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PROCESS OF DYEING FUR SKINS WITH
INSOLUBLE AZO DYESTUFFS

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My present invention relates to a process of dyeing furskins with insoluble azo dyestuffs, and to the material dyed by this process. This application is a continuation-in-part of my co-pending application Serial No. 76,643, filed February 15, 1949, now abandoned.

Furskins are generally dyed with oxidation dyestuffs, with acid or basic dyestuffs, or with certain water-insoluble dyestuffs of the azo or anthraquinone series that are applied in suitable suspensions (e. g. "Celliton" and "Celliton Fast" dyestuffs).

Before dyeing there is usually applied a complicated pre-treatment process comprising:

(a) The dressing, as a rule a treatment with a pickle, mostly with a solution of sulfuric acid and sodium chloride, followed by a liquoring with an oil or fat emulsion (so-called Leipzig dressing);

(b) The so-called killing, i. e. a treatment with alkalis, in order to neutralize the acid previously used;

(c) A treatment with oxidizing agents;

(d) A mordanting with metal salt solutions.

Great experience is required for producing the dyeings with oxidation dyestuffs, particularly so if mixtures of dyestuffs are employed. Such mixtures generally do not yield the normal mixed shades to be expected, but often greatly differing shades with formation of complicated dyestuff compounds.

The mordanting with metal salts must be very carefully controlled so that a uniform covering of the long coarse hairs and the short undercoat of hair is guaranteed. In many cases, particularly with black, a special dyeing by blending or saddening of the long hairs or tips, i. e. by brushing on a concentrated dyestuff solution, is indispensable.

The dyeings with oxidation dyestuffs often have an unsatisfactory fastness to storing, i. e. in the course of time they alter their shades by the action of the atmospheric oxygen. Moreover, it is often necessary to prolong the clearing, namely the usual mechanical after-treatment with hardwood sawdust or sand, in order to attain a sufficient fastness to rubbing.

At the dyeing temperatures normally applied, basic and acid dyestuffs have only a slight affinity to the hair. Therefore, they yield only weak dyeings. For the production of deeper shades, higher temperatures must be applied, which again make a preliminary tannage of the skin with chromium salts necessary, as only chrome-tanned leathers have a sufficient sta-

bility to elevated temperatures. In addition, in order to enhance the affinity of the hair for the dyestuff, a chlorination is effected before the dyeing operation.

"Celliton" and "Celliton Fast" dyestuffs are suitable only for the production of delicate shades on a light ground.

Now I have found that all these complicated processes and the disadvantages involved thereby can be avoided by producing fast dyeings of water-insoluble azo dyestuffs on furskins in the following simple way. The ray, fleshed furskins are treated, either immediately or after the dressing and killing operations, if desired after a formaldehyde tanning, with a strongly alkaline solution of a coupling component having at least one hydroxy group and being capable of coupling, i. e. having a free unsubstituted hydrogen atom, in ortho-position to the hydroxy group, in the presence of formaldehyde, and developing the dyestuff by a subsequent treatment with a diazonium compound.

Fancy effects may also be produced by locally brushing, scraping on, spraying or printing on the skins a solution of the coupling components containing caustic alkali, formaldehyde, if desired solvents, wetting and thickening agents, and developing the dyestuff at the pre-treated places by a treatment with a diazonium compound.

Multicolored fancy effects may be produced by applying different coupling components side by side, or by applying locally on a material pre-treated with a coupling component, a second coupling component and then developing with a solution of a diazonium salt.

The new process not only avoids the complicated steps and other inconveniences of the processes hitherto used, but also offers advantages which highly surpass the results obtained with the processes hitherto known.

The dyeings produced by the process of this invention are distinguished by their depth. The dyed hairs preserve their natural gloss. The insoluble azo dyestuffs are very stable to the action of atmospheric oxygen and other reactive constituents of the atmosphere and, therefore, very fast to storing. If the coupling and diazo components are suitably selected they are also very fast to light. In view of the good fastness of the dyeings to acids and alkalis, it is possible to carry out the dressing after the dyeing process, whereby some of the hitherto usual operations may be shortened or omitted. Moreover, this method of working permits the pro-

duction of light-colored skins as the penetration of the dyestuffs into the skin is but small, and the undyed skin is exposed by the subsequent removal of a thin layer from the back of the skin. The good covering of the long hairs in a single operation according to the process of this invention, renders a blending or saddening of the long hairs or tips in most cases superfluous.

As a higher alkali concentration in the treatment with the coupling components facilitates the coupling whereby the dyestuff on the hairs is formed—and so does a slight increase of the bath temperatures—it is necessary during the treatment with the coupling components to use alkali concentrations corresponding to those usual on cellulose fibers, in order to obtain a good tipping of the long hairs. In practice I have found that one should use solutions of coupling components having a pH value above 11. These higher alkali concentrations, which usually would injure the skin and loosen the hair, even if chrome tanned furskins are used, may safely be applied, provided that formaldehyde is added to the solution of the coupling component. In practice I have found that one should use at least 2 mols of formaldehyde for each mol of the coupling component. Preferably I employ solutions containing from $\frac{1}{10}$ to $\frac{1}{3}$ mol per liter of caustic alkali in excess of that required to form a salt of the coupling component, and from 3 to 150 mols of formaldehyde for each mol of the coupling component.

If the dyeing is produced on dressed skins, for instance strongly acid Leipzig dressing, a thorough preliminary treatment with agents of alkaline reaction, such as sodium carbonate solution or caustic alkali solutions, is necessary for producing the alkaline medium required for the dyeing process. Diazonium compounds that contain strongly negative substituents, such as the nitro, cyano, trifluoromethyl and sulfoalkyl groups, penetrate the natural hair with difficulty. They may nevertheless be used in the process of this invention, if the hair is treated, before dyeing, with agents yielding oxygen such as hydrogen peroxide and sodium peroxide, or with a solution of an alkali or alkaline earth metal hypochlorite such as sodium hypochlorite and hypochlorite of lime.

Coupling components which may be used in the process of this invention are for instance: the hydroxy compounds, capable of coupling in ortho-position, of the benzene, naphthalene, anthracene series, and of carbocyclic or heterocyclic ring systems of lower and higher order and substitution products of such compounds, such as carboxylic acid amides, alkylamides and arylamides, acylamino compounds of hydroxy compounds, or the like. Preferably I employ arylamides of the hydroxy-naphthalene, hydroxycarbazole, hydroxy-benzocarbazole and hydroxy-anthracene series.

Diazonium compounds suitable for the process of this invention are, for instance, the diazonium compounds of benzene, diphenyl, terphenyl, naphthalene, carbazole, quinoline, indole, indazole, fluorene, diphenylene oxide, azobenzene, and their substitution products. I prefer to use those diazonium compounds which are free from strongly negative substituents and which contain a single diazonium group.

The diazonium compounds are usually applied at normal temperature. When using certain classes of such compounds, such as diazonium compounds of diphenylamines, it is however use-

ful to work at an elevated temperature. In this case the coupling is improved by an addition of chromium acetate or monosodium phosphate.

The following examples serve to illustrate the process of the invention without in any way limiting it to the products and working conditions specified.

Example 1

Raw, fleshed rabbit furskins are treated, in a liquor ratio 1:2 (one skin per 2 liters), at about 35° C. for 2 hours in a bath containing per liter of bath

3 grams of the dry product obtained from sulfite waste liquor after freeing it from iron and calcium salts,
1.5 grams calcined sodium carbonate,
5 cc. formaldehyde 30%
20 grams of sodium chloride.

There are then added per liter of bath

12 cc. caustic soda solution 38° Bé. and
2.5 grams 1-(Bz-2'-hydroxy-1''2''-benzocarbazole-3'-carbonylamino)-4-methoxybenzene,

dissolved with

5 cc. denaturated alcohol,
1.25 cc. caustic soda solution 38° Bé.,
2.5 cc. water, and
1.25 cc. formaldehyde 30%

Treatment is continued at about 35° C. for 1 hour. The furskins are then hydroextracted and treated in a cold bath containing per liter

2 grams 4-amino-3,5-dichlorophenyl-1-diazonium chloride in the form of the zinc chloride double salt, adjusted to neutral reaction with sodium bicarbonate, and

0.2 gram of the condensation product of dodecyl alcohol and 20 mols of ethylene oxide.

The material is well rinsed. The black dyed furskins are then placed overnight into a pickle solution containing per liter of water

110 grams sodium chloride,
10 grams ammonium chloride,
10 grams concentrated sulfuric acid.

They are coated on the skin side in the usual manner with a fat-liquor, dried, drummed with sawdust and finished. In this manner there is obtained a black dyeing that possesses excellent fastness to storing, light and rubbing, while the skins possess an excellent hand and elasticity.

Example 2

Dressed rabbit furskins (Leipzig dressing) are killed by placing them overnight in a solution of 10 grams of sodium carbonate per liter. At a liquor ratio of 1:2 they are treated at 38° C. for 2 hours with a solution containing per liter

1 gram 1-(2'-hydroxycarbazole - 3' - carbonylamino)-4-chlorobenzene,
5 grams sodium Turkey red oil 50%,
12 cc. caustic soda solution 38° Bé.,
6 cc. formaldehyde 30%,
20 grams sodium chloride.

The furskins are well squeezed and treated for half an hour in a bath containing per liter

2 grams of the diazonium compound of 1-amino-4-chloro-2-methylbenzene, adjusted with sodium bicarbonate solution to a neutral reaction, and

0.2 gram of the condensation product of dodecyl alcohol and 20 mols of ethylene oxide.

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The brown-colored furskins are well rinsed and finished in the usual manner. The resultant furskins are characterized by the same excellent properties as described in Example 1.

Example 3

Fleshed rabbit furskins are treated for 2 hours at 35° C. in a bath containing per liter

1 gram oleylmethyltaurine,
4 cc. sulfite waste liquor,
1.5 grams sodium carbonate, and
20 grams sodium chloride,
10 cc. formaldehyde 30%

There are then added

12 cc. caustic soda solution 38° Bé. and
3 grams 1-(2'.3'-hydroxynaphthoylamino) - 2 -
omega-dimethylaminomethylbenzene, dissolved
in
10 cc. ethyl alcohol,
1.5 cc. caustic soda solution 38° Bé.,
3 cc. water, and
1.5 cc. formaldehyde 30%,

and treatment is continued for 1 hour. The furskins are hydro-extracted, and developed during half an hour to a dark-brown shade in a cold solution containing per liter about 2 grams 4-amino-3,5-dichloro-1-phenyldiazonium chloride in the form of the zinc chloride double salt, adjusted to a neutral reaction by the addition of sodium bicarbonate.

The furskins are finished in the manner described in Example 1 by pickling, fat-liquoring and clearing or sawdusting.

Example 4

Rabbit furskins, lightly tanned with formaldehyde and dressed with a pickle of sodium chloride and sulfuric acid, are killed, before dyeing, with 10 grams of sodium carbonate per liter and brushed with a mixture of

500 cc. hydrogen peroxide 3% and
400 cc. of a solution of 1 part of ammonia solution 25% and 10 parts of water.

After one hour they are dried. After soaking, the furskins in the proportion of 1 furskin to 2 liters of water, are treated in a solution containing per liter 2 grams 1-(bz-2'-hydroxy-1''-2''-benzocarbazole-3'-carboylamino) - 4 - methoxybenzene, dissolved with

5 grams denaturated alcohol,
2 cc. caustic soda solution 38° Bé.,
4 grams water, and
2 cc. formaldehyde 30%,

which is added to a solution of

10 grams Turkey red oil 50%,
12.5 cc. caustic soda solution 38° Bé., and
10 cc. formaldehyde 30%.

After one hour's treatment at 36-33° C. the furskins are hydroextracted. Development is effected in a solution containing per liter about

2 grams 2-methoxy-4-nitro-1-phenyldiazonium chloride in the form of the zinc chloride double salt, and
0.1 gram of the condensation product of dodecyl alcohol and 20 mols of ethylene oxide.

The black dyeings are rinsed, acidified, the furskin is brushed with sodium chloride solution, dried and finished. Other kinds of furskin, such

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as lamb, calf, etc., may be dyed in an analogous manner.

Example 5

For producing fancy effects on furskins, rabbit furskins are locally brushed or sprayed with a dyestuff solution containing per kilogram

10 grams 1-(Bz-2'-hydroxy-1''-2''-benzocarbazole-3'-carboylamino) - 2 - methyl-4-methoxybenzene,
60 grams ethylenediglycol,
34 cc. caustic soda solution 38° Bé.,
30 grams Monopol Brilliant Oil (sodium salt of sulfonated castor-oil)
15 10 cc. formaldehyde 30%, and
300 grams of a tragacanth thickening 50:1000 and water to yield 1000 grams.

The furskins are stored for 2 hours in a moist room at about 35° C. to 40° C. and then developed in an aqueous bath containing per liter about

1.5 grams 4-amino - 3,5 - dichlorophenyl - 1 - diazonium chloride and
25 4 grams monosodium phosphate.

Pickling is carried out in a pickle of sodium chloride and sulfuric acid, and the furskins are finished in the usual manner. Black fancy effects are obtained at the treated parts of the furskins.

Example 6

Fleshed lamb furskins if desired, after a combined chrome tanning, are treated for 1 hour in a bath containing per liter water of 38-40° C.

1 gram oleylmethyltaurine,
4 cc. sulfite waste liquor,
40 1.5 grams sodium carbonate,
10 cc. formaldehyde 30%

There are then added

12.5 cc. caustic soda solution 38° Bé. and
45 2.5 grams 1-(Bz-2'-hydroxy-1''-2''-benzocarbazole-3'-carboylamino) - 4 - methoxybenzene,

dissolved with

5 cc. denaturated alcohol,
50 1.25 cc. caustic soda solution 38° Bé.,
2.5 cc. water, and
1.25 cc. formaldehyde 30%.

Treatment is continued at about 38° C. for 1 hour. The furskins are then rinsed in a solution containing per liter 50 grams of common salt and 3 grams of sodium carbonate or bicarbonate, the excess rinsing solution is drained off, and the skins are treated in a bath at 40° C. containing per liter of water

3 grams 4'-methoxy-diphenylamine-4-diazonium chloride
1 gram of the condensation product of dodecyl alcohol and 20 mols of ethylene oxide, and
65 3.5 grams chromium acetate (greenish).

The black furskins are well rinsed, treated with a solution of 2 grams of sulfuric acid and 60 grams of common salt per liter water of 40° C., again rinsed, dried and finished in the usual manner.

The following table gives some further examples of a wide range of shades which may be produced on furskins by the process of this invention.

Coupling component	Diazonium compound	Shade
1-hydroxynaphthalene-4-diethylsulfonamide	4-chloro-2-methylphenyl-1-diazonium chloride	red.
1-(2',3'-hydroxynaphthoyl-amino)-4-chloro-2-methylbenzene	do	Do.
Do	naphthalene-2-diazonium-chloride	Do.
Do	naphthalene-1-diazonium chloride	wine-red.
1-(2'-hydroxyanthracene-3'-carbonylamino)-2-methylbenzene	4-amino-3,5-dichlorophenyl-1-diazonium chloride	black.
2-(2',6'-dihydroxynaphthalene-3'-carbonylamino)-naphthalene	do	dark brown.
4-hydroxynaphthylphenylketone	4-chloro-2-methylphenyl-1-diazonium chloride	red.
2-hydroxynaphthalene	do	Do.
1-(2'-hydroxycarbazole-3'-carbonylamino)-4-aminobenzene	do	brown.
1-(2'-hydroxycarbazole-3'-carbonylamino)-4-chlorobenzene	2-chlorophenyldiazonium chloride	Do.
Do	3-chlorophenyl-diazonium chloride	Do.
Do	5-chloro-2-methylphenyl-diazonium chloride	Do.
Do	3-chloro-2-methylphenyl-diazonium chloride	Do.
Do	5-chloro-2-methoxyphenyl-diazonium chloride	Do.
Do	4-diphenylamine diazonium chloride	dark brown.
1-(Bz-2'-hydroxy-1'',2''-benzocarbazole-3'-carbonyl-amino)-4-methoxybenzene	2-chlorophenyl-diazonium chloride	violet brown.
Do	3-chlorophenyl-diazonium chloride	dark brown.
Do	5-chloro-2-methyl-phenyl-diazonium chloride	Do.
Do	4-chloro-2-methylphenyl-diazonium chloride	Do.
Do	5-chloro-2-methoxy-phenyldiazonium chloride	Do.
Do	2,5-dichlorophenyl-diazonium chloride	Do.
1-(2',3'-hydroxynaphthoylamino)-ethanol-(2)	4-amino-3,5-dichloro-phenyldiazonium chloride	brown.
2',3'-hydroxynaphthoylamino-n-butane	do	Do.
2-hydroxy-3-benzoylamino-naphthalene	4-chloro-2-methylphenyldiazonium chloride	red.
2-hydroxy-5,6,7,8-tetra-hydronaphthalene	do	yellow brown.
2-hydroxycarbazole	do	brown.
3-hydroxydiphenyleneoxide	do	orange.
1-(2',3'-hydroxy-5',6',7',8'-tetrahydronaphthoylamino)-naphthalene	do	red brown.
1-(2',3'-hydroxynaphthoylamino)-phenyl-6-ethanol	do	red.
2',3'-hydroxynaphthoylamino-N-ethylhexylamine	do	Do.
2',3'-hydroxynaphthoylamino-benzene	do	Do.
6-hydroxynaphthoquinolindine	do	brown orange.
5-hydroxyquinoline	do	orange.
1-(Bz-2'-hydroxy-1'',2''-benzocarbazole-3'-carbonyl-amino)-4-methoxybenzene	azobenzene-4-diazonium chloride	black.
1-(2'-hydroxycarbazole-3'-carbonylamino)-4-chlorobenzene	do	red brown.
Do	carbazole-2-diazonium chloride	brown.
1-(Bz-2'-hydroxy-1'',2''-benzocarbazole-3'-carbonylamino)-4-methoxybenzene	do	black.
1-(2',3'-hydroxynaphthoylamino)-4-chloro-2-methylbenzene	do	purple.
Do	quinolinediazonium chloride	red.
6-benzoylamino-2-naphthol	4-chloro-2-methylphenyldiazonium chloride	Do.
Do	3-chlorophenyldiazonium chloride	orange.
Do	4-amino-3,5-dichlorophenyldiazonium chloride	red brown.
5-benzoylamino-1-naphthol	4-chloro-2-methylphenyldiazonium chloride	brown.
Do	3-chlorophenyldiazonium chloride	Do.
Do	4-amino-3,5-dichlorophenyldiazonium chloride	Do.
3-benzoylamino-2-naphthol	5-chloro-2-methylphenyldiazonium chloride	red.
Do	4-amino-3,5-dichlorophenyldiazonium chloride	wine-red.
Do	3-chlorophenyl-1-diazonium borofluoride	orange.
2-(1'-hydroxy-4',5'-dimethylbenzene-2'-carbonylamino)-naphthalene	4-chloro-2-methylphenyldiazonium chloride	orange brown.
2-(1'-hydroxy-4'-methylbenzene-2'-carbonylamino)-naphthalene	do	orange yellow.
bis-4,4'-(1'-hydroxy-4'',5''-dimethylbenzene-2''-carbonylamino)-3,3'-dimethoxydiphenyl	4-chloro-2-methylphenyl diazonium chloride	brown.
3-hydroxy-4'-chlorodiphenylamine-4-carboylaminobenzene	do	brown orange.
bis-4,4'-(1'-hydroxy-4''-methylbenzene-2''-carbonylamino)-3,3'-dimethoxydiphenyl	do	Do.
1-(6'-methoxy-2',3'-hydroxynaphthoylamino)-4-methylbenzene	do	wine-red.

Since an object of the present invention is to provide dyeings of furskins stable under the conditions of the usual dressing of such materials, such dyeings especially being insoluble in acids and alkalis, it is to be understood that the coupling and the diazonium components named in the appended claims do not contain groups which are known to reduce the stability of organic compounds to acids and alkalis, especially free sulfonic acid or carboxylic acid groups.

I claim:

1. A process of dyeing furskins with insoluble azo dyestuffs, which comprises treating the furskins with an alkaline solution of a coupling component having at least one hydroxy group and being capable of coupling in ortho-position to the hydroxy group, said solution containing at least 2 mols of formaldehyde for each mol of the coupling component and having a pH value in excess of 11, and thereafter developing the dyestuff on the furskins by treatment with a solution of a diazonium compound.

2. A process as claimed in claim 1, wherein the coupling component is selected from the group consisting of arylamides of the hydroxy-naphthalene, hydroxy-carbazole, hydroxy-benzocarbazole and hydroxy-anthracene series.

3. A process as claimed in claim 1, wherein the diazonium compound is free from strongly nega-

tive substituents and contains a single diazonium group.

4. A process as claimed in claim 1, wherein the diazonium compound contains strongly negative substituents, and the process is preceded by a treatment with agents yielding oxygen.

5. A process as claimed in claim 1, wherein the diazonium compound contains strongly negative substituents, and the dyeing process is preceded by a treatment with a solution of hypochlorite of a metal of the group consisting of alkaline and alkaline earth metals.

6. A process of dyeing furskins with insoluble azo dyestuffs, which comprises treating the furskins with a solution of a coupling component having at least one hydroxy group and being capable of coupling in ortho-position to the hydroxy group, said solution containing from $\frac{1}{2}$ to $\frac{1}{3}$ mol per liter of caustic alkali in excess of that required to form a salt of the coupling component, and from 3 to 150 mols of formaldehyde for each mol of the coupling component, and thereafter developing the dyestuff on the furskins by treatment with a solution of a diazonium compound.

7. A process as claimed in claim 6, wherein the coupling component is selected from the group consisting of aryl-amides of the hydroxy-naphthalene, hydroxy-carbazole, hydroxy-benzocarbazole and hydroxy-anthracene series.

8. A process as claimed in claim 6, wherein the diazonium compound is free from strongly negative substituents and contains a single diazonium group.

9. A process of dyeing furskins with insoluble azo dyestuffs, which comprises immersing the furskins in a solution of a coupling component having at least one hydroxy group, being capable of coupling in ortho-position to the hydroxy group and being selected from the class consisting of arylamides of the hydroxy-naphthalene, hydroxy-carbazole, hydroxy-benzocarbazole and hydroxy-anthracene series, said solution containing from $\frac{1}{20}$ to $\frac{1}{3}$ mol per liter of caustic alkali in excess of that required to form a salt of the coupling component, and from 3 to 150 mols of formaldehyde for each mol of the coupling component, then removing the excess coupling component from the furskins, and thereafter developing the dyestuff on the furskins by immersing them in a solution of a diazonium compound that is free from strongly negative

substituents and which contains a single diazonium group.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
13,206	Barrows	July 10, 1855
787,923	Kann	Apr. 25, 1905
1,628,484	Wilkinson	May 10, 1927
1,718,882	Schwenk	June 25, 1929
1,978,800	Levy	Oct. 30, 1934
2,183,752	Mendoza	Dec. 19, 1939

FOREIGN PATENTS

Number	Country	Date
451,264	Great Britain	Oct. 25, 1934
457,798	Great Britain	Dec. 7, 1936