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DYEING OF LEATHER

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This invention relates to a new process for dyeing leather, and more particularly to a process for dyeing leather on one side only with vat dyestuffs.

Dyestuffs which have been employed for dyeing leather have up to the present been restricted for the most part to those of the acid, basic and direct dyestuffs. The brightness, wash-fastness and light-fastness properties of leather dyed with such dyestuffs have not been entirely satisfactory. Vat dyestuffs are known to have good wash-fast and light-fast properties, and to be capable of yielding bright shades, and their use for dyeing leather would be highly desirable. However, since ordinary dyeing with vat dyestuffs involves application of the reduced or leuco form of the dyestuff from an alkaline vat, and since the substantivity of such alkaline vats is low in view of the usually acid character of the leather, such methods have found little use in dyeing leather. It has been previously proposed to dye leather with sulfuric acid ester salts of leuco vat dyestuffs but the results have not been entirely satisfactory and the use of such a process has been limited in view of the general understanding that the oxidizing treatment must be applied as a separate step. Leather is usually of an acid character due to its inherent chemical composition and/or its previous tanning and other treatments, whereby dyebaths in contact therewith generally have or acquire an acid reaction. Addition of an oxidizing agent to an acidic dyebath containing a sulfuric acid ester salt of a leuco vat dyestuff would accordingly result in hydrolysis and oxidation of the dyestuff to the final pigment form in the dyebath thereby preventing proper penetration or impregnation of the leather.

The dyeing of certain types of leather on only one side is highly desirable. This is particularly true of glove leathers in addition to shoe, garment and upholstery leathers, where bleeding and/or rubbing off of a color from the opposite surface would be often objectionable.

It is an object of this invention to provide a novel process for dyeing leather with vat dyestuffs. Another object of this invention is the dyeing of leather on only one side with vat dyestuffs. Still another object of this invention is the provision of a process wherein a sulfuric acid ester salt of a leuco vat dyestuff is applied to only one side of leather. Other objects and advantages will appear as the description proceeds.

The attainment of the above objects is made possible by the instant invention which comprises a process for coloring leather comprising spraying the leather with an aqueous bath containing a sulfuric acid ester salt of a leuco vat dyestuff and an oxidizing agent, and then treating the sprayed leather with an acid solution. It has been found that the process of this invention enables the attainment of more level dyeings having improved properties with respect to wash-fastness, light-fastness and the like. The problems of low substantivity of the dyestuff to the leather, and of uneven exhaustion of components from the dyebath, are hereby eliminated since the dyebaths employed in the instant invention are maintained

separately from the leather and only sufficient dye solution is sprayed on the leather to achieve the desired depth of shade. Better control of the dyeing process and better dyeings are attained. Relatively expensive padding and/or impregnating equipment is eliminated, and plant space is conserved. In addition, the process enables the dyeing of only one side of the leather in an easily controlled and expeditious manner.

The type of leather which may be dyed in accordance with the process of this invention is relatively immaterial, the process being operative on leather which has been tanned in any known manner. It will of course be understood that the particular manner in which the leather has been previously tanned or treated may have some effect on the depth of shade or brightness of the dyeings produced.

The sulfuric acid ester salts of leuco vat dyestuffs employed in the instant invention are well known in the art, being in general available on the market under, for example, the trademark "Algosol" (General Aniline and Film Corporation). They may be made by various methods and with the use of various assistants disclosed in the prior art. The alkali metal salts such as those of sodium and potassium are usually preferred, although other water-soluble or readily water-dispersible salts may be employed such as those with triethanolamine, and the like. Illustratively, the sulfuric acid ester salts of the following vat dyestuffs, identified in the 1954 Technical Manual and Year Book of the American Association of Textile Chemists and Colorists (A. A. T. C. C.) may be employed in accordance with this invention.

Algosol Blue IBC Pst CF (C. I. 1113)
Algosol Brown IBR–CF (Pr. 118)
Algosol Blue O–CF (C. I. 1178)
Algosol Golden Yellow IGK (Pr. 291)
Algosol Golden Yellow IRK (Pr. 292)
Algosol Blue 04B (C. I. 1184)
Algosol Orange HR–CF (C. I. 1217)
Algosol Brilliant Violet 14R–CF (C. I. 1104)
Algosol Pink IR Fine–CF (Pr. 109)
Algosol Brown IRRD Supra (Pr. 121)
Algosol Golden Orange IRR–CF (C. I. 1098)
Algosol Red Violet IRRN–CF (Pr. 503)
Algosol Grey IBL–CF (Pr. 295)
Algosol Scarlet HB–CF (Pr. 107)
Algosol Green IBW Pst CF (C. I. 1101)
Algosol Yellow GCA–CF (Pr. 9)
Algosol Olive Green IB–CF (Pr. 293)
Algosol Red IFBB–CF (Pr. 296)

In the above list, the term "Pr." refers to the corresponding foreign prototype, and the term "C. I." refers to the dyestuff listed in Rowe's Color Index.

The concentration of dyestuff in the spray solution may vary considerably depending upon the strength of the dyeing desired, and may vary from about 0.2 to 7% by weight of the solution, concentrations of about 0.5 to 2% being preferred. In making the spray solution, the dyestuff may be dissolved in water at any convenient temperature from room temperature up to near the boil. However, completely satsifactory results have been obtained in making and spraying the dyebaths employed in the instant invention at room temperature.

While other oxidizing agents may be added to the dyebath, sodium nitrite has been found to yield highly desirable results. Sufficient nitrite must be added to the dyebath to oxidize the amount of leuco ester salt contained therein. In general, concentrations of about 0.5 to 5% of the alkali nitrite may be employed by weight in the dyebath, although about 0.7 to 2% is usually sufficient.

To provide improved solubility of the dyestuff in the dyebath and to aid in increasing surface penetration of the leather and level dyeing results, a surface active agent is preferably added to the dyebath. Cationic surface active agents should not be employed since they tend to precipitate the anionic leuco ester salt dyestuffs. Water-soluble anionic surface active agents are preferred, although water-soluble non-ionic surface active agents may also be employed.

The anionic surface active agents which may be employed in the instant invention are well known in the art and are in general organic sulfates and sulfonates containing at least 10 carbon atoms. Included in this group are the alkyl arylsulfonates such as dodecylbenzene sulfonate, isopropylnaphthalene sulfonate, diisobutylnaphthalene sulfonate, and the like, N-higher acyl taurines such as N-oleoyl-N-methyl taurine, N-tallow acyl-N-methyl taurine, N-tall oil acyl-N-ethyl taurine, N-palmitoyl-N-methyl taurine, and the like, higher aliphatic sulfates and sulfonates such as lauryl sulfate, Oxo tridecyl sulfate, sulfonated and sulfated castor oil and other higher fatty acids or esters, higher fatty acid esters of isethionic acid and the like and sulfonated polycarboxylic acid esters such as diamyl sulfosuccinate, dioctylsulfosuccinate, and the like. All of these sulfates and sulfonates are preferably employed in the form of their alkali metal salts with sodium or potassium, although other salts may be employed such as those with alkaline earth metals such as calcium or magnesium, ammonia or amines such as methylamine, ethanolamine, cyclohexylamine, morpholine, piperidine, and the like.

The water-soluble non-ionic surface active agents which may be employed in the instant invention may be represented by the general formula

$$R—(—CHR^1—CHR^1—O—)_n—H$$

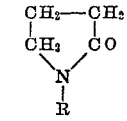
wherein R represents the residue of an organic compound containing a reactive hydrogen atom, R^1 represents hydrogen or lower alkyl, and n has a value of from 2 to 100 or more and usually from about 4 to 30. Compounds of this type are well known in the art and are disclosed along with suitable methods for their preparation in numerous patents, including U. S. 1,970,578, 2,002,613, 2,085,706, 2,205,021, 2,213,477, 2,266,141, 2,593,112, etc. and other publications. In general, they may be obtained by condensing a polyglycol ether containing the required number of alkenoxy groups or an alkylene oxide such as propylene oxide, butylene oxide, or preferably ethylene oxide, with an organic compound containing a reactive hydrogen atom. As such compounds containing a reactive hydrogen atom there may be mentioned alcohols, phenols, thiols, primary and secondary amines, carboxylic and sulfonic acids and their amides. The amount of alkylene oxide condensed with the reactive hydrogen-containing compound, i. e., the length of the polyoxyalkylene chain, will depend primarily upon the particular compound with which it is condensed. The optimum amount of alkylene oxide may readily be determined in any particular instance by preliminary test and routine experimentation.

As specific examples of suitable water-soluble non-ionic surface active agents which may be employed in the instant invention, there may be mentioned the reaction product of 1 mole of nonylphenol with 9 to 11 moles of ethylene oxide, the reaction product of 1 mole of castor oil with 20 moles of ethylene oxide, the reaction product of 1 mole of tall oil with 18 moles of ethylene oxide, the reaction product of 1 mole of olelyl alcohol with 20 moles of ethylene oxide, the reaction product of 1 mole of dodecyl mercaptan with 9 moles of ethylene oxide, the reaction product of 1 mole of soybean oil amine with 10 moles of ethylene oxide, the reaction product of 1 mole of rosin amine with 32 moles of ethylene oxide, the reaction product of 1 mole of cocoanut fatty acid amine with 7 moles of ethylene oxide, and the like. The non-ionic agent should be employed in sufficient amount, and should contain a high enough content of alkyleneoxy groups to yield a stable dispersion, preferably a clear solution of aqueous dyebath.

In general, about .01 to 2% of the anionic or non-ionic surface active agent by weight of the dyebath is sufficient, when employed, to yield the desired results.

While the sulfuric acid ester salts of leuco vat dyestuffs are generally soluble in water in the required degree, their degrees of solubility vary considerably and in some cases turbid solutions are obtained at the required concentrations. As a further feature of this invention, it has been found that addition to the dyebath of a small amount of an N-lower alkyl-2-pyrrolidone or an N,N-disubstituted formamide such as N,N-dimethyl-formamide, N,N-diethyl-formamide, or N,N-dihydroxyethyl-formamide, clears up the turbidity. The use of these amides has also been found to yield improved dyeings with respect to levelness and uniformity. The mechanism by which these improved results is attained is not fully understood, although it may be due to the solvent action of these amides on the dyestuffs and/or their alkaline or buffering action in the bath. These amides may be employed in amounts ranging from about 2 to 12% by weight of the dyebath, although amounts of about 4 to 6% are usually sufficient.

The N-lower alkyl-2-pyrrolidones which may be employed in the dyebaths of the instant invention have the formula



wherein R is an alkyl radical of from 1 to 4 carbon atoms such as ethyl, propyl, isopropyl, butyl, isobutyl and especially methyl. Such pyrrolidones and their methods of production are well known in the art and no claim is made thereto per se.

The formamide compounds are also well known in the art. The N,N-dihydroxyethyl-formamide may be readily made for example by amidation of formic acid with diethanolamine in known manner.

In carrying out the process of the instant invention, the leuco ester salt is usually first dissolved in water followed by addition to the dye solution of the surface active agent and sodium nitrite. In case an N-lower alkyl-2-pyrrolidone or formamide compound of the type above described is called for, it is usually added before addition of the sodium nitrite. The bath should be maintained at a neutral or alkaline pH. After the dyebath is diluted with water to the concentration required for proper spray consistency and the attainment of the desired depth of shade, it is sprayed on the leather in the usual manner, for example with an ordinary spray gun, or any other spray device suitable for applying liquids in finely divided form. The leather may be sprayed with up to 3 or more passes, depending upon the results desired, 1 gallon of dyebath per 200 to 500 sq. ft. of leather being usually sufficient. The leather is then preferably partially dried and subjected to an acid treatment to develop the dyestuff. A dilute inorganic acid solution such as dilute hydrochloric acid has been found very effective, although other dilute acid solutions may be employed such as sulfuric acid, in from 1 to 5%, and preferably 2 or 3% concentration. This acid treatment may be accomplished by padding, dipping, or, preferably, brushing or spraying.

Following the acid treatment, the leather is air-dried in known manner to develop the color, and then neutralized by a weakly alkaline treatment with, for example, a 2% ammonium hydroxide solution by padding, dipping, or, preferably, brushing or spraying or the like. If desired, urea or thiourea or other antioxidant may be added to the neutralizing solution in amounts of about

2 to 10% by weight of the solution, preferably about 5%, in order to obtain improved dyeings in some instances.

The following examples, in which parts are by weight unless otherwise indicated, are illustrative of the instant invention and are not to be regarded as limitative.

Example 1

A solution is made up by dissolving .75 g. Algosol Golden Yellow IGK in 50 cc. water. To this is added 7½ cc. 10% sodium nitrite solution and .5 cc. wetting agent (20% solution of sodium dioctylsulfosuccinate). Water is added to make up 100 cc.

This solution is sprayed, in three passes, on chrome tanned grain glove leather, formaldehyde tanned grain glove leather, a grain glove leather that has been tanned with a syntan (synthetic tanning agent), chrome tanned upholstery leather, chrome tanned grain shoe leather and chrome tanned garment leather.

After partially drying, the leather is brushed with a 2% solution of hydrochloric acid. The leather is allowed to dry in air and is then sprayed with a 2% solution of ammonium hydroxide.

Excellent level yellow dyeings are obtained on the treated side of the leather.

Example 2

The process of Example 1 is repeated except that 5 cc. of N-methyl-2-pyrrolidone is added to the dyebath prior to addition of the sodium nitrite. The resulting dyebath is much clearer and the dyeings are of excellent quality and of improved uniformity and levelness.

Example 3

The process of Example 2 is repeated except that instead of a final 2% ammonium hydroxide solution spray, a 2% ammonium hydroxide solution containing 5% urea is brushed on the leather. The resulting dyeings are of excellent quality and improved properties.

Excellent dyeings are also obtained when the processes of Examples 1 and 2 are repeated using the other Algosol dyestuffs listed hereinabove.

This invention has been disclosed with respect to certain preferred embodiments, and various modifications and variations thereof will become obvious to those skilled in the art. It is to be understood that such modifications and variations are to be included within the spirit and purview of this application and the scope of the appended claims.

I claim:

1. A process for coloring leather comprising spraying the leather with an aqueous bath containing a sulfuric acid ester salt of a leuco vat dyestuff, an agent selected from the group consisting of water-soluble anionic and non-ionic surface active agents, a member of the group consisting of N-lower alkyl-2-pyrrolidones, N,N-dimethylformamide, N,N-diethylformamide, and N,N-dihydroxyethylformamide, and sodium nitrite, and then treating the sprayed leather with an acid solution.

2. A process as defined in claim 1 wherein said agent is a water-soluble anionic surface active agent.

3. A process as defined in claim 1 wherein the aqueous bath contains an N-lower alkyl-2-pyrrolidone.

4. A process as defined in claim 3 wherein said N-lower alkyl-2-pyrrolidone is N-methyl-2-pyrrolidone.

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