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2,913,301

AZOIC DYEING OF LEATHER

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8 Claims. (Cl. 8—13)

This invention relates to a method for dyeing leather and more particularly to a method for dyeing leather with azoic dyestuffs.

It has long been the desire in the trade to be able to dye leather in such a manner that the color is fast to washing, crocking and light. The conventional acid, direct and basic colors frequently lack the necessary fastness properties and often tend to bleed considerably when treated in a soap liquor. Such bleeding is of course detrimental to the color properties of the dyestuff in addition to introducing problems in connection with staining of adjacent areas or garments. Attempts have been made to dye leather by the azoic method, as for example by application of a Naphthol AS type coupling component and coupling with a diazo component. However, due to the high alkalinity of the coupling component treating liquor, the coupling component exhausted poorly, the conditions for efficient coupling with the diazo component were improper, and the shades obtained were dull, weak, and of poor wash-, crock- and light-fastness. Moreover, the quality of the leather was adversely affected, desirable properties therein being destroyed.

It is an object of this invention to provide a process for the azoic dyeing of leather. Another object of this invention is the provision of a process for the production of leather dyed with azoic colors having good wash-, crock-, dry-cleaning and/or light-fastness properties. Still another object of this invention is the provision of a process for the azoic dyeing of leather which will produce uniform, level shades and will not adversely affect desirable properties in the 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, in an azoic dyeing method, the step of treating leather with an azoic coupling component devoid of solubilizing groups from an aqueous solution having an initial pH of more than 7 and less than 11, preferably less than 9, and a final pH of no more than 7, for example from 3 to 7 and preferably about 5. It has been found that application of the coupling component in this manner enables the attainment of wash-, crock-, and/or light-fast dyeings having good penetration and having no detrimental effects on desirable properties in the leather. In contradistinction to the usual dyeing methods which emphasize surface imperfections in the leather, the instant process minimizes such imperfections whereby an upgrading effect is attained. As a further feature of this invention, it has been found that when the azoic coupling component employed in the instant invention contains at least one aromatically bound free amino group, even more uniform, level dyeings are obtained having improved fastness to dry cleaning.

In carrying out the process, the leather is first wet out in the usual manner with water which may desirably contain a wetting agent. If the leather is highly acid, the addition of some sodium bicarbonate or other alkaline material to the wetting-out liquor is desirable to aid

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in neutralizing the acidity and preventing it from unduly affecting the pH of the coupling component treating liquor. The aqueous solution containing the coupling component is prepared by dissolving the coupling component with sufficient alkali, such as sodium or potassium hydroxide, to form the alkali metal salt of the coupling component plus a small excess to prevent too early hydrolysis, but insufficient to raise the pH value of the solution over the above-mentioned maximum allowable values. During impregnation of the leather with this solution, the pH of the solution is controlled to drop to about 7 or less. In most cases this must be accomplished by addition of acid, such as acetic, hydrochloric or preferably formic acid, during and preferably towards the end of the impregnation treatment. In some cases, this addition of acid may be dispensed with where the leather is sufficiently acid, for example as a result of a previous tanning or other treatment. The temperature of treatment may vary from about room temperature to about 150° F., with durations of about 15 minutes to 2 hours. Optimum conditions are dependent in any particular instance upon the nature of the leather and the treating agents employed, being readily determinable by a worker skilled in the art. With some coupling components, the addition of a small amount of a water soluble organic solvent such as ethyl alcohol, isopropyl alcohol, ethylene glycol and its monoethyl ether or the like may be desirable to facilitate solution thereof. The addition of a wetting agent to the solution, or other additives, may be desirable in some instances.

From the above, it will be understood that the instant process, instead of employing a highly alkaline coupling liquor, requires regulation of the initial pH thereof, by direct adjustment and/or by suitable treatment of the particular leather being dyed in such manner that it has a value of more than 7 and less than 11, preferably less than 9 and that the drop in the pH during treatment is sufficient to bring it to about 3 to 7, preferably about 5.

The coupling components operative in the instant invention are the usual ice color coupling components well known in the art and devoid of solubilizing groups such as carboxylic or sulfonic acid groups. In general, these coupling components may be characterized as compounds having an active methylene group, an enolizable keto group or an aromatic hydroxy group including coupling, usually in ortho- or para-position, preferably the former, to said hydroxy group. Such compounds are typified by the acylacetarilides, the pyrazolones, and aromatic hydroxy compounds capable of coupling. As acylacetarilides there may be mentioned acetoacetic acid arylides, furoyl acetic acid arylides, terephthaloyl-bis-acetic acid arylides, and the like. As pyrazolones, there may be mentioned 1-phenyl-3-methyl-5-pyrazolone, 1-p-tolyl-3-methyl-5-pyrazolone, 3-methyl-5-pyrazolone, 5-pyrazolone, 1,3-dimethyl-5-pyrazolone, 1-(p-chlorophenyl)-3-methyl-5-pyrazolone, 1-(p-nitrophenyl)-3-methyl-5-pyrazolone, 1-(o-methoxyphenyl)-3-methyl-5-pyrazolone, 1-(m-aminophenyl)-3-methyl-5-pyrazolone, 1-methyl-5-pyrazolone, 1-phenyl-5-pyrazolone, 1-phenyl-5-pyrazolone-3-carboxylic acid methyl ester, 1-phenyl-5-pyrazolone-3-carboxylic acid ethyl ester, and other pyrazolones unsubstituted or substituted in the 1- and/or 3-positions by non-solubilizing radicals. The aromatic (carbocyclic or heterocyclic) hydroxy compounds useful as coupling components herein generally include phenols, resorcinols, 1- and 2-naphthols, benzonaphthols, hydroxybenzofluorenones, and the like, in addition to arylides of β -hydroxy aromatic carboxylic acids. Illustratively, examples of arylides of β -hydroxy aromatic carboxylic acids which may be employed in the process of the instant invention are 3-hydroxy-2-naphthoic acid arylides, 3-hydroxy-2-

anthroic acid arylides, 3-hydroxy-2-carbazole carboxylic acid arylides, 3-hydroxy-2-furane carboxylic acid arylides, 2-hydroxy-11H-benzo-[a]carbazole-3-carboxylic acid arylides, hydroxydibenzothiophene carboxylic acid arylides and the like. Many such coupling components operative herein are disclosed in Diserens, "Chemical Technology of Dyeing and Printing," volume 1, pages 213 to 224 (Reinhold Publishing Corp., 1948); Lubs, "Chemistry of Synthetic Dyes and Pigments," pages 182 through 192 (Reinhold Publishing Corp., 1955); and Adams, "Journal of the Society of Dyers and Colorists," volume 67 (1951), beginning at page 223. As stated above, those azoic coupling components containing an aromatically bound free amino group enable the attainment of further improved results. Typical amino substituted couplers include aminonaphthols, such as 1-amino-7-naphthol; aminophenols, such as m-diethylaminophenol, aminoresorcinol, m-aminophenol; aminoazophenols and naphthols, such as 6-hydroxy-4(o-nitrophenyl-azo)-1-naphthylamine; aminophenylpyrazolones, such as methyl m- and p-aminophenylpyrazolone; acylacetarilides substituted in the aryl radical by an amino group, such as acetoacet-m-toluylenediamine; o-hydroxycarboxylic acid arylides having an amine substituent in the aryl radical, such as 3'-amino-3-hydroxy-2-naphthanilide.

To produce the azoic color on the leather, the coupling component must be reacted with a diazotized aromatic primary amine compound also devoid of solubilizing groups such as carboxylic or sulfonic acid groups. As examples of such primary amine compounds useful in the instant invention, there may be mentioned aminozotoluene, 4-chloro-2-nitroaniline, 5-chloro-o-toluidine, 4-nitro-o-toluidine, 2,5-dichloroaniline, 4-benzamido-2,5-diethoxyaniline, 4-nitro-m-anisidine, 4-nitro-o-anisidine, 4-chloro-o-anisidine, 1-aminonaphthalene, 1-aminoanthraquinone, dianisidine, 5-chloro-4-nitro-o-anisidine, aminobenzophenones, aminosulfones such as aminobenzosulfones and aminodiphenylsulfones, aminodiphenyl ethers, aminocarbazoles, and other similar cyclic compounds containing at least one diazotizable primary amine group. These and other carbocyclic and heterocyclic azoic bases operative in the process of this invention are well known in the art.

The diazotizable aromatic primary amine compound to be reacted with the coupling component may be applied subsequent to application of the coupling component to the leather, or simultaneously therewith. In either case, the final azoic dyestuff is produced by treatment of the leather containing the coupling component and diazotizable amine with sodium nitrite and an acid, preferably formic acid, whereby diazotization of the diazotizable amine and reaction of the resulting diazo compound with the coupling component takes place in situ on and/or in the leather.

Even better results are obtained by application to the leather containing the coupling component of the said aromatic amine in the form of its already diazotized compound, whereby a subsequent diazotization treatment with sodium nitrite and acid is avoided. The diazo compound may be employed as a solution freshly prepared from a diazotizable amine or as a solution of one of its stabilized salts, e.g. as a hydrochloride or sulfate of one of the relatively stable diazos, as a double salt employing such salts as zinc chloride, zinc sulfate, cadmium chloride, tin tetrachloride, fluoroborates and the like, or as a salt with an organic sulfonic acid such as benzene disulfonic acid, β -naphthalenesulfonic acid and naphthalenetrisulfonic acid. In some instances wherein solubility may be insufficient a dispersing agent may be added to improve dispersion and penetration. Or the subsequent application of the said amine may be in the form of its nitroso compound or as the stabilized diazo amino compound, e.g. the Levamines. All of these forms of stabilized diazotized primary amino compounds or nitrosoamines

are to be regarded as the equivalent of the freshly prepared diazotized primary amine compounds since they react as such with the coupling component.

Alternatively, said aromatic primary amine compound can be applied to the leather in its diazotized form simultaneously with the coupling component in known manner. Thus, the coupling component can be combined with a stabilized form of the diazotized primary amine compound, such stabilized compound being then activated by a drop in the pH to 7 or less whereby the coupling reaction takes place in situ on and/or in the leather. Examples of known types of combinations of coupling components and stabilized diazotized primary amine compounds are the Rapidazols (mixtures of couplers and diazosulfonates), the Rapid Fast colors (mixtures of couplers and antidiazotates) and preferably, the Rapidogens (mixtures of couplers and diazo amino compounds).

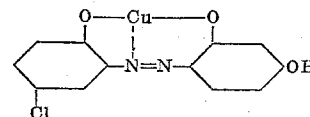
In carrying out the process of this invention, the initial pH of the solution containing the coupling component may be as high as 11 if the leather is highly acid. However, in most cases, wherein the leather has been washed free of salts or neutralized with an alkaline substance, the initial pH is usually in the alkaline range, and about 9-11. Where Rapidogens are used, the pH range should be between about 7.5 and 8 for optimum treatment since if the pH is lower the diazo tends to split, and if higher, on subsequent addition of acid, acidification occurs unevenly which results in dull dyeings.

In general, the diazo component and the coupling component are employed in amounts sufficient to react in approximately equivalent proportions, although in some cases it may be desirable to use an excess of one. The reaction products thereof, i.e., the azo dyestuff, is employed in amounts ranging from about 0.1 to 10%, and preferably from about 0.1 to 5% based on the weight of the leather.

The following examples are illustrative of the instant invention and are not to be regarded as limitative. They disclose various embodiments and means for carrying out the basic process of the invention more fully described above.

Example 1

1 g. of an azoic coupling component of the formula



2 cc. alcohol and 0.75 cc. caustic soda 40° Bé. were pasted and then diluted to about 2000 cc. with warm water. 80 g. chrome tanned suede calf leather pre-wet was immersed in the bath for 15 minutes, during which time the pH dropped from about 11 to about 10. A mixture of 1.6 g. of azo-o-toluidine, as the sulfate, and 0.5 g. of sodium N-oleoyl-N-methyl tauride dispersing agent was dissolved in warm water and added to the bath. After immersing the leather in this bath for about 30 minutes at 130° F., the pH dropped to about 8-9. 8 cc. of a 5 percent formic acid solution was then added. The impregnation was continued for another 30 minutes at about 130° F., at which time the pH had dropped to about 5.

The leather was removed from this bath, rinsed in fresh water and developed in a bath containing 30 cc. of a 10% sodium nitrite solution and 75 cc. of a 5% formic acid solution for 30 minutes at room temperature. The pH was adjusted to about 4.5 and the dyeing continued for another 30 minutes. The leather was finished in usual manner.

A brown shade was obtained having excellent light and wash fastness.

Example 2

4 g. m-diethylaminophenol was pasted with 1 cc. al-

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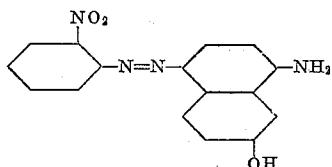
cohol and .5 cc. caustic soda 40° Bé., and diluted to 2000 cc. with water. The bath had a pH of about 11. 80 g. pre-wet chrome tanned suede calf skin was entered into this bath for 15 minutes, at which time the pH of the bath was about 10. Then 3 g. 1-naphthylamine dispersed with a small amount of sodium N-oleoyl-N-methyl tauride was entered in the bath and impregnation continued for 60 minutes at 130° F., at which time the pH had dropped to about 6. The leather was withdrawn, rinsed and diazotized in a bath containing 25 cc. of a 10% sodium nitrite solution and 60 cc. of a 5% formic acid solution. The bath was maintained for 1 hour at room temperature, the leather withdrawn, rinsed and finished as usual. A greenish tan product was obtained of good fastness to light, washing and crocking. Also the penetration was good.

Example 3

1 g. Naphthol AS-E (p-chloroanilide of 3-hydroxy-2-naphthoic acid) was pasted with 2 cc. alcohol and 1 cc. caustic 40° Bé. and diluted to 2000 cc. with water. 80 g. pre-wet chrome tanned grain glove leather was impregnated in this bath for 10 minutes, during which time the pH dropped from about 11 to about 10. 1.3 g. 5-chloro-o-toluidine hydrochloride dissolved in a small amount of water with the assistance of 0.5 g. sodium N-oleoyl-N-methyl tauride was added to the bath. After soaking for 30 minutes at 130° F., the pH dropped to about 8-9. 8 cc. of a 5% formic acid solution was then added. After impregnation at 130° F. for an additional 30 minutes, the pH had dropped to about 5. The leather was then withdrawn, rinsed and diazotized in a bath containing 25 cc. of a 10% sodium nitrite solution and 60 cc. of a 5% formic acid solution. The leather was maintained in this bath at room temperature for 60 minutes, withdrawn, rinsed and finished as usual. A yellow red coloration was obtained of good properties.

Example 4

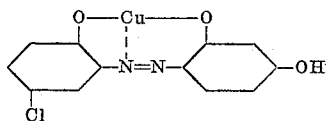
1.2 g. of the compound



was dissolved with 3 cc. alcohol and $\frac{3}{4}$ cc. caustic soda 40° Bé. Water was added to about 2000 cc., yielding a bath having a pH of 10-11. 80 g. chrome tanned suede calf skin was soaked in this bath for 30 minutes at 130° F., during which time the pH dropped to about 9-10. 8 cc. of a 5% formic acid solution was added and impregnation was continued for another 30 minutes, at which time the pH had dropped to about 6-7. The leather was withdrawn, rinsed and entered into a fresh bath containing 5 g. zinc chloride double salt of 4-benzamido-2,5-diethoxybenzene diazonium chloride and 25 cc. of a 10% sodium bicarbonate solution made up to about 2000 cc. with water. Dyeing was continued for 60 minutes at 130° F. The leather was withdrawn, rinsed and finished as usual. The leather was dyed a uniform, level black and had good quality. The light and wash fastness was excellent, in addition to the fastness to dry cleaning.

Example 5

1 g. of the compound



was dissolved with 3 cc. alcohol and $\frac{1}{2}$ cc. caustic 40° Bé. and diluted with warm water to about 2000 cc. The

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bath had a pH of about 10. 80 g. chrome tanned suede calf skin was entered into the bath at 130° F. for about 30 minutes, during which time the pH dropped to about 9-10. 8 cc. of a 5% formic acid solution was added and soaking continued for another 30 minutes, at which time the pH had dropped to about 6-7. The leather was withdrawn, rinsed and entered into a bath consisting of 3.5 g. of the diazonium sulfate of azo o-toluidine dissolved in about 2000 cc. cold water. Dyeing was continued for 1 hour and the leather rinsed, dried and finished as usual. A deep brown shade was obtained of excellent light and wash fastness.

Example 6

1 g. bis-acetoacet-o-toluidide was dissolved with 2 cc. alcohol and $\frac{1}{2}$ cc. caustic soda 40° Bé. The volume was diluted with water to about 2000 cc., yielding a bath having a pH of about 10. 80 g. chrome tanned grain glove leather was immersed in this bath for 30 minutes at 130° F., during which time the pH dropped to about 8-9. 8 cc. of a 5% formic acid solution was added and the treatment continued for another 30 minutes, at which time the pH had dropped to about 5-7. The leather was rinsed and treated for 1 hour in a bath consisting of 5 g. zinc chloride double salt of 3-chloro-5-methoxybenzene diazonium chloride made up to 2000 cc. at 130° F. The leather was rinsed and finished as usual. A beautiful yellow shade was obtained of good all around properties.

Example 7

4 g. of a Rapidogen, which consisted of 5-chloro-o-toluidine diazotized and stabilized with 4-sulfoanthranilic acid and 3-hydroxy-2-naphthoic-o-phenetide, was dissolved with 2 cc. alcohol and $\frac{3}{4}$ cc. caustic soda 40° Bé., made up to 2000 cc. with water and the pH adjusted to about 7.5-8. 80 g. chrome tanned suede calfskin was impregnated in this bath for 30 minutes at 130° F., and the pH remaining about the same. At this time an addition was made of about 5 cc. of a 5% formic acid solution, the pH dropping to about 6. Dyeing was continued for another 30 minutes, then the leather was rinsed and finished as usual. A brilliant scarlet resulted, and the leather was of excellent quality.

Part of the dyed leather was exposed in a fadeometer for 50 hours and showed no fading. Finally the dyed leather was treated for 1 hour at 120° F. in a $\frac{1}{2}$ % soap solution. Very little loss of color was observed.

Example 8

4 g. of a Rapidogen which consisted of a mixture of diazotized cresidine stabilized with sarcosine and the copper complex of o-aminophenol-resorcinol was made into a bath as in Example 7. 80 g. chrome tanned suede calf was treated as in Example 7.

A deep dark brown was obtained. The leather possessed good qualities.

No fading was noticeable after 50 hours in the fadeometer. There was practically no color loss after treating the leather for 1 hour in a $\frac{1}{2}$ % soap solution at 140° F.

Example 9

80 g. chrome tanned suede was dyed as in Example 7 with 4 g. of a Rapidogen which consisted of tetrazotized and stabilized (with N-methyltaurine) dianisidine and 3-hydroxy-3-naphthoic-o-phenetide. A deep navy was obtained. The leather was of excellent quality.

Only a very slight fading was apparent after 50 hours in the fadeometer. Wash fastness was very good.

Example 10

80 g. chrome tanned grain glove leather was dyed as in Example 7 with 4 g. of a Rapidogen, which consisted of 5-chloro-o-anisidine diazotized and stabilized with 4-sulfoanthranilic acid, and bis-(acetoacet)-o-toluidide,

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A bright yellow shade resulted. The leather had excellent properties.

Example 11

80 g. combination tanned (chrome tanned and further treated with quebracho or other natural tanning extract) suede sheep garment leather was dyed as in Example 7, using the same dye mixture. A brown shade was obtained of good light and wash fastness.

Example 12

80 g. combination tanned suede sheep garment leather was dyed as in Example 7 with a Rapidogen, which consisted of 5-chloro-o-toluidine diazotized and stabilized with 4-sulfoanthranilic acid, and 3-hydroxy-2-naphthoic-o-toluidide. A tan shade was obtained. The properties of the dyed leather were excellent.

Example 13

An 80 g. sample of chrome tanned grain glove leather, previously wet back as usual, was treated in the dye bath with 4 cc. monoethanolamine at 110° F. A solution, containing 1 g. acetoacet-m-toluylenediamine dissolved with 2 cc. alcohol and ½ cc. caustic soda 40° Bé., was added to the dye bath. The total volume was about 2,000 cc., pH about 10.5. Naphtholating continued at 110° F. for 20 minutes, during which time the pH dropped to about 9. 4 cc. of a 5% formic acid solution was added and the immersion continued for 20 minutes. An additional 4 cc. of a 5% formic acid solution was added and the immersion continued for 20 minutes at which time the pH had dropped to 5-7. The leather was rinsed and developed cold for 30-40 minutes in a bath consisting of 5 g. zinc chloride double salt of 3-chloro-6-methoxybenzenediazonium chloride made up to 2,000 cc. The leather was rinsed and finished as usual. A uniform yellow shade was obtained of good all around properties.

Example 14

The procedure of Example 6 was repeated, but employing instead of the bis-acetoacet-o-toluidide, 1 g. m-aminophenyl methyl pyrazolone. The initial pH was about 10.5, the second pH around 9 and the third about 5-7. A beautiful yellow color was produced of good all around properties.

Example 15

The procedure of Example 7 was repeated but employing as the coupler 3'-amino-3-hydroxy-2-naphthanilide and as diazo, dianisidine tetrazo stabilized with methyl taurine. A high quality leather having a navy blue coloration resulted.

Example 16

4 g. m-diethylaminophenol was pasted with 1 cc. alcohol and .5 cc. caustic soda 40° Bé., and diluted to 2000 cc. with water, approximate pH about 10.5-11. 80 g. chrome tanned suede calfskin which had been pre-wet was entered into this bath for 15 minutes, at which time the pH of the bath was about 10. Dyeing continued for 45 minutes. Due to the inherent acidity of the leather, the pH dropped to about 6. The leather was rinsed and added to a bath made up of 3 g. 1-naphthylamine dissolved with 5.5 cc. HCl 20° Bé. in 2000 cc. cold water. After about 5 minutes; 20 cc. of a 10% sodium nitrite solution was added. After about 20 minutes, 4 g. sodium acetate anhydrous was added and the leather left to soak another 20 minutes. The leather was withdrawn, rinsed and finished. A greenish tan product was obtained of good fastness to light, washing and crocking.

Example 17

1 g. Naphthol AS-D (3-hydroxy-2-naphthoic acid o-toluidide) was pasted with 2 cc. alcohol and 1 cc. caustic soda 40° Bé. and diluted to 2000 cc., pH about 10.5. To this bath was added an 80 g. swatch of chrome tanned grain glove leather which had been pre-wet. The pH

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dropped to about 10 after about 20 minutes. 8 cc. of a 5% formic acid solution was added. After about 30 minutes, at which time the pH was about 5-7, the leather was rinsed. It was then added to a bath which was made by dissolving 1.5 g. 3-butylsulfamyl-o-anisidine with 1.5 cc. HCl 20° Bé. and 2000 cc. water. After about 5 minutes, 5 cc. of a 10% sodium nitrite solution was added to the bath. After an additional 20 minutes, 4 g. sodium acetate anhydrous was added. After about 20 minutes, the leather was rinsed and finished as usual. A bright red dyeing was obtained, having good fastness properties.

Example 18

Leather was treated with coupler as in Example 5. It was then removed from the bath (pH 6-7), rinsed and refloats in cold water. To the dye bath was added a solution containing 1.5 g. 3-butylsulfamyl-o-anisidine, 1.5 cc. HCl 20° Bé. and cold water to a total volume of about 2000 cc. ½ g. sodium nitrite was added. After 20 minutes, 4 g. sodium acetate was added. After another 20 minutes, the leather was rinsed and finished as usual. A bright red coloration was obtained which had good fastness properties.

Example 19

A 10 g. sample of chrome tanned syntan stained sheep-skin was wet back, and at a temperature of 120° F. there was added to the dye bath .19 g. 3-hydroxy-2-naphthoic acid m-aminoanilide, .3 cc. alcohol, .2 cc. caustic soda 34° Bé. and sufficient water to float the skins. The pH was about 9. After about 30 minutes .3 cc. formic acid was added. After about 30 minutes, the pH was 4-5 and the skin was rinsed and refloats. To the bath was added .1 g. 3,3'-diaminobenzanilide pasted with .5 cc. warm water and dissolved with .2 cc. HCl. After a few minutes there was added .07 g. sodium nitrite, followed in 10 minutes by addition of .2 g. sodium acetate. After about 30 minutes the skin was rinsed and finished as in Example 1. The skin was dyed an orange shade of very uniform grain. The dyeing is fast to washing and dry cleaning.

Example 20

A 10 g. sample of chrome tanned syntan stained goat-skin was wet back. To the dye bath was added .13 g. 1-(m-aminophenyl)-3-methyl-5-pyrazolone, .3 cc. alcohol, .2 cc. caustic soda 34° Bé. and sufficient warm water to float the leather. The pH was about 9. After about 30 minutes there was added .3 cc. formic acid. After 30 minutes the pH was about 6, and the skin was rinsed and refloats. To the bath there was added .14 g. 1-(m-aminophenyl)-3-methyl-5-pyrazolone pasted with 1.0 cc. water and dissolved with .2 cc. HCl. After a few minutes there was added .06 g. sodium nitrite, and after 10 minutes .2 g. sodium acetate. After 30 minutes the skin was rinsed and finished as in Example 1. A deep greenish yellow was obtained of good light, wash and dry cleaning properties. The grain was dyed unusually level.

This invention has been disclosed with respect to certain preferred embodiments, and various modifications and variations thereof will become obvious to the person 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.

This application is a continuation-in-part of application Serial No. 534,628, filed on September 15, 1955, now abandoned.

I claim:

1. A process for the azoic dyeing of leather comprising treating leather with an azoic coupling component devoid of sulfonic and carboxylic acid solubilizing groups from an aqueous solution having an initial pH of more than 7 and less than 11, while lowering the pH of said aqueous solution to a final pH of no more than 7 while

controlling the rate at which such pH is so lowered so that a pH of more than 7 is maintained for from about 15 minutes to two hours, and then treating the leather with a diazotized aromatic primary amine compound devoid of sulfonic and carboxylic acid solubilizing groups to produce its reaction product with said coupling component in situ.

2. A process as defined in claim 1 wherein said azoic coupling component contains an aromatically bound free amino group.

3. A process as defined in claim 1 wherein said coupling component is an acylacetic acid arylide.

4. A process as defined in claim 1 wherein said coupling component is a pyrazolone.

5. A process as defined in claim 1 wherein said coupling component is an aromatic hydroxy compound capable of coupling.

6. A process as defined in claim 5 wherein said coupling component is a β -hydroxy aromatic carboxylic acid arylide.

7. A process for the azoic dyeing of leather comprising treating leather with an azoic coupling component devoid of sulfonic and carboxylic acid solubilizing groups

from an aqueous solution having an initial pH of more than 7 and less than 11, while lowering the pH of said aqueous solution to a final pH of no more than 7 while controlling the rate at which such pH is so lowered so that a pH of more than 7 is maintained for from about 15 minutes to two hours, and then treating the leather with a stabilized form of a diazotized aromatic primary amine compound devoid of sulfonic and carboxylic acid solubilizing groups to produce its reaction product with said coupling component in situ.

8. A process as defined in claim 7 wherein said azoic coupling component contains an aromatically bound free amino group.

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UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION

Patent No. 2,913,301

November 17, 1959

Clemens Streck

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 44, for "including" read -- inducing --;
column 6, line 14, and column 7, line 40, for "toluidide",
each occurrence, read -- tolidide --.

Signed and sealed this 13th day of June 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD

Commissioner of Patents