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PROCESS FOR PRODUCING TWO-COLOR EFFECTS ON SKINS OR FURS

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Our present invention relates to a process for dyeing skins or furs and more particularly to such a process which produces beautiful and permanent two-color effects on the said materials.

One of the objects of our invention comprises the pretreatment of the skins and furs which are to be dyed in two-color effects.

Another object is a method for producing pelts having white tips.

Further objects of our invention may be seen from the detailed specification following hereafter.

White-tipped furs have been produced essentially by either of two methods. By one of these the fur is treated in a solution of a lead salt and then in a solution of alkali sulfide or polysulfide whereby, according to conditions, brown or black lead sulphide is precipitated on the hair of the pelt. To produce the white tips the pelt is superficially painted with an acid solution of hydrogen peroxide which bleaches the lead sulfide to lead sulfate. By the other method, to the parts of the pelt which are to remain white there is applied by means of a coarse or fine brush a certain paraffin mixture in molten condition and then the pelt is mordanted in the usual manner and dyed with an oxidation dye. The paraffin reserve is then removed by means of warm water.

Now we have found that beautiful white and variegated effects can be produced on skins and furs by a specific pretreatment of these materials before dyeing. This pretreatment comprises the following procedure:—

The pelt which has been softened and killed in the usual manner, is treated with a chromium mordant. Then a solution of an alkali metal carbonate or bisulfite, which may be thickened if desired, is applied to the pelt in order to remove the mordant at the tips or certain spots. After the material has been thoroughly rinsed, it is immersed in a bath of an oxidation dye which does not dye the tips or spots thus treated, or dyes them in a color other than that of the hair still containing the chromium mordant. These white or variegated effects can be improved by a reducing bleaching bath.

As compared with the lead sulfide method associated with the danger of poisoning by lead salts and sulphuretted hydrogen, this new process has the advantage that it is completely harmless. Moreover, it does not suffer from the gradual yellowing of the white tips, a defect which nearly always occurs in the lead sulfide process by a reversion of the lead sulfate to lead sulfide. As compared with the paraffin method there is the advantage of a simpler operation, more easily applicable in practice.

The following example illustrates the invention:—

An unshorn lambskin is killed in a solution containing per liter 3 grams of calcined sodium carbonate and 5 cc. of ammonia solution of 24 per cent. strength for 2 hours at a temperature of 24° C. and is then rinsed in the usual manner and freed from adhering alkali in an acid bath. The skin thus treated is laid overnight in a bath containing per liter 2 grams of potassium bichromate, 0.5 gram of tartaric acid and 30 grams of common salt. It is then centrifuged, stretched and painted on the places to be reserved with a solution, containing per liter, 100 grams of calcined sodium carbonate, 50 grams of potato starch and 20 grams of a fiber protective agent described in German Patent No. 480,898, this solution being applied with a brush. After several hours the skin is carefully rinsed to remove the paste and dyed in a bath of the following composition per liter: 2 grams of a mixture of 40 parts of the compound made by dissolving 1 mol. 2.7-dihydroxy-naphthalene and 2 mols 3-chloro-1.4-diaminobenzene in alcohol and evaporating the solvent, 60 parts of a dispersing agent and 2 cc. of hydrogen peroxide of 30 per cent. strength, the liquor ratio being 1:50. After dyeing for 20 minutes at 28° C., the skin is removed, carefully rinsed and bleached for a quarter of an hour in a bath containing, per liter, 3 grams of zinc salt of formaldehyde-sulfoxylate and 1 cc. of acetic acid of 30 per cent. strength. There is obtained a deep grey-brown ground with white tips.

If instead of the oxidation dye prescribed above there is used the analogous product from 1 mol. 1.5-dihydroxynaphthalene and 1 mol. metatoluenediamine there is obtained, by the same procedure, white tips on a deep brown ground.

In the tables following hereafter, we enumerate a number of other oxidation dyes useful for producing the two-color effects on pelts or skins pretreated as indicated in the foregoing example.

In Table A such dyes are indicated which do not dye the tips or spots of the pelts from which the mordant has been removed by the said process, so that white effects are produced.

The products enumerated in Table B likewise yield two-color effects with a coloration of the tips or spots other than that of the parts still containing the mordant.

In these tables certain of the dyeing materials (marked by brackets) do not constitute mixtures;

these materials are salt-like products which are obtainable similar to the dye mentioned in the example, namely by dissolving the ingredients in an organic solvent, such as in an alcohol, and evaporating the latter. If not otherwise indicated, these ingredients are used in molecular proportions when preparing the dyeing materials.

The dyeing process with these materials is the same as that of the example.

Table A

	Dye preparation	Coloration of— The fur	The tips or spots respectively
1	2.6-dihydroxynaphthalene (1 mol.) +4-aminodiphenylamine (½ mol.) +1.4-diaminobenzene (½ mol.)	Grey	White
2	2.6-dihydroxynaphthalene (1 mol.) +4-aminodiphenylamine (½ mol.) +chloro-4-aminodiphenylamine (½ mol.)	Grey	White
3	2.7-dihydroxynaphthalene + 4-aminodiphenylamine + 1.5-diaminonaphthalene	Grey	White
4	2.7-dihydroxynaphthalene (1 mol.) +2-chloro-1.4-diaminobenzene (2 mol.)	Grey	White
5	2.7-dihydroxynaphthalene +2-chloro-1.4-diaminobenzene	Grey	White
6	2.7-dihydroxynaphthalene +3.5-diamino-4-methoxy-1-methylbenzene	Brown	White
7	2.7-dihydroxynaphthalene +1-methyl-2.4-diaminobenzene	Brown	White
8	2.7-dihydroxynaphthalene +8-aminoquinoline	Brown	White
9	2.5-dihydroxynaphthalene +3.5-diamino-4-chlor-1-methylbenzene	Brown	White
10	3.5.8.10-tetrahydropyrene +2.6-diaminonaphthalene	Brown	White
11	1.5-dihydroxynaphthalene +8-aminoquinoline	Red	White
12	2.6-dihydroxynaphthalene +1.5-diaminonaphthalene	Red	White
13	1.5-dihydroxynaphthalene +benzidine	Red	White
14	1.5-dihydroxynaphthalene +1.5-diaminonaphthalene	Red	White
15	1.5-dihydroxynaphthalene +2-amino-1-(dimethylamino)-benzene	Red	White
16	1.5-dihydroxynaphthalene +4-aminodiphenylamine-3-sulfonic acid	Violet-brown	White
17	1.6-dihydroxynaphthalene +1-(dimethylamino)-2-chlor-4-aminobenzene	Violet-brown	White
18	1.7-dihydroxynaphthalene + 1.3-diaminobenzene or 1-methyl-2.4-diamino-benzene	Black-brown	White
19	1.5-dihydroxynaphthalene +2-dimethylamino-4-amino-1-chlorobenzene	Red-brown	White
20	1.4-dihydroxybenzene-2-phenylsulfone+1.4-diaminobenzene	Red-brown	White
21	Dimethylgallic acid	Beige	White
22	1.3-dihydroxybenzene+2.2'-diamino-1.1'-dinaphthyl	Beige	White

Table B

	Dye preparation	Coloration of— The fur	The tips or spots respectively
1	1.5-dihydroxynaphthalene + 2.4-diamino-1-nitrobenzene	Yellow-brown	Yellow
2	1.6-dihydroxynaphthalene+2-nitro-5-dimethylaminoquinoline	Brown-olive	Yellow
3	1.5-dihydroxynaphthalene+1-amino-2-dimethylamino-4-nitrobenzene	Red-brown	Yellow
4	1.6-dihydroxynaphthalene+1-amino-2-dimethylamino-4-nitrobenzene	Brown	Yellow
5	1.5-dihydroxynaphthalene+4-amino-1-(methylethylamino)-benzene	Dark-blue	Light-blue
6	1.5-dihydroxynaphthalene+1-methylamino-2-chloro-4-aminobenzene	Dark-violet	Light-violet
7	2.6-dihydroxynaphthalene (1 mol.) +1-(dimethylamino)-4-aminobenzene	Dark-green	Light-green
8	2.7-dihydroxynaphthalene + 2-amino-4.6-dinitro-4'-(dimethylamino)-diphenylamine	Brown	Pink
9	1.6-dihydroxynaphthalene + 4-amino-2-chloro-1-(dimethylamino)-benzene	Violet-brown	Pink
10	1.5-dihydroxynaphthalene + 1.3-di-(dimethylamino)-4-aminobenzene	Brown	Light-red
11	2.7-dihydroxynaphthalene + 2.4.6-triamino-4'-(dimethylamino)-diphenylamine	Brown	Violet
12	3.5.8.10-tetrahydroxypyrene + 4-aminodiphenylamine	Brown	Green

From the example and from the tables it may be seen that many of pelt dyes are suitable for producing the two-color effects on the pelts pretreated according to our invention. It is obvious, however, that our invention is not limited to these specific dyes, and other oxidation dyes suitable for the same purpose are considered to be within the scope of the claims following hereafter.

What we claim is:—

1. The process which comprises treating a fur or pelt in a chromium modanting bath, tipping or spotting the mordanted hairs with an agent of the group consisting of alkali metal carbonate and alkali metal bisulfite for removing the mordant, rinsing the pelt and dyeing it with an oxidation dye yielding different colorations on the mordanted and unmordanted places.

2. The process which comprises treating a fur or pelt in a chromium mordanting bath, tipping or spotting the mordanted hairs with an agent of the group consisting of alkali metal carbonate and alkali metal bisulfite for removing the mordant, rinsing the pelt and dyeing it with an oxidation dye which dyes only the mordanted parts of the pelt.

3. The process which comprises treating a fur or pelt in a chromium mordanting bath, tipping or spotting the mordanted hairs with an agent of the group consisting of alkali metal carbonate and alkali metal bisulfite for removing the mordant, rinsing the pelt, dyeing it with an oxidation dye which dyes only the mordanted parts of the pelt, and subjecting it to a reducing bath.

4. The process which comprises mordanting a

fur or pelt with an alkali metal bichromate, tipping of spotting it with a thickened solution containing an alkali metal carbonate and thus removing the mordant, rinsing it and then dyeing it in an aqueous solution containing an oxidizing agent with the product, obtainable by dissolving one molecular part of 2.7-dihydroxynaphthalene and two molecular parts of 3-chloro-1.4-diaminobenzene in alcohol and evaporating the solvent, rinsing the dye thus colored in two-color effects and finally subjecting it to a reducing bleach.

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