Patented June 17, 1947

2,422,586

UNITED STATES PATENT OFFICE

2,422,586

DYEING NITROGENOUS FIBERS WITH PRE-METALLIZED DYES AND ALDEHYDES

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No Drawing. Application September 29, 1944, Serial No. 556,482

10 Claims. (Cl. 8—43)

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This invention relates to a new method of dyeing metallized azo dyes containing an ortho-amino group and to new dyeing compositions.

Metallized azo dyes have achieved widespread use, particularly in the dyeing of basic nitrogenous fibers. These dyes are frequently dyed by forming the metal complex and then dyeing with the thus pre-metallized dyes. Other methods involve metallization during dyeing or after.

A completely metallized dye will normally have one atom of metallizing metal for each metallizable azo group and, when dyeing with pre-metallized dyes, it is important to prevent decomposition or de-metallization during dyeing which otherwise results in a change of shade and frequently in a dulling of the shade. The problem is particularly acute with metallized dyes having an amino group ortho to the azo group.

According to the present invention metallized dyes having an amino group ortho to the azo group are dyed in the customary acid bath in the presence of an aliphatic aldehyde containing not more than 3 carbon atoms or a compound which will set free such an aldehyde under the specified dyeing conditions. The dye bath is otherwise unchanged and the temperatures are not critical, the range from 20° C. to 160° C. giving good results.

The present invention is applicable to metallized dyes generally which contain an amino group ortho to the azo group and is particularly useful with chromium dyes, although improved results are also obtained with dyes metallized with copper, iron, manganese, cobalt, and other metallizing metals.

When the process of the present invention is used the dyes undergo substantially no de-metallization, particularly in the case of dyes containing chromium, and the dyeings do not change shade and are not dulled. We believe that the improved results of the present invention depend primarily on prevention of the loss of metal content of the dye during the dyeing operation. However, the mechanism of dyeing with metallized dyes is somewhat complex and it is not desired to limit the present invention to any theory of action as other factors may also be involved.

It is an advantage of the present invention that not only are improved dyeings obtained, but there is less tendering of wool, particularly in goods which have to be rehandled, for example, stripped and redyed. In a typical case when wool was dyed, stripped and redyed with a pre-metallized dye in 8% sulfuric acid without an aldehyde liberating agent such as para-formaldehyde, the

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loss in tensile strength was 45% greater than when para-formaldehyde was present. In another typical case the loss was about 36% greater when no aldehyde liberating agent was present. We do not know just why the aldehydes protect wool in dyeing and do not wish to limit the invention to any theory of action.

Another advantage of the use of aldehyde liberating products is to protect the wool fiber from becoming harsh. This harshness of the wool which is developed during the dyeing in the 8% sulfuric acid solution is probably caused by the action of the sulfuric acid on the wool. Whatever the reason the presence of the aldehyde liberating product imparts a softness to the fiber that is not obtained when the sulfuric acid only is used.

The present invention is not sensitive to the particular aldehyde liberating agent used. Thus, for example, ordinary aqueous formaldehyde solutions give good results as does para-formaldehyde. Other aldehydes having not more than 6 carbon atoms are also suitable, such as acetaldehyde, metaldehyde, butyraldehyde, glyoxal, and the like. Typical compounds which set free aliphatic aldehydes under dyeing conditions are methylol ureas, methylol melamines and their alkyl or aralkyl ethers, reaction products of methylol melamines and alkylolamines, condensation products of phenol formaldehyde and the like. Products which are solid, such as para-formaldehyde, hexamethylenetetramine, methylol ureas and methylol melamines present some advantage because it is possible to blend them dry with the metallized dyestuff to produce a product in a form in which it is ready for dyeing without the necessity of measuring out and adding suitable amounts of the aldehyde liberating substance. This is a definite commercial advantage and hence the solid aldehyde liberating substances are preferred.

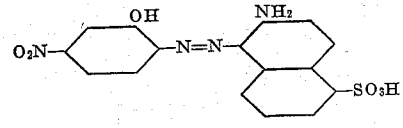
While as small an amount as 0.5% aldehyde on the weight of the wool shows substantial stabilization of the metallized dye during the dyeing operation, amounts as high as 10% in many cases show no objectionable features. However, in the latter case it is preferable to add the aldehydes in smaller portions and at various intervals during the dyeing operation as it appears that better stabilization of the metallized color is obtained. Thus, in one experiment which lasted over a period of 6 hours, the dyeing was started with 2% of para formaldehyde, and additions of 2% were made at intervals of 1 and 1½ hours. Thus in spite of the long boiling period, the metallized

dye appeared to be stabilized during the entire dyeing operation and the shade remained yellow and bright. Obviously for the more volatile aldehydes, some escape into the atmosphere during the boiling operation and it is an advantage to have an excess present.

If desired the wool can be pretreated by boiling in a bath containing about 5% formaldehyde or its equivalent for several hours. Such pretreatment usually does not give results quite equal to that obtained by an equivalent addition of the aldehyde to the dye bath. There is, however, a real improvement and this modification is included in the scope of the invention, although it is not in the preferred modification.

The invention will be described in greater detail in conjunction with the following specific examples.

Example 1



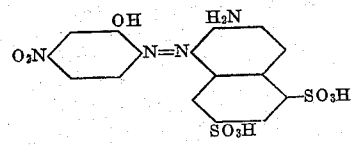
The azo dyestuff of the above formula, metallized with one atom of chromium per mole of dyestuff, was used in dyeing wool in a dye bath at 2% strength in 8% sulfuric acid, both percentages being based on the weight of the wool. 2% of para-formaldehyde, also based on the weight of the wool, was added to the dye bath which was brought to a boil and boiled until dyeing was complete and uniform.

The wool dyed a beautiful bright yellow green, whereas when the dyeing was effected under identical conditions without the para-formaldehyde, the green had no yellowish shade but was blue and dull.

Example 2

The process of Example 1 was repeated with 5% of a 40% aqueous formaldehyde instead of para-formaldehyde. The results were essentially the same as in Example 1.

Example 3



The procedure of Example 1 was repeated with the dyestuff of the above formula, fully metallized with chromium. When wool was dyed in the presence of para-formaldehyde an excellent yellow green shade was obtained. In the absence of the para-formaldehyde the shade was blue and dull.

Example 4

Example 3 was repeated exactly except a 5-gram skein of a casein fiber (Aralac) was used in place of the wool. Spectrophotometric data show that the Aralac dyed in the presence of the para-formaldehyde is definitely brighter than when no para-formaldehyde is present in the dye bath.

Example 5

The procedure of Example 3 was repeated, substituting 5% of formalin solution for the para-formaldehyde. The results were in general the same.

Example 6

The procedure of Example 3 was repeated using hexamethylene tetramine instead of the para-formaldehyde. Again the results were essentially the same.

Example 7

The procedure of Example 3 was repeated but a formaldehyde equivalent of methylol melamine was substituted for the para-formaldehyde. During the dyeing operation the odor of formaldehyde was present, indicating that the methylol melamine was liberating some formaldehyde. A very desirable bright yellowish-green shade was obtained with the methylol melamine, whereas in its absence the shade was blue, dull and commercially unsatisfactory.

Example 8

A 5-gram skein of wool was pre-boiled in 400 cc. water containing 12.5 cc. of a 40% solution of formaldehyde for 1 hour. This was then dyed with 2% of the color of Example 3, using 8% sulfuric acid. Both percentages are based on the weight of the wool. A second 5-gram skein was dyed with 2% of the color of Example 3 using 8% sulfuric acid only. The skein in this experiment received no pre-treatment with formaldehyde.

A third skein was dyed as in the immediate above experiment except 5 cc. of a 40% solution was present in the dyebath.

The shade of the skein which was pre-treated in the formaldehyde solution was brighter and yellower than the shade of the untreated skein, but was not quite as yellow as the shade of the skein dyed in the solution which contained formaldehyde during the dyeing operation.

Example 9

A melamine resin (tri-methylol melamine) was used in place of the methylol melamine of Example 7, the procedure being the same. The results obtained were practically the same as in Example 7.

Example 10

The procedure of the preceding example was repeated with a reaction product of methylol melamine and mono ethanolamine. This reaction product is prepared by heating 71 parts of methylol melamine and 48 parts of mono ethanolamine at 75–80° C. for 10 minutes. The solvents and excess reagents were then removed by distillation. The results of the dyeing were essentially equivalent to those obtained in Example 7.

Example 11

30 parts of urea and 60 parts of 40% formaldehyde solution were mixed in the cold and brought to a pH of 8 with ammonium hydroxide. This was boiled under a reflux for a few minutes and rapidly cooled. 5% of this water-soluble product was used in the procedure of Example 7 in place of the methylol melamine. An excellent yellow-green shade was obtained.

Example 12

15 parts of sodium sulfate were added to 85 parts of the reaction product of the preceding example. This product was air-dried and blended with the metallized dyestuff of Example 3 in an amount so that when the procedure of Example 3 was followed the urea formaldehyde resin and sodium sulfate amounted to 6% of the weight of the wool. A bright yellow green shade was

obtained and in the absence of the urea formaldehyde resin the shade was blue and dull.

Example 13

The procedure of Example 3 is repeated except that 4% butyraldehyde is added to the dye bath instead of the 2% para-formaldehyde. The dyeing obtained from the solution containing butyraldehyde is much yellower than the dyeing obtained from the solution in which no butyraldehyde was present.

Example 14

The procedure of Example 3 is repeated, except that 4% metaldehyde is added to the dye bath instead of the 2% para-formaldehyde solution. The dyeing obtained from this dye bath is yellower than that obtained from a dyeing solution in which no metaldehyde is present.

Example 15

The procedure of Example 1 is repeated, except that 4% acetaldehyde is used in place of the 2% para-formaldehyde. The resultant dyed woolen skein is yellower and brighter than when no acetaldehyde is present. It is not as yellow and bright as when 2% para-formaldehyde is used.

Example 16

The procedure of Example 3 is repeated, except a water soluble phenol-formaldehyde resin, such as Bakelite resin 15100 is used. Results are generally the same as obtained in experiment in Example 3.

Example 17

The procedure of Example 3 is repeated except 2% of mono methylol urea is used. A bright yellowish-green color is obtained. Dimethylol urea can be used in place of the mono methylol urea.

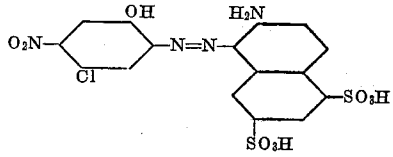
Example 18

The procedure of Example 3 is repeated except 2.5% tetra hydroxy dioxane is used in place of the para-formaldehyde of Example 3. The shade of the dyeing obtained is much yellower than that obtained from a similar dyeing in which no tetra-hydroxy-dioxane is present.

Example 19

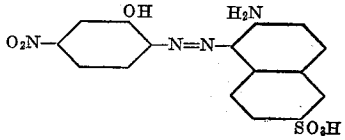
The procedure of Example 3 is repeated except 2% of glyoxal is used in place of the para-formaldehyde of Example 3. The shade of the dyeing obtained when the glyoxal is present is yellower than that obtained in which no glyoxal is in the dye bath.

Example 20



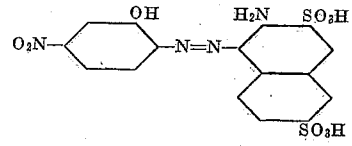
The procedure of Example 1 was repeated using the dyestuff of the above formula fully metallized with one atom of chromium. A bright, clean yellow-green shade was obtained.

Example 21



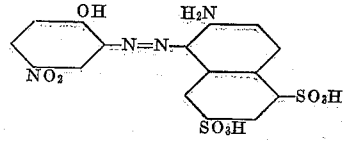
The procedure of Example 1 was repeated, using the above dyestuff metallized with one atom of chromium. Again the shade was a bright yellow-green, whereas under the same conditions without para-formaldehyde a blue, dull shade was obtained.

Example 22



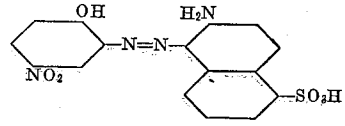
The procedure of Example 1 was followed, using the dyestuff of the above formula, metallized with one atom of chromium. A bright yellow shade of green was obtained, whereas under the same conditions without para-formaldehyde, the shade was blue and dull.

Example 23



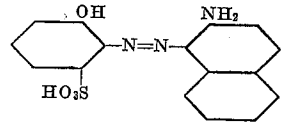
The procedure of Example 1 was followed using the dyestuff of the above formula metallized with one atom of chromium. When dyed in the presence of para-formaldehyde a bright slate green was obtained, whereas when para-formaldehyde was absent the shade was a dull gray-green.

Example 24



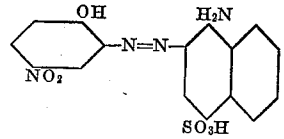
The procedure of the preceding example was followed using the chromium complex of the dyestuff of the above formula, the results being substantially the same as those of the preceding example.

Example 25



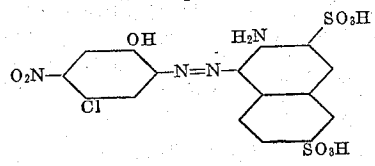
The procedure of Example 14 was followed substituting the chromium complex of the dyestuff of the above formula. The results were similar to those of Example 14.

Example 26



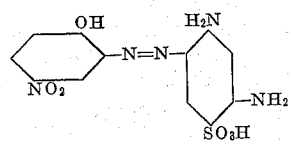
The procedure of Example 16 was followed, substituting the chromium complex of the dyestuff of the above formula. In the presence of formaldehyde de-metallization of the dyestuff was prevented, as is shown by the fact that a gray green shade was obtained instead of the reddish-brown shade of the unmetallized dyestuff.

Example 27



The procedure of Example 1 was followed, substituting the chromium complex of the dyestuff of the above formula. In the presence of paraformaldehyde a brighter and yellower green shade was obtained than when the dyeing was carried out in sulfuric acid only and which caused a blue green shade to be obtained.

Example 28



The procedure of Example 1 was followed substituting the chromium complex of the dyestuff of the above formula. In the presence of paraformaldehyde de-metallization of the color was prevented, as is shown by the fact that a rich taupe shade is obtained whereas in the absence of paraformaldehyde a reddish-tan shade is obtained.

We claim:

1. A method of dyeing basic nitrogeneous fibers with metallized acid monazo dyes containing an amino group and a hydroxy group ortho to the azo group which comprises effecting dyeing in the presence of an effective amount of a substance which, on contact with the dyebath, introduces therein aliphatic aldehydes having less than 6 carbon atoms.

2. A method of dyeing basic nitrogeneous fibers with metallized acid monazo dyes containing an amino group and a hydroxy group ortho to the azo group which comprises effecting dyeing in the presence of an effective amount of a substance which, on contact with the dyebath, introduces therein formaldehyde.

3. A method according to claim 2 in which the effective amount of formaldehyde is obtained from para-formaldehyde.

4. A method according to claim 2 in which the formaldehyde is obtained from a methylol urea.

5. A method according to claim 2 in which the formaldehyde is obtained from a methylol melamine.

6. A dyestuff composition comprising a metallized monazo dyestuff having an amino group and a hydroxy group ortho to the azo group and an amount of a solid capable of liberating an aliphatic aldehyde of less than 6 carbon atoms on contact with an acid dyebath.

7. A dyestuff composition comprising a metallized monazo dyestuff having an amino group and a hydroxy group ortho to the azo group and an amount of a solid capable of liberating a formaldehyde on contact with an acid dyebath.

8. A composition according to claim 7 containing para-formaldehyde as the formaldehyde liberating component.

9. A composition according to claim 7 in which the formaldehyde liberating substance is a methylol urea.

10. A composition according to claim 7 in which the formaldehyde liberating material is a methylol melamine.

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REFERENCES CITED

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

FOREIGN PATENTS

Number	Country	Date
502,314	France	Feb. 19, 1920