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2,974,000

FAT-LIQUORING PROCESS

Clinton Edward Retzsch, Caldwell, Jacob Levy, Livingston, and Charles Herbert Lighthipe, Bernardsville, N.J., assignors to Nopco Chemical Company, Harrison, N.J., a corporation of New Jersey

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This invention relates, in general, to the fat-liquoring of leather. More particularly, it relates to a class of compounds which has been found to be very effective when used to fat-liquor leather.

As a general rule, a series of distinct and separate operations are involved in the processing of hides and skins in the manufacture of leather. Included among these operations are the preliminary steps of soaking and fleshing the hides and skins and the steps of pickling, tanning, neutralizing, washing, and fat-liquoring the leather. The fat-liquoring step with which the present invention is primarily concerned serves to replenish the natural oils and greases that are unavoidably removed from the leather during the various stages in its processing. By replacing, with comparable lubricating materials, the natural lubricants that are lost during its processing, the pliability or suppleness, the tensile strength and the tear-resistance of the finished leather is greatly enhanced.

In the past, very many chemical compounds, and various mixtures containing such compounds, have been disclosed as being suitable for use as fat-liquoring agents. These include raw and sulfonated oils and fats, soaps made from oils and fats, waxes, resins, moellon degars and egg yolk. To a limited extent these and various other materials have proven to be satisfactory for such use. However, since the fat-liquoring operation contributes greatly to the quality, utility and marketability of the finished leather, efforts to develop products that will improve the effectiveness of the operation, and ultimately, the characteristics of the product, are never ending.

To be satisfactory for use as a fat-liquoring agent, a product must be such that it will penetrate the surface of the leather and properly lubricate the interior thereof. This is accomplished in the art by carrying out the fat-liquoring operation in a bath comprising water and the fat-liquoring agent or agents. The bath may also contain other ingredients. In order to insure complete and proper lubrication of the leather, the lubricant or lubricants must be distributed properly throughout the aqueous fat-liquor bath. A proposed fat-liquoring agent, therefore, must be soluble, or at least dispersible, in water. Thus, in addition to its lubricating properties, the solubility or the dispersibility of a proposed product in water is a prime factor to be considered in evaluating its suitability for use as a fat-liquoring agent.

There are a number of effective fat-liquoring compositions on the market today. However, many of the compositions that have been suggested in the art as being suitable for use as fat-liquoring agents have been found to be far less than satisfactory. For the most part this is attributable either to the fact that the proposed products did not lubricate the leather to the extent desired or to the fact that the products were either insoluble or not readily emulsifiable in water. However, certain other of the fat-liquoring agents of the art were unsuitable for use due to their tendency to darken or discolor the leather that was treated therewith.

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It is the object of this invention to provide a method for improving the fat-liquoring of leather.

It is a further object of the invention to provide improved compositions which are suitable for use in the fat-liquoring of leather.

It is a more particular object of the invention to provide a composition which, alone or in combination with known constituents of fat-liquoring compositions, effectively fat-liquors leather imparting thereto vastly improved pliability, tensile strength and tear-resistance without discoloring or darkening it.

Other objects of the invention will be obvious and will, in part, appear hereinafter.

It has been found that certain water-soluble or water-dispersible products derived from fatty acid-dialkanolamine condensates can be used successfully, either alone or in combination with other suitable materials, to fat-liquor leather. For convenience, in this specification, these water-soluble or water-dispersible derivatives will be referred to collectively as the "solubilized condensates."

The fatty acid-dialkanolamine condensates, the water-soluble or water-dispersible derivatives of which are used in the practice of this invention, are produced by reacting a fatty acid having a carbon chain length of from about 10 to about 20 carbon atoms, or a glyceride containing such fatty acids, with a dialkanolamine or with a mixture thereof. In addition, such condensates can be produced by reacting a dialkanolamine or a mixture of dialkanolamines, with a mixture of the aforementioned fatty acids or with a mixture of glycerides containing those fatty acids. Moreover, if desired, one may carry out the condensation of the dialkanolamine using fatty acid esters other than esters of glycerol, as, for example, esters produced from a fatty acid having a carbon chain length of from about 10 to about 20 carbon atoms and aliphatic monohydric alcohols having from 1 to 5 carbon atoms in their structure. For convenience, and to distinguish them from the solubilized condensates which are produced therefrom, the fatty acid-dialkanolamine reaction products will be referred to herein as the "base condensates." Thus, in the practice of the invention, a base condensate produced by reacting a dialkanolamine, or a mixture of dialkanolamines, with a saturated, unsaturated or hydroxylated fatty acid having a carbon chain length of from about 10 to about 20 carbon atoms, or with a mixture of such fatty acids, can be used. Included among the group of fatty acids that can be used are saturated fatty acids, such as, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, or arachidic acid; unsaturated fatty acids, such as, oleic acid, linoleic acid or linolenic acid; and hydroxylated fatty acids, such as, ricinoleic acid. As used herein, the expression fatty acid should be construed as including those products which are available commercially as "fatty acids." These, of course, are mixtures of various fatty acids. Thus, whenever or wherever in the present specification reference is made to oleic acid, stearic acid, etc., mixtures containing those acids in combination with other higher and lower molecular weight saturated and unsaturated fatty acids are included. The glycerides that can be used in producing the base condensates include any of the various animal, vegetable, marine or marine animal oils, as, for example, palm oil, coconut oil, rice bran oil, tallow, castor oil, cod-liver oil, whale oil, etc., both raw and hydrogenated. In addition, the fatty acids, and the natural mixtures of fatty acids, that are derived from such glycerides can be employed in the production of the base condensates. The esters other than glycerol esters than can be used in producing the base condensates include esters of methyl, ethyl, propyl, butyl and amyl alcohol with fatty acids, such as, capric acid, lauric acid, oleic acid, stearic acid, etc. The preferred solubilized condensates of the inven-

tion are derivatives of base condensates produced by reacting a dialkanolamine either with oleic acid or with a natural mixture of fatty acids containing large quantities of oleic acid.

In general, any dialkanolamine can be reacted with a fatty acid, a glyceride or some other fatty acid ester to produce the base condensates. However, it has been found that a solubilized condensate derived from a base condensate produced by condensing a fatty acid with a lower molecular weight dialkanolamine, that is, a dialkanolamine, the alkyl radicals of which do not exceed about four carbon atoms in length, is an excellent fat-liquoring agent. Outstanding results are achieved, for example, when a solubilized condensate derived from a base condensate produced by reacting a fatty acid, a glyceride or some other fatty acid ester with diethanolamine or diisopropanolamine, is used in the practice of the invention. In the preferred embodiment of the invention a solubilized condensate derived from a base condensate produced by condensing a fatty acid, such as, oleic acid, with diethanolamine is employed.

The precise manner in which the fatty acid, the glyceride or other fatty acid ester and the dialkanolamine are reacted to give the desired base condensate will be quite apparent to those skilled in the art. Such condensates, and the process by which they are produced, are described in U.S. Patent 2,089,212. For the purposes of this invention the fatty material is condensed with the dialkanolamines in such quantities that the mol ratio of fatty acid to dialkanolamine is about one to two. When a glyceride, or a mixture of glycerides, is employed as the source of the fatty acid, it is substituted for the fatty acid on an equivalent basis, that is, one mole of glyceride should be used for each six moles of dialkanolamine. Thus, in all embodiments of the invention, the ratio of carboxyl groups, as supplied either by the fatty acid or ester or by the glyceride, to nitrogen atoms, as supplied by the dialkanolamine, will be about one to two, respectively. Under ordinary circumstances, the reaction conditions employed in carrying out the reaction will be the same regardless of whether a fatty acid or an ester, including a glyceride, is employed. Generally, the base condensate can be prepared successfully by heating the reactants at a temperature of at least about 100° C. However, it has been found that optimum results will be obtained if the condensation is carried out at a temperature within the range of from about 135° C. to about 210° C. The duration of the heating step will depend primarily upon the temperature used. At higher temperatures, that is, at temperatures of about 210° C., the reaction will proceed more quickly and a shorter heating period will be needed.

The reaction conditions employed in preparing the base condensates are such that, for each mol of fatty acid that is present originally in the reaction mixture, from about one mol to about two mols of water are formed during the condensation. The exact nature of the condensation products thus obtained has not been determined. It is believed, however, that one mol of water is liberated when an amide linkage is formed between the carboxyl group of the fatty acid and the secondary nitrogen atom of one mol of the dialkanolamine and that the second mol of water is split out when a pentavalent nitrogen atom is formed between the hydroxyl groups of the alkanolamide and the secondary nitrogen atom of the second mole of dialkanolamine. Generally, prolonged heating or heating at a temperature at or near the extreme temperature limitation, that is, 210° C., will result in the liberation of the second mol of water. For the purposes of the present invention, a base condensate from which up to about two mols of water are actually split out can be employed. Thus, the formation of water during the condensation reaction provides an excellent control standard for the reaction. The water formed during the reaction can be collected,

as, for example, by the use of a Dean-Stark trap. When at least one mol, and up to about two mols of water, for each mol of fatty acid used has been collected, the condensation reaction can be considered as being complete.

As disclosed heretofore, the solubilized condensate that is used in the practice of the present invention is a water-soluble or water-dispersible product derived from the fatty acid-dialkanolamine condensate heretofore described. It is prepared by reacting the base condensate with a compound that will either render it soluble or dispersible in water or enhance its solubility therein. In general, such compounds include alkylating agents, as, for example, alkyl halides, alkyl sulfates, alkyl phosphates, dialkyl sulfates, etc.; aralkylating agents, as, for example, benzyl halides, etc.; and organic and mineral acids. Thus, a suitable solubilized condensate can be prepared by condensing the fatty acid-dialkanolamine condensate with an alkylating agent such as, ethyl bromide, ethylene chlorhydrin, dimethyl sulfate, diethyl sulfate, triethyl phosphate. A comparable result will be obtained by substituting in the reaction an aralkylating agent, such as, benzyl chloride or benzyl sulfate, for the alkylating agent. In another embodiment of the invention, suitable solubilized condensates can be obtained by neutralizing the fatty acid-dialkanolamine condensate with an acid, either mineral or organic. In general, any acid capable of reacting with the base condensate to form therewith the desired water-soluble or water-dispersible product can be used. More specifically, any of the various mineral acids or any organic acid having up to about 3 carbon atoms in its structure can be employed. Acids such as formic acid, acetic acid, glycolic acid, hydrochloric acid, sulfuric acid, et. are all well suited for use. However, irrespective of whether an alkylating agent, an aralkylating agent or an acid is employed, the desired solubilized condensate is obtained by reacting the fatty acid-dialkanolamine condensate with approximately equimolecular quantities of the solubilizing agent.

The method by which such solubilized condensates are prepared is well known in the art. The production of products having a somewhat similar structure is disclosed in U.S. Patent 2,496,640 and U.S. Patent 2,496,641. As a general rule, the desired compound can be obtained by heating the fatty acid-dialkanolamine condensate with the solubilizing agent at an elevated temperature. The temperature used in this step will depend upon the particular solubilizing agent in use. Thus, for example, using a strong alkylating agent, as, for example, diethyl sulfate, temperatures exceeding about 60° C. need not be employed. However, using an alkylating agent, such as, ethylene chlorhydrin, triethyl phosphate, etc., temperatures approximating 170° C. are needed to initiate the reaction, which is exothermic in nature. Since excellent results are obtained thereby we prefer to use diethyl sulfate as the solubilizing agent and to carry out the reaction at a temperature of about 60° C. However, when diethyl sulfate is employed, lower temperatures, as, for example, any temperature above ordinary room temperatures, can be used but at such lower temperatures the reaction rate is slower and a longer heating period is needed.

Our invention is noteworthy in that we have discovered products, namely, the solubilized condensates described herein, which, either alone or in combination with other materials, have outstanding utility as fat-liquoring agents. A particular feature of the invention is the fact that the solubilized condensates can be used in the fat-liquoring of any type of leather, regardless of the manner in which the leather was tanned, without necessitating any change whatsoever in the conventional fat-liquoring processes of the art. Moreover, since the fat-liquoring compositions of this invention are compatible with the various mineral tanning agents, as, for example, with alum and chrome tanning agents, the fat-liquor can be added directly to

the tanning bath and thus obviate the necessity for the step of washing the leather after tanning. In such an instance, there is no need for a separate fat-liquoring step. The "take-up" by the leather of the fat-liquoring agents of this invention, or of compositions containing them, is extremely high regardless of whether the fat-liquoring agent is added to the tanning bath or used in a separate fat-liquoring step.

The manner in which leather is fat-liquored using the products disclosed herein will be quite obvious to those skilled in the art. When the solubilized condensate is used alone, its water-solubility or dispersibility permits it to be employed in the form of an aqueous solution or dispersion. When the derivative is used in combination with a water-immiscible material, as, for example, in combination with any of the many known constituents of the fat-liquors of the art, the mixture is employed to fat-liquor leather in the form of an aqueous emulsion. In a composition of the latter type, the solubilized condensate performs a dual function. First, it serves to emulsify the water-immiscible ingredient in water thus providing even distribution of the ingredient throughout the bath and insuring proper penetration of the ingredient throughout the leather. Secondly, but of no lesser importance, in such a composition, the solubilized condensate functions as a fat-liquoring agent. In short, in a composition of this nature, the solubilized condensate itself lubricates the leather and makes it possible for the added water-immiscible ingredient or ingredients to do likewise.

Several classes of compounds are well suited for use in conjunction with the solubilized condensates of this invention. It has been found that aqueous emulsion concentrates containing our solubilized condensates in combination with various fatty oils and/or mineral oils are highly effective fat liquoring agents. Thus, for example, the solubilized condensates of the invention can be blended with fatty oils, that is, oils from animal, vegetable, marine and marine animal sources, such as, neat's-foot oil, rice bran oil, whale oil, herring oil, codliver oil, coconut oil, castor oil, etc. In addition blown fatty oils, such as, blown sperm oil, blown tallow, etc. can be used. When such a blend is employed in the form of an aqueous emulsion, extremely noteworthy properties are imparted to the leather fat-liquored therewith. Moreover, if desired, the solubilized condensates described herein, either alone or in combination with a fatty oil, can be blended with a mineral oil, such as, paraffin oil, white mineral oil, yellow mineral oil, etc. and, in the form of an aqueous emulsion, used to fat-liquor leather. Hereinafter, the expression "raw oils" will be used collectively and it should be construed as including both the various types of fatty oils enumerated heretofore and mineral oils.

In addition, the solubilized condensates of the invention, either alone or in combination with any of the aforesaid raw oils, can be blended with an anionic surface active agent and the blend thus obtained employed, in the form of an aqueous emulsion, to fat-liquor leather. Some of the anionic surface active agents that can be employed in such embodiments of the invention are the various sulfonated oils, as, for example, sulfonated sperm oil, sulfonated neat's-foot oil, sulfonated cod oil, sulfonated herring oil, sulfonated whale oil, sulfonated tallow, etc. It should be understood that although the expression "sulfonated oil" is used to designate the anionic surface active agents that are suitable for use herein, technically it would be more proper to refer to these oils as sulfated oils. However, since, in the trade, these oils are commonly referred to as "sulfonated oils," we will employ that expression in this specification. Procedures suitable for producing sulfonated oils are well known in the art and sulfonated products produced by any of the known methods can be used in the practice of this invention. The organic "SO₃" content of the sulfonated oils

employed can be varied to some extent. However, sulfonated oils having an "SO₃" content of from about 4% to about 10% are preferably used. Moreover, since they are generally available commercially as such, sulfonated oils containing quantities of water admixed therewith can be used. In the practice of the present invention sulfonated oils having a water content of about 25% by weight are employed usually. However, sulfonated oils having a water content of as low as 0.5% by weight, or lower, are also suitable for use. Quite obviously, since our novel compositions are, prior to use, diluted with rather large quantities of water, the presence of sulfonated oils in our products having a water content greatly in excess of 25% by weight is not objectionable. However, since the presence of an extremely large quantity of water in the sulfonated oil would serve to decrease the proportion of active fat-liquoring ingredients in the product while increasing shipping costs and presenting storage problems for the product, seldom, if ever, will it be desirable to use a sulfonated oil having a water content which is greatly in excess of about 25% by weight.

Furthermore, non-ionic surface active agents can be used in combination with the solubilized condensates, either alone or in combination with the raw oils and/or the anionic surface active agents. Such non-ionic materials include mono- and diesters produced by reacting a polyethylene glycol having a molecular weight of from about 200 to about 1000 either with a saturated, unsaturated or hydroxylated fatty acid having a carbon chain length of from about 8 to about 22 carbon atoms, and preferably about 12 to about 16 carbon atoms, or with a glyceride containing such fatty acid radicals. Thus, for example, polyethylene glycol (200) monolaurate, polyethylene glycol (400) monooleate, polyethylene glycol (600) distearate, polyethylene glycol (800) dilaurate, polyethylene glycol (800) dioleate, polyethylene glycol (1000) monoricinoleate, etc. can be used. It has been found that when such esters are used in combination with the solubilized condensates of this invention, they function not only to improve the emulsion stability of the product but also to enhance the fat-liquoring properties thereof.

In addition, aqueous emulsion concentrates, in which esters produced by reacting a fatty acid with a low molecular weight aliphatic monohydric alcohol are blended with the solubilized fatty acid-dialkanolamine condensates, are included within the scope of the invention. Specifically, esters prepared by reacting a fatty acid having from about 8 to about 22 carbon atoms, or a glyceride containing such fatty acids, with a monohydric alcohol having from 1 to 4 carbon atoms in its chain can be used in formulating our products. Methyl oleate, butyl stearate and butyl oleate have been found to be extremely well suited for such use. Such esters can be mixed with the solubilized condensates of this invention, either alone or in combination with any of the various raw oils and/or the anionic and non-ionic surface active agents, and, in the form of an aqueous emulsion, used to fat-liquor leather.

As indicated heretofore, the fat-liquoring agents of this invention, namely, the solubilized fatty acid-dialkanolamine condensates, can be used, as it, in the form of an aqueous solution or dispersion. Such solutions and dispersions, without the assistance of any added ingredients, can be employed to fat-liquor leather. It will be demonstrated in the examples that leather treated with a solution or a dispersion of this nature will be characterized by its improved pliability or suppleness, that is, its soft feel, and by the absence of discoloration and darkening. It has been found that the solubilized condensates of this invention are such that these results can be achieved, often using quantities of the solubilized condensate which are smaller than those ordinarily employed to accomplish a similar result using one of the conventional fat-liquoring compositions of the art.

Furthermore, we have found that results of a comparable nature are obtained when leather is fat-liquored using an aqueous emulsion containing a blend of the solubilized condensate with other materials commonly used in the art. In such blended products, the solubilized fatty acid-dialkanolamine condensate should comprise at least about 2% of the total weight of the non-aqueous ingredients in the aqueous emulsion. The remaining 98% of the total weight of the non-aqueous ingredients in the blend can comprise the various raw oils, surface active agents, esters, etc., mentioned heretofore. Thus, the invention contemplates a product in which the solubilized condensate comprises from about 2% to about 100% of the weight of the non-aqueous ingredients therein. It further contemplates blends of the solubilized condensate with a raw leather-treating oil in which the oil comprises from 30% to 70% by weight of the non-aqueous ingredients therein. The invention also encompasses blends of the solubilized condensates, either alone in combination with a raw oil or a mixture of raw oils, with polyethylene glycol esters, which esters comprise from about 4% to about 20% of the weight of the non-aqueous ingredients of the blend. In addition, the invention includes products containing mixtures of the solubilized condensates, either alone or with raw oils and/or polyethylene glycol esters, with sulfonated oils and/or the fatty acid esters of low molecular weight aliphatic alcohols in which products the sulfonated oil comprises from about 25% to about 50%, and the ester of the lower aliphatic alcohol from about 10% to about 50%, of the weight of the non-aqueous ingredients. Water generally comprises at least about 5.0% of the total weight of the aqueous emulsion concentrates of the invention. However, in certain embodiments of our invention blends are produced which are water-free or substantially so. Prior to their use, such water-free blends can be emulsified in water to the desired concentration. The precise ratios in which the added ingredients should be present in any particular product can best be determined by experimentation. Quite obviously, the nature of the added ingredient or ingredients, and the quantity of the solubilized condensate employed, will determine the quantity of added ingredient or ingredients that may be employed in any particular instance. However, in determining the quantity of added ingredients to be used, due regard must be given to the emulsifiability of the product, the stability of the aqueous emulsions of that product and the ability of the ingredients of the product to penetrate the surface of leather when, in the form of an aqueous emulsion, that product is employed to fat liquor leather. The formulation of a product having completely satisfactory properties using the ingredients disclosed herein is within the skill of the art. In general, however, products produced by blending the solubilized condensate of this invention with other ingredients, when used to fat liquor leather, greatly enhances the suppleness of the leather without causing it to discolor or darken. In these respects, the present products are superior to certain products of the art which contain ingredients which are somewhat similar to those used in the formulation of our products.

Other incidental, but highly significant benefits, accrue from the practice of this invention. In the case of the solubilized condensate itself, the product can be supplied to the leather manufacturer for use either as is or in the form of concentrated aqueous solution or dispersion. In the case of a blend which contains the solubilized condensate in combination with one or more water-immiscible materials, it can be supplied in the form of a relatively highly concentrated aqueous emulsion. Immediately prior to the time that the fat-liquoring operation is to be carried out, the leather manufacturer can adjust the solution or the emulsion so that the concentration of the non-aqueous ingredients in the fat-liquoring bath will meet his own requirements. This, of course, has con-

siderable commercial significance. As a result of the low water content of the products, savings accrue to the leather manufacturer because of lower freight and handling charges. Moreover, due to their low water content, our products require much less storage space than is sometimes needed for the products of the prior art. Furthermore, the solubilized condensates, the relatively concentrated aqueous solutions and dispersions thereof and the relatively concentrated aqueous emulsions which contain our solubilized condensates in admixture with other ingredients are all highly stable and their fat-liquoring properties are not adversely affected by prolonged storage under ordinary conditions. In this respect, the present products are a vast improvement over many of the products of the art.

For a fuller understanding of the nature and the objects of this invention, reference may be had to the following examples which are given merely as further illustrations of the invention and are not to be construed in a limiting sense. Unless otherwise indicated, all parts given in the examples are parts by weight.

Example I

A base condensate was produced by heating diethanolamine (2.0 mols) and oleic acid (1.0 mol) at a temperature of from about 155° C. to about 170° C. The water that evolved as the condensation reaction progressed was collected in a Dean-Stark trap. The reaction mixture was heated for a period of about four hours, the time of heating being measured from the beginning of the evolution of water. At the end of the four hour heating period, about 1½ mols of water had been collected. An acid value and an alkali value were determined on the product of the example. It was found that the condensate had an acid value of about 8.9 and an alkali value of 12.3% (calculated as percent KOH).

Thereafter, equimolecular proportions of the condensate thus produced and diethyl sulfate were heated at a temperature of about 60° C. for a period of about two hours. Being exothermic, the reaction, once initiated, proceeded to completion without the application of additional external heat. The product thus prepared was a viscous liquid-like composition which formed a slightly milky dispersion in water. It was determined that this product had an actual alkali value of 1.8% (calculated as percent KOH). A 2% aqueous solution of this product had a pH of 3.2.

This product was evaluated as a fat-liquor for vegetable tanned upholstery leather. However, so that the product could be tested under conditions which would most closely approximate the conditions that would be encountered in a leather tannery, as, for example, where the fat liquoring operation would take place immediately after tanning, the leather was retanned prior to fat-liquoring using quebracho extract as the tanning agent, the quantity of the extract used being equivalent to about 10% of the drained weight of the leather. In this retanning step, the leather was placed in an aqueous solution of the extract, heated to a temperature of about 90° F., drummed for a period of about two hours and allowed to stand in that solution overnight. The following morning the leather was removed from the tanning bath and washed in water for ten minutes at a temperature of about 120° F.

The retanned leather was thereafter fat-liquored. The fat-liquoring operation was carried out in the following manner. The retanned upholstery leather, the solubilized condensate produced in this example and water were placed in a tumbling drum. The weight of the solubilized condensate employed was equivalent to about 5.0% of the wet drained weight of the retanned leather present. The weight of the water used in the fat-liquoring bath was approximately three times the weight of the wet drained leather. The leather was thereafter tumbled in this bath continuously for a period of about two

hours at a temperature of about 120° F. At the end of this period, the leather was removed from the bath, allowed to cool to room temperature, drained and finally dried.

It was found that the retanned upholstery leather that was fat-liquored using the product of this example had outstanding properties and characteristics. The leather was exceedingly pliable and supple and it was not at all darkened or discolored by the treatment.

For comparative purposes, the product of this example was compared with a diethyl sulfate condensate of oleic acid and aminoethylethanolamine. Using the same procedure and the same conditions of the fat-liquoring operation described in Example I, chrome vegetable retanned leather was fat-liquored using each of the aforesaid products. The leather that was fat-liquored using the product of this example was greatly superior to the leather fat-liquored with the other product. It had a much lighter color and softer feel than the leather that was fat-liquored using the oleic acid-aminoethylethanolamine derivative.

It was also found that the product of this example fat-liquored leather to an exceedingly high degree when it was added directly to chrome tannage during the tanning operation.

Example II

Equimolecular quantities of the oleic acid-diethanolamine condensate of Example I and benzyl chloride were heated at a temperature of about 120° C. for a period of about two hours. It was determined that the product thus produced had an actual alkali value of 2.89% (calculated as percent KOH). A 2% aqueous solution of this product had a milky appearance and it was determined that such a solution had a pH of 4.4. The product was evaluated as a fat-liquor on the vegetable tanned upholstery leather which was retanned using quebracho extract as described in the previous example. The fat-liquoring procedure, including the relative proportions of the leather, the fat-liquoring agent and the water, was the same as that used in evaluating the product of Example I. It was found that the solubilized condensate of this example possessed fat-liquoring properties. However, it was found that, as a fat-liquor, the product of this example possessed properties which were less outstanding than those of the products of Example I. Leather treated using product of this example did exhibit the characteristics of a fat-liquored leather. However, it was somewhat less supple and pliable and somewhat darker in color than the leather that was treated with the product of Example I.

Example III

A base condensate was produced by heating 299 parts by weight of castor oil and 210 parts by weight of diethanolamine at a temperature of from about 160 to about 180° C. for a period of about 10 hours. During the progress of the reaction about 10 grams of water were removed. At the end of the heating period the base condensate had an alkali value of 15.6% (calculated as percent KOH).

Thereafter, 137 parts by weight of the base condensate thus produced and 47 parts by weight of the diethyl sulfate were heated at a temperature of about 60° C. for a period of about 2 hours. The alkali value of the solubilized condensate thus produced was determined to be 2.5% (calculated as percent KOH). A 2% aqueous solution of this product had a pH of 3.5. The product was a viscous amber liquid which formed a light opalescent solution in water.

This product was evaluated as a fat liquor for the retanned, vegetable tanned upholstery leather described in Example I. The fat-liquoring procedure, and the conditions under which the tests were conducted, were identical to the procedure and conditions described in Example I.

It was found that solubilized condensate of this example possessed outstanding fat-liquoring properties. Leather treated therewith was characterized by an exceedingly soft feel and by the absence of any darkening or discoloration.

Example IV

In this example, 215 parts by weight of coconut oil fatty acids were heated at a temperature of from about 160° C. to about 180° C. with 266 parts by weight of diisopropanolamine for a period of about ten hours. During the progress of the reaction, the water formed by the condensation was collected. At the end of the heating period, about 25 grams of water had been recovered. The product had an acid value of 17.0% and an alkali value of 12.6% (calculated as KOH).

Thereafter, 74.3 parts by weight of the base condensate thus produced were mixed with 25.7 parts by weight of diethyl sulfate and heated at a temperature of about 60° C. for a period of about 2 hours. The product thus produced was a clear, pale amber liquid which gave a clear solution in water. This product had an alkali value of 2.5% (calculated as percent KOH) and a 2% aqueous solution of the product had a pH of 4.0.

This product was evaluated as a fat-liquor for retanned, vegetable tanned upholstery leather by the method described in Example I. It was found that the product had excellent fat-liquoring properties. Leather treated with this material was extremely soft and pliable and it was not to any extent darkened or discolored by the fat-liquoring operation.

Example V

In this example, a triethyl phosphate derivative of a base condensate that was produced by reacting 215 parts by weight of coconut oil with 210 parts by weight of diethanolamine was prepared. The base condensate was prepared by heating the coconut oil and the diethanolamine at a temperature of from about 165° C. to about 170° C. About 5 parts by weight of water were collected from the reaction mixture during the condensation reaction. The base condensate had an alkali value of 15.5% (calculated as percent KOH). The solubilized condensate was produced by heating 31.9 parts of triethyl phosphate with 68.1 parts by weight of the coconut oil-diethanolamine condensate. The reactants were heated at a temperature of from about 160° C. to about 170° C. for a period of about 2 hours. It was determined that the product of this example had an alkali value of 5.1% (calculated as percent KOH) and that a 2.0% aqueous solution of this product had a pH of 7.3.

The solubilized condensate of the invention was a clear, dark amber liquid which in water formed an opalescent emulsion. It was found that retanned vegetable tanned leather fat-liquored with this product, in the manner described in Example I, had outstanding properties. The leather thus treated had an exceedingly soft feel. It was not, to any extent, darkened or discolored by the treatment with this product.

Example VI

In this example, an aqueous emulsion was produced using the solubilized condensate produced in Example I. This emulsion was produced by mixing 30 parts by weight of the solubilized condensate of Example I with 5 parts by weight of polyethylene glycol (400) monooleate, 20 parts by weight of neat's-foot oil and 45 parts by weight of water. The blend was thoroughly stirred at room temperature until a uniform product was obtained. The product thus produced was found to be an exceedingly stable emulsion.

This emulsion was employed to fat-liquor retanned vegetable tanned leather using the procedure described in Example I. In the fat-liquoring operation, the emulsion was used in such quantities that the combined weight of the non-aqueous ingredients therein was equivalent to

about 5.0% of the wet drained weight of the retanned leather being treated. It was found that very satisfactory results were obtained using this product as a fat-liquoring agent. The leather treated therewith was extremely supple and pliable, that is, it had a soft feel, and it was characterized in that during the operation it did not become darkened or discolored.

Example VII

In this example, a blend comprising 2 parts by weight of the solubilized condensate produced in Example V, 8 parts by weight of polyethylene glycol (200) monooleate, 5 parts by weight of white mineral oil, 55 parts by weight of blown fish oil and 30 parts by weight of sulfonated sperm oil were blended. The sulfonated sperm oil employed had a water content of about 25% by weight. The blend was stirred thoroughly at room temperature until homogeneous. The product thus produced was a clear, slightly viscous liquid which was readily dispersible to form a stable emulsion in water.

The product was evaluated as a fat liquor for retanned vegetable tanned leather in the manner described in Example I. The combined weight of the non-aqueous constituents of the emulsion used in the fat-liquoring operation was equivalent to about 5% of the wet drained weight of the leather. It was found that leather fat-liquored with the product of this example had outstanding properties. The leather had an exceedingly soft feel and was free from any discoloration or darkening.

Example VIII

In this example, 35 parts by weight of the solubilized condensate of Example IV, 20 parts by weight of sperm oil and 45 parts by weight of water were blended and thoroughly stirred at room temperature to form a stable aqueous emulsion. This product was evaluated as a fat liquor for retanned, vegetable tanned leather in the manner described in Example I. It was found that the leather fat-liquored using this product was completely free of any darkening or discoloration and had an excellent soft feel.

Example IX

In this example, 40 parts by weight of the solubilized condensate that was produced in Example III, 20 parts by weight of a blown peanut oil, 20 parts by weight of butyl oleate and 20 parts by weight of white mineral oil were admixed and thoroughly stirred at room temperature until homogeneous. The product thus produced was a clear, slightly viscous liquid which was readily emulsifiable in water. This product was evaluated as a fat liquor for retanned, vegetable tanned leather in the manner described in Example I. It was found that leather treated with this product was entirely satisfactory in every regard. It had the desired soft feel and it was entirely free of darkening or discoloration.

Example X

In this example, 88.5 parts by weight of the base condensate produced in Example I were reacted with 11.6 parts by weight of glacial acetic acid. The reaction was carried out at a temperature of about 60° C. for a period of about two hours. The product thus produced was a viscous liquid which, in the form of a 2% aqueous solution, had a pH of 5.2. In water, the product formed an opalescent solution.

As was the case with the products of each of the preceding examples, this product was evaluated as a fat-liquoring agent. The procedure followed in this evaluation was the procedure described in Example I. The product proved to be a highly satisfactory fat-liquor for leather. It was noted that the retanned, vegetable tanned upholstery leather that was fat-liquored using this product had an exceptional soft feel. The leather was neither darkened nor discolored when treated with the product.

Having described our invention what we claim is new and desire to secure by Letters Patent is:

1. A process for fat-liquoring leather which comprises contacting said leather with a composition comprising water and a cationic amine salt of a condensate produced by heating at temperatures between about 100° to 210° C., (a) a fatty material selected from the group consisting of fatty acids having carbon chain lengths of from about 10 to about 20 carbon atoms, glycerides composed of said fatty acids and esters of said fatty acids and aliphatic monohydric alcohols having a carbon chain length of from 1 to about 5 carbon atoms and (b) a dialkanolamine, the alkyl groups of which contain up to about 4 carbon atoms, said (a) and (b) being reacted in such quantities that the ratio of acyl groups to nitrogen atoms in the reaction mixture is about 1 to 2.

2. A process for fat-liquoring leather which comprises contacting said leather with a composition comprising water and a cationic amine salt of a condensate produced by heating, at temperatures of from about 135° to 210° C., (a) a fatty acid having a carbon chain length of from about 10 to about 20 carbon atoms and (b) a dialkanolamine selected from the group consisting of diethanolamine and diisopropanolamine, said (a) and (b) being reacted in such quantities that the ratio of acyl groups to nitrogen atoms in the reaction mixture is about 1 to 2.

3. A process for fat-liquoring leather which comprises contacting said leather with a composition comprising water and a cationic amine salt of a condensate produced by heating, at temperatures of from about 135° C. to about 210° C., (a) a glyceride composed of fatty acids having a carbon chain length of from about 10 to about 20 carbon atoms and (b) a dialkanolamine selected from the group consisting of diethanolamine and diisopropanolamine, said (a) and (b) being reacted in such quantities that the ratio of acyl groups to nitrogen atoms in the reaction mixture is about 1 to 2.

4. A process for fat-liquoring leather which comprises contacting said leather with a composition comprising water and a cationic amine salt of a condensate produced by heating at temperatures of from about 135° C. to about 210° C., (a) oleic acid and (b) a dialkanolamine selected from the group consisting of diethanolamine and diisopropanolamine, said (a) and (b) being reacted in such quantities that the ratio of acyl groups to nitrogen atoms in the reaction mixture is about 1 to 2.

5. A process for fat-liquoring leather which comprises contacting said leather with a composition comprising a blend of water, a leather-treating raw oil selected from the group consisting of mineral oils, fatty oils and mixtures thereof and a water-soluble cationic amine salt of a condensate produced by heating, at temperatures between about 100° to 210° C., (a) a fatty material selected from the group consisting of fatty acids having carbon chain lengths of from about 10 to 20 carbon atoms, glycerides composed of said fatty acids and esters of said fatty acids with aliphatic monohydric alcohols having from 1 to 5 carbon atoms in the structure, and (b) a dialkanolamine, the alkyl groups of which contain up to about 4 carbon atoms, said (a) and (b) being reacted in such quantities that the ratio of acyl groups to nitrogen atoms in the reaction mixture is about 1 to 2.

6. A process for fat-liquoring leather which comprises contacting said leather with a composition comprising a blend of water, a leather-treating raw oil selected from the group consisting of mineral oils, fatty oils and mixtures thereof, a sulfonated oil and a water-soluble cationic amine salt of a condensate produced by heating, at temperatures of from about 135° C. to about 210° C., (a) a fatty acid having a carbon chain length of from about 10 to 20 carbon atoms and (b) a dialkanolamine selected from the group consisting of diethanolamine and diisopropanolamine, said (a) and (b) being reacted in such

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quantities that the ratio of acyl groups to nitrogen atoms in the reaction mixture is about 1 to 2.

7. A process for fat-liquoring leather which comprises contacting said leather with a composition comprising a blend of water, a leather-treating raw oil selected from the group consisting of mineral oils, fatty oils and mixtures thereof, a sulfonated oil and a water-soluble cationic amine salt of a condensate produced by heating, at temperatures of from about 135° C. to about 210° C., (a) a glyceride composed of fatty acids having from about 10 to about 20 carbon atoms and (b) a dialkanolamine selected from the group consisting of diethanolamine and diisopropanolamine, said (a) and (b) being reacted in such quantities that the ratio of acyl groups to nitrogen atoms in the reaction mixture is about 1 to 2.

8. A process for fat-liquoring leather which comprises contacting said leather with a composition comprising a blend of water, a leather-treating raw fatty oil, a sulfonated oil and a water-soluble cationic amine salt of a condensate produced by heating at temperatures of from about 135° C. to about 210° C., (a) a glyceride composed of fatty acids having from about 10 to about 20 carbon atoms and (b) diethanolamine, said (a) and (b) being reacted in such quantities that the ratio of acyl groups to nitrogen atoms in the reaction mixture is about 1 to 2.

9. A process for fat-liquoring leather which comprises contacting said leather with a composition comprising a blend of water, a leather-treating raw fatty oil, a sulfonated oil and a water-soluble cationic amine salt of a condensate produced by heating, at temperatures of from about 135° C. to about 210° C., (a) a fatty acid having a carbon chain length of from about 10 to about 20 carbon atoms and (b) diethanolamine, said (a) and (b) being reacted in such quantities that the ratio of acyl groups to nitrogen atoms in the reaction mixture is about 1 to 2.

10. A process for fat-liquoring leather which comprises contacting said leather with a composition comprising a blend of water, neat's-foot oil, a sulfonated oil and a water-soluble cationic amine salt of a condensate produced by heating, at temperatures of from about 135° C. to about 210° C., (a) oleic acid and (b) diethanolamine, said (a) and (b) being reacted in such quantities that the ratio of acyl groups to nitrogen atoms in the reaction mixture is about 1 to 2.

11. The process of claim 4 wherein (b), the dialkanolamine, is diisopropanolamine.

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12. The process of claim 4 wherein (b), the dialkanolamine, is diethanolamine.

13. The process of claim 12 wherein the salt forming agent is dimethyl sulfate.

14. The process of claim 12 wherein the salt forming agent is diethyl sulfate.

15. The process of claim 12 wherein the salt forming agent is acetic acid.

16. The process of claim 6 wherein a product produced by reacting a polyethylene glycol having a molecular weight of from about 200 to about 1000 with a fatty material selected from the group consisting of fatty acids having a carbon chain length of from about 8 to about 22 carbon atoms and glycerides composed of said fatty acids, is present.

17. The process of claim 7 wherein a product produced by reacting a polyethylene glycol having a molecular weight of from about 200 to about 1000 with a fatty material selected from the group consisting of fatty acids having a carbon chain of from about 8 to about 22 carbon atoms and glycerides composed of said fatty acids is present.

18. The process of claim 10 wherein a compound produced by reacting a polyethylene glycol having a molecular weight of about 400 with oleic acid is present.

19. The process of claim 18 wherein the sulfonated oil is sulfonated sperm oil.

20. The process of claim 19 wherein the salt forming agent is dimethyl sulfate.

21. The process of claim 19 wherein the salt forming agent is diethyl sulfate.

22. The process of claim 19 wherein the salt forming agent is acetic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,089,212	Kritchevsky	Aug. 10, 1939
2,496,640	Schiller	Feb. 7, 1950
2,555,684	De Castro	June 5, 1951
2,772,967	Padbury et al.	Dec. 4, 1956

OTHER REFERENCES

- Schwartz et al.: "Surface Active Agents," vol. 1, 1949, Intersci. Pub. Inc., N.Y., pp. 212, 213.