

# UNITED STATES PATENT OFFICE

2,610,103

## DYEING PROCESSES FOR WOOL AND PREPARATIONS THEREFOR

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20 Claims. (Cl. 8—26)

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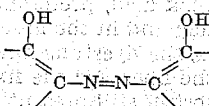
This invention relates to improvements in dyeing processes and preparations therefor.

Ortho:ortho'-dihydroxymonoazo dyestuffs are known which are of relatively good solubility in a neutral to alkaline medium but are of insufficient solubility in an acid medium. Accordingly these dyestuffs can as a rule not be dyed in a useful process from an acid bath because for the most part they are precipitated by the acid in relatively coarse form and thus even if they still take on the fiber from the suspension, they give non-uniform dyeings and as a rule dyeings of poor fastness properties, for example fastness to rubbing. Moreover undesired deposits frequently occur in the dye bath and especially on the walls of the dye vat. However many dyestuffs of this type, when they are not dyed from acid baths but for example according to the known single bath chroming process, give very valuable dyeings which are often distinguished by quite particularly good fastness properties. The fact that such valuable products cannot be utilised in a commercially applicable manner for dyeing from an acid bath, for example, for dyeing by the known after-chroming process, constitutes a considerable disadvantage.

The present invention is based on the observation that the dyestuffs of the specified type can also be dyed from an acid bath in a manner satisfying all commercial requirements when the operation is conducted according to a new process to be outlined below. By means of this process the hitherto limited scope of application of the dyestuffs of this type is extended in a valuable manner.

The new process for the dyeing from an acid bath consists in that ortho:ortho'-dihydroxymonoazo dyestuffs, which are suitable per se for dyeing from a neutral to weakly alkaline, but not from an acid bath, are dyed in the presence of an ortho-ortho'-dihydroxymonoazo dyestuff which is actually suitable for dyeing from an acid bath.

Under the term ortho:ortho'-dihydroxymonoazo dyestuffs are to be understood such monoazo dyestuffs as contain in the molecule the atom grouping

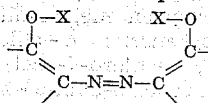


As acid dye baths are designated in the present case those the pH-value of which lies below 6.3, while the expression neutral to weakly alkaline comprises the region between 6.3 and about 8.0.

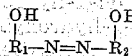
Ortho:ortho'-dihydroxymonoazo dyestuffs which are suitable for dyeing from a neutral to weakly alkaline but not from an acid bath, are for example those which although they contain no actual solubilizing groups such as sulfonic

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acid or carboxyl groups are still sufficiently soluble for application in dye baths, for example in the form of their alkali compounds



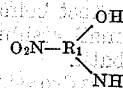
(wherein one X indicates hydrogen and the other X an alkali metal). Such dyestuffs are for example the monoazo dyestuffs free from sulfonic acid and carboxyl groups but containing a single nitro group of the general formula



wherein R<sub>1</sub> and R<sub>2</sub> both indicate an aromatic radical of the benzene series in which the azo group and the hydroxyl group are in ortho-position to one another. Further ortho:ortho'-dihydroxymonoazo dyestuffs which are suitable for dyeing from a neutral to weakly alkaline but not from an acid bath, are those which are free from sulfonic acid and carboxyl groups and contain in the molecule a single sulfonic acid amide group (ortho:ortho'-dihydroxymonoazo dyestuffs with more than one sulfonic acid amide group are as a rule also sufficiently soluble for dyeing from an acid bath).

Furthermore there may also be mentioned as dyestuffs of this type those ortho:ortho'-dihydroxymonoazo dyestuffs which contain the radical of a dihydroxynaphthalene.

A number of ortho:ortho'-dihydroxymonoazo dyestuffs, which are suitable for dyeing from a neutral to weakly alkaline but not from an acid bath, are known (see for example German Patent No. 445,888). Further such dyestuffs can be produced by methods known per se. Those of the last given formula can be obtained for example by coupling a diazo compound of an amine of the general formula



wherein R<sub>1</sub> indicates an aromatic radical of the benzene series in which the hydroxyl group and the amino group are in ortho-position to one another, with hydroxybenzenes coupling in ortho-position to the hydroxyl group, starting materials being employed which are free from sulfonic acid and carboxyl groups.

The mentioned ortho:ortho'-dihydroxyazo dyestuffs containing sulfonic acid amide groups can be produced by coupling ortho-hydroxydiazo compounds (in this case also preferably such of the benzene series) with compounds coupling in adjacent position to a hydroxyl group, as for example 1-phenyl-3-methyl-5-pyrazolones or hydroxy-naphthalenes, starting materials being employed which are free from sulfonic acid and car-

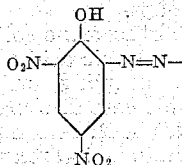
boxyl groups and either the diazo compound or the coupling component containing a sulfonic acid amide group.

The ortho:ortho' - dihydroxyazo dyestuffs which contain the radical of a dihydroxy-naphthalene can be obtained by coupling ortho-hydroxydiazo compounds with dihydroxynaphthalenes coupling in adjacent position to a hydroxyl group. As diazo components for the production of ortho:ortho' - dihydroxymonoazo dyestuffs which are suitable for dyeing from a neutral to weakly alkaline but not from an acid bath there are concerned for example: 4- or 5-nitro-2-amino-1-hydroxybenzene, 5-nitro-4-methyl-2-amino-1-hydroxybenzene, 6-acetylamino-4-nitro-2-amino-1-hydroxybenzene, 4-acetylamino-6-nitro-2-amino-1-hydroxybenzene, 5-nitro-4-chloro-2-amino-1-hydroxybenzene, 6-nitro-4-chloro-2-amino-1-hydroxybenzene, 4-nitro-6-chloro-2-amino-1-hydroxybenzene, 4-chloro-2-amino-1-hydroxybenzene, 4-nitro-6-chloro-2-amino-1-hydroxybenzene, 4-chloro-2-amino-1-hydroxybenzene, 2-amino-1-hydroxybenzene-4-sulfonic acid amide; as coupling components there may be employed: hydroxybenzenes substituted in para-position to the hydroxyl group by alkyl or alkoxy groups, as for example 4-methyl-1-hydroxybenzene, 4-tertiary amyl-1-hydroxybenzene, 3:4-dimethyl-1-hydroxybenzene, 2-acetylamino-4-methyl-1-hydroxybenzene, 2-acetylamino-4-methoxy-1-hydroxybenzene, 4-isopropyl-1-hydroxybenzene, 4-n-butyl-1-hydroxybenzene; furthermore pyrazolones such as 1-phenyl-3-methyl-5-pyrazolone-3'-sulfonic acid amide, 1-phenyl-3-methyl-5-pyrazolone-3'-sulfonic acid anilide and further also polynuclear systems such as 2:4-dihydroxyquinoline, 2:3-, 2:4-, 2:6-, 2:7-, 1:5-dihydroxynaphthalene, 1-hydroxynaphthalene-3-, -4- or -5-sulfonic acid amide, 2-hydroxynaphthalene-6-sulfonic acid amide, 2-hydroxynaphthalene-6-sulfonic acid anilide.

Such dyestuffs are as a rule suitable for dyeing, especially for the dyeing of wool from a neutral to weakly alkaline bath. They are primarily suitable for dyeing by the known single bath chroming process, in which dyeing is carried out in the presence of an alkali chromate and of ammonium sulfate and in which in contradistinction to certain earlier literature references it is not an acid but normally a neutral to weakly alkaline dye bath which is used.

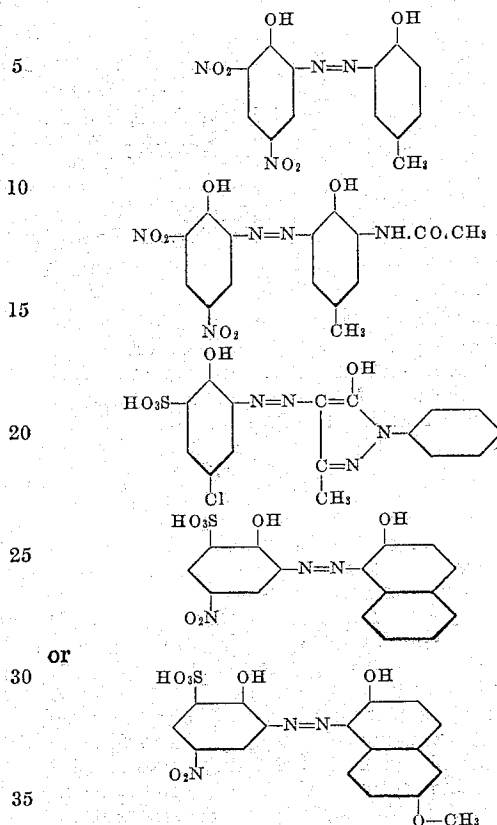
It is certainly customary in this process to add acetic acid in the course of the dyeing operation; the addition in general only takes place when the majority of the dyestuff is already fixed on the fiber and the dyeing process is thus practically complete, its effect being to cause to take on the fiber those small residues which are still present in the dye bath.

As ortho:ortho'-dihydroxymonoazo dyestuffs suitable per se for dyeing from an acid bath and in the presence of which dyeing is conducted in accordance with the present process, suitably such are employed as contain as solubilizing groups a carboxyl group or a sulfonic acid group or the atom grouping



Such products are known in large numbers; as known products of this constitution there may be mentioned for example the products given in

Color Index under Nos. 172, 202 and 652, and the dyestuffs of the formula



The ratio of the quantity of the dyestuff not suitable for dyeing from an acid bath to the quantity of the dyestuff which is suitable for dyeing from an acid bath can in the present process vary within wide limits. An addition of 30 parts of a dyestuff suitable for dyeing from an acid bath to 70 parts of a dyestuff which is not suitable for dyeing from an acid bath already renders possible a commercially satisfactory dyeing and yields a good result. If approximately equal quantities of the two dyestuffs are employed then from an acid bath dyeings are obtained which are for practical purposes as uniform as those obtained with the dyestuff which is suitable for dyeing from an acid bath used alone.

The combined application of the two types of dyestuff according to the present process is in no way limited to the application of one only of the dyestuffs of each type. With equally good results two or more can be employed at the same time of the dyestuffs suitable for dyeing from an acid bath and/or of the dyestuffs which are not suitable for dyeing from an acid bath.

In general it is advantageous to carry out the dyeing according to the present process in the presence of a weak acid, preferably in the presence of acetic acid and in the absence of mineral acid. As soon as the dyestuffs have for the most part taken on the fiber, for the fixation of small quantities of dyestuff still present in the dye bath it is however possible to add without disadvantage and in many cases with advantage a quantity of sulfuric acid.

The preparation of the dye baths serving for the execution of the present process suitably takes place using the customary stock solutions which contain the dyestuffs dissolved in the desired mixture ratio and in considerably higher concentration than is customary for the dye baths

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themselves. If desired the acid can subsequently be added to such stock solutions which are suitably of approximately neutral reaction.

By the mixing of the dyestuffs, advantageously in dry form, valuable dye preparations are obtained. These dye preparations are characterized in that they contain an ortho:ortho'-dihydroxymonoazo dyestuff which per se is suitable for dyeing from a neutral to weakly alkaline but not from an acid bath and an ortho:ortho'-dihydroxymonoazo dyestuff suitable per se for dyeing from an acid bath.

It is in general to be recommended not to admix with these dye preparations substances having a salting out effect as for example sodium sulfate or sodium chloride, as otherwise the good solubility of the preparations is reduced and the production of concentrated solutions, for example of the above-mentioned stock solutions may be rendered more difficult.

The present process and the preparations of the specified constitution suitable for carrying it out, are primarily suitable for the dyeing of animal fibers, especially for the dyeing of wool and preferably of loose wool or carded wool. The ortho:ortho'-dihydroxymonoazo dyestuffs which are per se unsuitable for dyeing from an acid bath and which are to be employed in this process, when dyed alone from an acid bath on such fiber material yield quite particularly non-uniform and very often completely useless dyeings. This is easily understandable since these dyestuffs are precipitated by the acid present in the dyebath in coarse form and in this condition cannot penetrate sufficiently deeply into the material to be dyed; they are retained by the outermost fiber layers which act as a filter. However by working according to the present process, in a surprising manner the dyestuffs remain in solution even in the acid medium or at least in such a fine state of division that the material to be dyed is no longer capable of acting as a filter and becomes uniformly dyed throughout. The new process and the new preparations are accordingly of especial advantage for machine dyeing in which as a rule concentrated dyebaths are used and the material to be dyed is treated in relatively close form in the bath so that the filter effect tends to be large. Under machine dyeing are to be understood in this case those dyeing methods in which the material to be dyed remains stationary and the dyebath is caused to move, for example by means of a circulating pump.

Among the dye preparations of the constitution set forth above those are of special advantage which contain ortho:ortho'-dihydroxymonoazo dyestuffs which are suitable per se for dyeing according to the single bath chroming process but are not suitable for dyeing according to the after-chroming process on account of insufficient solubility in the acid medium, and at the same time such ortho:ortho'-dihydroxymonoazo dyestuffs as are suitable both for dyeing according to the single bath chroming process and also for dyeing according to the after-chroming process.

With these multiple purpose preparations very valuable fast and level dyeings are obtained for example on wool both by the single bath chroming process and also by the after-chroming process, the result being to a far reaching extent independent of the nature of the wool to be dyed.

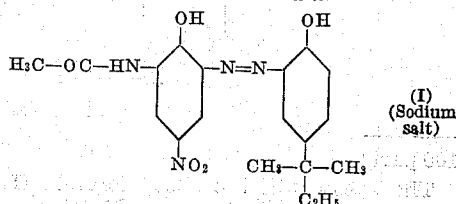
The following examples illustrate the invention, the parts and percentages being by weight unless otherwise stated:

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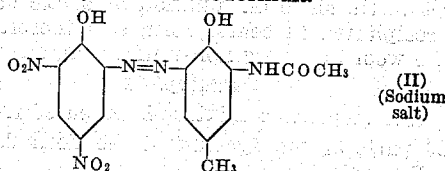
## Example 1

A dye preparation is prepared by producing a uniform powder mixture from:

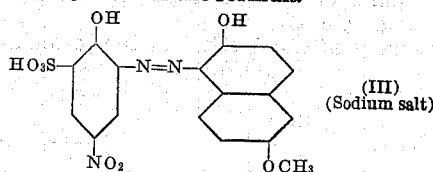
50 parts of the dyestuff of the formula



35 parts of the dyestuff of the formula



15 parts of the dyestuff of the formula



100 parts

Wool can be dyed in an advantageous manner with this mixture according to the following dyeing directions.

100 parts of loose wool are dyed in the following manner with 1.3 parts of the dyestuff mixture obtained according to this example in the dye machine (by this is to be understood a dyeing apparatus in which the material to be dyed is not moved while the dyebath is circulated):

1.3 parts of the mixture are dissolved in about 100 times the quantity of hot water and with this stock solution a dyebath produced which contains in 2500 parts of water at 50° C. in addition to the dyestuff mixture 10 parts of crystalline sodium sulfate and 3 parts of acetic acid of 40 per cent. strength. This dyebath is now run into the apparatus containing 100 parts of loose wool. With continuous circulation of the dyebath heating to boiling is effected within half an hour, after 45 minutes' boiling 5 parts of 10 per cent. sulfuric acid are added and the whole further treated at the boil for a quarter of an hour. Cooling is then carried out to 70-80° C., 1.3 parts of potassium bichromate are added and chroming effected for 40 minutes at boiling temperature. Finally the wool is rinsed with cold water and dried. It is dyed a level brown shade.

Instead of employing the mixture produced according to the above directions for the production of the stock solution, the dyestuffs can also be dissolved consecutively in corresponding quantity proportion in about 100 parts of water and the stock solution produced in this way employed according to the same directions, whereby practically the same result is obtained.

Instead of dyeing with 1.3 parts of the above specified mixture, the loose wool can also be dyed with 1.3 parts of the following mixture in the same way, a level, reddish brown dyeing then likewise being obtained.

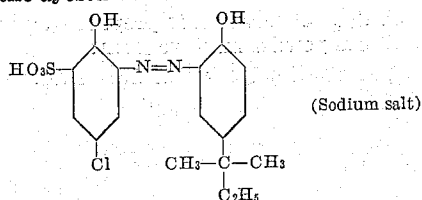
50 parts of the dyestuff of the Formula I (see above)

36 parts of the dyestuff of the Formula II (see above)

75

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14 parts of the dyestuff of the formula



100 parts.

The dyestuff of the above formula (I) is not per se suitable for dyeing by the process above set forth, since on addition of acetic acid it is precipitated in coarse form and therefore dyes the wool in a very non-uniform manner.

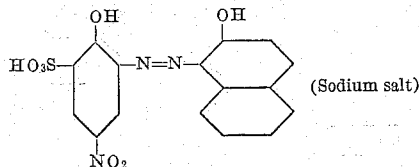
*Example 2*

A homogeneous mixture is prepared from

50 parts of the dyestuff of the Formula I (see Example 1)

36 parts of the dyestuff of the Formula II (see Example 1)

14 parts of the dyestuff of the formula



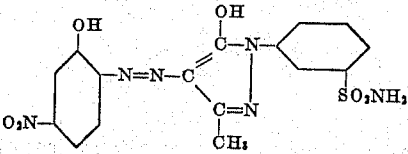
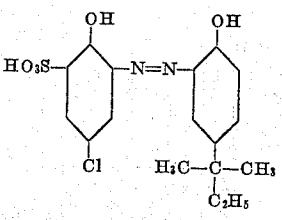
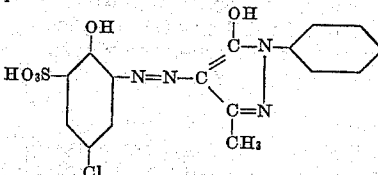
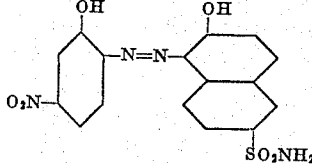
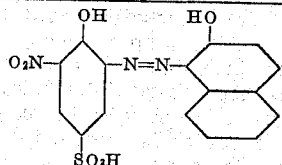
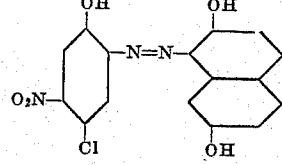
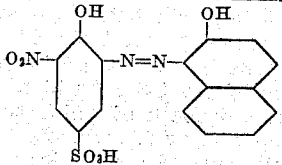
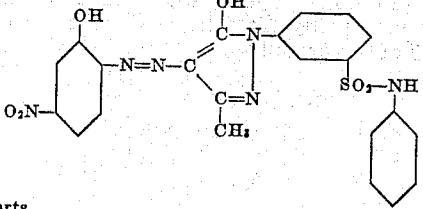
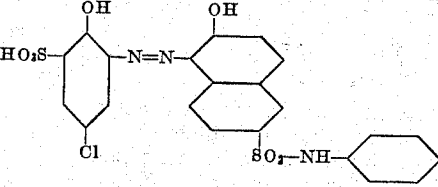
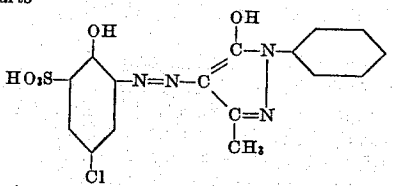
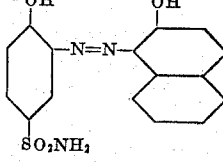
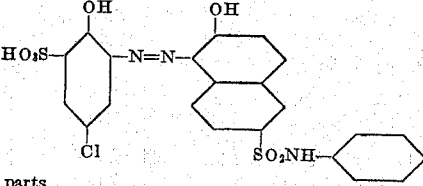
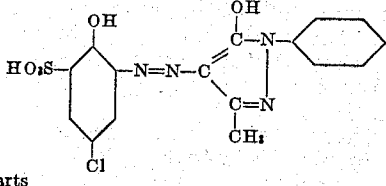
100 parts.

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1.1 parts of this mixture are dissolved in 100 parts of hot water. This stock solution is diluted with water to 4000 parts by volume and 10 parts of crystalline sodium sulfate and 4 parts of 40 per cent, acetic acid added. 100 parts of loose wool are entered into the dyebath thus obtained at 50° C., heating is effected within half an hour to boiling and dyeing at the boil carried on for 45 minutes. 5 parts of 10 per cent, sulfuric acid are now added and boiling continued for a further 15 minutes. At this point the whole is cooled to 70-80° C., 1.3 parts of potassium bichromate introduced and chroming carried out at boiling temperature for 40 minutes. Finally the wool is rinsed in cold water and dried. It is uniformly dyed in reddish brown shades.

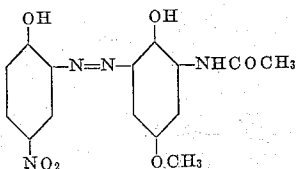
Further valuable dyeings are obtained with the mixtures set out in the following table. In these cases it is possible either, as stated above, to produce powder mixtures or to dissolve the dyestuffs in corresponding mixture ratio in about 100 parts of water and to employ for dyeing the stock solution thus obtained. Column I contains the data relating to the dyestuffs which are not suitable for dyeing from an acid bath and column II the data relating to dyestuffs which are suitable for dyeing from an acid bath. In column III is given the color shade which is obtained in the dyeing of wool with these mixtures according to the dyeing methods above set forth.

I	II	III
<p>60 parts</p>	<p>40 parts</p>	black brown.
<p>55 parts</p>	<p>45 parts</p>	brown.
<p>50 parts</p>	<p>50 parts</p>	black brown.
<p>50 parts</p>	<p>50 parts</p>	brown.

I	II	III
 <p>57 parts</p>	 <p>28.5 parts</p>  <p>14.5 parts</p>	<p>bordeaux.</p>
 <p>36 parts</p>	 <p>64 parts</p>	<p>black grey.</p>
 <p>36 parts</p>	 <p>64 parts</p>	<p>navy blue.</p>
 <p>40 parts</p>	 <p>40 parts</p>  <p>20 parts</p>	<p>bluish bordeaux.</p>
 <p>30 parts</p>	 <p>30 parts</p>  <p>40 parts</p>	<p>violet brown.</p>

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Level dyeings are also obtained when in one of the mixtures set forth above (Examples 1 and 2) the dyestuff of the Formula I is replaced by the dyestuffs of the formula

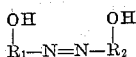


and the process is conducted according to the dyeing directions set out in either of Examples 1 and 2. This dyestuff also, when employed alone, is not of good suitability for dyeing from an acid bath.

What we claim is:

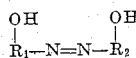
1. A process for dyeing wool which comprises conducting the dyeing from an acid bath with an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value greater than 6.3 and up to about 8 but which is practically insoluble in a dyebath of which the pH value lies substantially below 6.3, in the presence of an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value below 6.3.

2. A process for dyeing wool which comprises conducting dyeing from an acid bath with an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value greater than 6.3 and up to about 8 but which is practically insoluble in a dyebath of which the pH value lies substantially below 6.3, which dyestuff is free from sulfonic acid and carboxylic acid groups, contains a single nitro-group and corresponds to the formula



wherein  $R_1$  and  $R_2$  each stand for an aromatic radical of the benzene series in which the azo group and the hydroxyl group are in ortho-position to one another, in the presence of an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value below 6.3.

3. A process for dyeing wool which comprises conducting dyeing from an acid bath with an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value greater than 6.3 and up to about 8 but which is practically insoluble in a dyebath of which the pH value lies substantially below 6.3, which dyestuff is free from sulfonic acid and carboxylic acid groups, contains a single sulfonic acid amide group and corresponds to the formula

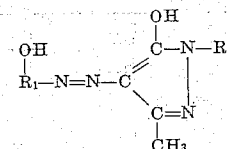


wherein  $R_1$  stands for an aromatic radical of the benzene series and  $R_2$ -OH for the radical of a coupling component, both -OH groups being in adjacent position to the azo group, in the presence of an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value below 6.3.

4. A process for dyeing wool which comprises conducting dyeing from an acid bath with an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value greater than 6.3 and up to about 8 but which is practically insoluble in a dyebath of which the pH value lies substantially below 6.3, which dyestuff is free from sulfonic acid and carboxylic

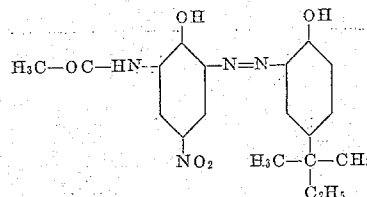
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acid groups, contains a single sulfonic acid amide group and corresponds to the formula

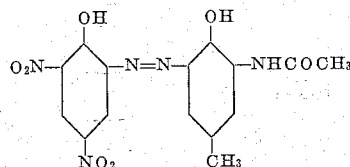


wherein  $R_1$  stands for an aromatic radical of the benzene series in which the azo group and the hydroxyl group are in ortho-position to one another and  $R_2$  stands for a phenyl radical, in the presence of an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value below 6.3.

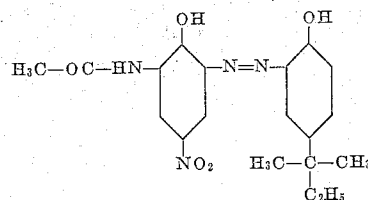
5. A process for dyeing wool which comprises conducting dyeing from an acid bath with the dyestuff of the formula



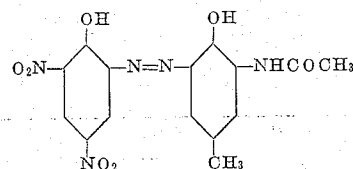
in the presence of the dyestuff of the formula



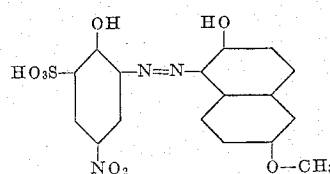
6. A process for dyeing wool which comprises conducting dyeing from an acid bath with the dyestuff of the formula



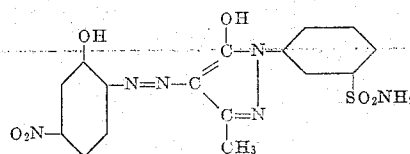
in the presence of the dyestuff of the formula



and the dyestuff of the formula

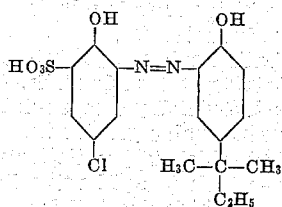


7. A process for dyeing wool which comprises conducting dyeing from an acid bath with the dyestuff of the formula

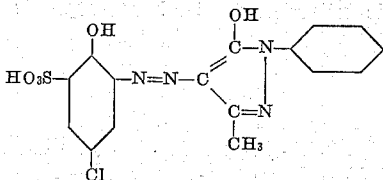


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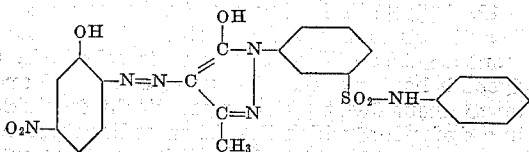
in the presence of the dyestuff of the formula



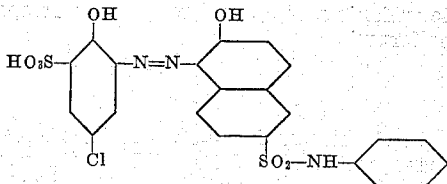
and the dyestuff of the formula



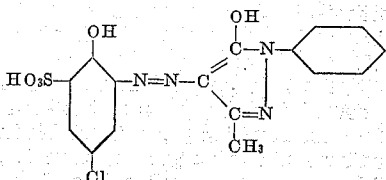
8. A process for dyeing wool which comprises conducting dyeing from an acid bath with the dyestuff of the formula



in the presence of the dyestuff of the formula

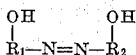


and the dyestuff of the formula



9. A dyestuff preparation containing an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value greater than 6.3 and up to about 8 but which is practically insoluble in a dyebath of which the pH value lies substantially below 6.3, and an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value below 6.3.

10. A dyestuff preparation containing an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value greater than 6.3 and up to about 8 but which is practically insoluble in a dyebath of which the pH value lies substantially below 6.3, which dyestuff is free from sulfonic acid and carboxylic acid groups, contains a single nitro group and corresponds to the formula

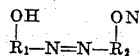


wherein  $\text{R}_1$  and  $\text{R}_2$  each stand for an aromatic radical of the benzene series in which the azo group and the hydroxyl group are in ortho-position to one another, and an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value below 6.3.

11. A dyestuff preparation containing an

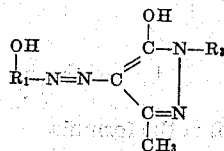
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ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value greater than 6.3 and up to about 8 but which is practically insoluble in a dyebath of which the pH value lies substantially below 6.3, which dyestuff is free from sulfonic acid and carboxylic acid groups, contains a single sulfonic acid amide group and corresponds to the formula



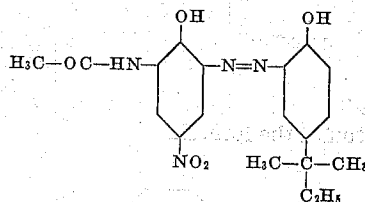
wherein  $\text{R}_1$  stands for an aromatic radical of the benzene series and  $\text{R}_2-\text{OH}$  for the radical of a coupling component, both  $-\text{OH}$  groups being in adjacent position to the azo group, and an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value below 6.3.

12. A dyestuff preparation containing an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value greater than 6.3 and up to about 8 but which is practically insoluble in a dyebath of which the pH value lies substantially below 6.3, which dyestuff is free from sulfonic acid and carboxylic acid groups, contains a single sulfonic acid amide group and corresponds to the formula

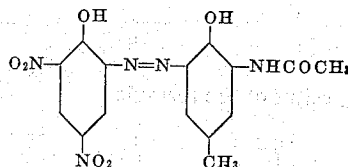


wherein  $\text{R}_1$  stands for an aromatic radical of the benzene series in which the azo group and the hydroxyl group are in ortho-position to one another and  $\text{R}_2$  stands for a phenyl radical, and an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value below 6.3.

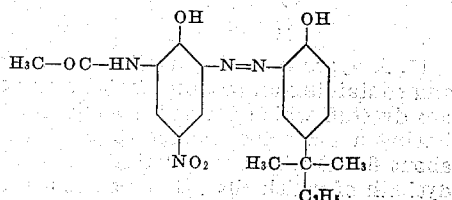
13. A dyestuff preparation containing the dyestuff of the formula



and the dyestuff of the formula

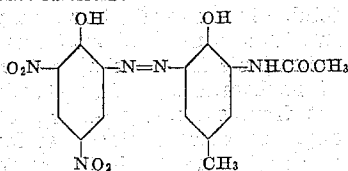


14. A dyestuff preparation containing the dyestuff of the formula

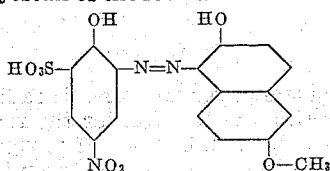


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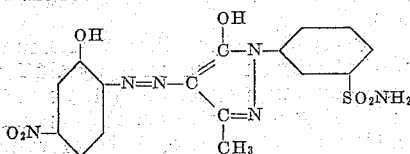
the dyestuff of the formula



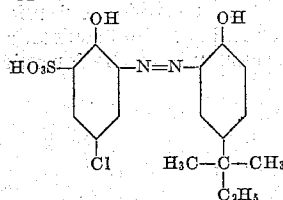
and the dyestuff of the formula



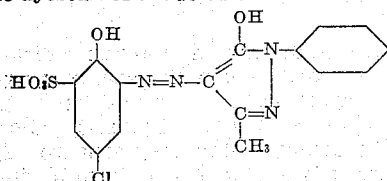
15. A dyestuff preparation containing the dyestuff of the formula



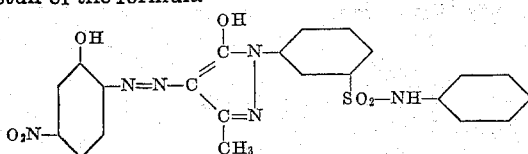
the dyestuff of the formula



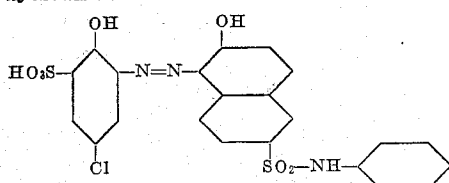
and the dyestuff of the formula



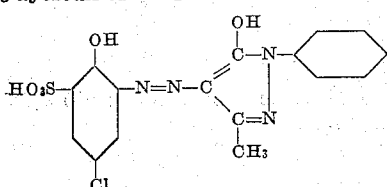
16. A dyestuff preparation containing the dyestuff of the formula



the dyestuff of the formula



and the dyestuff of the formula



17. A dyebath having a pH value from 3 to 5 and containing an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value greater than 6.3 and up to about 8 but which is practically insoluble in a dyebath of which the pH value lies substantially

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below 6.3 and an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value below 6.3.

18. A dyebath having a pH value from 3 to 5 and containing an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value greater than 6.3 and up to about 8 but which is practically insoluble in a dyebath of which the pH value lies substantially below 6.3, which dyestuff is free from sulfonic acid and carboxylic acid groups, contains a single nitro group and corresponds to the formula



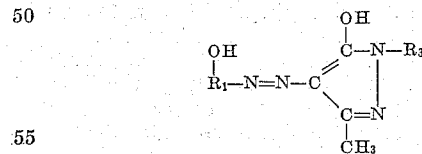
wherein R<sub>1</sub> and R<sub>2</sub> each stand for an aromatic radical of the benzene series in which the azo group and the hydroxyl group are in ortho-position to one another, and an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value below 6.3.

19. A dyebath having a pH value from 3 to 5 and containing an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value greater than 6.3 and up to about 8 but which is practically insoluble in a dyebath of which the pH value lies substantially below 6.3, which dyestuff is free from sulfonic acid and carboxylic acid groups, contains a single sulfonic acid amide group and corresponds to the formula



wherein R<sub>1</sub> stands for an aromatic radical of the benzene series and R<sub>2</sub>-OH for the radical of a coupling component, both -OH groups being in adjacent position to the azo group, and an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value below 6.3.

20. A dyebath having a pH value from 3 to 5 and containing an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value greater than 6.3, which dyestuff is free from sulfonic acid and carboxylic acid groups, contains a single sulfonic acid amide group and corresponds to the formula



wherein R<sub>1</sub> stands for an aromatic radical of the benzene series in which the azo group and the hydroxyl group are in ortho-position to one another and R<sub>3</sub> stands for a phenyl radical, and an ortho:ortho'-dihydroxymonoazo dyestuff which per se is soluble in a dyebath having a pH value below 6.3.

WILLI WIDMER.  
FRITZ SCHUETZ.  
ALPHONSE HECKENDORN.

## REFERENCES CITED

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

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