Patented July 16, 1935 2,008,602

UNITED STATES PATENT OFFICE

2,008,602

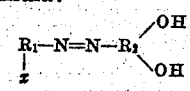
PROCESS OF DYEING LEATHER

Fritz Straub and Hans Mayer, Basel, Switzerland, assignors to Society of Chemical Industry in Basle, Basel, Switzerland

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12 Claims. (Cl. 8—5)

This invention relates to a process of dyeing leather fast shades by means of complex metallic compounds of mono-azo-dyestuffs which have the general formula:



wherein R_1 and R_2 represent aryl residues and x a lake-forming group in ortho-position to the azo-group.

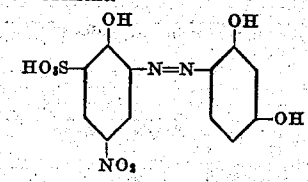
Complex metallic compounds of mono-azo-dyestuffs of this general formula are, for example, aluminium-, titanium-, vanadium-, chromium-, copper-, manganese-, iron-, cobalt-, nickel- and uranium-compounds of azo-dyestuffs which are obtainable by coupling the diazotized ortho-hydroxy- or ortho-alkoxy- or ortho-carboxy-aminobenzenes or ortho-hydroxy- or ortho-alkoxy- or ortho-carboxyaminonaphthalenes or a derivative of one of these, for example, a chlorine-, bromine-, nitro-, sulfo-, carboxy-, methoxy- or ethoxy-substitution product with a dihydroxybenzene or a dihydroxynaphthalene for example 1:3-dihydroxybenzene, 1:3-dihydroxybenzene-4-carboxylic acid, 1:3-dihydroxybenzene-5-carboxylic acid, 1:2:3-trihydroxybenzene-5-carboxylic acid, 1:5-dihydroxynaphthalene, 2:6-dihydroxynaphthalene or 2:7-dihydroxynaphthalene as well as the sulfonic acids and nitro-, alkyl- or halogen-substitution products of any of these. These complex metallic compounds may contain one or more metals.

The complex metallic compounds to be used dye leather, tanned in any manner, for example, vegetable-tanned leather or chrome-leather, very various tints which are very level and excellently fast.

The following examples illustrate the invention:—

Example 1

100 parts of neutralized chrome-leather (box calf, chrome sides, goat, kid and sheep) are tumbled in a drum in a bath of 3-400 parts of water at 60° C. During the rotation of the drum, there is run in, through the hollow axle, a solution (1 part of dyestuff in 50 parts of boiled water) of the nickeliferous dyestuff from the azo-dyestuff of the formula



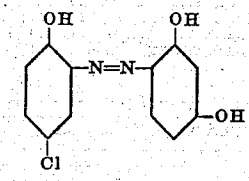
obtainable by coupling diazotized 4-nitro-2-amino-1-hydroxybenzene-6-sulfonic acid with 1:3-dihydroxybenzene. After about 40 minutes the dyestuff has been adsorbed by the leather which is then fatliquored as usual.

The leather thus dyed has a brown shade which is very fast.

The leather is dyed through.

Example 2

Well tumbled vegetable-tanned sheep or goat leather is dyed, as described in Example 1, with the iron compound of the azo-dyestuff of the formula



obtainable by coupling diazotized 4-chloro-2-amino-1-oxybenzene with 1:3-dihydroxybenzene. When the dyeing is completed there is added formic acid amounting to half the weight of the dyestuff used and dyeing is continued for 10–15 minutes; the leather is then rinsed.

The leather thus dyed has a level full brown-olive shade which is very fast to light.

The dyeing can also be conducted by the brushing process with a neutral, cold liquor.

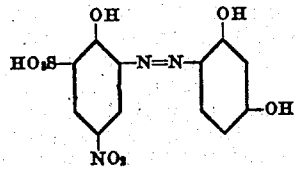
The following table gives a series of the dyestuffs serving for the present process and the colours obtained therewith:—

	Diazo-component	Coupling component	Metal	Colours obtained
(1)	4-nitro-2-amino-1-hydroxybenzene-6-sulfonic acid.	1:3-dihydroxybenzene	Uranium	Yellowish brown.
(2)	4-nitro-2-amino-1-hydroxybenzene	do	Manganese	Brown-orange.
(3)	do	do	80% chromium and 20% nickel.	Janus red.
(4)	do	do	Iron	Yellow-brown.
(5)	do	do	Cobalt	Brown-red.
(6)	do	do	Nickel	Orange.
(7)	4-chloro-2-amino-1-hydroxybenzene	do	do	Do.
(8)	do	do	Cobalt	Bordeaux.
(9)	5-nitro-2-amino-1-hydroxybenzene	do	Iron	Blackish-brown.
(10)	do	do	Cobalt	Bordeaux.
(11)	do	do	Nickel	Pink.
(12)	do	do	Manganese	Brown-orange.
(13)	6-nitro-2-amino-1-hydroxybenzene-4-sulfonic acid.	do	Cobalt	Brown-violet.

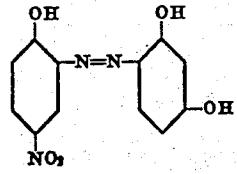
	Diazo-component	Coupling component	Metal	Colours obtained
(14)	6-nitro-2-amino-1-hydroxybenzene-4-sulfonic acid.	1:3-dihydroxybenzene	Nickel	Wine-red.
(15)	do	do	Iron	Blackish-brown.
(16)	do	do	Manganese	Violet.
(17)	4-nitro-2-amino-1-hydroxybenzene-6-sulfonic acid.	do	Iron	Brown.
(18)	do	do	Manganese	Red-brown.
(19)	do	do	Cobalt	Do.
(20)	2-amino-1-hydroxy-benzene-4-sulfonic acid.	do	Iron	Brown-orange.
(21)	do	do	Manganese	Orange-brown.
(22)	do	do	Cobalt	Brown-red.
(23)	do	do	Nickel	Brown-orange.
(24)	do	do	Chromium and cobalt	Bordeaux.
(25)	4-methyl-2-amino-1-hydroxybenzene-6-sulfonic acid.	do	Cobalt	Brown-violet.
(26)	do	do	Uranium	Brown.
(27)	do	do	Nickel	Yellow-brown.
(28)	do	do	Iron	Olive-brown.
(29)	do	do	Manganese	Yellow-brown.
(30)	4-chloro-2-amino-1-hydroxybenzene-5-sulfonic acid.	do	Cobalt	Brown-violet.
(31)	do	do	Nickel	Red-brown.
(32)	do	do	Iron	Brown-olive.
(33)	do	do	Manganese	Red-brown.
(34)	4-chloro-2-amino-1-hydroxybenzene-6-sulfonic acid.	do	Cobalt	Bordeaux.
(35)	do	do	Nickel	Brown-red.
(36)	do	do	Iron	Olive-brown.
(37)	do	do	Manganese	Brown.
(38)	do	do	Uranium	Red-brown.
(39)	5-chloro-2-amino-1-hydroxybenzene-3-sulfonic acid.	do	Iron	Yellowish-brown.
(40)	4-chloro-2-amino-1-hydroxybenzene	do	Chromium	Bordeaux.
(41)	5-nitro-2-amino-1-hydroxybenzene	do	do	Violet.
(42)	6-nitro-2-amino-1-hydroxybenzene-4-sulfonic acid.	do	do	Brown-red.
(43)	do	do	Copper	Violetish-brown.
(44)	4-nitro-2-amino-1-hydroxybenzene	do	50 percent chromium and 50 percent nickel.	Janus red.
(45)	4-chloro-2-amino-1-hydroxybenzene-6-sulfonic acid.	do	Chromium and copper	Brown-red.
(46)	4-nitro-2-amino-1-phenol	1:3-dihydroxybenzene-4-carboxylic acid.	Chromium	Bordeaux-red.
(47)	do	do	Cobalt	Bluish-red.
(48)	do	do	Nickel	Dull red-brown.
(49)	do	do	Manganese	Reddish dark-brown.
(50)	do	do	Iron	Olive-brown.
(51)	5-nitro-2-amino-1-phenol	2:6-dihydroxy-naphthalene	Chromium	Green-grey.
(52)	do	do	Nickel	Dull violet.
(53)	do	do	Manganese	Dark grey.
(54)	do	do	Iron	Beige-grey.
(55)	do	do	Cobalt	Grey-green.
(56)	6-nitro-2-amino-1-phenol-4-sulfonic acid	2:7-dihydroxynaphthalene	do	Reddish-violet.
(57)	do	do	Nickel	Red violet.
(58)	do	do	Manganese	Violet brown.
(59)	do	do	Iron	Brown blue-violet.
(60)	do	do	Chromium	Bluish-violet.
(61)	1-aminobenzene-2-carboxylic acid	2:4-dihydroxybenzene	do	Full orange.
(62)	do	do	Cobalt	Dull light brown.
(63)	do	do	Manganese	Reddish-yellow.
(64)	do	do	Iron	Light brown.
(65)	do	do	Nickel	Reddish-yellow.
(66)	1-amino-2-ethoxybenzene	do	Chromium	Flesh-colored red.
(67)	do	do	Cobalt	Light brown.
(68)	do	do	Nickel	Do.
(69)	do	do	Manganese	Yellow brown.
(70)	do	do	Iron	Reddish-yellow.

The azo-dyestuffs of the above table have the following formulas:—

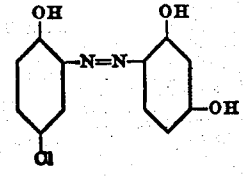
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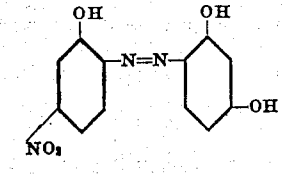
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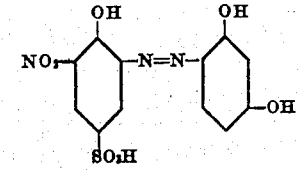
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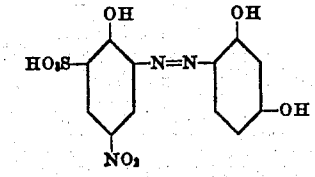
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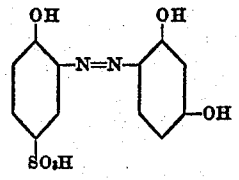
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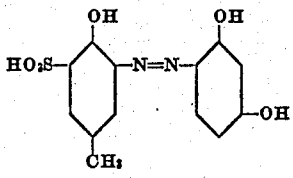
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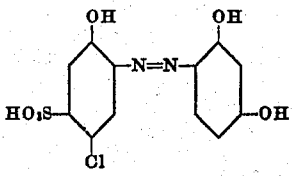
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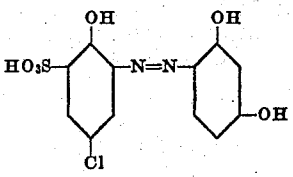
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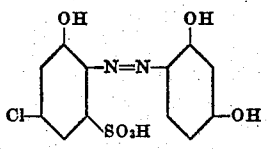
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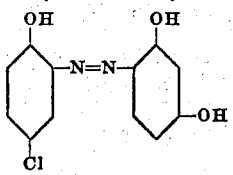
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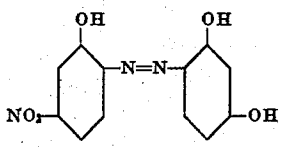
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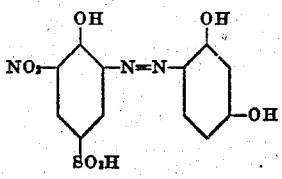
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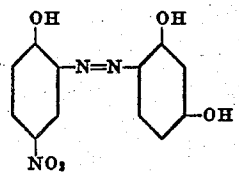
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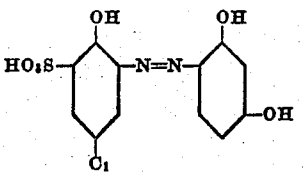
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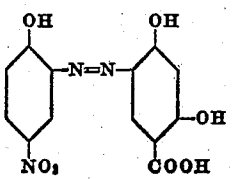
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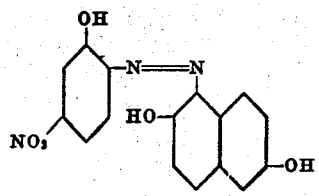
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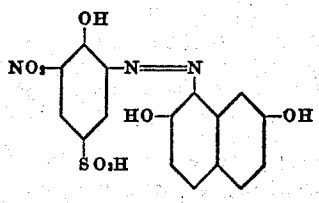
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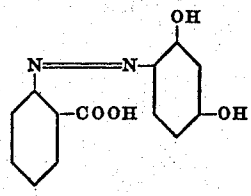
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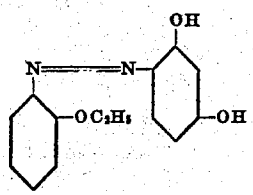
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(61-65)

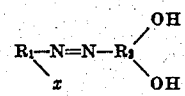


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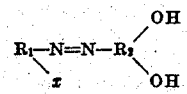
What we claim is:—

1. Process of dyeing leather, consisting in using the complex metal compounds of such monoazo-dyestuffs which correspond to the general formula



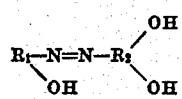
wherein x represents a lake-forming group standing in ortho-position to the azo-bridge, R_1 is a phenyl radical free from a carboxylic acid group in ortho-position to the lake-forming group and R_2 is a phenyl or naphthyl radical.

2. Process of dyeing leather, consisting in using the complex metal compounds of such monoazo-dyestuffs which correspond to the general formula



wherein x represents a lake-forming group standing in ortho-position to the azo-bridge, R_1 is a phenyl radical free from a carboxylic acid group in ortho-position to the lake-forming group, and R_2 is a phenyl radical.

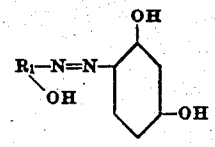
3. Process of dyeing leather, consisting in using the complex metal compounds of such monoazo-dyestuffs which correspond to the general formula



wherein R_1 is a phenyl radical free from a carboxylic acid group in ortho-position to the hydroxyl group, R_2 is a phenyl radical, and the hydroxyl group of the phenyl radical R_1 stands in ortho-position to the azo-bridge.

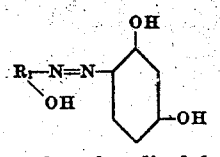
4. Process of dyeing leather, consisting in using

the complex metal compounds of such monoazo-dyestuffs which correspond to the general formula



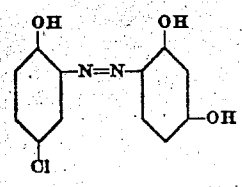
wherein R_1 is a phenyl radical free from a carboxylic acid group in ortho-position to the hydroxyl group, and the hydroxyl group of the phenyl radical R_1 stands in ortho-position to the azo-bridge.

5. Process of dyeing leather, consisting in using the complex iron compounds of such monoazo-dyestuffs which correspond to the general formula

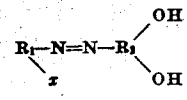


wherein R_1 is a phenyl radical free from a carboxylic acid group in ortho-position to the hydroxyl group, and the hydroxyl group of the phenyl radical R_1 stands in ortho-position to the azo-bridge.

6. Process of dyeing leather, consisting in using the complex iron compound of the monoazo-dyestuff of the formula

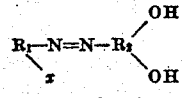


7. As new compositions of matter of yellow, brown, red, violet and green tint, the coloured leather dyed fast with the complex metal compounds of such monoazo-dyestuffs which correspond to the general formula



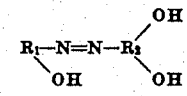
wherein x represents a lake-forming group standing in ortho-position to the azo-bridge, R_1 is a phenyl radical free from a carboxylic acid group in ortho-position to the lake-forming group and R_2 is a phenyl or naphthyl radical.

8. As new compositions of matter of yellow-brown, brown, red and violet tint, the coloured leather dyed fast with the complex metal compounds of such monoazo-dyestuffs which correspond to the general formula



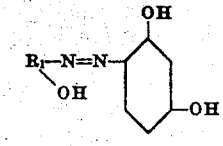
wherein x represents a lake-forming group standing in ortho-position to the azo-bridge, R_1 is a phenyl radical free from a carboxylic acid group in ortho-position to the lake-forming group, and R_2 is a phenyl radical.

9. As new compositions of matter of yellow-brown, brown, red and violet tint, the coloured leather dyed fast with the complex metal compounds of such monoazo-dyestuffs which correspond to the general formula



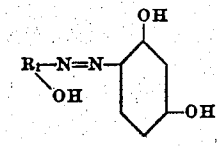
wherein R_1 is a phenyl radical free from a carboxylic acid group in ortho-position to the hydroxyl group, R_2 is a phenyl radical, and the hydroxyl group of the phenyl radical R_1 stands in ortho-position to the azo-bridge.

10. As new compositions of matter of yellow-brown, brown, red and violet tint, the coloured leather dyed fast with the complex metal compounds of such monoazo-dyestuffs which correspond to the general formula



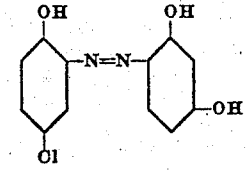
wherein R_1 is a phenyl radical free from a carboxylic acid group in ortho-position to the hydroxyl group, and the hydroxyl group of the phenyl radical R_1 stands in ortho-position to the azo-bridge.

11. As new compositions of matter of brown tint, the coloured leather dyed fast with the complex iron compound of such monoazo-dyestuffs which correspond to the general formula



wherein R_1 is a phenyl radical free from a carboxylic acid group in ortho-position to the hydroxyl group, and the hydroxyl group of the phenyl radical R_1 stands in ortho-position to the azo-bridge.

12. As new composition of matter of brown tint, the coloured leather dyed fast with the complex iron compound of the monoazo-dyestuff of the formula



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