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METHOD OF DEGREASING SKINS

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This invention relates to an improved method for the degreasing of skins in the manufacture of leather.

This conversion of crude hide to finished leather consists of a series of procedures based largely on experience. Crude hides are usually received at the tannery in a dry, salted condition and before being subjected to any treatment are swelled back into shape by soaking in water. Extraneous matter such as salt, tissue, dried blood, fat, hair and soluble protein matter is then removed from these soaked hides. The original hides contain variable quantities of fatty substances such as grease and it is desirable to remove these prior to the tanning operation, because their removal permits better penetration of the tanning liquor.

Heretofore, the degreasing of skins has been accomplished by the use of solvents such as various petroleum-hydrocarbon cuts obtained from crude oil, such as kerosene, having a boiling range from about 400° F. to about 500° F. and a solvent known in the trade as "Varnolene," which is a petroleum hydrocarbon cut having a boiling range of about 300° F. to about 400° F. However, because of the aqueous salt solution present in the hides, it is difficult for a non-miscible liquid, such as a petroleum hydrocarbon to penetrate the skins so as to remove the grease to the desired degree.

Degreasing of skins has also heretofore been carried out with liquid hydrocarbon solvents of fat or grease, admixed with a non-drying oil of such nature that the mixture will form an emulsion with water. While such a method is an improvement over one in which only an organic degreasing solvent is used, it suffers from a similar disadvantage in that it still does not remove sufficient of the grease for most practical purposes.

It is an object of this invention to provide a degreasing method with which the fatty substances may be removed from crude hides or skins more easily, more uniformly, more thoroughly and more economically than heretofore. Other objects and advantages of the invention will be apparent during the course of the following description.

In accordance with my invention, the degreasing of skins is accomplished by the use of a water emulsifiable composition comprising a solvent for the fatty substances present in the skins and a minor amount of an emulsifiable pine oil, with or without the addition of a protective colloid to stabilize the emulsion. I have found that skins treated with my compositions are more

thoroughly degreased than when the same skins are treated with prior art degreasing compositions. I have also found that there is a more even deposition of the remaining grease so that a more even dyeing may be obtained, especially in the case of sheepskins.

In proceeding in accordance with my invention I may take, for example, water-wet pickled sheepskins, which have been treated in a pickling solution composed of about 3% sulfuric acid and about 10-15% of sodium chloride, and add thereto a solvent for the grease, and from about 1% to about 15%, preferably about 4% to about 10%, by weight of the solvent of an emulsifiable pine oil. The skins together with the solvent and the emulsifiable pine oil are treated in a rotating degreasing drum for a certain period depending on the particular skins being treated. At the end of this period, the greasy solvent is removed from the skins and these are then washed with several salt water washes. A mild tanning extract is added to the last salt water solution and the skins are treated with this solution for approximately 30 minutes after which they are removed and sent to the tannery.

The particular solvent used in the degreasing operation may vary, depending upon the practice of the individual commercial plants. It is, of course, possible to use any organic solvent which is capable of dissolving oils, fats or greases, but from a practical standpoint, I prefer using a liquid petroleum hydrocarbon and more particularly one having a boiling range within about 300° F. to about 500° F. Among the latter are kerosene and a product known under the trade name of "Varnolene."

The emulsifiable pine oil which I add to the solvent consists of pine oil to which a small amount of a suitable dispersing agent has been added. I have found that this combination is a good dispersing and emulsifying agent so that this property plus the fact that pine oil itself is an excellent wetting-out and penetrating agent makes the combination unique for use with grease solvents in the degreasing of leather in accordance with this invention. Among the dispersing agents particularly effective are sulfonated castor oil, sodium oleate, and the alkylamine esters of a higher fatty acid, such as oleic, ricinoleic and stearic acid. These esters may be prepared using either the acids or the glyceryl esters thereof. The amount of the dispersing agent will in general not be in excess of about 10% by weight of the pine oil. It will be appreciated, of course, that the amount used in

each particular case will depend on the condition of the skins as well as upon the specific dispersing agent used with the pine oil.

Since the aqueous phase present in the degreasing process is always slightly acid in character and since pine oil emulsions tend to be unstable in acid media, it may be desirable to add certain protective colloids to act as stabilizers for the dispersions. As stabilizers, a great variety of mostly water-soluble colloidal substances may be used, among which are the following: gum arabic, albumin, agar-agar, and methyl cellulose. The choice of the latter will depend not only on the properties of the stabilizer itself but also upon the properties of both the dispersion medium and the dispersing agent.

In this connection, however, it must also be remembered that the stability of pine oil emulsions in any medium is also affected by the dispersing agent used with the pine oil. For example, when the reaction product of castor oil-triethanolamine is added to the pine oil and this is emulsified in an aqueous acid medium, such as present in the degreasing operating, the emulsion formed is stable without the addition of protective colloids.

With reference to the terms "protective colloid" and "dispersing agent" as used in the present application, I mean by the former a lyophilic colloid which assists in stabilizing the emulsion. An explanation which has been offered for the effect produced by protective colloids, is that these colloids form protective films around the droplets of the dispersed phase, thereby preventing coalescence. The term "dispersing agent" as used herein refers to a material soluble in the pine oil and which is added for the purpose of making the pine oil emulsifiable by reducing its interfacial tension against water.

The following examples will give a more detailed description of this invention.

Example 1

To 125 pounds of pickled sheepskins in a degreasing drum there were added 7.5 gallons of "Varnolene" and 2.9 pounds of an emulsifiable pine oil consisting of 90% pine oil and 10% of sulfonated castor oil and the drum rotated for 10 minutes. Then 0.26 pound of gum arabic dissolved in one pint of water was added to stabilize the emulsion and the drum rotated for an additional period of 1 hour and 20 minutes. The greasy "Varnolene" was then removed and the skins treated in the drum with a warm (110° F.) salt solution composed of 5 pounds of salt dissolved in 87 pounds of water. After 15 minutes treatment this solution was drained and the skins were given 5 warm salt water washes of the same concentration of salt as before. After these washes, a cold salt water solution of the same concentration as before was added to the skins in the degreasing drum which was then rotated for 15 minutes. This salt solution was retained and a mild tanning extract added thereto after which the drum was rotated for an additional 30 minutes. The skins were then taken out and sent to the tannery after which they were made into finished leather by dyeing, glazing, etc.

The superior and more uniform degreasing obtainable by treatment in accordance with my invention over that of the prior art was clearly indicated by inspection of the skins. The superiority was particularly indicated after dyeing because there was a very level distribution of the color which has not been the case with prior art

degreasing, especially when some particularly difficult color is desired.

In the following examples a large batch of sheepskins were treated in the manner described below. These skins originally had a grease content of 35.22% as determined by subjecting a sample of these skins to a chloroform extract under reflux conditions over night. After each of the degreasing operations shown below, a sample of the degreased skins, taken from the same portions of the hides on which the original grease content was determined, was subjected to the same chloroform extraction under the same conditions in order to determine the amount of grease still left in the skins.

Example 2

About 700 pounds of pickled sheepskins (being approximately 350 pounds of dry skins and 350 pounds of salt water, containing about 15% sodium chloride and 3% sulfuric acid) were placed in a degreasing drum and 33 gallons of "Varnolene" and 2 gallons of an emulsifiable pine oil consisting of 85% pine oil, 10% sodium oleate and 5% water were added thereto. The drum was then rotated for about 1 hour with this degreasing medium after which the greasy salt water solution was drained to the sewer. The degreased skins were then given a salt water wash for ½ hour with 800 pounds of a 4% salt solution by rotating the degreasing drum with the outlet closed, and after draining this, were further washed with a total of 1600 pounds of a 4% salt solution having the outlet of the degreasing drum partially open for the salt water to wash through. A mild tanning extract was then added to a fresh salt solution of the same concentration and the skins were treated with this in the revolving degreasing drum for ½ hour, after which the skins were removed and sent to the tannery. A chloroform extraction of the degreased skins showed that they contained 21.29% grease or fatty substances. This is to be compared with the original grease content of 35.22% before degreasing as shown. The skins thus contains 40% less oil than the untreated skins.

Example 3

About 700 pounds of pickled sheepskins were treated in the same manner as shown in Example 2 by using an emulsifiable pine oil composed of 90% pine oil and 10% of the reaction product of castor oil and triethanolamine. A chloroform extraction of a sample of these degreased skins showed that they contained 15.17% grease or fatty substances. This means that my degreasing composition has removed about 57% of the original grease present.

Example 4

About 700 pounds of pickled sheepskins were treated in the same manner as shown in Example 2 by using an emulsifiable pine oil composed of 90% pine oil and 10% of sulfonated castor oil. A chloroform extraction of a sample of these degreased skins showed that they contained only 9.03% grease or fatty substances. This means that my degreasing composition has removed nearly 75% of the grease originally present in the skins.

Example 5

About 700 pounds of pickled sheepskins of the same original stock as used in Example 2 were placed in a degreasing drum and 33 gallons of "Varnolene" and 2 gallons of a sulfonated corn

oil were added thereto. The degreasing procedure was then carried out in the same manner as in the previous examples. A chloroform extraction of a sample of the degreased skins showed that they still contained 26.06% grease or fatty substances after the treatment as shown. This means that only about 26% of the original grease content has been removed.

The marked improvement in grease removal from skins when using my compositions containing a minor amount of an emulsifiable pine oil is clearly demonstrated when the results shown in Examples 2, 3, and 4 are compared with those shown in Example 5, where the grease removal was carried out with a degreasing composition heretofore used by the art.

It will be understood that the details and examples hereinbefore set forth are illustrative only and in no way limiting on my invention as broadly described hereinbefore and in the appended claims.

What I claim and desire to protect by Letters Patent is:

1. A method of degreasing water-wet pickled skins which comprises agitating said skins with a composition comprising a petroleum hydrocarbon grease solvent and a small proportion of emulsifiable pine oil, said emulsifiable pine oil being composed of pine oil and a small proportion of a water-soluble emulsifying agent therefor, and thereafter removing said skins from said composition.

2. A method of degreasing water-wet pickled skins which comprises agitating said skins with a

composition comprising a petroleum hydrocarbon grease solvent boiling within the range from about 300° F. to about 500° F. and a small proportion of emulsifiable pine oil, said emulsifiable pine oil being composed of pine oil and a small proportion of a water-soluble emulsifying agent therefor, and thereafter removing said skins from said composition.

3. A method of degreasing water-wet pickled skins which comprises agitating said skins with a composition comprising a petroleum hydrocarbon grease solvent and a small proportion of emulsifiable pine oil, said emulsifiable pine oil being composed of pine oil and a small proportion of sodium oleate, and thereafter removing said skins from said composition.

4. A method of degreasing water-wet pickled skins which comprises agitating said skins with a composition comprising a petroleum hydrocarbon grease solvent and a small proportion of emulsifiable pine oil, said emulsifiable pine oil being composed of pine oil and a small proportion of sulfonated castor oil, and thereafter removing said skins from said composition.

5. A method of degreasing water-wet pickled skins which comprises agitating said skins with a composition comprising a petroleum hydrocarbon grease solvent and a small proportion of emulsifiable pine oil, said emulsifiable pine oil being composed of pine oil and a small proportion of an alkylolamine ester of a higher fatty acid, and thereafter removing said skins from said composition.

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