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PLUMPING LEATHER WITH A SOL OF LARGE SILICA PARTICLES

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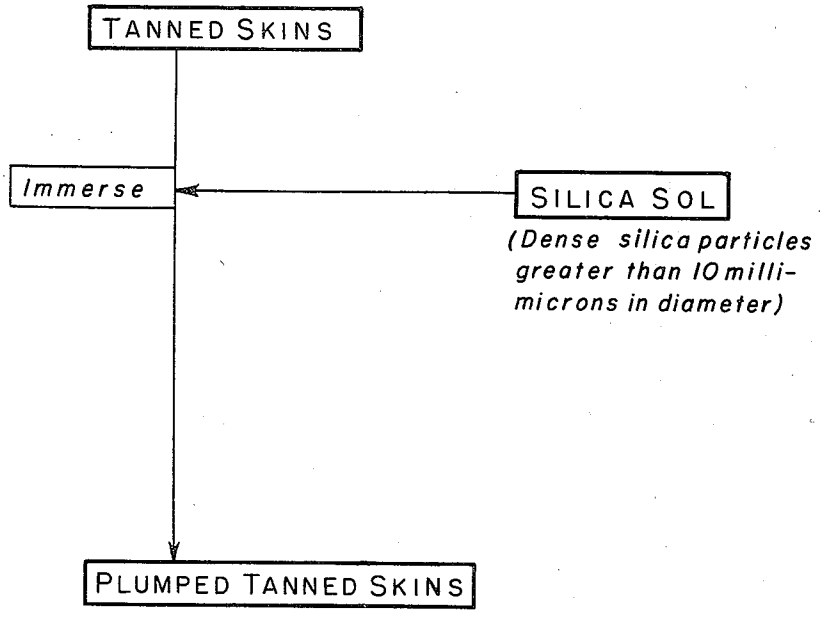

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PLUMPING LEATHER WITH A SOL OF LARGE SILICA PARTICLES

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This invention relates to leather treatment and more particularly to processes for plumping skins with silica in which the pH of the tanned skins is adjusted to from 1.7 to 5.0, or preferably, from 2.8 to 5.0, the skins are agitated in a substantially stable colloidal solution of silica having a combined SiO_2:Na_2O ratio greater than 10, the agitation of the skins being continued until they have taken up an appreciable quantity of silica, and the pH of the skins is thereafter raised.

Skins of the kind ordinarily converted into leather are characterized by a lack of physical uniformity. Parts of a skin, such as the backbone areas, may be converted by tanning into tight, firm leather, while other parts, such as the flanks, may give weak, loose, and flabby leather. Non-uniformity and looseness of the flanks is objectionable with any tanning process and is particularly troublesome in chrome-tanning. Sorting of the tanned skins and selection of particular areas of each skin for particular purposes must be resorted to on account of this lack of uniformity. It is an object of this invention to provide processes for tightening the flanks and improving the uniformity of tanned skins and, particularly, of chromed-tanned skins.

Plumpness is a highly desirable quality in leather. Plump leather has good body and thickness. Improvement of plumpness is acceptable with any tannage and is a necessity with certain tannages, such as chrome and alum-formaldehyde. Thus, while chrome tannage gives leather in many respects superior to that from other tannages, chrome leather is unfortunately characterized by an emptiness, that is, by a lack of plumpness. For many uses an empty leather is entirely unsuitable and expensive expedients, such as retanning with vegetable tannins or syntans, must be employed. Unfortunately retanning with vegetable tannins gives dark leather unsuitable for finishing into light or pastel shades of leather, while the use of syntans in many cases gives leather which is not color-stable to ultraviolet light. It is an object of this invention to provide processes for improving the plumpness of leather, and particularly of chrome leather without resorting to retanning.

Even leather which is of good quality with regard to plumpness can be advantageously treated using processes of the invention. For example, leather which has been tanned with a maleic anhydride-styrene polymer, as shown in Graves U. S. Patent No. 2,205,882, can be treated with colloidal silica according to the invention to give it improved suedeing characteristics.

It is therefore a further object of the invention to improve the suedeing characteristics of leather. More generally, it is an object of the invention to use colloidal silica for the improvement of leather.

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Colloidal silica or silicic acid is an inexpensive, inorganic material which is known to have an affinity for skins. It has already been proposed to tan skins with colloidal silica sols or solutions and it has also been proposed to use sodium silicate for treating skins and leather in various ways. Unfortunately, methods hitherto proposed for incorporating silica in combination with chrome in leather have led to undesirable properties other than lack of plumpness. Thus, while the leather might be plump it was also characterized by harshness, crackiness, lack of tensile strength, lack of unctuous feel, and poor aging properties. In short, no method has heretofore been available for plumping leather, and particularly chrome leather, with silica without at the same time imparting undesirable qualities to the leather. It is an object of this invention to provide such a method.

Now according to the present invention it has been found that leather, and especially chrome-tanned leather, may be plumped, and uniformity and tightness, especially of flanks, may be obtained, without any deleterious effect on the other qualities of the leather, by adjusting the pH of the tanned skins to from 1.7 to 5.0, or preferably, from 2.8 to 5.0, agitating them in a substantially stable colloidal solution of silica having a combined SiO_2:Na_2O ratio greater than 10, the agitation of the skins being continued until they have taken up an appreciable quantity of silica, and thereafter raising the pH of the skins. In treating chrome-tanned and other skins it is particularly preferred to use a silica solution prepared by a process in which sodium ions in a sodium silicate solution are replaced with hydrogen ions by passing the silicate solution through a mass of ion-exchange material which has been treated with an acidic reagent. Such solutions are preferably heat-treated in manners set out in more detail hereinafter.

Throughout the description of this invention, the terms "silica sols" and "silica solutions" and "colloidal silica solutions" are used interchangeably.

The processes of this invention are applicable to improve the quality of leather produced by any tannage. Especial advantages are realized when the processes are applied to tanned skins which are characteristically empty, loose, and non-uniform, such as might be obtained by chrome- or alum-formaldehyde tannage. The

term "tanned skins" will be understood to include tanned hides and other tanned animal membranes. Desirably, though not necessarily, the processes may be applied after the skins have been shaved as well as tanned, and they may be applied even after the tanned skins have been dried, although the latter is not preferred.

To treat tanned skins with silica according to this invention the pH of the skins is first adjusted to from 1.7 to 5.0, or preferably, from 2.8 to 5.0 by adding an acid, such as hydrochloric, or an alkali, such as sodium bicarbonate, as may be required. If the skins have been dried they must, of course, be wetted back. Chromed skins ideally may be treated "in the blue"—that is, after they have been tanned, shaved, and horsed or piled down for a day or longer, but before they have been neutralized. The pH of chromed skins in the blue will be in the range from 3.0 to 3.5 and hence will not require any adjustment since for treating chromed skins a pH of 3.0 to 3.5 is preferred. The lower pH limit to use in a particular case will depend upon the stability of the tanned skin. With chrome-tanned skin, as indicated, a pH of about 2.8 is a practical operating minimum. With skins tanned with a maleic anhydride-styrene polymer, it is quite practical to operate at considerably lower pH.

The amount of colloidal silica solution used should be large enough to give good workability in the equipment used for agitation—usually a tanning drum—but should not be greatly in excess of such amount. Ordinarily, the weight of silica solution advantageously may be from 1 to 2 times the weight of the drained but wet skins. In the case of chrome tannage this will be 1 to 2 times the weight of skins in the blue, a weight of solution 1½ times the weight of skins being particularly preferred.

The solution used for plumping tanned skins according to this invention is a substantially stable colloidal solution of silica, the solvent being water. By "substantially stable" is meant that the solution may be allowed to stand for an extended period without gelling. This is a distinguishing characteristic over most colloidal silica solutions, such as those prepared by acidifying sodium silicate solution, which, in the absence of a stabilizer, may gel in a few weeks at best. Moreover, this stability of the colloidal solutions used according to this invention is observed even when the solutions are relatively concentrated, that is, when they contain 10 per cent or more of silica.

When added to the skins the silica solution may contain any desired concentration of silica, good results, for instance, following the use of solutions containing from 1 to 15 per cent. Ordinarily it is preferred to employ a relatively dilute solution, and when particularly applied to chromed skins it should, for best results, contain from 2 to 6% of silica.

It will be understood, as described below in more detail, that the silica sols used in making up a treating solution may contain 30% or 40% or even more SiO_2. These sols can suitably be diluted before addition to the skins, or as will commonly be the case, they can be added to the skins which already contain water from preceding operations. It will be understood that a considerable variation in the silica content of the treating solution is permissible, and in a particular case the strength can be adjusted to conform to the type of skin to give the desired retention in the skin.

The 30% or 40% SiO_2 sols described, or even more dilute sols prepared by ion-exchange and subsequent concentration, can be added to drained, pickled skins. These can be washed so that they are comparatively free from salts and other impurities, but more customarily, they will contain considerable amounts of sodium sulfate or other such materials. Again, they may also contain sulfuric acid or another acid which is used in adjusting the pH. The sols used, then, must take into account the amount of water already present and they should be used in such proportion as to give a workable mixture with the skins and to obtain a desired degree of retention.

The silica solution should contain combined sodium in such an amount that the mol ratio of silica to sodium is greater than about 10, the silica being expressed as SiO_2 and the sodium as Na_2O. It will be understood that the combined sodium referred to is associated with the silica and is not to be confused with the sodium present, for instance, as sodium sulfate in a silicate solution made by acidifying sodium silicate with sulfuric acid. The solution cannot be regarded merely as a solution of high ratio sodium silicate because it is well known that sodium silicates prepared by usual procedures, such as fusing silica with soda ash, are unstable in aqueous solution when the ratio exceeds about 4.

Instead of combined sodium, another combined alkali metal, such as potassium or lithium, or ammonia or an amine, may be employed as the alkali associated with the silica. These, as well as the combined sodium, are generically referred to as the "alkali." The combined alkali may be determined, according to conventional analytical procedures, by titration with acid, and may be calculated by stoichiometry to Na_2O. Thus, when reference is made to silica:alkali mol ratio in describing this invention, the mol ratio of colloidal silica, calculated as SiO_2, to sodium hydroxide, calculated as Na_2O, or other hydroxide such as potassium hydroxide, similarly calculated, is meant, and as described in the preceding paragraph, only the alkali associated with the silica is included.

More specifically the ratio SiO_2:Na_2O may advantageously be greater than 25, particularly satisfactory results being obtained with chromed skins using a ratio of from 25 to 100 or even higher. Solutions with these preferred ratios are characterized by extreme stability against gelling because of the specific nature of the silica.

Colloidal silica solutions of the above-described character may be prepared by removing sodium ions from a sodium silicate solution having a lower ratio—say 3.25 SiO_2:Na_2O—and replacing such sodium ions with hydrogen ions. One method for effecting such removal is by dialysis through a semi-permeable membrane, the sodium silicate being on one side of the membrane and an acid on the other, and the sodium ions diffusing out and being replaced by hydrogen ions from the acid. The membrane so used has a permeability which does not permit diffusion of silicate ions, at least in the polymerized condition.

It is particularly preferred to employ a colloidal silica solution prepared by removing sodium ions from a sodium silicate solution by passing the solution through a mass of ion-exchange material which has been treated with an acidic reagent. Such solutions may be prepared according to the teachings of Bird U. S.

Patent 2,244,325 and have been referred to as "Colosil" in Carter U. S. Patent 2,329,589. In particular, the colloidal silica may be prepared by passing a 3.3 ratio (SiO_2:Na_2O) sodium silicate solution through a bed of a carbonaceous zeolite in the hydrogen form as described at page 2, column 1, paragraphs 1 to 4, of the Bird patent.

Relatively concentrated silica sols which have sufficient stability to make their use practical may be prepared, for instance, by redispersing a silica gel with an alkali as described in the White U. S. Patent 2,375,738. According to this method silica sols which are relatively stable and which contain up to about 18% SiO_2 may be prepared.

Becktold and Snyder U. S. Patent application 65,536, now Patent No. 2,574,902, filed December 15, 1948, discloses methods for preparing concentrated stable silica sols from the ion-exchange effluent of the Bird patent. These sols have been found to be particularly useful in plumping tanned skins. They are also remarkably stable, and contain substantially spherical, discrete, non-agglomerated, dense particles of amorphous silica which may have an average diameter of 15–130 millimicrons.

The Bechtold and Snyder sols are produced by processes comprising forming a heel, by heating to a temperature above 60° an aqueous sol of silica particles of less than 10 millimicrons diameter, adding to said heel a silica sol containing particles of less than 10 millimicrons diameter, and continuing the addition and heating until at least 5 times as much silica has been added to the heel as was originally present. By such build-up processes sols may be produced which are amenable to concentration even to as high as 35 per cent SiO_2 without gelling, the sols being characterized by having a silica:alkali ratio of from 60:1 to 130:1, by containing discrete, dense silica particles having a molecular weight, as determined by light-scattering, of more than one-half million, and by having a relative viscosity, at 10 per cent SiO_2, of from 1.15 to 1.55.

A particularly preferred sol which may be prepared according to the process of Bechtold and Snyder has the following characteristics: The sol is practically clear having only a slight opalescence. It is stable indefinitely under ordinary conditions of storage. Electron microscopic examination shows that the sol contains substantially spherical, discrete, non-agglomerated dense ultimate particles of amorphous silica, substantially all of which have an average diameter in the range of 15 to 30 millimicrons, and at least 80% of which have an average diameter of from 0.5 to 1.7 times the arithmetic mean particle diameter. The sol has a relative viscosity of 1.15 to 1.25 as measured at 10% SiO_2 concentration and a pH of 10. When the silica sol is adjusted to pH 3.5 with dilute HCl and evaporated to dryness, the resulting powder possesses a specific surface area as measured by nitrogen adsorption of from 100 to 200 $m.^2/g.$ The mol ratio of SiO_2 to Na_2O in the sol is from 80:1 to 100:1 and the pH of the sol is from 9.7 to 10.3. The concentration of SiO_2 in the sol is about 30%. A typical product has the following chemical analysis:

	Percent
SiO_2	30.07
Na	0.34
SO_4	0.06
Cl	0.03
Sulfated non-siliceous ash before leaching	1.02

The co-pending application of Joseph M. Rule, Serial No. 183,901, filed September 8, 1950, discloses processes for producing stable silica sols which comprise preparing an active silica sol by effecting contact, successively, between a sodium silicate solution and a cation-exchanger in the hydrogen form and an anion-exchanger in the basic form, adding a suitable amount of sodium hydroxide to adjust the SiO_2:Na_2O mol ratio of the sol to from 130:1 to 500:1, boiling a portion of the adjusted sol under atmospheric pressure to form a heel, adding to the heel an additional quantity of the original active silica sol, while maintaining the pH in the range from 7.5 to 10.7 and the temperature at the boiling point of the sol, whereby water is evaporated, the additional quantity of active silica sol being added at such a rate, relative to the rate of evaporation, that the volume of the combined sols remains substantially constant, and the amount of silica added being at least 3 to 15 times as much as that originally present, whereby build-up of the added silica upon that present in the heel is effected to give a sol product stable against gelation, and concentrating the sol to upwards of 35% by weight of silica.

The products prepared according to the previous application may be characterized as aqueous silica sols having a silica:sodium oxide mol ratio of from 130:1 to 500:1, a relative viscosity of from 1.15 to 1.55 as measured at 10% Si_2O and pH 10, and a specific conductance, as measured at 10% SiO_2 and 28° C., of less than

$$\left(\frac{10{,}000}{R}+30\right)\times 10^{-5}\ \text{mho/cm.}$$

where R is the silica:sodium oxide mol ratio, and containing amorphous silica in the form of dense, non-agglomerated, spherical particles having an average diameter of 10 to 30 millimicrons, in a concentration of from 35% to upwards of 50% SiO_2 by weight.

These products may also be prepared according to the processes disclosed in the co-pending application of Rule, Serial No. 183,902, now Patent No. 2,577,485, filed September 8, 1950, wherein sodium hydroxide is added to a silica sol containing amorphous silica particles which are dense, non-agglomerated, spherical, and have an average diameter of 10 to 130 millimicrons, the sol having a relative viscosity, as measured at 10% SiO_2 and pH 10, of 11.15 to 1.55 and a specific conductance, as measured at 10% SiO_2 and 28° C., of lesss than 4×10^{-4} mho/cm., the amount of hydroxide added being enough to adjust the silica:sodium oxide mol ratio to from 130:1 to 500:1.

A particularly preferred sol which may be prepared according to either of the Rule processes has the following characteristics: The sol is practically clear, having only a slight opalescence. It is stable indefinitely under ordinary conditions of storage and does not gel after one month of heated storage at 95° C. Electron microscopic examination shows that the sol contains substantially spherical, discrete, non-agglomerated, dense, ultimate particles of amorphous silica, substantially all of which have an average diameter of from 0.5 to 1.7 times the arithmetic mean particle diameter. The sol has a viscosity of 250 centistokes and when diluted to a concentration of 10% SiO_2 and adjusted to a pH of 10, the relative viscosity is 1.2. When such a silica sol is adjusted to pH 3.5 with dilute hydrochloric acid and evaporated to dryness, the resulting powder has a specific surface area, as

measured by nitrogen adsorption, of from 100 to 200 m.²/g. The specific conductance of the sol which contains 40% SiO_2 is 4.8×10^{-4} mho/cm. at 28° C. The pH of the sol is 9.6. The mol ratio of SiO_2:Na_2O in the sol is 150 to 1. A typical product has the following analysis:

	Percent
SiO_2	40.8
Sulfated non-siliceous ash:	
Before leaching	0.67
After leaching	0.08
Cl	0.001
Na	0.19
SO_4	Less than 0.005

In the foregoing description of the silica sols which may be employed in processes of the invention, certain properties of the sols, such as specific conductance and relative viscosity, have been mentioned. These properties are determined, under the conditions specified, by conventional techniques of physical chemistry. The method for measuring the sizes of silica particles by means of the electron microscope is that described by J. H. L. Watson in Analytical Chemistry, 20, p. 576 (June 1948), the calculation method being that described in an article by L. R. Sperberg and H. M. Barton in "Rubber Age," 63, pp. 45 to 51 (April 1948). From electron micrographs one can also determine whether the particles of silica are substantially discrete or agglomerated, and whether they are spherical or some other shape. The specific surface area of the silica may be calculated from the size of particles as observed in the electron micrographs. The specific surface area may also be determined directly, by a nitrogen adsorption method, as described in an article, "A New Method for Measuring the Surface Areas of Finely Divided Materials and for Determining the Size of Particles" by P. H. Emmett in the publication, Symposium on New Methods for Particle Size Determination in the Sub-Sieve Range, published by the American Society for Testing Materials, March 4, 1941, p. 95. (The value of 0.162 square millicron for the area covered by our surface-adsorbed nitrogen molecule is used in calculating the specific surface areas, the latter being reported in square meters per gram, m.²/g.) If the particles of silica in the sol are substantially individual and discrete, the specific surface areas as calculated from electron micrographs and as determined by nitrogen adsorption will be in close agreement—that is, within about 25%—if the silica particles are dense. If the silica particles are not dense, the specific surface area by nitrogen adsorption will be more than about 25% greater than the value calculated from electron micrographs.

The colloidal silica solutions suitable for use according to the invention thus may be prepared as above-described by a variety of routes. The products, however, are all characterized by being silica sols made up of colloidal particles of greater than 10 millimicrons diameter, the particles being dense.

According to a process in the present invention the tanned skins are agitated in the silica solution until they have taken up an appreciable amount of silica. Marked effects are observed when the skins have taken up about two per cent of silica based on their tanned and drained but wet weight. With chromed skins this is two per cent on the "blue" weight. Larger amounts than 2 per cent may, of course, be used advantageously, the amount sometimes exceeding 8 per cent when a substantial loading of the leather is desired.

After the skins have been agitated in the silica solution and the desired amount of silica has been taken up, the pH is raised, preparatory to finishing off the leather. The pH may be raised by adding an alkali. While any alkali may be used, sodium bicarbonate has been found to be particularly desirable in this capacity. The pH may be raised to any value desired for finishing; with chromed skins the value may advantageously be from 4.5 to 5.0.

Tanned skins treated with silica according to this invention may be finished off into leather in any desired manner. Ordinarily they will be washed, fatted, and dried according to practices customary in the art, but it will be understood that the finishing step may be varied, depending on the particular character of finished leather desired.

The processes of this invention will be better understood from the following illustrative examples.

Example I

To 145 parts by weight of blue shaved chrome-tanned skins having a pH of 3.3 and contained in a tanning drum there was added 198.6 parts of water and 18.9 parts of a substantially stable colloidal solution of silica having a combined SiO_2:Na_2O mol ratio of 50:1 containing 30% silica and prepared by passing a sodium silicate solution through an acid-regenerated zeolite as described in Bird U. S. Patent 2,244,325. The solution and skins were agitated together for one-half hour. The pH was then raised to 5.0 by addition of sodium bicarbonate, and the skins were removed, washed, fatted, and dried according to usual practice for finishing chrome leather.

Upon examination, the leather was found to be of excellent quality, having an unctuous feel and being plump, uniformly tight and firm, and showing no tendency to drawn grain, harshness, crackiness, or instability on aging. As compared with corresponding sections of the same skins which had been processed in identical manner, except that the silica solution was omitted, the treated skins showed a 21 per cent increase in thickness.

The treated skins were found to contain 6.25% by weight of silica, equivalent to a 2.3% take-up of silica based on the original blue-chrome weight.

Example II

A batch of blue shaved chrome-tanned skins was treated with silica exactly as in Example I except that 38.7 parts of silica solution and 179.7 parts of water was used, that is, the silica concentration was doubled.

Again it was found that the leather was of excellent quality, having an unctuous feel and being plump, uniformly tight and firm, and showing no tendency to drawn grain, harshness, crackiness, or instability upon aging. The increase in thickness in this case was 29 per cent. The treated skins contained 13.6% by weight of silica, equivalent to a 5.5% take-up of silica based on the original blue-chrome weight.

Example III

Colloidal silica solutions were made containing, respectively, 5.8% SiO_2 and 19% SiO_2, and having ratios of SiO_2 to Na_2O greater than 10, by passing sodium silicate solutions through an acid-regenerated ion-exchange medium of the

zeolite type. Separate solutions, each containing 3% SiO_2, were made, respectively, by diluting 183 parts by weight of the 5.8% SiO_2 solution with 174 parts of water and by diluting 56 parts of the 19% SiO_2 solution with 300 parts of water.

In each of the solutions thus prepared separate quantities of chrome-tanned skins, in the blue state, at a pH of 3.3, were agitated for 25 minutes. The pH was then raised by adding sodium bicarbonate, after which the skins were fatted and dried.

By chemical analysis the skins treated with the diluted 5.8% SiO_2 solution were found to contain 8.9% SiO_2 on the dry weight, while those treated with the diluted 19% SiO_2 solution were found to contain 10.2% SiO_2. The finished leather, in each case, was plump, uniformly tight and firm, had an unctuous feel, and showed no tendency to drawn grain, harshness, crackiness, or instability upon aging.

Example IV

This example illustrates the practice of the invention as applied to the improvement of the properties of leather tanned with a synthetic tanning agent, namely, a hydrolyzed co-polymer of styrene and maleic anhydride.

A quantity of pickled goat skins of the type known as "Nigerian" was tanned with the synthetic tanning agent in the following manner, all percentages mentioned being by weight, based on the drained pickled weight of the original skins and the amount of water initially present being between 20 and 30 gallons per hundred pounds of skins.

The skins were depickled to a pH of 4.8 with sodium acetate. They were then tanned with 30% of a 20% solution of a hydrolyzed co-polymer of styrene and maleic anhydride prepared as described in Example 5 of Graves U. S. Patent 2,205,882, the tanning step requiring two hours. The skins were then acidified to a pH of 3.0 by adding sulfuric acid. The tannage was then fixed by adding 12% of alum and agitating for one hour in the tanning drum, then raising the pH to 4.5 by adding sodium bicarbonate, all as explained in Kirk U. S. Patent 2,205,901.

The tanned skins were treated with colloidal silica solution, according to the present invention, as follows:

The pH of the skins was lowered to 2.1 by adding sulfuric acid. There was then added 50% by weight, based on the original drained pickled weight of skins, of a colloidal silica solution containing 30% by weight of silica expressed as SiO_2, the silica solution having been prepared by passing a sodium silicate solution, containing 2.3% SiO_2, through a cation-exchange resin in the hydrogen form, adjusting the SiO_2:Na_2O weight ratio of the effluent to about 85:1 by adding sodium silicate, and concentrating the solution to 30% SiO_2 by a constant volume evaporation process in which eight volumes of feed sol were added, as required, to the original volume of sol in the evaporator and water was boiled off at atmospheric pressure, all as described in Example 3 of Bechtold and Snyder U. S. application Serial No. 65,536, filed December 15, 1948. The skins were tumbled in the colloidal silica solution in a tanning drum for one hour. The pH was then raised to 4.5 by adding sodium bicarbonate. Thereafter, the treated skins were set out, shaved, washed, fat-liquored, and finished in accordance with conventional practices.

The finished, treated leather had excellent plumpness and other properties. In particular, the suedeing properties were noted to be remarkably improved as compared to similarly prepared leather without silica treatment. This was particularly noticeable in that the nap of the sueded leather was unusually fine.

Example V

This example was similar to Example IV except in the particulars set forth below.

A quantity of pickled goat skins of the type known as "Batti" was depickled to pH 4.8 with sodium acetate and was then tanned with hydrolyzed styrene-maleic anhydride co-polymer, the amount of tanning agent used being 25% by weight of a 20% aqueous solution, based on the drained pickled weight of skins. The skins were then acidified to pH 3.2 with sulfuric acid and treated for one hour with 10% of alum, after which the pH was raised to 4.5 by adding sodium bicarbonate. The tanned skins were then set out and shaved and returned to the tanning drum with a solution of sodium acetate (3%) and sulfuric acid (5%) to give a pH of 2.0.

The tanned skins thus prepared were treated, by a process of this invention, with a colloidal silica solution containing 30% by weight of SiO_2 and prepared as described in Example IV, the amount of solution used being 25% by weight, based on the drained pickled weight of skins, and the time of treatment being one hour. The pH was then raised to 4.5 by adding sodium bicarbonate and the skins were washed, fat-liquored and finished in accordance with the customary practices of the art.

Again it was found that the finished, treated leather had excellent plumpness and other properties. The properties of suede leather made from the skins were especially good, the nap being unusually fine.

This application is a continuation-in-part of my co-pending application U. S. Serial No. 582,179, now forfeited, filed March 10, 1945.

I claim:

1. In a process of treating tanned skins the step comprising immersing a skin in a sol of dense, colloidal silica particles greater than 10 millimicrons in diameter.

2. In a process of treating tanned skins the step comprising immersing a skin in a sol of dense, colloidal silica particles greater than 15 millimicrons in diameter.

3. In a process of treating tanned skins the step comprising immersing a skin in a sol of dense, colloidal silica particles greater than 10 millimicrons in diameter, the sol having an SiO_2:alkali mol ratio greater than 60:1.

4. In a process of treating tanned skins the steps comprising adjusting the pH of the tanned skins to from 1.7 to 5.0 and immersing the skins in a sol of dense, colloidal silica particles greater than 10 millimicrons in diameter.

5. In a process of treating tanned skins the step comprising immersing a skin in a sol of dense, discrete, colloidal silica particles greater than 15 millimicrons in diameter, the sol having an SiO_2:alkali mol ratio of from 60:1 to 130:1 and a relative viscosity of from 1.15 to 1.55 as measured at 10% SiO_2 and pH 10.

6. In a process of treating tanned skins the step comprising immersing a skin in a sol of dense, discrete, colloidal silica particles 10 to 30 millimicrons in diameter, the sol having an SiO_2:alkali mol ratio of from 130:1 to 500:1, a relative viscosity of from 1.15 to 1.55 as measured

at 10% SiO_2, and pH 10, and a specific conductance, before immersion of the skins, of less than

$$\left(\frac{10,000}{R}+30\right)\times 10^{-5}\ \text{mho/cm.}$$

as measured at 10% SiO_2 and 28° C., where R is the silica:alkali mol ratio.

7. In a process for plumping tanned skins with silica the steps comprising adjusting the pH of the tanned skins to from 2.8 to 5.0, agitating the skins in a substantially stable colloidal solution of silica particles which are dense and greater than 10 millimicrons in diameter, the solution having a combined SiO_2:Na_2O ratio greater than 10 and being prepared by removing sodium ions from a sodium silicate solution and replacing them with hydrogen ions, the agitation of the skins being continued until they have taken up an appreciable quantity of silica, and thereafter raising the pH of the skins.

8. In a process for plumping chrome-tanned skins with silica the steps comprising adjusting the pH of the chrome-tanned skins to from 3.0 to 3.5, agitating the skins in a substantially stable colloidal solution of silica particles which are dense and greater than 10 millimicrons in diameter, the solution having a combined SiO_2:Na_2O ratio greater than 10 and prepared by removing sodium ions from a sodium silicate solution and replacing them with hydrogen ions, the agitation of the skins being continued until they have taken up an appreciable quantity of silica, and thereafter raising the pH of the skins.

9. In a process for plumping chrome-tanned skins with silica the steps comprising adjusting the pH of the chrome-tanned skins to from 3.0 to 3.5, agitating the skins in a substantially stable colloidal solution of silica particles which are dense and greater than 10 millimicrons in diameter, the solution having a combined SiO_2:Na_2O ratio greater than 10 and prepared by passing a solution of sodium silicate through a mass of ion-exchange material which has been treated with an acidic reagent, the agitation of the skins being continued until they have taken up an appreciable quantity of silica, and thereafter raising the pH of the skins.

10. In a process for plumping chrome-tanned skins with silica the steps comprising adjusting the pH of the skins, in the blue shaved state, to from 3.0 to 3.5, agitating them in about from 1 to 2 times their weight of a substantially stable colloidal solution of silica particles which are dense and greater than 10 millimicrons in diameter, the solution having a concentration of from 1 to 15 per cent SiO_2, having a combined SiO_2:Na_2O ratio greater than 25, and prepared by passing a solution of sodium silicate through a mass of ion-exchange material which has been treated with an acidic reagent, the agitation of the skins being continued until they have taken up at least 2 per cent of their weight of silica, and thereafter raising the pH of the skins to from 4.5 to 5.0.

11. In a process for plumping chrome-tanned skins with silica the steps comprising adjusting the pH of the skins, in the blue shaved state, to from 3.0 to 3.5, agitating them in from 1 to 2 times their weight of a substantially stable, colloidal, solution of silica particles which are dense and greater than 10 millimicrons in diameter, the solution having a concentration of from 2 to 6 per cent SiO_2, having a combined SiO_2:Na_2O ratio greater than 25 and prepared by passing a solution of sodium silicate through a mass of ion-exchange material which has been treated with an acidic reagent, the agitation of the skins being continued until they have taken up at least 2 per cent of their weight of silica, and thereafter raising the pH of the skins to from 4.5 to 5.0.

12. In a process for plumping chrome-tanned skins with silica the steps comprising adjusting the pH of the skins, in the blue shaved state, to about 3.3, agitating them in about 1½ times their weight of a substantially stable, colloidal, solution of silica particles which are dense and greater than 10 millimicrons in diameter, the solution having a concentration of from 2 to 6 per cent SiO_2, having a combined SiO_2:Na_2O ratio of from 25 to 100 and prepared by passing a solution of sodium silicate through a mass of ion-exchange material which has been treated with an acidic reagent, the agitation of the skins being continued until they have taken up at least 2 per cent of their weight of silica, raising the pH of the skins to about from 4.5 to 5.0 by adding sodium bicarbonate, and washing, fatting, and drying the skins.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,127,304	Mauthe et al.	Aug. 16, 1938
2,244,325	Bird	June 3, 1941
2,276,314	Kirk	Mar. 17, 1942
2,276,315	Kirk	Mar. 17, 1942
2,375,738	White	May 8, 1945
2,408,656	Kirk	Oct. 1, 1946
2,443,512	Powers	June 15, 1948

OTHER REFERENCES

"Science News Letter," page 28, November 1, 1947.