and top chrome processes, as it is carried out with chromium complexes of azo dyes which have been entirely metallized before addition to the dye bath. The chromium complexes may be produced by treatment of azo dyestuffs with salts of trivalent chromium or by any other suitable method.

The anion of the trivalent chromium salt added to the dyeing bath according to the present invention, does not appear to be critical. Comparable results are obtained with trivalent chromium salts of a wide number of acids and except for anions which might react with the dyestuffs themselves, any salt may be used so long as it possesses sufficient water solubility. Among typical salts which may be effectively used may be mentioned: chromic acetate, chromic formate, chromic fluoride, chromic chloride, chromic sulfate, chromic potassium sulfate, chromic benzene sulfonate, dichromic naphthalene disulfonates. While good results are obtained with all the above salts we prefer to use chromic acetate which gives the best results.

It is an advantage of the present invention that the amount of chromic salt to be used is not critical. In general as little of a chromic salt as corresponds to 0.5 part of chromium to 10 parts of dye produces a notable improvement in shade. A somewhat greater amount of the chromic salt is preferred as it will show further shade improvement and the preferred range is from .6 to 15 parts of chromium for 10 parts of dyestuff. The proportions within this range will vary somewhat with the nature of the particular dyestuff and also with the strength of the dyeing. In general, as the strength of the dyeing increases, the amount of chromic salt relative to the weight of the dye necessary for optimum results decreases. The reason for this behavior is not fully known, but it is possible that a certain minimum amount of chromic salt is necessary regardless of how light a dyeing is made.

Any of the monoazo dyestuffs having one hydroxyl or carboxyl radical and one amino group ortho to the azo bridge may be used in the present invention. Typical diazo components are the following:

2 - amino - 4 - nitrophenol, 2-amino-4-nitro-6-

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sulfo phenol, 2-amino-4-sulfo-6-nitro phenol, 2-amino-5-nitro phenol, 2-amino-4-nitro-5-sulfo phenol, 2-amino-4-chlorophenol, 2-amino-4-chloro-6-sulfo phenol, 2-amino-4-chloro-5-sulfo phenol, 2-amino-4-sulfo phenol, anthranilic acid, the sulfo anthranilic acids, 1-amino-2-hydroxy naphthalene-4-sulfonic acid, 2-amino-4-methyl-6-nitro phenol, 2-amino-4-methyl-5-sulfo phenol, 2-amino-4-methyl phenol, and 3-amino-4-hydroxy benzene sulfonamide.

As appropriate coupling components there may be mentioned:

Naphthionic acid, 1-amino naphthalene-5-sulfonic acid, 2-amino naphthalene, 2-amino naphthalene-5-sulfonic acid, 2-amino naphthalene-6-sulfonic acid, 2-amino naphthalene-7-sulfonic acid, 2-amino naphthalene-5,7-disulfonic acid, 2-amino naphthalene-3,6-disulfonic acid, m-phenylene diamine, m-phenylene diamine sulfonic acid, 2-amino-8-hydroxy naphthalene-6-sulfonic acid, 2-amino-5-hydroxy naphthalene-7-sulfonic acid, 1-hydroxy-8-amino naphthalene 3,6-disulfonic acid, and 1-amino-8-hydroxy naphthalene-4-sulfonic acid. This list of diazo components and coupling components is merely illustrative and is not intended to limit the scope of this invention.

The improved results obtained with the limited group of metallized azo dyes by the procedure of the present invention is all the more surprising since the addition of salts of trivalent chromium to the dye bath does not have beneficial results on the shade of chromium complexes of other types of azo dyes which do not have an amino group ortho to the azo group. However, the presence of other types of chromium derivatives of azo dyes does not inhibit the action of the trivalent chromium salts on the particular class of chromium complexes of azo dyes to which the present invention relates. On the contrary, when mixtures of the chromated dyes of the present invention with other chromated dyes are used in the same bath improved results are obtained in the dyeing of the mixed shades which come out fuller, brighter and more easily reproducible than is the case when the dyeing takes place from a bath containing no chromic salt.

The present invention does not appear to require any particular sequence of operations; thus it does not make any material difference whether the trivalent chromium salt is added to the bath after dissolving the chromated dyestuff or whether the salt and dyestuff are mixed together and then dissolved. This property of the present invention permits enjoying a further advantage in that the proper amount of water soluble salt of trivalent chromium may be blended with the chromated dye so that the dyer does not have to make up his own dye composition but can dissolve the blend in the customary way and obtain the improved results of the present invention.

Blending operations require no new technique and can be effected in simple, well-known apparatus for blending or grinding. If preferred, the mixture may be effected by wet mixing in a dough mixer or other type of apparatus for handling a stiff cake.

The dye manufacturer frequently employs inert agents for purposes of shade standardization, such as for example, sodium sulfate, sodium chloride, dextrin, glucose, sugar, etc. These standard blending agents can be incorporated with the dyestuff together with the added chromic salt and the improvements are obtained in the same manner. It is also possible to incorporate a small

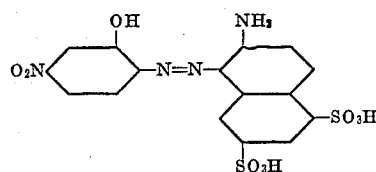
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amount of soda ash where this is desirable in order to enhance the solubility of the chromium complex in water. Dyeing assistants to improve the levelness of dyeing may also be incorporated in dye compositions according to the present invention and it is an advantage that all of these operations can be carried out without any particular new technique and without in any way interfering with the improvements obtained by the process of the present invention which thus represents one of the few chemical processes where an improvement is obtained without any compensatory disadvantage.

The invention will be further illustrated by the following examples, the parts being by weight.

Example 1

5.0 parts of the chromium complex of the azo dyestuff, which in the form of the free acid has the following formula:

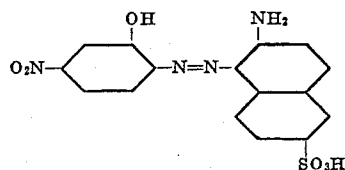


(obtained from diazotized 5-nitro-2-amino phenol and 2-amino naphthalene-5,7-disulfonic acid) are added to 200 parts of hot water. 1.0 part of anhydrous sodium carbonate is added and the mixture is stirred until the dyestuff is all dissolved. This solution is diluted with about 40,000 parts of water. Then 300 to 400 parts of a dilute sulfuric acid solution (equivalent to 30 to 40 parts of 66° Bé. sulfuric acid) and a solution of 5.0 parts of chromic acetate (equivalent to 1.6 parts of Cr₂O₃) in 50 parts of water are added to the bath. 500 parts of the material to be dyed (wool slubbing, wool raw stock, wool skeins, knitted woolen goods or woven woolen goods) are well wet out and placed in this solution. The solution is heated to the boil and boiled for 1½ to 2 hours. The material is turned or the solution is stirred from time to time to permit access of the dye solution to all parts of the material. The goods are lifted from the solution, rinsed well with water and dried. The pure blue-green dyeings obtained by this process are clearer, brighter, fuller, yellower, and more reproducible than the dyeings obtained by the same process in the absence of chromic acetate or any other commercially used dyeing process.

Similar improved dyeings are also obtained by substituting for chromic acetate in the above process equivalent amounts of the following chromic salts: chromic formate, chromic sulfate, potassium chromium sulfate, and chromic fluoride.

Example 2

2.5 parts of the chromium complex of the azo dyestuff, which in the form of the free acid has the following formula:



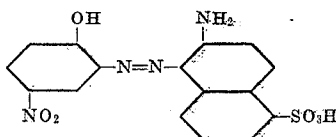
(obtained from diazotized 5-nitro-2-amino phe-

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not and 2-amino naphthalene-6-sulfonic acid) are added to 200 parts of hot water. 0.75 part of anhydrous sodium carbonate is added and the mixture is stirred until the dyestuff is all dissolved. The woolen goods are dyed as outlined in Example 1 with the exception that 2.5 parts of chromic acetate (equivalent to 0.8 part of Cr_2O_3) are used. By this dyeing process, pure bright green shades are obtained on wool. If the process of this example is repeated using no chromic acetate, the dyeings obtained are bluer, duller and much more difficult to reproduce.

Example 3

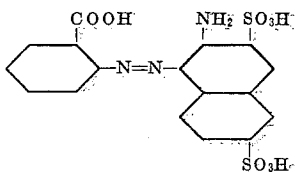
2.5 parts of the chromium complex of the azo dyestuff, which in the form of the free acid has the following formula:



(obtained from diazotized 4-nitro-2-amino phenol and 2-amino naphthalene-5-sulfonic acid) are added to 200 parts of hot water. 0.5 part of anhydrous sodium carbonate is added and the mixture is stirred until the dyestuff is all dissolved. The woolen goods are then dyed as outlined in Example 1 with the exception that 2.5 parts of chromic acetate (equivalent to 0.8 part of Cr_2O_3) are used. A green shade is obtained on wool. The dyeings produced by this process in the absence of chromic acetate are duller and less attractive.

Example 4

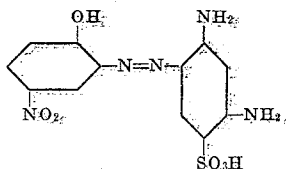
5.0 parts of the chromium complex of the azo dyestuff, which in the form of the free acid has the following formula:



(obtained from diazotized anthranilic acid and 2-amino naphthalene-3,6-disulfonic acid) are added to 200 parts of hot water. The mixture is stirred until the dyestuff is all dissolved. The woolen goods are then dyed as directed in Example 1. A bright shade of violet is obtained which is much brighter, fuller, and more level than the dyeing obtained by the same method in the absence of chromic acetate.

Example 5

5.0 parts of the chromium complex of the azo dyestuff, which in the form of the free acid has the following formula:



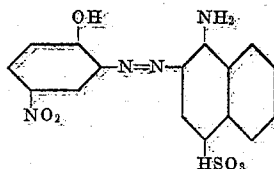
(obtained from diazotized 2-amino-4-nitro phenol and m-phenylene diamine sulfonic acid) are added to 200 parts of hot water. 1.0 parts of an-

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hydrous sodium carbonate are added and the mixture is stirred until the dyestuff is all dissolved. Woolen goods are then dyed by the method outlined in Example 1. A rich reddish brown shade is obtained. The dyeings produced by the same method in the absence of chromic acetate are very much yellower.

Example 6

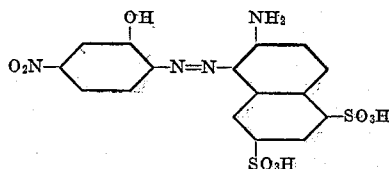
2.5 parts of the chromium complex of the azo dyestuff, which in the form of the free acid has the following formula:



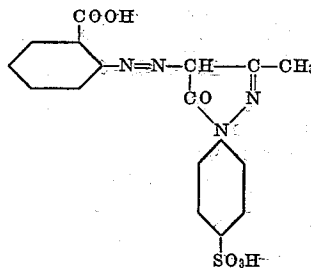
(obtained from diazotized 4-nitro-2-amino phenol and naphthionic acid) are added to 200 parts of hot water. 0.75 part of anhydrous sodium carbonate is added and the mixture is stirred until the dyestuff is dissolved. Woolen goods are then dyed by the method outlined in Example 1 with the exception that 2.5 parts of chromic acetate (equivalent to 0.8 part of Cr_2O_3) are used. Reddish-gray dyeings are obtained which are much greener and more easily duplicated than dyeings obtained by the same process in the absence of chromic acetate.

Example 7

2.00 parts of the chromium derivative of the azo dyestuff, which in the form of the free acid has the following formula:



(obtained from diazotized 5-nitro-2-amino phenol and 2-amino naphthalene-5,7-disulfonic acid) and 1.75 parts of the chromium derivative of the azo dyestuff which in the form of the free acid has the following formula:

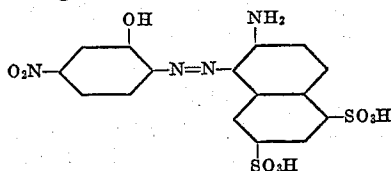


(obtained from diazotized anthranilic acid and 1-(4-sulfo phenyl)-3-methyl-5-pyrazolone) are added to 200 parts of hot water. 1.0 part of anhydrous sodium carbonate is added and the mixture is stirred until all the material has dissolved. Woolen goods are then dyed by the method outlined in Example 1 with the exception that 2.00 parts of chromic acetate (equivalent to 0.64 part of Cr_2O_3) are used. A bright pea green shade is obtained on wool, which is fuller, brighter, yellower and more easily reproducible than the shade obtained by the same method without the addition of chromic salt.

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Example 8

10.0 parts of the chromium complex of the azo dyestuff, which in the form of the free acid has the following formula:



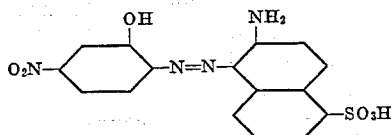
(obtained from diazotized 5-nitro-2-amino phenol and 2-amino naphthalene-5,7-disulfonic acid) are blended with 10.0 parts of chromic acetate (equivalent to 3.0 parts of Cr_2O_3), 3.0 parts of anhydrous sodium sulfate, and 2.0 parts of anhydrous sodium carbonate. The new dyeing composition obtained is a dark powder easily soluble to a deep blue-green solution in hot water. It gives pure blue-green dyeings on wool when dyed from a bath containing sulfuric acid which are clearer, brighter, fuller and more easily reproducible, than the dyeings obtained from a similar blend containing no chromic acetate.

In place of chromic acetate in the above formula, the following chromic salts can be used:

Chromic formate, chromic sulfate, chromic fluoride, chromic potassium sulfate, and chromic chloride.

Example 9

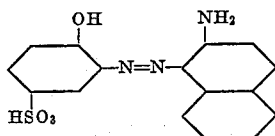
10.0 parts of the sodium salt of the chromium complex of the azo dyestuff which in the form of a free acid has the following formula:



(obtained from diazotized 5-nitro-2-amino phenol and 2-amino naphthalene-5-sulfonic acid) are blended with 10.0 parts of chromic acetate (equivalent to 3.0 parts of Cr_2O_3), 3.0 parts of dextrine, and 1.0 parts of anhydrous sodium carbonate. The new dyeing composition is a dark powder, soluble in hot water to a blue-green solution. It gives green dyeings on wool when dyed from a bath containing sulfuric acid which are clearer, brighter, fuller, yellower and more easily reproducible than the dyeings obtained from a similar blend containing no chromic acetate.

Example 10

10.0 parts of the chromic complex of the azo dyestuff, which in the form of the free acid has the following formula:



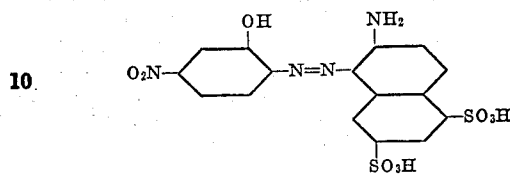
(made from diazotized 2-amino phenol-4-sulfonic acid and 2-naphthylamine) are blended with 10.0 parts of chromic acetate (equivalent to 3.0 parts of Cr_2O_3), 3.0 parts of anhydrous sodium sulfate and 2.0 parts of anhydrous sodium carbonate. The new dyeing composition obtained is a dark powder easily soluble in water to a dark blue solution. It gives greenish-gray dyeings on wool when dyed from a bath containing sulfuric acid, which are greener, brighter and more easily reproducible than the dyeings obtained from a similar blend containing no chromic acetate.

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Example 11

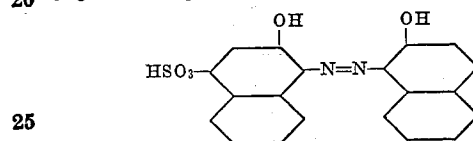
The following materials are intimately blended together:

- 5 7.5 parts of the chromium derivative of the azo dyestuff which in the form of the free acid has the following formula:



- 10 15 (obtained from diazotized 5-nitro-2-amino phenol and 2-amino naphthalene-5,7-disulfonic acid).

- 15 15.0 parts of the chromium complex of the azo dyestuff, which in the form of the free acid has the following formula:



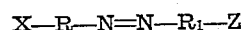
- 20 25 (obtained from diazotized 1-amino-2-hydroxy naphthalene-4-sulfonic acid and 2-naphthol).

- 30 Chromic acetate (equivalent to 2.25 parts of Cr_2O_3) 7.5
Anhydrous sodium sulfate..... 8.5
Anhydrous sodium carbonate..... 1.5

- 35 The dyeing composition obtained is a blue-black powder which dissolves in hot water to a deep blue solution. It dyes wool from a bath containing sulfuric acid blue shades, which are smoother, greener, and brighter than the shades
40 obtained from similar blends containing no chromic acetate.

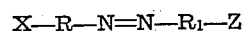
We claim:

1. A method of dyeing basic nitrogenous fibers with chromium complexes of azo dyestuffs having the formula



- where R and R_1 are radicals included in the group consisting of benzene and naphthalene radicals; X is a radical included in the group consisting of hydroxyl and carboxyl radicals and is situated in the ortho position to the azo bridge; Z is an amino group situated in the ortho position to the azo bridge; and where the dyestuff contains at least one radical included in the group consisting of sulfonic and sulfonamide radicals, which comprises applying the chromium complex of the dyestuff to the material to be dyed in a bath containing an effective amount of a water soluble salt of trivalent chromium.

2. A method of dyeing basic nitrogenous fibers with chromium complexes of azo dyestuffs having the formula



- where R and R_1 are radicals included in the group consisting of benzene and naphthalene radicals; X is a radical included in the group consisting of hydroxyl and carboxyl radicals and is situated in the ortho position to the azo bridge; Z is an amino group situated in the ortho position to the azo bridge; and where the dyestuff contains at least one radical included in the group consisting of sulfonic and sulfonamide radicals, which comprises applying the chromium complex of the dyestuff to the material to be dyed in bath contain-

ing a water soluble chromic salt having from .6 to 15 parts of chromium to 10 parts of dyestuff.

3. A method according to claim 1 in which the dye bath also contains a chromium complex of an azo dyestuff of a different formula not included in the formula of claim 1.

4. A method according to claim 2 in which the dye bath also contains a chromium complex of an azo dyestuff of a different formula not included in the formula of claim 2.

5. A method according to claim 1 in which the salt is chromic acetate.

6. A method according to claim 2 in which the salt is chromic acetate.

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MAX EMERSON NESTLER.

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