UNITED STATES PATENT OFFICE

2,123,832

TREATMENT OF HIDES, SKINS, AND LEATHER

Alphons O. Jaeger, Mount Lebanon, and Richard Herrlinger, Bridgeville, Pa., assignors to American Cyanamid & Chemical Corporation, New York, N. Y., a corporation of Delaware

No Drawing. Application August 10, 1936, Serial No. 95,280

8 Claims. (Cl. 149—5)

This invention relates to the use of certain polycarboxylic acids and their water soluble salts and ester salts in preparing hides and skins for tannages such as mineral and vegetable tannage, formaldehyde tannage, tannage with synthetic tanning agents and the like, as well as in the tanning and finishing operations themselves. In accordance therewith, any of the steps of washing the limed hides, deliming, bating, pickling, buffering for pH adjustment, setting of mineral tannages, bleaching, neutralizing the leather, fatliquoring the tanned leather or dyeing the leather, or any combination of these steps, may be carried out in the presence of members of the class consisting of phthalic acid, maleic acid, fumaric acid and succinic acid and their water soluble salts which are the ammonium, ethanolamine, and alkali metal salts.

We have found that the dicarboxylic acids of the above group and the water soluble neutral and acid salts thereof are important agents for improving the above steps in leather manufacture when incorporated with the materials ordinarily used therein, and that leather of improved characteristics will result from their use. Accordingly, it is an object of the invention to improve each of the above steps of leather manufacture in the manner which will be pointed out in the present specification, to the end that leather having a better grain, a better feel, lessened deterioration upon storage or subjection to light and other improved characteristics will result.

The four acids which constitute the class dealt with by the present invention are so similar in their action in the above enumerated steps of leather manufacture that they may be used interchangeably, as will be explained in the following examples, and the same is true of their water-soluble salts. They are also closely related chemically, and are all obtained commercially fom the same parent material, which is naphthalene. Upon the vapor phase partial oxidation of this hydrocarbon and treatment of the reacted gases with water a solution containing phthalic acid, maleic acid and fumaric acid is obtained, and upon treatment of this solution with metallic zinc a part or all of the maleic and fumaric acids are reduced to succinic acid. On the other hand, they distinguish from all other dicarboxylic acids by their pH values in aqueous solutions and by the solubility of their salts, and particularly by the remarkable advantages we have found them to possess in leather manufacture as will now be explained.

We have found that these acids and their water soluble salts have very desirable cleansing and deliming properties on hides and skins, and produce a desirable pH for further operations.

By reason of the buffering range which is possessed by these acids and their salts, and especially by phthalic acid and its salts, they are very useful in the bating of skins with enzymes such as proteolytic enzymes.

In pickling, particularly with sheepskins, dicarboxylic acids and especially phthalic acid produce a cleaner and firmer grain when the skins are tanned, because their preserving action eliminates the necessity of extreme acidification for the prevention of mold and bacterial growth. Much stronger acidification is necessary for pickling if sulfuric acid or other mineral acids are used.

Phthalic acid in saturated solution has a pH of 2.2, which is low enough for any acidification in modern leather manufacture. It has considerable advantages over mineral acids in operations involving hide substance. A most important characteristic for this purpose is its buffering capacity, making it very valuable where gradual acidification is required. This is important not only in pickling operations but also in all other operations of leather manufacture due to the necessity of protecting the collagens against destruction during the relatively great changes in hydrogen ion concentration to which the hide is subjected.

Compared with other organic acids used in leather manufacture, the dicarboxylic acids of the above class have greater buffering capacity due to the availability of the second hydrogen ion, at least doubling the buffering range. In the use of alkali metal salts of dicarboxylic acids, and particularly sodium acid phthalate, advantage is taken of the reverse effect in accomplishing a gentle and limited neutralization. Phthalic acid has two buffering maxima at 2.92 and 5.41 respectively.

Sodium phthalate or other alkali metal phthalates, when used in chrome tannage or other mineral tannages, operates to set the chrome or other metal and thus to convert the hide or skin into leather. When so used it avoids the development of a drawn grain and produces fuller flanks with more uniform distribution during subsequent fat-liquoring, as compared with conventional neutralizing agents. Similar results are obtained by the use of maleic acid, fumaric acid and succinic acid in the form of their alkali metal salts.

The above mentioned dicarboxylic acids have the additional important property, especially when applied in water solution, of bleaching vegetable and mineral tanned leather.

In fat-liquoring or stuffing compositions the addition of polycarboxylic acids and their salts, especially sodium phthalate, impart greater stability against auto-oxidation and rancidification of the finished leather and prevents spewing and rancidification during storage by reason of their resistance to the action of light. Better distribution of the fat-liquor or stuffing composition, fuller feel and a finer grain are also produced.

From the above it will be seen that the present invention provides a class of organic polybasic acids all of which may be used, either in the free state or in the form of their neutral or acid water soluble salts, in each of the steps of leather manufacture. The employment of these materials throughout the process wherever changes of acidity or alkalinity are to be made will result in a finished leather of much better characteristics, for there is never a sudden or drastic change of pH with its resulting uneven action on the outer and inner layers of the hides being treated.

In the following examples the methods whereby the group of substances constituting the subject matter of the invention are used in leather manufacture will be illustrated in greater detail by a description and discussion of each of the individual steps. It will be found that these steps, although discussed separately, will constitute a single unitary process giving final products of improved characteristics. Accordingly, it should be understood that the invention includes the combination of any two or more of these novel steps collectively as well as the novel features of each individual step, and this is sought to be protected by the appended claims.

EXAMPLE 1

Washing and deliming

1000 pounds of a white hide or skin in a limed, unhaired and fleshed condition are paddled in a solution containing from 0.25 to 5% of an ammonium salt of phthalic acid, maleic acid or succinic acid, based on the weight of the hides. For example, a solution of ammonium phthalate or ammonium maleate may be used, depending upon the nature of the skin and the following treatment to which it is to be subjected. By this procedure a simultaneous removal of lime and adjustment of the pH for the following bating step is obtained.

Instead of ammonium phthalate, the acid ammonium salts, the corresponding free acid or the sodium, potassium or triethanolamine salts may be used in the presence or absence of other salts such as ammonium sulfate and other acids such as lactic acid, formic acid or mineral acids such as boric acid or sulfuric acid.

When hard water difficulties are encountered, for example when the water supply of the tanner contains carbonates, bicarbonates and sulfates which would react with lime to form insoluble compounds, the steady flow of water in the washing operation which is ordinarily used before bating may cause the surface of the skins to become blasted. This phenomenon is known in the tannery as "lime blast". In accordance with the present invention, this blast can be removed as follows: after transferring the stock to the bate paddle or drum, phthalic, maleic, fumaric or succinic acid is added until the bate liquor reacts acid to methyl orange and remains acid for 3 minutes. The bate may then be added and no difficulties will be experienced, since all the lime blast is sufficiently dissolved and the obstacle to proper enzyme action is removed. This method is successful even in the case of thin skins, such as sheep and goatskins where it is necessary to carry some lime into the bate, for the organic dicarboxylic acids of the above described class do not inhibit the bating action. On the contrary, they perform the double function of removing the raspy feel of the blasted hides and at the same time reducing the pH of the leather to a range most suitable for the subsequent bating step.

EXAMPLE 2

Bating

In this step, phthalic acid, maleic acid, fumaric acid and succinic acid and the ammonium, ethanolamine and alkali metal salts thereof form an excellent medium for control of the operation, since they automatically provide a proper control of the hydrogen ion concentration. By choosing the right salt of the right dicarboxylic acid a bate of any desired pH within the ordinary bating range may be maintained.

For example, calf-skins are bated in the production of upper leather by the following procedure: 100 pounds of the calf-skins are paddled for 30 to 45 minutes in a solution containing 2½ pounds of ammonium phthalate to which one-fourth pound of a concentrated proteolytic enzyme preparation such as pancreatic enzymate has been added, the temperature being maintained at 90° F. At the end of this period an examination of the hide will show that all keratinous substances have been removed and that the skin has reached a proper degree of lime depletion and has a clean and clear grain. Such a skin will show uniformity after tanning with no undertone or cast and with a strong and pliable grain.

As another example, 100 pounds of hides are charged to a solution containing 500 g. of phthalic acid and are run for 10 minutes in order to reduce the pH of the outer layers of the hide. 200 grams of papaine are then introduced and the hides are paddled in this bate from 45 minutes to 1 hour at 90° F. Phthalic acid, maleic acid and the other acids of the present invention, or properly selected mixtures of these with their salts will show a different action from other acids, and particularly from mineral acids in bating. When used in the above described manner they will neutralize the outside layer of leather to the desired pH for enzyme action while leaving the inside at a different pH and so prevent over-bating and the resulting difficulties from loose flanks.

EXAMPLE 3

Pickling

After the bating step, skins are pickled in acid solutions to prevent mold and bacterial growth and enable them to be stored. We have found that skins treated with phthalic acid, maleic acid, fumaric acid and succinic acid have excellent storing properties and that subsequent tanning of the skins so pickled will yield leather having good color, fine texture, strong fiber and a clear and clean grain. This result is obtained because the above organic acids are all inhibitors of mold and bacterial growth, and by their use a satisfactory pickle is obtained at a much higher pH value than would be necessary with mineral acid. Accordingly, the amount of neutralization with alkali for subsequent tannage is greatly reduced, and can be dispensed with in some tannages, thereby avoiding a drawn grain and obtaining leather having the above described characteristics.

As an example, 100 pounds of bated sheepskins are washed in a paddle wheel for one hour and are then transferred to a pickle liquor containing 10% sodium chloride and 2% phthalic acid, which is maintained at room temperatures. An amount of pickle liquor equal to 6 times the weight of the wet skins is used, and the skins remain in the pickle liquor for 6 hours or longer, and preferably over-night. It will then be found that the skins have taken up approximately 1.7% of the phthalic acid, based on the weight of the bated skins, and have attained a pH of about 2.9.

Where skins requiring a lower pH for subsequent acid tannages are required, for example where an acid syntan tannage is to be used, maleic or succinic acids or a mixture thereof may be substituted for the phthalic acid in the above process. Mixtures of the acids of the present invention with other acids such as sulfuric acid may also be used in pickling processes, where a very low pH is not objectionable.

In the pickling of sheepskins, phthalic acid is probably the most valuable pickling agent among the acids of the present invention, as it is self-regulating and requires no accurate control, but it is apparent that maleic acid, fumaric acid and succinic acid may be substituted if desired. All of these acids possess the great advantage that they may be brought into direct contact with the human skin without damage thereto, which makes them much easier to handle than strong mineral acids, and they cannot damage the skins to be pickled under any circumstances. Being solid acids, they are easy to store, handle and ship which is another great advantage over the mineral acids.

EXAMPLE 4

Setting mineral tannages

In mineral tannages such as chrome tannage and the like, alkalies are used to reduce the acidity of the chrome solution and thus cause the resulting basic chrome salt to combine with the animal fibers and produce leather. When the alkali salts of dicarboxylic acids of the present invention are used for this purpose, with or without the addition of other alkaline reacting agents, they give a distinctive color to the resulting leather and improve the cut thereof.

As an example of the one-bath process, calf skins are tumbled in 75% of their weight of water together with 5% of sodium chloride for one-half hour, and then a 33% basic chrome solution containing a total of 2% chromium oxide is added in three portions, one hour apart. A solution containing 3% of sodium phthalate, based on the weight of the hides, is added in three portions, one-half hour apart, the first portion being added shortly after the last addition of chrome to the solution. The mixture is run for several hours until the desired heat resistance is obtained, after which the completely tanned calf skins are removed, washed and are ready for fat-liquoring.

The total amount of ammonium, ethanolamine, or alkali metal salt of the dicarboxylic acid to be used depends upon the final acidity of the leather desired and upon the original basicity of the chrome solution.

As an example of the two-bath process, bated calf skins are paddled in a liquor containing from 3½ to 7½% of their weight of sodium bichromate together with 2½% of their weight of phthalic or succinic acid. Preferably this acid is added in three portions, the first immediately after solution of the chrome in the water containing the hides, but it is also possible to add all the acid at one time by reason of its relatively mild acidity.

The skins are run in the above bath until a uniform yellow color is obtained throughout the leather. They are then horsed up overnight with exclusion of light and are then ready for the fixing bath.

This bath may consist, in accordance with the present invention, of a solution containing from 10 to 15% of sodium thiosulfate and approximately 3 to 5% of maleic or succinic acid, based on the weight of the skins. If necessary, additional amounts of these acids, or of phthalic or fumaric acids may be added during the treatment of the hides in order to produce a uniform blue color therein.

When all the chrome has been fixed in the skins they are removed from the bath, horsed up, and washed with cold running water in a wheel until a pH of approximately 4–5 is obtained, and are then ready for further operations.

EXAMPLE 5

Neutralization of finished leathers

After chrome tannage, the chrome salts in the leather sometimes hydrolyze and keep the pH at a value which may be too low for subsequent operations. This is particularly true when leather is stored for several days after the chrome tannage.

In practice the prior art has used alkalies, such as sodium bicarbonate, ammonium bicarbonate, borax and the like to raise the pH of chrome tanned leather. However, considerable care is necessary when using these materials, as their alkalinity is so high that they may over-neutralize the surface of the leather and produce a drawn grain. Moreover, they tend to neutralize the looser parts of the hides, for example, the flanks to a greater degree than the denser parts. This over-neutralization results in turn in too great a penetration during the subsequent fat-liquoring or stuffing of the leather and produces over-lubrication of these parts.

We have found that the neutral salts of the dicarboxylic acids of the present invention, such as sodium and ammonium phthalates and maleates, are excellent neutralizing agents for use in place of the alkalies above mentioned. They have a mild and gentle neutralizing action by reason of their relatively low pH and great buffering capacity and yet a thorough neutralization can be obtained by soaking the hides in solutions containing these substances.

The salts of phthalic, maleic, fumaric and succinic acids are also valuable agents for the neutralization of tanned leather which has been bleached with a syntan such as a sulfonated diaryl methane. They may be used with much greater safety than the conventional neutralizing agents of the type above mentioned and present the important advantage that re-darkening of the leather does not occur as is sometimes the case when free alkalies are used.

We have found that the subsequent dyeing of the leather is also greatly influenced by the neutralization step. When the leather is neutralized deeply the penetration of acid dyestuffs is also deepened and the dyes do not tend to collect on the surface of the leather. Such neutralization is difficult or impossible when strong alkalies are used, for the surface of the leather becomes over-neutralized, with the resulting difficulties noted above, when this is attempted. Salts of the dicarboxylic acids of the present invention, on the other hand, have a definite upper limit of alkalinity and will never over-neutralize any part of the leather no matter how long it remains in contact with them. Accordingly, they may be employed for such times and in such concentrations that the entire thickness of the leather is neutralized, and may even be added to the dyebath if desired.

What we claim is:

1. In the treatment of hides, skins and leather by a process including any of the steps of washing limed hides, deliming, bating, pickling, setting of mineral tannages, bleaching, fat-liquoring or dyeing with acid dyes, the method of adjusting the hydrogen ion concentration of the hides, skins or leather which comprises introducing therein a suitable compound comprising a member of the group consisting of phthalic acid, maleic acid, fumaric acid and succinic acid and their water soluble salts.

2. The method of washing and deliming hides and skins which comprises soaking them in an aqueous solution containing a neutral or acid salt of a compound, selected from the group consisting of phthalic acid, maleic acid, fumaric acid and succinic acid.

3. The method of removing lime blast resulting from the washing of limed skins in hard water which comprises soaking the blasted skins in an aqueous solution containing a compound, selected from the group consisting of phthalic acid, maleic acid, fumaric acid and succinic acid.

4. A method of controlling the hydrogen ion concentration of a bating preparation during the bating of hides or skins which comprises incorporating therein a compound containing the radical of an organic dicarboxylic acid selected from the group consisting of phthalic acid, maleic acid, fumaric acid and succinic acid.

5. A method of pickling hides and skins which comprises soaking them in an aqueous solution containing an organic dicarboxylic acid selected from the group consisting of phthalic acid, maleic acid, fumaric acid and succinic acid.

6. A method of mineral tannage which comprises impregnating hides and skins with a solution of a mineral tanning agent and introducing into the hide or skin a compound containing the radical of an organic dicarboxylic acid selected from the group consisting of phthalic acid, maleic acid, fumaric acid and succinic acid.

7. A method of chrome tannage which comprises impregnating hides and skins with a solution of a water soluble chromate and introducing into the hide or skin a compound containing the radical of an organic dicarboxylic acid selected from the group consisting of phthalic acid, maleic acid, fumaric acid and succinic acid.

8. A method of neutralizing leather preparatory to finishing operations which comprises soaking it in a solution containing a neutral or acid salt of an organic dicarboxylic acid selected from the group consisting of phthalic acid, maleic acid, fumaric acid and succinic acid.

ALPHONS O. JAEGER.
RICHARD HERRLINGER.