The present invention relates to the art of depilating or unhairing hides or skins.

In unhairing skins or hides it is usual to soak the hides or skins with the assistance of various chemicals or treating agents to loosen the hair therein, so that such hair may be readily removed by scraping or other mechanical defainting processes or to destroy or dissolve the hair away from the skin or hide.

The most frequent treating agent utilized in the defainting of skins and hides is lime, with or without the addition of other alkaline materials, such as caustic soda.

These alkaline treatments are preferably carried out in such a manner that the hair of the skin or hide will be readily removed without injury to the pelts, and the pelts so treated are then subjected to baking, puering and tanning processes to produce the final leather.

Instead of the alkaline treatment, for the purpose of loosening the hair, the skins or hides may also be subjected to a sweating process, in which the skin or hide is subjected to the action of bacteria.

The skins or hides, preferably after the alkaline treatment, may be subjected to the action of proteolytic enzyme preparations for loosening of the hair, which may also have a bating or softening action.

These alkaline depilatory processes, however, are relatively slow and it has been customary to speed them up with sharpening agents, such as sodium sulphide, the form of arsenical sulphide known as red arsenic, and various amnies such as methylamine. It has been found, however, that such sharpening agents can be used only in limited quantities because excessive quantities result in damage to the hides or skins.

It is an object of the invention to provide a method of defainting or unhairing hides and skins that materially shortens the time of treatment without danger of damage to the hides and that makes possible the production of leather and hair of improved quality and texture.

Other objects of the invention will be apparent from the following description.

I have discovered that certain reducing sulphur-oxygen combinations, when added to the unhairing bath, not only act as accelerators to decrease materially the time required for loosening the hair, but also make possible the production of leather of improved quality after the subsequent operation of baking, puering and tanning.

These sulphur-oxygen combinations are characterized by being stable in dry condition and having a substantially greater reducing power in solution than that of the sulphates, sulphanates, sulphides or thio-sulphates. While various such compounds may be used, I prefer using compositions of the class of the hydrosulphites and sulphonylates and corresponding organic compounds of sulphur and oxygen. I have found, for example, that sodium hydrosulphite (\( \text{Na}_2\text{S}_2\text{O}_3 \)), sodium sulphonylate, sodium formaldehyde sulphoxide or zinc calcium hydroly sulphite are suitable and satisfactory.

The compounds referred to may be added to liquid baths or to paste compositions that can be applied to the hides and skins. The relative proportions of the materials used may vary within a considerable range. The reducing sulphur-oxygen compounds may be added in amounts ranging from 0.1 to 70% or in some cases from 1 to 10% of the amount of alkali added, including lime, caustic soda, sodium carbonate, and so forth or in amounts ranging from 0.05 to 50% or in some cases from 0.1 to 3%, based upon the weight of the cow hides, goat skins, sheep skins, calf skins or other hides or skins being processed. The lower portions of the range are most applicable to liquid baths and the upper portions most applicable to paste compositions.

These ranges are just given by way of example and even smaller or larger quantities of these reducing compounds may be employed depending upon the character of the hides or skins being treated, the time permitted for the treatment, the character of the bath or paste utilized and the ingredients therein, and the temperature at which the treatment is carried out.

Where the skins and hides are also subjected to treatments with bacterial or enzyme preparations, or where sharpening agents are employed, the amount of the hydrosulphite or sulphonylate or other compound may be decreased, but, as a general rule, it is preferable to use between 0.5 and 50 or in some cases between 2 to 10 parts of sodium hydrosulphite or sodium sulphonylate or similar compound for every thousand parts of the skins or hides or for every hundred parts of lime, which may be employed.

When the reducing sulphur-oxygen compounds herein described are used, the result is a substantial decrease in the amount of time required in the alkaline soaking operation or generally required in the complete defainting process.
Where sharpening agents, such as sulphides of sodium or arsenic or amines are employed, the action of these sharpening agents is greatly enhanced by the action of the hydro sulphite or sulphonate.

Not only may the reducing sulphur-oxygen combination of the present invention be added to the alkaline treating bath, but in addition, it may be employed in subsequent or in prior treatments accompanying the alkaline treatment as above described, in which case, the hydro sulphite or sulphonate or similar compound may be also included in the alkaline bath in decreased quantities or omitted altogether.

In addition, it is also possible to make pastes of the alkaline material, whether it be lime, soda ash, ammonia or caustic soda, and to add to such pastes suitable quantities of the hydro sulphite or sulphonate or similar compound; for example in amounts varying from 1 to 50% or more desirably from 1 to 20%. These pastes are then applied or painted upon the flesh sides of the hides or skins and the hair loosening occurs in a much shorter interval without injuring the hair or the hides.

Not only is the quality of the skin or hide greatly improved with resultant production of a better grade of leather, but in addition, the hair, which is removed, is of high quality.

In addition to the sodium hydro sulphite or sulphonate, it is also possible to use the corresponding zinc, calcium, magnesium, and other salts and the formaldehyde or other aldehyde and ketone derivatives of the hydro sulphites and sulphonates.

In addition to the sulphonates or hydro sulphites specifically above mentioned, it is also possible to utilize calcium, zinc or magnesium formaldehyde sulphonate, sodium, calcium, magnesium or zinc acetone sulphonate, or hydro sulphite, and various other hydro sulphites and sulphonates of sodium, calcium, magnesium and zinc. These compounds may be added as such, or generated in solution or during the unhairing process, for example by adding zinc or iron and bisulphite, or by electrolytic reduction of bisulphite.

In general; all sulphinic or disulphinic acid derivatives whether of inorganic or organic origin—aromatic or sulphonate—may be employed.

As a general rule, the sulphur should at all times be combined with the oxygen to form a reducing power in aqueous solution than is the case with sulphonates, bisulphites, sulphides, hydro sulphides, sulphates, thiosulphates and other similar compounds.

While the invention may be carried out in various ways, the following specific processes are given by way of examples. They illustrate various ways of carrying out the invention successfully but it is to be understood that the invention is not to be restricted by or limited to such exemplifications:

**Example 1.**—1200 pounds of salted cow hides are soaked and then put in a paddle containing a solution of 30 pounds of caustic soda and 100 pounds of soda ash with sufficient water so that the proportion of skins to water by weight is about 1 to 4. Then 5 pounds of sodium hydro sulphite are added and the paddle is operated for a few minutes to obtain a uniform mixture. After two or three days, the hair is perfectly loosened and may be removed by unhairing machines in exceptionally good condition.

The skins may then be bated and tanned and the resultant leather is of very good quality.

The addition of soda ash is only to prevent exorbitant swelling of skins with the caustic, but it may be omitted or replaced by other alkali metal salts, such as sodium chloride or sodium sulphate.

In carrying out the same operation without the addition of hydro sulphite, satisfactory loosening of the hair is only obtained after six days, and even then, it is not possible to achieve the most desirable mechanical unhairing operation. In addition, both the hair and final leather are not in as good a condition.

**Example 2.**—1000 pounds of dry goat skins are soaked for two days and then put into a paddle. To the paddle is added 120 pounds of lime and the temperature is then raised to about 60° F. Then there is added 5 pounds of sodium hydro sulphite, together with 20 pounds of caustic soda. About after two days a perfect hair loosening occurs and the hair and flesh are readily removed by mechanical dehaulers or fleshing machines from the skins.

The skins and hair after depliation are in excellent condition and the final leather, after puning and tanning, is of high quality.

Under the same conditions and with the same reagents in the same proportions, but with the omission of sodium hydro sulphite, hair loosening is only satisfactorily obtained after ten days and both the removed hair and the final leather are of inferior quality.

**Example 3.**—5000 pounds of salted cow hides are soaked for one day and then to the soaked hides is added about three times their weight of water together with 25 pounds of zinc calcium hydro sulphite. After several hours, there is added 400 pounds of fresh slaked lime and the hides are kept in this solution for about two days. After two days, the hair is sufficiently loosened so as to render mechanical depliation relatively easy and the hair and unhairled pelts are in good condition.

Without the hydro sulphite, the loosening of the hair and the unhairing operation is unsatisfactory, even though the hides are kept in a bath for over four days.

**Example 4.**—10 dozen sheep skins are soaked and then painted upon the flesh side with a paste containing lime and 5% sodium hydro sulphite. The painted skins are kept in moist condition for twenty-four hours. The wool then is readily removed by pulling. The wool and the pelt are both in excellent condition. The saving in time is substantial.

**Example 5.**—1000 pounds of goat skins by dry weight are soaked for two days and then put into a solution of 6000 pounds of water containing 35 pounds of caustic soda. To this solution is then added two pounds of sodium formaldehyde hydro sulphite or sodium formaldehyde sulphonate.

After three days the hair is considerably loosened. Without unhairing at this stage, the skins are partly neutralised by sodium bicarbonate, boric acid, ammonium sulphate or any other similar reagent to a pH of around 9.0 and there are then added 20 pounds of an antiseptic enzymatic dehauling preparation of bacterial origin. After twelve hours, the skins are capable of being dehaired most readily and both the hair and the pelt are in excellent condition.

**Example 6.**—500 pounds of salted calf skins are washed in a paddle for ten minutes and then
soaked in water containing 2¾ pounds of sodium hydrosulphite and 3 pounds of ammonia. When the hair commences to slip after twenty-four hours, 50 pounds of lime are added and after another twenty-four hours, the skins are taken out and mechanically unhaired.

Example 1: 1000 pounds of dry goat skins are soaked for two days and then put in a paddle so that the proportion of goat skins to water is about 1 to 8 by weight.

Then there is added 5 pounds of sodium hydrosulphite. After one hour there is further added 120 pounds of fresh slaked lime and 2 pounds of sodium sulphide.

After forty-eight hours the hair loosening has set in to such a degree that the hair may be removed with a brush.

Instead of sodium sulphide, other sharpeners might be employed, such as red arsenic and amines.

As amines there may be used mono-, di- or triethanolamine, ethyl- or methyl-amin, diaminopropanol, various hydroxy-, carboxy- or other substituted amines.

In carrying out the above processes, it is found that various antiseptic agents may be readily included without hindering the action of the reducing sulphur-oxygen combination, such antiseptic agents being, for example, phenols, cresols, naphthalins, various halogenated or chlorinated benzenes, toluene, xylene or naphthenalene derivatives, pine oil or other terpene derivatives, and so forth.

As enzymatic products in the above procedures, there may be utilized enzymes, such as pancreatin, trypsin, papain, cathepsin, bromelin or enzymes derived by the growth and cultivation of bacteria, fungi and molds, such as B. subtilis, B. mesentericus, mycoides and liquefaciens, Aspergillus oryzae or niger, Penicillium glaucum, Mucor delemar or mucido, Amylomyces rouzii, Trychotis tenuis and so forth.

Many other changes could be effected in the particular features of process and treatment described, substantially departing from the invention intended to be defined in the claims, the specific description herein merely serving to illustrate various ways of successfully carrying out the invention. What is claimed is:

1. A process of loosening the hair of skins and hides which comprises subjecting said skins or hides to treatment with an alkaline material and to the action of a compound selected from the group consisting of hydrosulphites, sulphoxylates and their organic derivatives.

2. A process of loosening the hair of skins and hides which comprises treating the skins or hides with an alkaline bath containing a compound selected from the group consisting of hydrosulphites, sulphoxylates and their organic derivatives.

3. A process of loosening the hair of skins and hides which comprises subjecting the skins or hides to the action of an alkaline material selected from the group consisting of lime and caustic soda, and a compound selected from the group consisting of hydrosulphites, sulphoxylates and their organic derivatives.

4. A process of accelerating the loosening of hair of skins and hides in alkaline soaking operations which comprises adding a hydrosulphite to the bath.

5. A process of accelerating the loosening of hair of skins and hides which comprises immersing the skins or hides in a bath containing an alkaline material and a hydrosulphite, about 0.1 to 70 parts of the hydrosulphite being utilized for every 100 parts of said alkaline material.

6. A process of accelerating the loosening of hair of skins and hides which comprises immersing the skins or hides in a bath containing an alkaline material and a hydrosulphite, about 0.1 to 70 parts of the hydrosulphite being utilized for every 100 parts of said alkaline material.

7. A process of accelerating the loosening of hair of skins and hides which comprises adding a formaldehyde sulphoxylate to the bath.

8. A process of accelerating the loosening of hair of skins and hides which comprises adding a formaldehyde sulphoxylate to the bath.

9. A process of accelerating the loosening of hair of skins and hides which comprises applying to the flesh sides of said skins or hides a paste of an alkaline material including an accelerator selected from the group consisting of hydrosulphites, sulphoxylates and their organic derivatives.

10. A process of accelerating the loosening of hair of skins and hides which comprises applying to the flesh sides of the skins or hides a paste of lime containing about 1 to 50% of sodium hydrosulphite.

11. A process of accelerating the loosening of hair of skins and hides which comprises adding a sulphoxylate to the bath. 12. A process of accelerating the loosening of hair of skins and hides which comprises adding a sulphoxylate to the bath.

13. A process of accelerating the loosening of hair of skins and hides which comprises subjecting said skins or hides to the action of an enzyme, an alkaline material and a compound selected from the group consisting of hydrosulphites, sulphoxylates and their organic derivatives.

14. A process of accelerating the loosening of hair of skins and hides which comprises subjecting said skins or hides to the action of an enzyme, an alkaline material and a compound selected from the group consisting of hydrosulphites, sulphoxylates and their organic derivatives.

15. A process of accelerating the loosening of hair of skins and hides which comprises subjecting said skins or hides to the action of an enzyme, an alkaline material and a compound selected from the group consisting of hydrosulphites, sulphoxylates and their organic derivatives.

16. A process of accelerating the loosening of hair of skins and hides which comprises subjecting said skins or hides to the action of an enzyme, an alkaline material and a compound selected from the group consisting of hydrosulphites, sulphoxylates and their organic derivatives.

17. In the process of loosening the hair of skins and hides by the action of lime the improvement which comprises adding to the lime a hydrosulphite of the group consisting of alkali and alkaline earth hydrosulphites.

18. In the process of loosening the hair of skins and hides by the action of lime the improvement which comprises adding to the lime an alkali hydrosulphite.

19. In the process of loosening the hair of skins and hides by the action of lime the improvement which comprises adding to the lime an alkali hydrosulphite.

20. In the process of loosening the hair of skins and hides by the action of lime the improvement which comprises adding to the lime an alkali hydrosulphite.

21. A process of accelerating the loosening of hair of skins and hides which comprises subjecting the skins or hides to the action of lime, caustic soda and a hydrosulphite.

22. A process of accelerating the loosening of hair of skins and hides which comprises subjecting the skins or hides to the action of lime, caustic soda and a hydrosulphite.
4. A compound selected from the group consisting of hydrosulphites, sulphonylates and their organic derivatives.

22. A hair-loosening composition comprising an alkaline material selected from the group consisting of caustic soda and lime and an accelerator selected from the group consisting of hydrosulphites, sulphonylates and their organic derivatives.

23. A process of loosening the hair of skins and hides which comprises treating the skins or hides with an alkaline bath containing a sharpening material selected from the group consisting of sodium sulphide, red arsenic and an amine, and an accelerator selected from the group consisting of hydrosulphites, sulphonylates and their organic derivatives.

24. A process of loosening the hair of skins and hides which comprises treating the skins or hides with an alkaline bath containing sodium sulphide and sodium hydrosulphite.

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