

UNITED STATES PATENT OFFICE

2,273,117

PROCESS OF PRODUCING FAST DYEINGS
AND THE DYED FIBER OBTAINED THEREBY

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14 Claims. (Cl. 8-46)

The present invention relates to a process of producing fast dyeings and to the dyed fiber obtained thereby.

We have found that valuable dyeings of good properties of fastness are obtained on animal fibers and on natural or artificial cellulose fibers as well as on mixtures of animal fibers with cellulose fibers and furthermore on foils by applying to the material to be dyed a compound derived from 1,3,5-triazine and containing either at least one substituted or unsubstituted radical which contains an amino-group capable of being diazotized and at least one radical capable of coupling with diazo-compounds, or a radical which contains simultaneously the amino-group capable of being diazotized and the position capable of coupling with diazo-compounds, as well as at least one group lending solubility in water, then diazotizing the compound and causing it to combine with itself. The self-coupling may be performed or completed, for instance, by adding to the diazo-bath an agent neutralizing the acid or having an alkaline action, after the diazotization is finished, or by passing the goods through a bath having an alkaline action subsequently to the diazotization process.

The radical containing the amino-group capable of being diazotized and the radical capable of coupling with diazo-compounds may be linked to the triazine radical by a carbon-, oxygen-, nitrogen- or sulfur-bond.

As radicals capable of coupling with diazo-compounds there may be mentioned, for instance, the radicals of naphthols, of ortho-hydroxycarboxylic acids, of beta-ketocarboxylic acids, of 2-amino-5-naphthol-7-sulfonic acid, of 2-amino-8-naphthol-6-sulfonic acid, of 1-amino-8-naphthol-3,6-disulfonic acid, of 1-amino-3-dimethylaminobenzene or of pyrazolones. As further radicals the most various inorganic or organic radicals may be used.

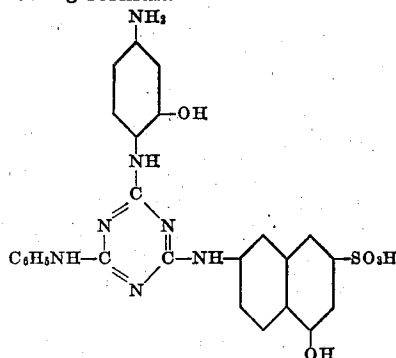
Most of the compounds used in the present process are substantive. Owing to the substantivity of these compounds it is possible to obtain on cellulose and regenerated cellulose as well as on mixtures of these fibers with animal fibers and, furthermore, on sheets from regenerated cellulose dyeings which are distinguished by their good properties of fastness. As far as the condensation products do not contain a sulfonic acid group, they have an affinity for cellulose esters and ethers. By treating the dyeings on the fiber with agents yielding metal, their properties of fastness may be improved.

The condensation products used as parent materials may, for instance, be prepared as described in German patent specification No. 485,185.

The following examples serve to illustrate the

invention, but they are not intended to limit it thereto.

(1) 1 kilo of mixed yarn consisting of 50 parts of wool and 50 parts of staple fiber from viscose is treated for 1 hour at 85° C. in a bath containing per 24 liters of water 40 grams of the compound obtained by reducing the tertiary condensation product from cyanuric chloride, 1 mol of 2-amino-5-naphthol-7-sulfonic acid, 1 mol of 5-nitro-2-aminophenol and 1 mol of aniline, of the following formula



and 80 grams of ammonium sulfate. 600 grams of sodium sulfate, dissolved in 6 liters of water, are then added and the material is further treated for half an hour at 70° C. It is then rinsed, diazotized in the cold for half an hour in a solution containing per 30 liters of water 25 grams of sodium nitrite, 25 grams of sodium dibutyl-naphthalene sulfonate and 75 cc. of hydrochloric acid of 20° Bé. The material is then treated for half an hour in a fresh bath containing per 30 liters of cold water 75 cc. of ammonia of 25 per cent strength and 10 grams of the condensation product from 1 mol of octodecylalcohol and 20 mols of ethyleneoxide, rinsed and dried. A leather-brown dyeing of good properties of fastness is obtained.

When this dyeing is after-treated for one hour at 95° C. with a solution containing per 30 liters of water 20 grams of potassium bichromate and 20 cc. of formic acid of 85 per cent strength, a deeper leather-brown tint of very good properties of fastness is obtained.

When the above leather-brown dyeing, diazotized and developed with ammonia, is after-treated for one hour at 80° C. with 20 grams of copper sulfate and 10 cc. of acetic acid of 50% strength, a greenish leather-brown tint of equally good properties of fastness is obtained.

(2) 1 kilo of wool is treated for 90 minutes at 85° C. with a solution containing per 30 liters of water 40 grams of the compound obtained by reducing the tertiary condensation product from

cyanuric chloride, 1 mol of 2-amino-5-naphthol-7-sulfonic acid, 1 mol of 5-nitro-2-amino-1-methoxybenzene and 1 mol of aniline, with addition of 80 grams of ammonium sulfate, 100 grams of sodium sulfate and 5 grams of the condensation product from 1 mol of octodecylalcohol and 20 mols of ethyleneoxide. The material is then rinsed, diazotized for half an hour with a solution containing per 30 liters of cold water 25 grams of sodium nitrite, 75 cc. of hydrochloric acid of 20° Bé. and 25 grams of sodium dibutyl-naphthalenesulfonate, and developed for half an hour in the cold with 75 cc. of ammonia of 25% strength in 30 liters of water. Finally the material is rinsed. A bluish Bordeaux dyeing is obtained whose good properties of fastness may be essentially improved by treating it in the heat with chromium or copper salts.

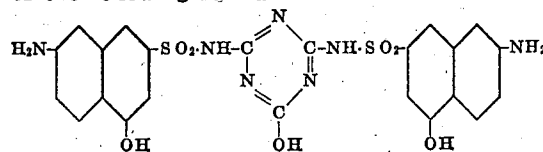
(3) 1 kilo of mixed yarn consisting of 50 parts of wool and 50 parts of staple fiber from cuprammonium cellulose is treated for one hour at 80° C. with a solution containing per 30 liters of water 40 grams of the compound obtained by reducing the tertiary condensation product from cyanuric chloride, 1 mol of 2-amino-5-naphthol-7-sulfonic acid, 1 mol of 5-nitro-2-naphthylamine and 1 mol of aniline, and 600 grams of sodium sulfate. The material is further treated for 30 to 45 minutes at a temperature falling to 65° C., rinsed and diazotized for half an hour with a solution containing per 30 liters of cold water 25 grams of sodium nitrite and 75 cc. of hydrochloric acid of 20° Bé. Thereupon the material is developed for half an hour in a fresh bath containing per 30 liters of cold water 75 cc. of ammonia of 25 per cent strength and 5 grams of the condensation product from 1 mol of octodecylalcohol and 20 mols of ethylene oxide, rinsed and dried. A garnet dyeing is obtained.

Dyeings of similar properties are obtained by using compounds which contain an α -naphthylamine radical or an α -aminoanthraquinone radical instead of the aniline radical.

(4) 1 kilo of mixed yarn consisting of 50 parts of wool and 50 parts of staple fiber from viscose is treated for 45 minutes at 85° C. with a solution containing per 30 liters of water 50 grams of the compound obtained by reducing the tertiary condensation product from cyanuric chloride, 1 mol of 1-amino-8-naphthol-3,6-disulfonic acid, 1 mol of 3-nitraniline and 1 mol of aniline, 80 grams of ammonium sulfate and 600 grams of sodium

sulfate. The material is further treated for 45 minutes at a temperature falling to 70° C., rinsed and diazotized for half an hour with a solution containing per 30 liters of cold water 25 grams of sodium nitrite and 75 cc. of hydrochloric acid of 20° Bé. Thereupon the material is treated for half an hour in the cold in a bath containing per 30 liters of water about 75 cc. of ammonia of 25 per cent strength, rinsed and dried. A Bordeaux dyeing of good properties of fastness is obtained. By an after-treatment with metal salts bluer tints with improved properties of fastness are obtained. When the yarn contains effects from acetate silk, these effects are reserved.

(5) 1 kilo of a mixture consisting of 50 parts of wool and 50 parts of acetyl cellulose is treated for one hour at 60-70° C. in 30 liters of a bath containing 50 grams of a condensation product of the following formula

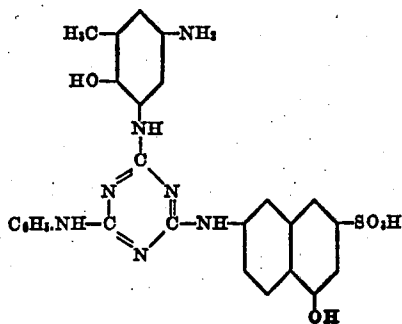


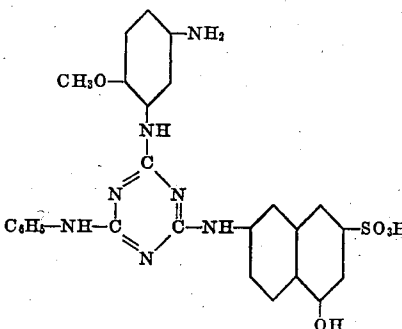
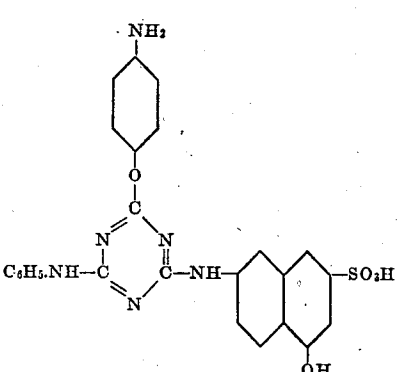
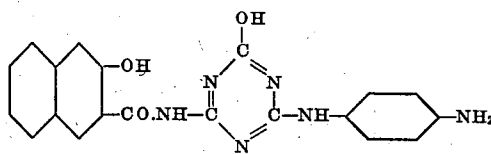
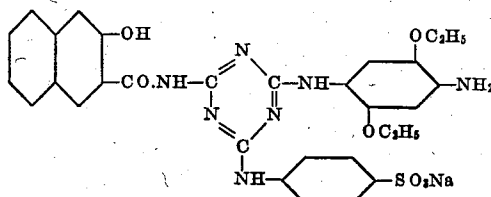
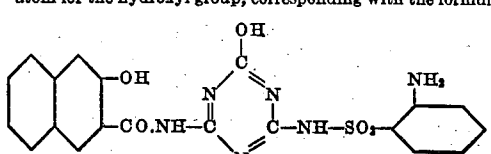
(obtainable by condensing cyanuric chloride with 2 mols of 2-acetyl-amino-5-(benzenesulfonyloxy)-naphthalene-7-sulfamide, subsequently saponifying the acyl groups by means of alkalis and exchanging the third chlorine atom for the hydroxyl group), 80 grams of ammonium sulfate and 200 grams of sodium sulfate. The material is then centrifuged, diazotized for half an hour in a bath containing per 30 liters of water 90 grams of sodium nitrite and 240 cc. of hydrochloric acid of 20° Bé., further treated for 10 minutes in a bath containing in 30 liters of water 150 cc. of ammonia of 25% strength, rinsed and dried. A currant dyeing is obtained.

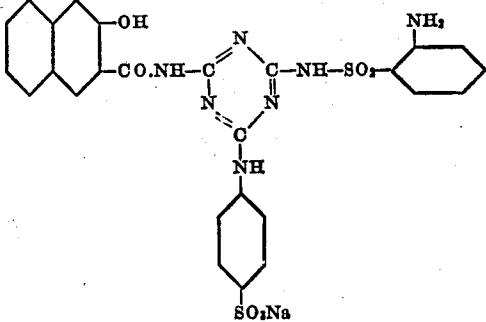
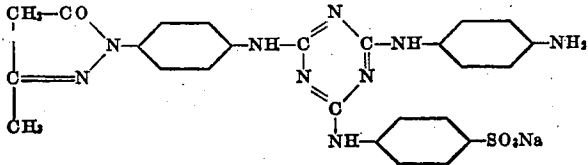
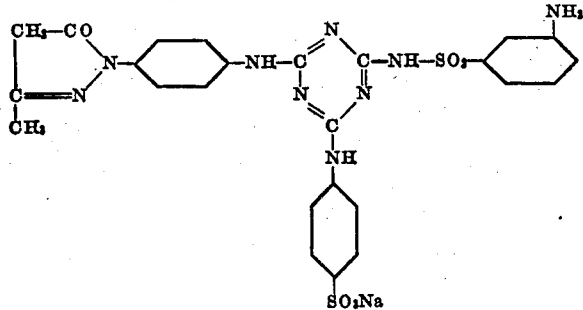
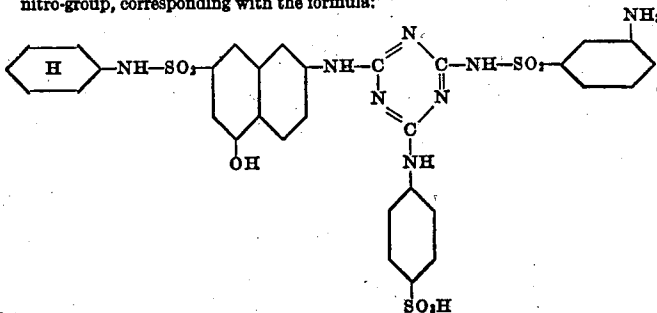
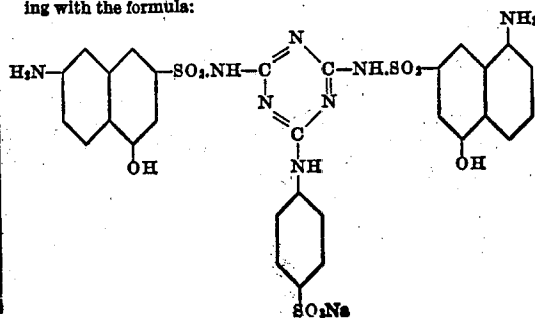
(6) 1 kilo of a sheet consisting of acetyl cellulose is treated for one hour at 60° C. with 50 grams of the condensation product described in Example 5. The material is then squeezed, treated for half an hour in 30 liters of water containing 90 grams of sodium nitrite and 240 cc. of hydrochloric acid of 20° Bé., squeezed again and developed for 10 minutes in 30 liters of water containing 150 cc. of ammonia of 25% strength, rinsed and dried. A currant dyeing is obtained.

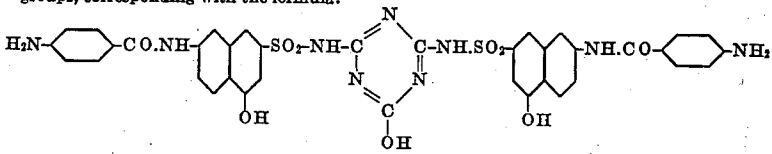
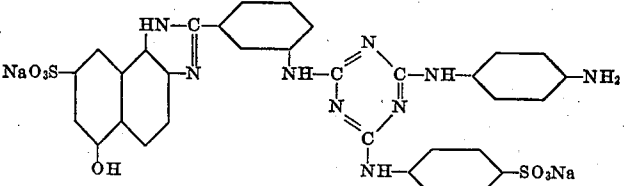
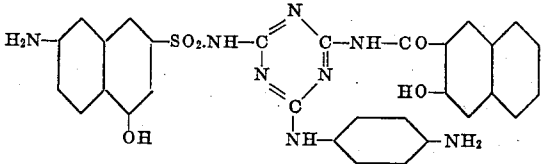
The following table illustrates the shades of a number of other dyeings obtainable by self-coupling according to the present invention:

	Parent component	Shade
1	Condensation product from cyanuric chloride, 1 mol of 2-amino-8-naphthol-6-sulfonic acid, 1 mol of 3-nitraniline and 1 mol of aniline with subsequent reduction.	Very bluish red; after-treated with metal salts: Bordeaux red.
2	Condensation product from cyanuric chloride, 1 mol of 2-amino-5-naphthol-7-sulfonic acid, 1 mol of 5-nitro-3-amino-2-hydroxytoluene and 1 mol of aniline with subsequent reduction, corresponding with the formula:	Leather-brown; after-treated with metal salts: brown.



	Parent component	Shade
3	Condensation product from cyanuric chloride, 1 mol of 2-amino-5-naphthol-7-sulfonic acid, 1 mol of 4-nitro-2-amino-anisole and 1 mol of aniline with subsequent reduction, corresponding with the formula:	Brownish Bordeaux.
		
4	Condensation product from cyanuric chloride, 1 mol of 2-amino-5-naphthol-7-sulfonic acid, 1 mol of 4-nitraniline and 1 mol of aniline with subsequent reduction.	Bordeaux.
5	Condensation product from cyanuric chloride, 1 mol of 2-amino-5-naphthol-7-sulfonic acid, 1 mol of 3-nitraniline and 1 mol of aniline with subsequent reduction.	Red.
6	Condensation product from cyanuric chloride, 1 mol of 2-amino-5-naphthol-7-sulfonic acid, 1 mol of 4-nitrophenol, and 1 mol of aniline with subsequent reduction, corresponding with the formula:	Scarlet; after-chromed: yellowish red; after-treated with copper salts: brown-orange.
		
7	Condensation product from cyanuric chloride, 1 mol of 2-amino-5-naphthol-7-sulfonic acid, 1 mol of 5-amino-3-nitro-2-hydroxy-benzoic acid and 1 mol of aniline with subsequent reduction.	Leather-brown; after-treated with copper salts: leather-brown.
8	Condensation product from cyanuric chloride, 1 mol of 2,3-hydroxynaphthoic acid amide and 1 mol of 1-amino-4-acetylamino-benzene with subsequent alkaline saponification of the acetyl group and exchange of the third chlorine atom for the hydroxyl group, corresponding with the formula:	Bluish red.
		
9	Condensation product from cyanuric chloride, 1 mol of 2,3-hydroxynaphthoic acid amide, 1 mol of 1-amino-4-acetylamino-2,5-diethoxybenzene and 1 mol of 1-aminobenzene-4-sulfonic acid with subsequent alkaline saponification of the acetyl group, corresponding with the formula:	Bordeaux.
		
10	Condensation product from cyanuric chloride, 1 mol of 2,3-hydroxynaphthoic acid amide and 1 mol of 1-acetylamino-benzene-2-sulfamide with subsequent alkaline saponification of the acetyl group and exchange of the third chlorine atom for the hydroxyl group, corresponding with the formula:	Yellowish red.
		

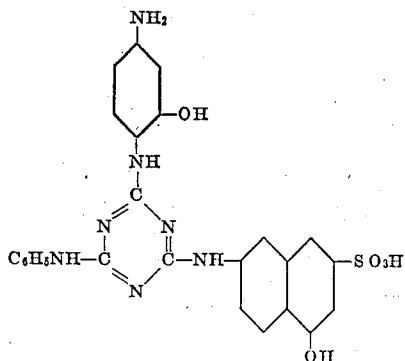
	Parent component	Shade
11	Condensation product from cyanuric chloride, 1 mol of 2,3-hydroxynaphthoic acid amide, 1 mol of 1-acetylaminobenzene-2-sulfamide and 1 mol of 1-aminobenzene-4-sulfonic acid with subsequent alkaline saponification of the acetyl group, corresponding with the formula: 	Yellowish red.
12	Condensation product from cyanuric chloride, 1 mol of 1-(4'-aminophenyl)-3-methyl-5-pyrazolone, 1 mol of 1-amino-4-acetylaminobenzene and 1 mol of sulfanilic acid with subsequent saponification of the acetyl group, corresponding with the formula: 	Brownish yellow.
13	Condensation product from cyanuric chloride, 1 mol of 1-(4'-aminophenyl)-3-methyl-5-pyrazolone, 1 mol of 1-nitrobenzene-3-sulfamide and 1 mol of 1-aminobenzene-4-sulfonic acid with subsequent reduction of the nitro-group, corresponding with the formula: 	Yellow.
14	Condensation product from cyanuric chloride, 1 mol of 2-amino-5-hydroxynaphthalene-7-sulfonyl-cyclohexylamine, 1 mol of 1-nitrobenzene-3-sulfamide and 1 mol of 1-aminobenzene-4-sulfonic acid with subsequent reduction of the nitro-group, corresponding with the formula: 	Yellowish red.
15	Condensation product from cyanuric chloride, 2 mols of 2-acetylaminobenzene-5-(benzenesulfonyloxy)-naphthalene-7-sulfamide and 1 mol of 1-aminobenzene-4-sulfonic acid with subsequent splitting off of the acyl groups, corresponding with the formula: 	Reddish blue.

	Parent component	Shade
16	Condensation product from cyanuric chloride and 2 mols of 2-(4'-nitrobenzoylamino)-5-(benzenesulfonyloxy)-naphthalene-7-sulfamide with subsequent reduction of the nitro-groups and alkaline saponification of the acyl groups, corresponding with the formula: 	Bluish red.
17	Condensation product from cyanuric chloride, 1 mol of 3'-amino-C-phenyl-1,2-(N)-imidazolo-5-hydroxynaphthalene-7-sulfonic acid, 1 mol of 1-amino-4-acetylaminobenzene and 1 mol of 1-aminobenzene-4-sulfonic acid with subsequent splitting off of the acetyl group, corresponding with the following formula: 	Subdued red.
18	Condensation product from cyanuric chloride, 1 mol of 2-acetyl-amino-5-(benzenesulfonyloxy)-naphthalene-7-sulfamide, 1 mol of 2,3-hydroxynaphthoic acid amide and 1 mol of 1-amino-4-acetylaminobenzene with subsequent saponification of the acyl radicals, corresponding with the following formula: 	Bluish red.

We claim:

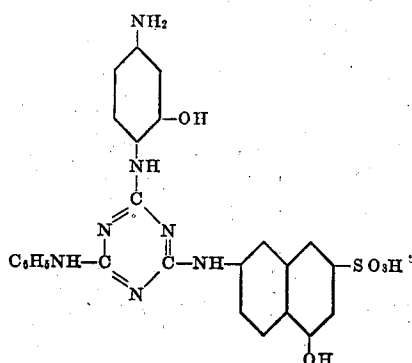
1. Process of producing fast dyeings on fibrous material of the group consisting of cellulose fibers, animal fibers and mixtures of animal fibers with cellulose fibers, which comprises applying to the fiber a compound derived from 1.3.5-triazine containing a group lending solubility in water, a diazotizable amino group and a grouping which is capable of coupling with a diazo compound, then diazotizing the compound on the fiber and causing self-coupling by an alkaline treatment.

2. Process of producing fast leather-brown dyeings on fibrous material of the group consisting of cellulose fibers, animal fibers and mixtures of animal fibers with cellulose fibers, which comprises applying to the fiber the compound obtained by reducing the condensation product from cyanuric chloride, 1 mol of 2-amino-5-naphthol-7-sulfonic acid, 1 mol of 5-nitro-2-aminophenol and 1 mol of aniline, corresponding with the following formula:



then diazotizing the compound on the fiber and causing self-coupling by an alkaline treatment.

3. Process of producing fast leather-brown dyeings on fibrous material of the group consisting of cellulose fibers, animal fibers and mixtures of animal fibers with cellulose fibers, which comprises applying to the fiber the compound obtained by reducing the condensation product from cyanuric chloride, 1 mol of 2-amino-5-naphthol-7-sulfonic acid, 1 mol of 5-nitro-2-aminophenol and 1 mol of aniline, corresponding with the following formula:

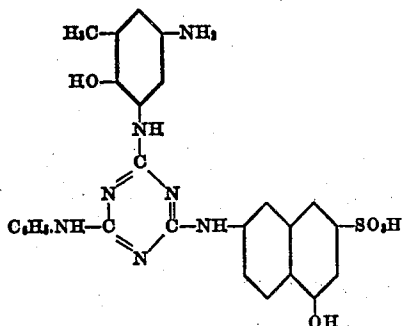


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then diazotizing the compound on the fiber, causing self-coupling by an alkaline treatment and treating the dyeing with an agent yielding metal.

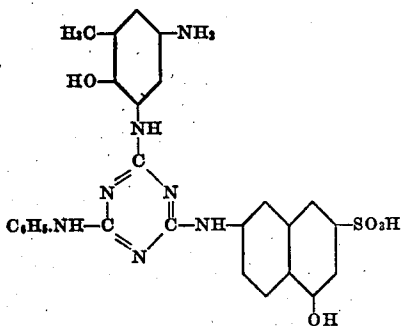
4. Process of producing fast leather-brown dyeings on fibrous material of the group consisting of cellulose fibers, animal fibers and mixtures of animal fibers with cellulose fibers, which comprises applying to the fiber the condensation product from cyanuric chloride, 1 mol of 2-amino-5-naphthol-7-sulfonic acid, 1 mol of 5-nitro-3-amino-2-hydroxytoluene and 1 mol of aniline

with subsequent reduction, corresponding with the formula:



then diazotizing the compound on the fiber and causing self-coupling by an alkaline treatment.

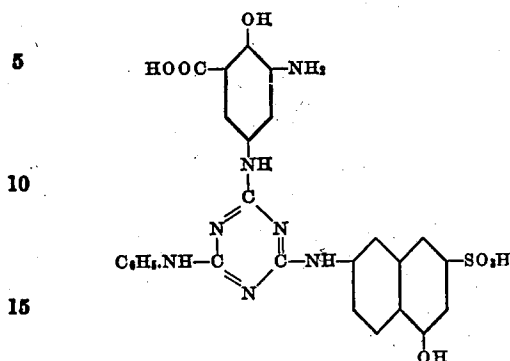
5. Process of producing fast brown dyeings on fibrous material of the group consisting of cellulose fibers, animal fibers and mixtures of animal fibers with cellulose fibers, which comprises applying to the fiber the condensation product from cyanuric chloride, 1 mol of 2-amino-5-naphthol-7-sulfonic acid, 1 mol of 5-nitro-3-amino-2-hydroxytoluene and 1 mol of aniline with subsequent reduction, corresponding with the formula:



then diazotizing the compound on the fiber, causing self-coupling by an alkaline treatment and treating the dyeing with an agent yielding metal.

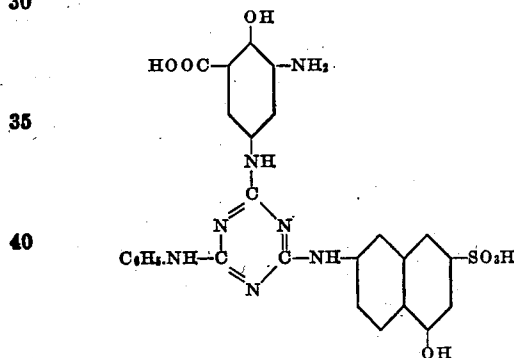
6. Process of producing fast leather-brown dyeings on fibrous material of the group consisting of cellulose fibers, animal fibers and mixtures of animal fibers with cellulose fibers, which comprises applying to the fiber the condensation product from cyanuric chloride, 1 mol of 2-amino-5-naphthol-7-sulfonic acid, 1 mol of 5-amino-3-nitro-2-hydroxy-benzoic acid and 1 mol of ani-

line with subsequent reduction, corresponding with the formula:



then diazotizing the compound on the fiber and causing self-coupling by an alkaline treatment.

7. Process of producing fast leather-brown dyeings on fibrous material of the group consisting of cellulose fibers, animal fibers and mixtures of animal fibers with cellulose fibers, which comprises applying to the fiber the condensation product from cyanuric chloride, 1 mol of 2-amino-5-naphthol-7-sulfonic acid, 1 mol of 5-amino-3-nitro-2-hydroxy-benzoic acid and 1 mol of aniline with subsequent reduction, corresponding with the formula:



then diazotizing the compound on the fiber, causing self-coupling by an alkaline treatment and treating the dyeing with an agent yielding metal.

8. Fiber dyed with an azo-compound obtainable on the fiber by the process claimed in claim 1.

9. Fiber dyed with an azo-compound obtainable on the fiber by the process claimed in claim 2.

10. Fiber dyed with an azo-compound obtainable on the fiber by the process claimed in claim 3.

11. Fiber dyed with an azo-compound obtainable on the fiber by the process claimed in claim 4.

12. Fiber dyed with an azo-compound obtainable on the fiber by the process claimed in claim 5.

13. Fiber dyed with an azo-compound obtainable on the fiber by the process claimed in claim 6.

14. Fiber dyed with an azo-compound obtainable on the fiber by the process claimed in claim 7.

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