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TREATMENT OF LEATHER

Henry Alfred Piggott and George Stuart James
White, Blackley, Manchester, England, as-
signors to Imperial Chemical Industries Lim-
ited, Westminster, England

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We have found that the properties of leather as regards colouring with dyestuffs may be altered by pre-treatment with an aqueous solution of a salt chosen from the group consisting of quaternary ammonium, quaternary phosphonium and sulphonium salts containing an aliphatic chain of not less than 10 carbon atoms.

The alteration in properties depends to some extent on the means by which the leather is treated with the solution. When the solution is brought into contact with the leather by spraying, stencilling, printing or like means, the treated portion generally shows much less affinity for the dyestuff, while in some cases it shows negligible affinity. When the solution is brought into contact with the leather by an immersing operation, for instance by a drumming, the leather may show an increased affinity for the dyestuff. According to either way of bringing the solution into contact the treated leather may take up the colour to a different hue.

Nigrosine G (Colour Index No. 865), Naphthalene black 12B (Colour Index No. 246), Lissamine green SF (Colour Index No. 670) are dyestuffs for which the leather shows markedly less affinity when treated by the spraying type of operation; Naphthalene orange G (Colour Index No. 27), Crocein scarlet 3B (Colour Index No. 252), and Tartrazine N (Colour Index No. 640) are dyestuffs for which the treated leather shows only slightly less affinity when treated by the same operation. The behaviour of any particular dyestuff can be easily ascertained by applying a solution of the colour to a test portion of leather, part of which has been suitably pre-treated with the quaternary salt.

According to the present invention we obtain new and valuable colour effects on leather by treating the leather with an aqueous solution of a salt chosen from the group consisting of quaternary ammonium, quaternary phosphonium salt and sulphonium salts containing an aliphatic chain of not less than 10 atoms of carbon and then colouring with an aqueous solution of a dyestuff. Suitable dyestuffs are acid, basic and direct dyestuffs. The leather may be pretreated in parts only with the salt. The aliphatic chains in the salts may be unsaturated.

Examples of suitable quaternary ammonium salts are:—dodecyltrimethylammonium chloride (from dodecylchloride and trimethylamine) cetyltrimethylammonium chloride, octadecylpyridinium iodide (see B. P. 379,396), stearylpyridinium bromide (see B. P. 379,396), stearamidophenyltrimethylammonium methyl sulphate

(made by condensing asymmetrical dimethyl-p-phenylenediamine with stearoyl chloride and then treating the condensation product with dimethyl sulphate), and methylcetyl piperidinium methyl sulphate (made by interacting 2 molecules of piperidine with 1 molecule of cetyl bromide, separating the cetyl piperidine and treating with dimethyl sulphate).

Examples of suitable quaternary phosphonium salts are cetyltrimethylphosphonium bromide (made by interacting trimethylphosphine and cetyl bromide), and dodecyltrimethylphosphonium bromide (similarly made from dodecyl bromide and trimethylphosphine).

Examples of suitable sulphonium salts are cetyldimethylsulphonium methyl sulphate (made by heating cetylmethyl sulphide with dimethyl sulphate; cetylmethyl sulphide is itself made by interacting equivalent quantities of cetyl mercaptan and dimethyl sulphate), benzylcetyl methylsulphonium methyl sulphate (made as hereinafter described), dodecylmethylsulphonium bromide (made by heating dodecylmethyl sulphide with methyl bromide until a completely water-soluble product is obtained; dodecyl methyl sulphide is itself made by interacting equivalent quantities of dodecyl mercaptan and dimethyl sulphate in aqueous alkaline medium).

Cetylmethylbenzylsulphonium methyl sulphate is made as follows:—1000 parts of cetylmercaptan are treated with 85 parts of sodium in methanol and then heated for 1 hour at about 80° C. with 470 parts of benzyl chloride. The product is poured into water, extracted with ether, the ethereal layer distilled, and the fraction B. P. 250-260° C/40 mm. collected. 100 parts of this cetylbenzyl sulphide are heated with 37 parts of dimethyl sulphate at about 80° C. for about ¾ hour and then cooled when the cetylbenzylmethylsulphonium methyl sulphate crystallizes.

In carrying the invention into practical effect very diverse methods may be used. Thus leather may be sprayed, stencilled or printed with an aqueous solution of the salt, then dyed by brushing, spraying, immersing or over-printing with either a solution of an individual dyestuff or a mixture of dyestuffs, especially interesting effects being obtained by using dyestuffs for which the treated leather shows different affinities as described above. In the pre-treating of suede leathers the salt is applied as a cold or warm aqueous solution by immersing the leather; this is followed by a rinsing with cold water and dyeing in the usual manner with the dyestuff.

The invention is illustrated but not limited by

the following examples, in which the parts are by weight.

Example 1.—Dry skivers (Sumac grain sheepskin splits are sprinkled with a 1% solution of stearylpyridinium bromide. When the spots are dry the leathers are dyed by immersion in a water solution of a mixture of Nigrosine G crystals (Colour Index No. 865) and Crocein scarlet 3B (Colour Index No. 252). The skins are then struck out and dried in the usual manner and finally an aqueous searson applied to the dry leathers if desired. The skivers show scarlet spots on a black background.

Example 2.—Sheepskins previously dyed with Naphthalene orange G (Colour Index No. 27) are spray-stencilled with a 1% solution of trimethylcetyl ammonium chloride and dried. The leather is then sprayed with a solution of Cardinal red S (Colour Index No. 176) and dried and finished in the usual manner. The skins show orange spots on a brown ground.

Example 3.—100 lbs. dry semichrome Persian suedes are treated by immersion for 30 minutes in a solution of 1% octadecylpyridinium iodide in 10 gallons of water circulating in a drum. The leathers are then rinsed with cold water for 10 minutes and drummed in a warm solution of 4% Lissamine green SF (Colour Index No. 670) calculated on the weight of the leather. After rinsing, fat liquoring and drying out in the usual manner, the shade on the suede side is found to be much stronger than that obtained without the pre-treatment.

Example 4.—A solution of 1 part of cetyldimethylsulphonium methyl sulphate in 100 parts of water is spotted on to East Indian tanned sheepskins. The skins are dried, immersed for about half a minute at 90° C. in a 1% aqueous solution of Naphthalene black 12B (Colour Index No. 246) and rinsed in running water. A coloured pattern of light undyed spots on a dull blue ground is obtained.

Example 5.—1 part of dodecyldimethylsulphonium bromide and 1 part of Auramine O (Colour Index No. 655) are dissolved in 100 parts of water. This solution is sprayed through stencils on to Sumac tanned grain sheepskin splits. The

skins are dried and dyed by immersion in a 1% solution of Methylene blue 2B, (Colour Index No. 922), a yellow pattern on a blue ground is obtained.

We claim:

1. The process which comprises treating leather in part with an aqueous solution of a salt chosen from the group consisting of quaternary ammonium, quaternary phosphonium, and sulfonium salts containing an aliphatic side chain having not less than ten carbon atoms, and dyeing the leather with an aqueous solution of a dyestuff.

2. The process which comprises treating leather in part with an aqueous solution of a quaternary ammonium salt containing an aliphatic side chain having not less than ten carbon atoms, and dyeing the leather with an aqueous solution of a dyestuff.

3. The process which comprises treating leather in part with an aqueous solution of a quaternary phosphonium salt containing an aliphatic side chain having not less than ten carbon atoms, and dyeing the leather with an aqueous solution of a dyestuff.

4. The process which comprises treating leather in part with an aqueous solution of a sulfonium salt containing an aliphatic side chain having not less than ten carbon atoms, and dyeing the leather with an aqueous solution of a dyestuff.

5. The process which comprises treating leather in part with a cetyl trimethyl ammonium halide and dyeing the leather with an aqueous solution of a dyestuff.

6. The process which comprises treating leather in part with a cetyl trimethyl phosphonium halide, and dyeing the leather with an aqueous solution of a dyestuff.

7. The method of dyeing leather which comprises treating leather in part with an aqueous solution of cetyldimethylsulfonium methyl sulfate, and treating the leather with an aqueous solution of a dyestuff.

HENRY ALFRED PIGGOTT.
GEORGE STUART JAMES WHITE.