

## UNITED STATES PATENT OFFICE

2,183,752

## DYEING OF FURS

Mordecai Mendoza and George Stuart James  
White, Blackley, Manchester, England, assign-  
ors to Imperial Chemical Industries Limited, a  
corporation of Great Britain

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5 Claims. (Cl. 8—10)

This invention relates to the dyeing of furs, pelts, hair and the like material and to new dyestuffs which are applicable for that purpose.

It is among the objects of the invention to provide dyes suitable for dyeing fur. Another object is to provide processes for making the dyes. Other objects are to provide fur dyed with the dye and processes for dyeing the fur. Still other objects will be apparent from the following description.

The objects of the invention are attained generally by coupling either in acid or alkaline medium diazotized picramic acid and a naphthol which is devoid of water-solubilizing groups and is substituted by a group, such as an amino, an hydroxylalkylamino or an acylamino group. In general, the fur to be dyed is immersed in a water solution of the dye which solution is heated to a suitable temperature, such as 60° C. and small amounts of acid, such as acetic and formic acid are added periodically with continued heating until the dyeing is completed.

According to the invention new and valuable colorings are produced on the said materials by dyeing with azo dyestuffs obtained by coupling diazotized picramic acid with an aminonaphthol devoid of sulphonie or carboxylic groups or an N-substituted derivative thereof.

Of the dyestuffs above defined, those obtained by coupling the said diazo component with N-substituted derivatives of naphthols devoid of sulphonie or carboxylic groups are new compounds and the manufacture of these is also a part of the present invention. As coupling components for this purpose we may use, for example, N-alkyl-, N-hydroxyalkyl-, N-aryl- or N-acylaminonaphthols.

Furs, pelts, hair or the like materials which are to be dyed according to the invention may previously be submitted to the so-called "killing process", that is, treatment with alkaline agents such as soda ash, ammonia, lime or caustic soda in order to degrease and purify the materials and make them more receptive of the dyestuffs to be applied. Where such "killing process" is to be followed by a chrome tannage treatment it is desirable first to remove from the materials any residual alkali remaining from the said "killing process". This may conveniently be done by rinsing the materials in a weakly acid bath.

It is advantageous to subject the furs or pelts before dyeing to a treatment (for example, the so-called "chrome tannage" process) with agents which enable the cutaneous portions to withstand the effect of moderately raised dyeing tempera-

tures. Such agents are, for example, chrome alum, alkali-bichromates and basic chromium sulphate. As is well known, furs or pelts which have been submitted to such chrome tannage processes tend to become strongly acid during wet storage. It is advantageous to neutralize this acidity, for example, with sodium bicarbonate, to approximately pH6 to pH7 before commencing the dyeing operation. In the case of freshly chrome-tanned pelts neutralization is not generally necessary.

The furs, pelts, hairs and the like may be submitted, if desired, to a further pre-treatment with agents which increase the dyeing capacity of the hairy portions and promote even dyeing. Among such agents are hypochlorites, as in the so-called "chlorinating" process, or phosphates.

It is preferred to commence the dyeing process under approximately neutral conditions and subsequently to complete the exhaustion of the dyebath by addition of acids such as acetic or formic acids. If desired, inorganic salts, buffering agents, wetting or dispersing agents, may be added to the dyebath. The choice of dyeing temperature is dependent on the materials to be dyed, and the effect desired. When it is desired to obtain a homogeneous shade on unshorn furs which still retain the horny guard hairs, a dyeing temperature of approximately 75°–80° C. is to be preferred. In the case of shorn furs or pelts lower dyeing temperatures, for example, 55°–60° C. may conveniently be used to obtain homogeneous shades. Lower dyeing temperatures than those indicated may be used but at temperatures below 40° C. there is an increasing tendency for a larger proportion of dyestuff to be taken up preferentially by the cutaneous parts of the fur or pelt. At temperatures higher than 80° C. the possibility of damage to the cutaneous parts is increased and a temperature of 90° C. should not be exceeded.

The colorings obtained according to the invention are characterized by solidity and evenness of shade and good fastness to light and rubbing.

The invention is illustrated but not limited by the following examples in which the parts are by weight.

*Example I*

The diazo derivative obtained in customary manner from 19.9 parts of picramic acid (4:6-dinitro-2-aminophenol) is added with stirring to a solution of 20.3 parts of 1- $\beta$ -hydroxyethyl-amino-5-naphthol (see Patent 2,078,960 dated



May 4, 1937) in 300 parts of water containing 12 parts of caustic soda at 10° C.

Coupling, which results in the formation of a deep brown solution, is allowed to complete in the course of 3 to 4 hours at the end of which time the dyestuff is isolated by adding 20% (weight for volume) of common salt. The new dyestuff is then filtered off, dried and ground. It forms a dark brown powder readily soluble in water to a dark brown solution and possesses good affinity for fur.

By using 18.7 parts of 1-dimethylamino-5-naphthol in the above example in place of 1-hydroxyethylamino-5-naphthol and proceeding in like manner, there is obtained a new dyestuff of similar good affinity for fur.

If in place of the 1-β-hydroxyethylamino-5-naphthol 20.1 parts of 1-acetylamino-5-naphthol are used, a further new dyestuff is obtained which gives Bordeaux colorings on fur.

#### Example II

The diazo derivative obtained in the customary manner from 19.9 parts of picramic acid (4:6-dinitro-2-aminophenol) is added with stirring to a cooled solution of 20.3 parts of 1-β-hydroxyethylamino-5-naphthol in 500 parts of water containing 10 parts of 36.5% hydrochloric acid. The temperature of the mixture is adjusted to 10° C. by addition of ice if necessary and after stirring for 1 hour the acidity to Congo Red paper is removed by adding the requisite amount of sodium acetate. Coupling is then allowed to complete in the course of 12 hours, keeping the temperature at 10° C. At the end of this time 25 parts of 40% caustic soda liquor are added dropwise during 15 minutes whereby the reaction is made alkaline to litmus paper.

After stirring for a further 15 minutes the new dyestuff is filtered off, pressed thoroughly, dried and ground. It forms a dark grey powder soluble in water and yields greyish shades on fur which build up to black in heavier concentration.

#### Example III

100 parts (damp weight) of long-haired, chrome-tanned white rabbit are entered at 40° C. into a dyebath consisting of 1 part of the monoazo dyestuff

Picramic acid—1:5-aminonaphthol (coupled in alkaline medium)

dissolved in 3000 parts of water.

During 20 minutes the temperature is raised to 75° C. After 30 minutes at this temperature 1 to 1.5 parts of glacial acetic acid are added, the dyeing continued for a further 30 minutes, after which 0.5 part of 80% aqueous formic acid is added and after a further 40 minutes at 75° C. the dyeing operation is complete. The dyed fur is removed and after drying is drummed in hardwood sawdust for 2 to 4 hours. The resulting fur is colored in a nigger brown shade on the under wool, the guard hairs and the skin.

#### Example IV

100 parts (damp weight) of shorn chrome-tanned white rabbit are entered at 40° C. into a dyebath consisting of 1 part of the monoazo dyestuff

Picramic acid—1-β-hydroxyethylamino-5-naphthol (obtained as in Example I above)

dissolved in 3000 parts of water. During 20 minutes the temperature is raised to 55°–60° C.

This temperature is maintained during the sub-

sequent additions of glacial acetic and 80% formic acids at periods corresponding to those specified in Example III and the dyed fur is subsequently dried and drummed in sawdust. The fur is colored a reddish nigger brown shade which has good fastness to rubbing.

Further examples of shades obtainable according to the invention are given in the following table.

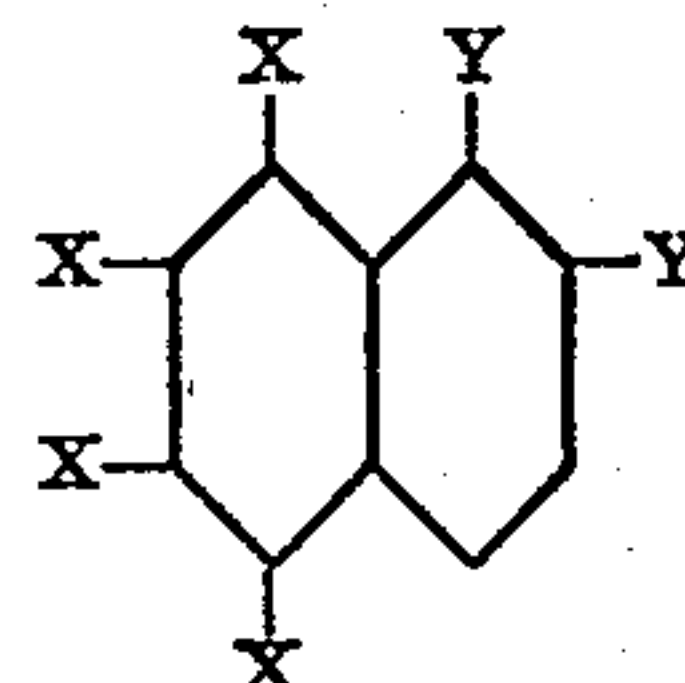
Diazo component	Coupling component	Coupling medium	Shade on fur
Picramic acid.....	1-dimethylamino-5-naphthol.	Alkaline..	Dull purple.
Do.....	1-acetylamino-5-naphthol.	do.....	Bordeaux.
Do.....	1-amino-7-naphthol.....	do.....	Greenish grey.
Do.....	1-acetylamino-7-naphthol.	do.....	Violet.
Do.....	1-β-hydroxyethylamino-7-naphthol.	do.....	Greenish grey.
Do.....	2-amino-5-naphthol.....	do.....	Dull red.
Do.....	2-amino-7-naphthol.....	do.....	Maroon.
Do.....	2-phenylamino-7-naphthol.	do.....	Violet.
Do.....	1:5-aminonaphthol.....	Acid.....	Reddish grey.
Do.....	1:6-aminonaphthol.....	do.....	Greenish grey.
Do.....	1-β-hydroxyethylamino-6-naphthol.	do.....	Greenish blue.
Do.....	1-7-aminonaphthol.....	do.....	Grey.
Do.....	1-β-hydroxyethylamino-7-naphthol.	do.....	Blue.
Do.....	2:7-aminonaphthol.....	do.....	Red.

It is to be understood that other substituent groups can be used, namely: 1-alkylamino groups, such as 1-propylamino and 1-butylamino; other 1-arylamino groups, such as 1-naphthylamino; other 1-acylamino groups, such as 1-propionylamino, butyrylamino, 1-benzoylamino and other aroylamino groups; 1- and 2-hydroxyalkylamino groups, such as 1- and 2-hydroxypropylamino and 1- and 2-hydroxybutylamino; 1-cycloaliphaticamino groups, such as cyclohexylamino; and 1-aralkyl groups, such as benzylamino. In these substituted naphthols the hydroxy may be in any position so long as it does not interfere with the coupling. In general it may be in the 5, 6, 7 or 8 position with respect to the substituted groups.

In the dyeing of furs, the dyes from the naphthols substituted by the described groups in both the 1- and 2- positions can be used advantageously in accordance with the described process of dyeing.

We claim:

1. The process of dyeing fur which comprises pre-treating the fur by the chrome tannage process, giving the fur a pH value between 6 and 7, immersing the pretreated fur in an approximately neutral solution of a dye heated to about 40° to about 90° C., said dyes being made by coupling diazotized 4:6-dinitro-2-aminophenol and a coupling component represented by the formula



in which one X is hydroxy and the other X's are hydrogen and one Y is hydrogen and the other Y is one of the group consisting of amino, NH-alkyl, NH-aryl, NH-hydroxyalkyl, dialkylamino and NH-acyl; and continuing the immersion with periodic additions of small amounts



of organic acids until the dyeing of the fur is completed.

2. The process of dyeing fur which comprises immersing the fur in an approximately neutral solution of a dye heated from about 40° C. to about 90° C., said dye being made by coupling in alkaline reaction medium diazotized 4-6-dinitro-2-aminophenol with an N- $\beta$ -hydroxyalkylamino-naphthol which is devoid of sulphonic and carboxylic acid groups, and continuing the treatment with periodic additions of small amounts of organic acids until the dyeing of the fur is completed.

3. The process of dyeing fur which comprises immersing the fur in an approximately neutral solution of a dyestuff heated from about 40° C. to about 90° C., said dyestuff being made by coupling diazotized 4-6-dinitro-2-aminophenol with an N- $\beta$ -hydroxyalkylamino-naphthol which is devoid of sulphonic acid and carboxylic acid groups, and continuing the treatment with periodic additions of small amounts of organic acids until the dyeing of the fur is completed.

4. The process of dyeing fur which comprises immersing fur in an approximately neutral solution of a dyestuff heated from about 40° C. to about 90° C., said dyestuff being made by coupling in acid reaction medium diazotized 4-6-dinitro-2-aminophenol with an N-hydroxyalkylamino- which is devoid of sulphonic acid and carboxylic acid groups, and continuing the treatment with periodic additions of small amounts of organic acids until the dyeing of the fur is completed.

5. The process of dyeing fur which comprises immersing the fur in an approximately neutral solution of a dye heated to about 40° to about 90° C., said dye being made by coupling diazotized 4:6-dinitro-2-aminophenol with 1-N- $\beta$ -hydroxyalkylamino-5-naphthol which is devoid of sulphonic acid and carboxylic acid groups.

MORDECAI MENDOZA.  
GEORGE STUART JAMES WHITE.

CERTIFICATE OF CORRECTION.

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December 19, 1939.

MORDECAI MENDOZA, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 5, claim 4, strike out the words "in acid reaction medium" and insert the same after "coupling" in first column, line 18, claim 3; second column, line 7, claim 4, for "amino-" read amino-naphthol; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office..

Signed and sealed this 13th day of February, A. D. 1940.

(Seal)

Henry Van Arsdale,  
Acting Commissioner of Patents.