METHOD OF MARKING ANIMAL SKINS AND RESULTING PRODUCT


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9 Claims. (Cl. 8—10)

This invention relates to marking animal skins or hides and, more particularly, to imparting permanent indicia to the non-fur sides of skins or hides.

Normally the term "hides" is reserved for skins of large animals while the term "skins" is used to designate the integument of an animal separated from the body. Although the teaching of this invention is applicable to both hides and skins as they are generally thought of in commerce, the invention will be described in connection with the marking of skins which are particularly valuable for the fur which they contain. However, it is to be understood that the invention is also equally applicable to hides and that the term "skins" as used hereinafter is meant to include also hides.

Animal skins which are to be used for fur vary in source and quality. The producer may desire to mark the skin to identify its source and the buyer may want to identify its quality. This, therefore, requires a marking on the skin which will remain permanent throughout the treatment of the skin and which can be put on a portion of the skin which becomes a part of the garment made from the fur. Inasmuch as any mark on the hair side (e.g., fur side of a fur-bearing animal) as prohibited for aesthetic reasons, the mark must be placed on the non-hair side. The animals have skins of non-uniform thickness and, in addition, the skins usually contain flesh and fat, at least over certain portions. These two conditions are corrected during tanning by the various operations including washing, fleshing, paring the leather, and by chemical treatment. The tanning operations expose the skins to water, wetting agents, tanning agents, oils, and considerable abrasion from such things as sawdust, paddles, starch, and other skins. Since it is highly desirable for an identifying mark to be applied before the skins are tanned, a problem of achieving permanent marking exists, particularly the achievement of permanent marking in an area of the skin which is later to be used in the garment to be made therefrom.

Several techniques for marking the skins have been known and tried. Among these may be listed puncturing of the skin, branding, and tattooing. However, these all possess one or more drawbacks which make them unsatisfactory for marking skins, particularly those parts which are to become part of a fur garment. For example, puncturing is widely used but is unsatisfactory because it damages the skin and reduces its strength. The same is true for branding. Tattooing is used on live animals by growers, but the mark is placed on an ear or some other disposable part of the animal and tattooing is not used on the raw fur skins.

During the tanning process, the skin is exposed to water and oils, and merely to contact the skin with an oil- or water-soluble ink is not sufficient to obtain a mark which will be visible after the tanning process. Reactive chemicals which would essentially pre-tan the skin are sometimes effective as marking media, but the pre-tanned sections then do not behave the same as the untreated sections in tanning and there is an irregularity in the resulting leather that is discernible and objectionable in its working effect, also changes the texture of the fur and is objectionable for aesthetic reasons. Other dyes, particularly alcohol-soluble dyes, are applied with rubber or metal stamps to raw skins, but none of these marks are completely satisfactory because of their limited penetration into the skins and their easy removal by the washing, abrading, or paring operations in the tannery. Finally, exposure of the skins to water before they are in the tanning process should be avoided because of the danger of initiating or promoting bacterial decay of the skin. In addition, water will swell the skin and the original dimensions are not regained on drying, a change that may lead to a textural change in the fur. Heat is also to be avoided because it will damage the skins.

Thus, there is in the prior art techniques known, no efficient and non-destructive method for permanently marking raw skins in such a manner that the marking will remain legible and appear on a finished garment made from the skins. In marketing skins it is highly desirable that they carry a permanent mark; and, therefore, it would be desirable to have available a marking composition and method which are capable of achieving such permanent marking on an untanned animal skin. The invention described herein provides such a composition and method.

It is, therefore, a primary object of this invention to provide a permanently marked, fur-bearing skin, the skin being marked in the raw or untanned state and retaining the mark through subsequent operations so that the skin is identifiable by this mark on the finished skin product. It is another object of this invention to provide a marking composition or ink which can be used to impart indicia to the non-fur or flesh side of animal skins, these indicia remaining permanent throughout tanning, handling, and subsequent use of the skins. It is another object of this invention to provide a marking composition of the character described which does not impair the strength of the skin or alter the aesthetic qualities of the fur in any way. It is yet another object of this invention to provide a method for marking animal skins to imprint on them marks which will remain permanent throughout tanning, handling, and use. Other objects of the invention will in part be obvious and will in part be apparent hereinafter.

The invention, accordingly, comprises the several steps and the relation of one or more such steps with respect to each of the others, the composition possessing the features, properties, and the relation of components which are exemplified in the following detailed disclosure. The scope of the invention will be indicated in the claims.

We have found that it is possible to permanently mark animal skins by introducing into the skin a dyestuff which is gradually embedded into the fibers forming the skin and reacted therewith. It is essential that the dye be introduced in a particular type of carrier medium and in such a way that the dye is permanently affixed to the fibers so that it will not be removed in subsequent treatment by the tannery or the furrier.

The ink or marking composition suitable for permanently marking animal skins in accordance with the teaching of this invention may be described as a gel-like composition comprising a non-volatile, organic carrier medium miscible with water and the lower aliphatic alcohols and a dye having a good solubility in the carrier but limited solubility in water, preferably held present in a quantity in excess of that which is soluble in the carrier at any room temperature or at temperatures at which it is applied. The gel-like characteristies may be entirely due to the physical state of the carrier or to this property of the carrier enhanced by the presence of an excess of dye which is suspended in the carrier and serves to thicken it.

In carrying out the method of this invention for permanently marking an animal skin, it is necessary to apply...
to the non-fur side of the skin a dye in a gel-like carrier in which it is at least partly soluble, convert the carrier to a viscous liquid, and finally to maintain the carrier in contact with the skin for a period of time sufficient to permit it to penetrate into the skin and carry dissolved dye into the skin for permanent attachment to the fibers forming the skin. The application of the ink to the skin may be carried out using any technique suitable for depositing a viscous liquid on a surface. Thus, it may be applied by stamping, printing, stencilling, brushing, or with a stylus, pen or the like. In some cases ink penetration may be enhanced by pretreating the skin surface to which the ink is to be applied. Such pretreatment takes the form of applying pressure over those areas where ink is to be introduced. Such pressure may be applied by rubbing the skin with any tool which does not rupture or tear the skin under the pressures used. For example, pressure has been applied by rubbing the skin with a comb, a wire wound metal rod, or a smooth glass rod.

The resulting permanently marked animal skin may be characterized as one which has indicia permanently attached thereto by virtue of the fact that the dye has penetrated into the fibrous material that is to be tanned and reacted or been physically attached thereto. By introducing the dye in this manner and by permanently attaching it to the fibers, it is no longer readily soluble in alcohol or water and it persists through the tanning or other processing of the skins. Moreover, the skin so marked retains its original integrity and strength; i.e., it is not damaged either by chemical degradation or physical weakening.

Because the carrier medium of the ink of this invention must be able to deposit the dye on the skin surface and to be available for continued and subsequent solution of the dye and to be able at the same time to carry the dye into the skin fibers, it must have certain characteristics. The carrier medium of this invention must have some gel properties; that is, it must possess the property of breaking down or becoming fluid upon working, shaking, or when other physical effort is put on it and subsequently coagulating or getting again when left at rest in order to prevent lateral spreading of the ink deposited on the surface of the skin. The carrier may therefore be described as thixotropic, a property which is explained by the fact that there is mechanical destruction of the zones of the oriented molecules; the breakdown and recovery of a gel may be compared with a grease that breaks down on working and rehardens at rest. Thus, the ink used at room temperature and standing assumes a gel-like consistency but at the time of application under pressure or increased temperature or other forms of working it takes on the property of a liquid. Moreover, this carrier should be one which is relatively non-volatile at room temperature, which is miscible with water and the lower aliphatic alcohols, and which is an solvent for the dye used. We have found that a particularly good carrier is a mixture of polyethylene glycols, the mixture being made to give the necessary thixotropic and gel-like physical characteristics noted above.

The polyethylene glycols may be defined as polymers of the general formula

\[
\text{HOCH}_{2}(\text{CH}_{2}O\text{CH}_{2})_{n}\text{CH}_{2}\text{OH}
\]

They are available as liquids, pastes and waxy solids with molecular weights ranging from about 200–6000. Those with molecular weights below 600 are generally liquids; those having molecular weights of 600 and above are wax-like; however, the melting point of those having molecular weights of about 600 is about 38° C., and so these polyethylene glycols may be more pasty than waxy depending on ambient temperatures. Molecular weights of 15,000 to 20,000 are obtained by joining polyethylene glycols of 6000 molecular weight with a diepoxide. These modified polyethylene glycols (which are solids) may also be used in formulating the carrier.

We have found in the practice of this invention that it is preferable to use a mixture of at least two of these polyethylene glycols; for example, a mixture of a liquid having a molecular weight of about 400 and of a solid having a molecular weight of about 1000. The various polyethylene glycols are mixed to give a carrier having the necessary thixotropic or gel-like properties noted above. In using these polyethylene glycols, it has been found suitable to use them in ratios such that the liquid polyethylene glycol is present in a weight percent ranging from about 50–98%, the remaining being the solid polyethylene glycols. We have also found that copolymers of propylene oxide and ethylene oxide, which are solids, may be used as a constituent of the ink to contribute the necessary gel-like qualities. In such copolymers, ethylene oxide should form at least 50% by weight of the solid material.

One example of such a copolymer is a solid having a molecular weight of between 1,500 and 1,800, in which ethylene oxide is present in a range of from about 80 percent to 90 percent by weight.

Other suitable solid components are those copolymers which may generally be described as ethylenediamine tetrapolypropylene polyethylene oxides and which may be represented as substituted compounds of the formula

\[
\text{R}_{1}-\text{N}-(\text{CH}-\text{CH}_{2})_{n}-\text{N}-\text{R}_{2}
\]

where the R's are polypropylene oxide and polyethylene oxide copolymers. In these copolymers, at least 50% by weight of the R components should be polyethylene oxides.

When solid copolymers of the type described are used with liquid polyethylene glycols to form the carrier medium these copolymers may comprise from 2 to 50% by weight of the carrier.

In compounding the inks using these copolymers of ethylene oxide and propylene oxide, it may be desirable in some compositions to add a small amount of water to adjust the viscosity and/or to adjust the dye solubility in the carrier.

The dyes used to mark the skins and which are carried in the medium described above may be any dye which is at least slightly soluble in the thixotropic carrier and which is capable of being affixed to the skin fibers such that they will not be subsequently freed during the tanning process. Such dyes are normally alcohol soluble; many such dyes are known and may be identified in the Colour Index.

Typical dyes include, but are not limited to, Methyl Violet (Colour Index No. 42535), Spirit Soluble Fast Blue B (Spirit Soluble Solvent Blue 29), Calcefast Spirit Black RB, Cibacron Brilliant Orange G (CI Name Reactive Violet 2), Resorcine Brown R (concentrated) (Acid Brown 14 CI20195), Calcecid Fast R A (concentrated) (Acid Red 88 CI15620), and the like. The color selected will, of course, depend upon that which is desired of the permanent marking and the amount used in the ink will vary with the solubility of the dye in the carrier.

Because the process of this invention depends upon the transfer of dye from the carrier medium to the fibers of the skin over a finite period of time, it is preferable that the dyes be present in at least a slight excess of that which is soluble in the carrier, thus having a portion of the dyestuff actually suspended in the carrier medium; that is, undissolved. Thus, the suspended dye apparently contributes to the fluid gel properties of the ink composition. Although it is not known precisely by what mechanism the ink composition of this invention achieves permanent marking, it seems logical to postulate that after application it sets up and without spreading laterally permits the
8,272,585 dye to gradually penetrate into the skin and react and/or physically attach itself to the fibers. As a portion of the dye migrates into the skin and in effect goes out of solution, some of the suspended (undissolved dye) goes into solution and continues the penetration in and affixing to the fibers. Where the carrier medium itself is highly gel-like, it is possible to use inks in which all of the dye is dissolved. The effect of dyestuff concentration may be illustrated by the following example. A carrier medium was made by mixing glycol monomethyl ethers having molecular weights of 400 and 1000 in an 85/15 weight ratio. Solvent Blue 6G (C138) was then added to this carrier to form inks having dye concentrations of 3, 5, 10, 15 and 20%. Microscopic examination of the inks with 10% to 20% dyestuff showed that undissolved dyestuff was present, and there was a sharp increase in the intensity of the color in the permanent mark made with these inks as compared with the intensity of the color obtained with inks having dyestuff concentrations below the solubility limit. The presence of dyestuff in excess of the solubility is therefore preferred, but suitable inks may be prepared with the dyestuff in solution.

In the preparation of the inks of this invention, it is only necessary to mix the carrier medium (i.e., the polyethylene glycols) and then stir in the dyestuff. Normally this is done by grinding it in order to thoroughly incorporate the dyestuff into the carrier. It is also possible to dissolve the excess dyestuff by the judicious application of heat. The resulting ink, when cooled to room temperature, is a rather viscous or gel-like liquid which can be readily deposited upon the skin by such techniques as stamping, writing, printing, or otherwise depositing a quantity on the skin surface.

As described above, it is believed that the carrier medium gradually penetrates into the skin fibers and as it does so it carries with it some of the dye. In doing this a portion of the dye is continually being put into solution in the carrier medium and being carried into the fibers forming the skin. Thus, it is possible over a period of time to penetrate the skin with the dyestuff and to have the dyestuff permanently adhere to the fibers. Generally, it is desirable to permit the ink to remain on the skin for at least 20 minutes before introducing it to the tanning process. Once the ink has penetrated to the desired level in the skin, the residual ink may be removed by washing with water and the skin is ready for further processing. In between animal skins with the invention, it is preferable to permit the ink to penetrate down to the hair follicles (which form a natural barrier to further penetration), since this is the limit to which the skin may be pared without weakening the bond of the fur to the leather. A lesser degree of penetration is usually satisfactory in actual practice.

The ink of this invention and the process for marking skins may be further illustrated in the following examples, which are meant to be illustrative and not limiting.

Example 1
Fifty parts by weight of a polyethylene glycol having a molecular weight of 1000 (a solid) and 50 parts by weight of a polyethylene glycol having a molecular weight of 400 (a liquid) were mixed with 15 parts by weight of a Methyl Violet dyestuff (C142235). Mixing was accomplished by grinding the dyestuff into the polyethylene glycol mixture. When this ink was permitted to stand, it gelled and pressed on the skin by means of a stamp and pressure, it become a liquid. The ink was permitted to remain on the non-fur side of the skin for approximately 20 minutes. At this time penetration was sufficient to allow further processing of the skin. It was found that after the skin had been tanned and dressed that the indicia put into the non-fur side with the ink remained and was entirely legible even after this rather drastic treatment.

Example 2
An ink was made up in accordance with this invention by mixing 95 parts by weight of a polyethylene glycol having a molecular weight of 400 and 5 parts by weight of a polyethylene glycol having a molecular weight of 15,000-20,000 (a solid) with 10 parts by weight of Solvent Blue 6G (C138). The mixture was heated to dissolve the dyestuff; then it was chilled to room temperature. In chilling, the material set up as a gel but could easily be broken down on working; i.e., by the pressure generated in stamping an indicia on a non-fur side of a mink skin.

In both Examples 1 and 2, the dyestuffs were in excess of that which was soluble in the polyethylene glycol mixture.

Example 3
An ink was prepared with 85 parts by weight of a polyethylene glycol having a molecular weight of 400, 15 parts by weight of a polyethylene glycol having a molecular weight of 1000, and 3 parts by weight of Solvent Blue 6G. Skins marked with this composition, which contained all of the dye in solution, were identifiable, but the intensity of the color retained was much less than for a similar ink containing 15 parts by weight of the dyestuff. It is therefore possible to mark a skin with an ink containing dissolved dyestuff, but the mark is improved when an excess is present.

Example 4
An ink was prepared as a mixture of 85 parts by weight of a polyethylene glycol having a molecular weight of 400, 15 parts by weight of a polyethylene glycol having a molecular weight of 1000, 2 parts by weight of a polyethylene glycol having a molecular weight of 20,000, and 10 parts by weight of Calcofast Spirit Black RB. The surface to be marked was rubbed with a smooth stylus and then the ink was applied to the animal skin from a rubber roller stamp and the indicia so affixed to the raw skin was readily identifiable on the dressed leather.

Example 5
An ink was prepared by first mixing 8.5 grams of a polyethylene glycol having a molecular weight of about 400 (a liquid) with 1.5 grams of a copolymer of ethylene oxide and propylene oxide having a molecular weight between 1,500 and 1,800 and an ethylene oxide content between 70 percent and 90 percent by weight (a solid). Into this carrier medium one gram of Solvent Blue 6G (C138) dye was ground to insure thorough mixing. The ink thus formed was applied to the non-fur side of a mink skin by means of a rubber stamp. It was permitted to remain on the skin for about 20 minutes before the skin was further processed.

Example 6
An ink was made as in Example 5 by substituting 1.5 grams of an ethylenediamine tetrapropylylene polyethylene oxide (sold under the trade name of Tretomix 908 by Wyandotte Chemical Company) for the copolymer of that example. The ink was applied to the non-fur side of a mink skin, as in Example 5, and successfully marked the skin with indicia which remained throughout the tanning process.

Mink skins marked with the ink compositions of these examples and in accordance with the teachings of this invention were entirely aesthetically acceptable inasmuch as no color from the ink was discernible on the fur of the mink skins. Moreover, by being permanent, the marking of this invention makes it possible to mark a raw skin and impart to it a permanent marking which will remain throughout normal skin processing such as used by the furrier or tailor in making the dressed skins into garments.

It will thus be seen that the objects set forth above, among those made apparent from the preceding descri-
tion, are efficiently attained; and since certain changes may
be made in carrying out the above method and in the
article set forth without departing from the scope of the in-
vvention, it is intended that all matter contained in the
above description shall be interpreted as illustrative and
not in a limiting sense.

We claim:

1. An ink suitable for permanently marking untanned
animal skins and hides, consisting essentially of:
(a) a thixotropic gel-like, non-volatile, oxygenated hy-
drocarbon carrier medium soluble in water and the
lower aliphatic alcohols and being further charac-
terized as consisting essentially of a mixture of at
least one liquid polyethylene glycol present in an
amount equivalent to from 50 to 98% by weight of
said carrier medium and at least one solid which
is a polyethylene glycol or a copolymer of ethylene
and propylene oxides forming the balance of said
carrier medium; and
(b) an alcohol-soluble dye having a limited solubility
in said carrier medium and suspended therein, said
dye being present in a quantity in excess of that which
is soluble in said carrier medium at normal room
temperatures.

2. Ink in accordance with claim 1 wherein said solid
copolymer is an ethylenediamine tetrapropylene poly-
ethylene oxide containing at least 50 percent ethy-
lene oxide by weight.

3. An ink in accordance with claim 1 wherein said dye
is reactive with the fibers in said skins.

4. An ink suitable for permanently marking untanned
skins and hides, consisting essentially of:
(a) an alcohol-soluble thixotropic gel-like carrier con-
sisting essentially of a mixture of liquid polyethylene
glycols and solid polyethylene glycols, said mixture
ranging in composition from about 50% to 98% by
weight of said liquid polyethylene glycols, the re-
maining being said solid polyethylene glycols; and
(b) a dye having a limited solubility in said carrier
and suspended therein, said dye being present in a
quantity which is at least substantially equivalent to
that which is soluble in said carrier.

5. Ink in accordance with claim 4 wherein said dye
is present in excess of that which is soluble in said
carrier.

6. Method of permanently marking an animal skin,
comprising the steps of:
(a) applying to the non-fur side of an untanned skin
a dye suspended in an alcohol-soluble, gelled, non-
volatile, oxygenated hydrocarbon carrier medium in
which it has a limited solubility, wherein said carrier
medium consists essentially of a mixture of at least
one liquid polyethylene glycol present in an amount
equivalent to from 50 to 98% by weight of said
carrier medium and at least one solid which is a
polyethylene glycol or a copolymer of ethylene and
propylene oxides forming the balance of said carrier
medium; and
(b) maintaining said carrier in contact with said skin
for a period of time sufficient to cause it to penetrate
into said skin and carry dissolved dye into said skin
for permanent attachment to fibers thereof.

7. Method in accordance with claim 6 wherein said
applying comprises contacting the ink with said skin
under pressure.

8. Method in accordance with claim 6 including the
step of applying pressure to said skin prior to applying
said dye.

9. An animal skin permanently marked in the raw un-
tanned state and having indicia visible on the non-fur
side whereby the skin retains the marking as well as its
original integrity and strength throughout further proces-
sing, the skin being marked by the process of claim 6.

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