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UNHAIRING OF HIDES AND SKINS

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This invention relates to the unhairing of hides and skins, which is a preliminary step in their conversion into leather. An object of the invention is to provide new classes of unhairing agents which are suitable for use in neutral or alkaline solutions or as unhairing accelerators in unhairing baths containing lime, baths containing arsenic, baths containing pancreatin or other enzymes or any other types of unhairing baths as will subsequently be explained. A further object of the invention is to provide classes of unhairing agents or accelerators which will effect the removal of hair roots as well as hair from hides and skins without damaging the hair or skin. A still further object of the invention is to provide classes of unhairing agents or accelerators which will contain or develop, in addition to groups having a reducing or hydrolyzing action on the keratin of the hair roots, also groups having a solvent or emulsifying action on the fat surrounding these roots in the hair pockets.

The invention in its broader aspects will be outlined and described in terms of certain commonly accepted principles of the mechanism of unhairing. We believe that these principles are correct and that their validity is further established by the experimental evidence contained in the present specification. It should be understood, however, that the invention as exemplified by this experimental evidence is not dependent upon any theory of operation but is limited only by the scope of the claims appended hereto.

The most successful unhairing agents or accelerators now in use are lime, sodium sulfide and red arsenic (As_2S_3). It is generally considered that the efficiency of these materials is due either to a reducing action or a hydrolyzing action, or both, on the disulfide linkages of the keratinous proteins of the hairs and hair roots. This theory was announced by H. B. Merrill in *J. Ind. Eng. Chem.* vol. 17, page 36 (1925).

An unhairing agent of the type of sodium sulfide, while rapid and effective, attacks the hair above the point where it enters the hair pocket. The result of this action is that the hair is weakened and breaks off above the surface of the hide, leaving the hair root embedded in the hide or skin from which it can be extracted only with difficulty.

Our investigations have shown that the failure of such unhairing agents or unhairing accelerators as sodium sulfide to remove the hair roots is due to a lack of penetration of the unhairing agent into the hair pockets containing these hair roots rather than to any lack of chemical action, for the hair roots consist of the same material as the hair itself.

In order to remove the hair roots without harming the hide or hair, and to produce a fine and clean grain, the unhairing agent or accelerator

must be capable of entering the hair pockets and dissolving the epithelial cells which line the walls and form the connecting binders for the hair bulb. After these cells have been hydrolyzed the hair bulb can slip from its sheath, leaving the hair pockets clean and open for the following scudding and bating operations. Unhairing agents which are strong alkalies have great difficulty in doing this because of the presence in these pockets of the fat provided by nature for protection and lubrication of the hair roots.

Lime, sodium sulfide and sodium hydroxide, which are the conventional unhairing agents, would in time saponify the fat in the hair pockets but the resulting soaps are bulky and tend to plug any available opening. At the same time the strong alkalinity of these agents hinders the removal of the hair by swelling the skin until the openings of the hair pockets are constricted, so that the thicker hair bulbs cannot get out and the alkali cannot enter.

For the above reasons the conventional alkaline unhairing agents are slow in action and must be used in such high concentrations that the hair is attacked. Most of its breaks off at its weakest part just above the hair bulb, leaving the hair bulbs embedded in the grain of the leather.

By a study of the above limitations in known unhairing agents and unhairing accelerators we have arrived at the principles of the present invention, which may be stated briefly, as follows:

(1) An unhairing agent or unhairing accelerator capable of liberating the hair roots must contain or develop in the unhairing bath one or more groups capable of disrupting the disulfide linkages of the keratinous matter surrounding the hair roots. This disruption is due to a chemical reduction and/or hydrolysis of these linkages by the unhairing agent, as stated by Merrill in the publication above referred to. Such reducing and/or hydrolyzing groups are usually polar in character.

(2) The unhairing agent or accelerator must contain or develop under unhairing conditions one or more fat-solvent groups; that is to say, groups which will have a solvent, emulsifying or penetrating action on the layer of fat surrounding the hair roots. Such fat-solvent groups are usually non-polar in character.

(3) The reagent should not be too alkaline; it should not develop during unhairing a pH such that alkali swelling becomes objectionable. In the following specification and claims, we shall use the term "non-swelling" to designate this characteristic.

(4) It should preferably have a relatively low molecular weight in order to facilitate penetration into the hair pockets, but this is not an absolute requirement in all cases.

(5) The fat-solvent group and the reducing

and/or hydrolyzing group must be in chemical combination; i. e., they must be contained in the same molecule. We have tested the action of mixtures of sodium sulfide with acetone and similar mixtures of fat-solvent with known un-
 5 hairing agents. It all cases the mixture was no better than the unhairing agent when used by itself.

(6) The unhairing agent or accelerator should be at least slightly water soluble or water-dis-
 10 persible, for obvious reasons.

We have found that any compound which fulfills the above conditions will be a good un-
 15 hairing agent. We have tested out a number of classes of compounds containing polar-non-polar groups that seemed to satisfy the above require-
 20 ments and in every case we found that all mem-
 bers of the class in question were operative. Naturally, some members of any given class were found to be more efficient than others, but any
 25 inferiority could always be traced to some defi-
 ciency in fulfilling one or more of the requisite conditions.

The above analysis has enabled us to identify
 25 entire classes of unhairing agents capable of liberating hair roots by an inspection of their type formula or by simple tests to determine if they contain groups of the necessary characteris-
 30 tics. Accordingly, we regard our invention in its broader aspects as including the use as an un-
 hairing agent or unhairing accelerator of any compound or class of compounds that fulfills the
 35 above requirements.

In some of its more limited and preferred as-
 35 pects our invention deals with certain classes of compounds which meet the above requirements of a satisfactory unhairing agent or accelerator
 40 and which we have found to be unusually effective for accomplishing the objects of the inven-
 45 tion. We will describe and discuss the charac-
 teristics of a number of such classes of compounds and illustrate their use in the following specific
 50 examples, but it should be understood that these examples are given primarily for the purpose of
 55 illustrating the invention as a whole and that our inventive concept is limited to their subject
 60 matter only in certain of the more limited claims
 appended hereto.

(a) Xanthates

This class of compounds is perhaps the best of
 50 all that we have tried, for all the relatively large number of xanthates which we have used appear
 55 to have a uniformly good unhairing action. Some of the higher alkyl xanthates such as the
 60 xanthates of dextrose, sucrose, and the like are not quite as efficient as are the lower xanthates
 by reason of their higher molecular weight but
 aside from this limiting factor the xanthates as
 65 a class comply with all the requirements of the
 present invention.

The xanthates have the following type for-
 mula:



in which Alk may be a primary, secondary or
 70 even a tertiary alkyl radical and Me is a positive group capable of forming a salt with the xan-
 75 thate such as sodium, potassium, calcium, am-
 monium or any other alkali or alkaline earth
 metal or basic groups such as methylamine, di-
 methylamine, guanidine, etc. They are prepared
 according to known methods by the interaction

of carbon bisulfide and alkali metal hydroxides
 in an excess of an alcohol corresponding to the
 desired alkyl radical, or by reacting a carbonate
 or other salt of the desired basic group, for ex-
 5 ample guanidine carbonate, with a mixture of
 the alcohol and carbon bisulfide in the presence
 of barium hydroxide.

It is evident from the association of groups con-
 10 tained in this class of compounds that its nucleus will have a strong affinity for fat and will readily
 15 penetrate the fat of the hair pockets. It is also evident that the compound will have both a re-
 ducing and hydrolyzing action on the disulfide
 linkages of the keratinous hair roots for it contains
 20 the group $-\text{SMe}$ which is known to have such an
 action. The xanthates as a class are neutral or
 only slightly alkaline, they are water-soluble,
 and of relatively low molecular weight. Accord-
 25 ingly, they fulfill all the conditions necessary for
 a successful unhairing agent capable of liberating
 hair at its roots in accordance with the present
 invention.

(b) Esters of thiocarbamic acid

These compounds have the type formula:



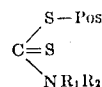
where A is alkyl, aryl, aralkyl, terpenyl, or in
 30 general any radical derived from an alcohol or
 phenol, and R_1 and R_2 are hydrogen or other
 positive groups capable of forming a substituted
 amide. In this class of compounds the group



is a fat-solvent or fat-emulsifying group and aids
 in the penetration of the compound into the
 hair pockets, while the group $-\text{NR}_1\text{R}_2$ is a hy-
 40 drolyzing agent of the type of dimethyl amine,
 which is known to be an unhairing agent.

(c) Salts and esters of dithiocarbamic acid

These compounds have the type formula:



in which Pos represents a positive group capable
 50 of forming a salt or an ester with the compound,
 such as alkoxy, aryloxy or a metal such as sodium,
 potassium, or other salt-forming group such as
 ammonium, etc., and R_1 and R_2 are hydrogen or
 55 other positive groups capable of forming a sub-
 stituted amide. This class of compounds con-
 tains as a hydrolyzing group the amido or sub-
 stituted amido group and also in the case where
 Pos is a salt-forming group they contain groups
 which are analogues of sodium sulfide. The com-
 60 pound has fat-solvent or fat-emulsifying prop-
 erties by reason of the group.



which resembles carbon bisulfide in its fat-solvent
 65 properties.

(d) Salts of trithiocarbonic acid

The type formula for this class of compounds
 is as follows:



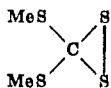
where Me is a positive salt-forming group. It is
 75 evident that the compounds of this class have

both fat-solvent, reducing and hydrolyzing properties since they contain groups of the MeS type as well as a group



(e) *Salts of tetrathiocarbonic acid*

The formula for this class of compounds is as follows:



In which Me is a positive, salt-forming group as previously defined.

These compounds are excellent unhairing agents for reasons which are apparent when their structure is compared with the salts of trithiocarbonic acid described under (d).

(f) *Salts and esters of thiolcarbamic acid*

These compounds have the type formula:



where the symbols have the same relative significance as in (e). In this class of compounds the amido group provides the reducing and hydrolyzing action and an affinity for fat is created by the —COS— group.

(g) *Ester salts of thiocarbonic acid*

These compounds have the type formula:



where A is as previously defined, and Me is a positive, salt-forming group. Here, as in several of the compounds previously discussed, the group —S.Me is a reducing and hydrolyzing group while the ester group creates an affinity for fat.

The similarity of the principles of operation of the above and similar classes of unhairing agents and accelerators to the modern theory of wetting agents may be helpful in explaining the advantages of the invention. It is well known that a good wetting agent causes water to wet an oily surface because it contains, in the same molecule, hydrophilic groups which have an affinity for water and hydrophobic groups which have an affinity for oil. Similarly the unhairing agents of the present invention, as has been demonstrated, contain groups which have an affinity for, and therefore a solvent action upon, the layer of fat surrounding the hair roots. These groups, therefore, facilitate the penetration of the unhairing agent into the hair pockets and aid in bringing the entire molecule into contact with the keratin of the hair roots. When this has been accomplished the reducing and/or hydrolyzing groups of the molecule are capable of directly attacking the disulfide linkages of the keratinous materials surrounding the hair roots and opening up the molecule for further attack by the lime or other hydrolyzing agent which may also be present in the bath.

METHODS OF APPLICATION

The unhairing agents or accelerators of the invention may be applied to the hides or skins by any known or approved method. Thus, for example, they may be incorporated in an unhairing bath of lime in which the hide is immersed or they may be applied in the form of a depilatory paste such as is frequently used in unhairing

sheepskins. In addition to their use as the chief unhairing agent we have also found that they are excellent unhairing accelerators for alkaline unhairing agents such as lime and sodium carbonate and that they may be used to advantage in admixture with known unhairing agents such as red arsenic or sodium sulfide; with reducing agents such as sodium hydrosulfite; and with proteolytic enzymes such as pancreatin.

The xanthates and other depilatories of the invention may be used in admixture with the above described materials or as a separate treatment preceding or following their use, or both. For example they may be used for extracting hair roots from stock which has been unhaird by other processes which leave some or all of the hair roots intact. This is sometimes done purposely in the manufacture of patent leather by treating light stock with a strong bath containing sodium sulfide to dissolve or weaken the hair and cause it to break off at the surface of the skin. The stock may then be treated with a bath containing one or more of the unhairing agents of the present invention in order to loosen the hair roots.

Unhairing baths or pastes containing the unhairing agents of the present invention may also contain auxiliary materials such as wetting agents, penetrating agents, emulsifying agents, softening agents and the like. An example of such an auxiliary material is the sodium salt of isopropyl naphthalene sulfonate, which is a well known wetting and penetrating agent.

The invention will be illustrated by the following specific examples, which show representative unhairing agents or accelerators included therein and representative methods of application. It should be understood, however, that these examples are given primarily by way of illustration and that the invention in its broader aspects is limited only by the claims appended hereto.

EXAMPLE 1

This example illustrates the use of xanthates as unhairing accelerators in conjunction with alkaline hydrolyzing agents. The xanthates were dissolved in lime solutions or suspensions and used according to standard commercial methods for unhairing steer and goatskins.

Procedure

a. *Steer hide*.—Domestic wet-salted steer hides were weighed and washed in running water for one-half hour, soaked overnight, and again washed for one-half hour in a drum. The hides were then suspended in four times their weight of lime solution containing an amount of lime equal to 8% of the weight of the hides before soaking and an amount of xanthate or other accelerator as indicated in this and other examples. The hides were agitated for about one-half minute every hour during several hours on the first and on the second day, and tested for hair looseness after 8, 24 and 48 hours.

b. *Goatskins*.—Dried goatskins were weighed and soaked for two days changing the soaking water once every day, then washed in running water for thirty minutes. The skins were then suspended in four times their weight of lime solution containing an amount of lime equal to 20% of the weight of the skins before soaking and an amount of accelerator as indicated.

In most cases the unhairing agents were tested in various concentrations. The percentage given in the following tables is the lowest quan-

tity which gave the results indicated. These percentages are based on the weight of the hides before soaking.

Terms used

The following terms have been adopted for the sake of simplicity and will be used in this and subsequent examples. The values represent the average results obtained by an experienced observer from several tests.

1. Unhairing acceleration.—

Excellent: On steer hide the hair comes off easily after 24 hours or less with practically no fine hair remaining when the skin is pressed with a dull unhairing knife in the direction of the

A. Clear, smooth grain, uniform color.

B. Good grain, but discolored.

C. Grain attacked.

5. **Odor of lime solution.**—The intensity and character of the predominating odor of the lime solution, skin and hair was observed and is noted under "odor of limes". The following terms are used:

Sl: Slight, inoffensive:

Notic: Noticeable, but not offensive. About the same as sodium sulfide.

Bad: Definitely disagreeable.

H₂S: Odor of hydrogen sulfide.

Amm: Odor of ammonia.

S: Undeterminable organic sulfur smell other than mercaptan.

Summary of results

Accelerator	Unhairing acceleration	Percent	Condition of—		Odor of lime
			Hair	Skin	
Sodium methyl xanthate.....	Excellent...	.5	A	A	Sl. S.
Potassium ethyl xanthate.....	do.....	.5	A	A	Do.
Sodium ethyl xanthate.....	do.....	.5	A	A	Do.
Sodium isopropyl xanthate.....	do.....	.5	A	A	Do.
Potassium sec. butyl xanthate.....	Very good...	.5	A	A	Do.
Xanthate of glycol.....	do.....	.5	A	A	Notic. H ₂ S and S.
Xanthate of glycerine.....	do.....	.5	A	A	Do.
Xanthate of glucose.....	do.....	1.5	A	A	Do.
Xanthate of sucrose.....	do.....	.5	A	A	Do.
Xanthate of molasses.....	do.....	1	A	B brown	Do.
Xanthate of hydrogenated sugar.....	do.....	1	A	A	Do.
Xanthate of aminated sugar.....	do.....	1	A	A	Do.
Xanthate of methylamine sugar.....	do.....	1	A	B brown	Do.
Xanthate of starch.....	do.....	1	A	A	Do.
Xanthate of cellulose.....	Good.....	1	A	B	Do.
Sodium sulfide.....	Excellent...	1	C-D	B-C	Notic. H ₂ S.
Dimethylamine.....	do.....	1	A	A	Bad.
Lime alone.....	Poor.....	1	A	A	Sl. Amm.

hair. After 48 hours the hair, including all fine hair, comes off very easily when the hide is simply rubbed with the finger. On goatskins, the same results are obtained after 48 hours and 62 hours respectively.

Very good: On steer hide the hair comes off with an unhairing knife after 24 hours, but some fine hair remains which after 48 hours can also be removed by using an unhairing knife with slight pressure. All the fine hair cannot be removed using finger pressure alone. For goatskins these times are 48 hours and 72 hours respectively.

Good: The hair is not sufficiently loose after 24 hours but can be satisfactorily unhaired after 48 hours for steer hide and 72 hours for goatskins, using medium pressure on the unhairing knife.

Fair: The hair is insufficiently loose after 48 hours for steer hide and 72 hours for goatskins, but considerably better than with pure lime solutions.

Poor: The hair looseness is no better than with lime alone.

2. **Plumping.**—The terms "much", "little" and "none" are self-explanatory.

3. **Condition of hair.**—The hair after 48 hours' unhairing was examined with a magnifying glass for the presence of hair roots and for signs of attack. It was tested for strength by pulling it apart with the fingers.

A. Excellent. Strong hair with roots intact.

B. Strong hair but with roots broken off.

C. Weak, hair attacked.

D. Hair destroyed.

4. **Condition of skin.**—The skin after unhairing and scudding was examined for clearness, smoothness of grain and for discoloration.

The above results show that the xanthates derived from monohydric alcohols are more effective as unhairing accelerators than those of polyhydric alcohols, which are in turn better than those derived from sugars. They also show that the effectiveness of the accelerator decreases with increasing molecular weight. Sucrose xanthate is apparently an exception to this rule, since it is better than the xanthates of glycol and glycerine.

It will be noted that all the xanthates as a class produce hair of excellent quality with the hair roots still attached after unhairing. The skin was in all cases clean, white and of good grain except when using the xanthates of molasses and methylaminated sugar. All the xanthates produce a degree of plumpness classified as "little"; the skin is less plump than with sodium sulfide but a little more plump than with dimethylamine.

Sodium sulfide, dimethylamine and lime alone were tested simultaneously with the xanthates for purposes of comparison and the results are given in the table. It will be noted that sodium sulfide attacks both the hair and the skin, and while the ease of unhairing after 24 and 48 hours was rated as "excellent" an examination of the hides after unhairing showed that most of the hair roots were still embedded in them. Dimethylamine, while a good unhairing accelerator, develops a bad odor.

EXAMPLE 2

This example illustrates the use of esters of thiocarbamic acid, salts and esters of dithiocarbamic acid, salts and esters of thiolcarbamic acid and ester salts of thiocarbonic acid, all as unhairing accelerators for alkaline hydrolyzing agents such

as lime. The tests were made on steer and goat-skins using the same procedure and type of lime bath as in Example 1, and the same terminology is used in expressing the results.

sible, painted uniformly on the flesh side with the depilatory paste, folded together flesh against flesh and tested for hair looseness after 8, 16 and 24 hours.

Summary of results

Accelerator	Unhairing acceleration	Percent	Condition of—		Odor of lime
			Hair	Skin	
10 Ethyl thiocarbamate.....	Good.....	1	A	A	Sl. Amm.
N, N'-dimethylthiourethane.....	Fair.....	1	A	A	Do.
Ammonium thiocarbamate.....	Very good.....	1	A	A	Notic. H ² S.
N, N'-dimethylthiocarbamic acid dimethylamine salt.....	Excellent.....	0.5	A	A	Sl. Amm.
15 Ammonium dithiocarbamate.....	do.....	0.5	A	A	Notic. H ² S.
N, N'-dimethyl dithiocarbamic acid dimethylamine salt.....	Very good.....	0.5	A	A	Sl. S.
Thiuram monosulfide.....	Good.....	0.5	A	A	Sl. H ² S.
Tetramethyl thiuram monosulfide.....	do.....	0.5	A	A	Sl. S.
Ethyl potassium monothiocarbonate.....	Excellent.....	0.5	A	A	Notic. H ² S.
Trithio ammonium carbonate.....	do.....	0.5	A	A	Do.
Potassium trithiocarbonate.....	do.....	0.5	A	A	Do.
20 Potassium trithiocarbonate.....	do.....	0.5	A	A	Do.
Sodium sulfide.....	do.....	1	C-D	B-C	Notic. H ² S.
Dimethylamine.....	do.....	1	A	A	Bad.
Lime alone.....	Poor.....	1	A	A	Sl. Amm.

These results show that the thiourethanes are not as effective accelerators as their isomers, the thiocarbamates, in which the sulfur is present in the form of the group



These latter compounds, especially in the form of their dimethylamine salts, are as effective as the best of the xanthates. Their reduction products containing a $-\text{C}-\text{S}-\text{C}-$ linkage, such as thiuram monosulfide, also gave good unhairing acceleration.

The thiocarbonates also showed very powerful unhairing action, being about equal in this respect to sodium ethyl xanthate. There was no noticeable difference between the potassium and ammonium salts of trithiocarbonate and tetra-thiocarbonate.

The action of these unhairing agents on the hair and skin was uniformly mild. Some of the tests were duplicated with the addition of 0.5% and 1.0% of such wetting agents as sodium dioctyl sulfosuccinate and isopropyl naphthalene sodium sulfonate. In these cases a cleaner skin was obtained, but the accelerating action was not greatly improved.

EXAMPLE 3

This example illustrates the use of the unhairing agents of the invention in depilatory pastes for use on sheep skins.

A standard depilatory paste consists of hydrated lime, unhairing accelerator and water. Equal volumes of pastes were made up using 30% of lime, based on the soak-weight of the sheep skins, and varying amounts of accelerator and water. In some cases kieselsguhr was added to increase the stiffness. Sodium ethyl xanthate, xanthate of sucrose and potassium trithiocarbonate were tested against a standard depilatory paste containing 30% of lime, 15% of crystal sodium sulfide and 55% of water. Additions of sodium hydroxide, red arsenic, pancreatin and sodium hydrosulfite to the xanthate were also tried.

Procedure

Domestic long-wool sheep skins were washed in a drum for one-half hour and soaked overnight at 15° C. The skins were then pressed by hand to remove as much of the surface water as pos-

Results

The following formulas gave as good unhairing as 15% sodium sulfide after 8 hours:

10% sodium ethyl xanthate+2% NaOH

10% sodium ethyl xanthate+1% NaOH+1% red arsenic

5% sodium ethyl xanthate+2% NaOH+2% Na₂S₂O₄

After 24 hours sodium ethyl xanthate alone gave excellent results in concentrations as low as 3%, while the potassium trithiocarbonate and xanthate of sucrose in concentrations of 5-10% gave as good results as sodium sulfide. In all cases the appearance of the skin was better when the xanthates and trithiocarbonate were used than with sodium sulfide and the wool was less attacked.

EXAMPLE 4

This example illustrates the use of the unhairing agents of the present invention in conjunction with other unhairing agents. In many cases the mild action of our unhairing agents will permit their use in admixture with cheaper and less satisfactory materials while still retaining at least some of the advantages of the invention.

The tests were made on goatskins and steer hide using the procedure and type of lime bath outlined in Example 1. However, the effect of variations of temperature in the unhairing bath was also noted. All percentages are based on the soak-weight of the hides or skins; that is to say, their weight before soaking.

Table of results

Sodium ethyl xanthate	Sulfide Na ₂ S	NaOH	Temp.	Unhairing	
				Steer	Goat
Percent	Percent	Percent	° F.		
1	1		70	Excellent.....	Very good.
.75	.75		70	Fair.....	Fair.
.50	.50		70	do.....	Poor.
.30	.75		70	Excellent.....	Good.
.30	.50		70	do.....	Do.
.50	.50		70	do.....	Very good.
.30	.50	.2	70	Very good.....	Good.
.50	.50	.2	70	Excellent.....	Very good.
.30	.50	.2	85	do.....	Do.
.30	.50	.2	85	do.....	Do.
.50	.50	.2	85	do.....	Do.
Red arsenic					
.30	.20		70	Excellent.....	Very good.
.30	.20	.2	70	do.....	Excellent.
.30	.20	.2	85	do.....	Do.
.30	.20	.2	85	do.....	Do.
do.....	.50	.2	85	Good.....	Good.

With 1% sulfide the hair was weak after 48 hours both on the steer and on the goatskins and the skin appeared stained. With 0.75% the skin was slightly stained, but the hair was strong. All other combinations gave strong hair and a clean skin.

The goatskin pieces used in these tests were not easy to unhair. While fine differences could not be detected between some of the variations used, it was very evident that the addition of sodium sulfide, sodium hydroxide and red arsenic considerably increased the unhairing action of sodium xanthate and made it possible to reduce the amount of the latter and obtain the same results. Increase of temperature also accelerated the unhairing action markedly. A combination effect seems to be best. The best results were obtained with .30% xanthate, .20% red arsenic, .2% sodium hydroxide at 85° F. Red arsenic was more effective than sodium sulfide. The

much better results than either of these agents alone. The combination .30% xanthate and 20% hydrosulfite gave the best unhairing, a clean skin and strong hair. Addition of sodium hydroxide was also beneficial, the most effective being .30% xanthate, .20% hydrosulfite and .2% sodium hydroxide.

Additional tests were made on goatskins and steer hides to show the effect on unhairing of additions of red arsenic (As_2S_3) and of varying amounts of sodium hydroxide. It was found that the combination of 0.5% sodium ethyl xanthate, 0.5% sodium hydrosulfite and 0.25% red arsenic in a lime bath containing 0.5% NaOH, all based on the soak-weight of the hides, gave the best unhairing after 24 hours, but that this combination attacked the hair after 48 hours.

The following table shows that larger amounts of xanthate and hydrosulfite will improve the unhairing during the first 24 hours, but that after

Table of results

Mixtures	Unhairing		Plumping 48 hrs.	Condition after 48 hrs.	
	24 hrs.	48 hrs.		Skin	Hair
.3 xanthate .2 hydrosulfite	Good	Excellent	Little	A	A
.5 xanthate .2 hydrosulfite	do	do	do	A	A
.5 xanthate .5 hydrosulfite	Good to excellent	do	Much	A	A
.5 xanthate .5 hydrosulfite	do	do	do	A	A
.25 red arsenic .5% NaOH 1 xanthate—.25 red arsenic .5% NaOH	do	do	do	A	A
.3 xanthate .2 hydrosulfite—.1% NaOH	Very good	do	Little	A	A
.3 xanthate .2 hydrosulfite—.2% NaOH	do	do	do	A	A
.3 xanthate—.2 hydrosulfite—.5% NaOH	do	do	Much	A	A
.3 xanthate—.25 red arsenic .2% NaOH	do	do	Little	A	A
.3 xanthate—.25 red arsenic .5% NaOH	do	do	Much	A	A

higher temperature and .2% NaOH gave also the best result in the sodium sulfide series.

All pieces where sodium hydroxide had been added were noticeably plumper than the others but none was excessively plump.

EXAMPLE 5

Good results are also obtained when the unhairing agents of the present invention are used in conjunction with sodium hydrosulfite, with or without the addition of alkalies such as sodium hydroxide. The procedure used and type of lime bath was identical with that described in Example 1.

Table of results

Sodium ethyl xanthate	Hydro-sulfite	NaOH	Results		Condition of after 48 hours		Plumbing
			Steer	Goat	Skin	Hair	
Percent	Percent	Percent					
1	.75		Excellent	Very good	A	D	Much.
	.50		Very good	Good	A	C	Do.
			Fair	Fair	A	A	Little.
			Excellent	Excellent	A	A	Do.
			do	Very good	A	A	Do.
			Very good	Good	A	A	None.
			Excellent	Very good	A	A	Little.
			do	Excellent	A	A	Do.
			do	Good	A	A	Much.
			do	Excellent	A	A	Do.
			do	do	A	A	Do.
			do	do	A	A	Do.
			do	Very good	A	A	Little.
			do	Excellent	A	A	Much.
			do	Very good	A	C	Do.

Sodium hydrosulfite had a very good unhairing action and produced a clean skin, but it attacked the hair when used in concentrations high enough for effective unhairing. Sodium xanthate in concentrations as high as 1% did not attack the hair.

The mixtures of xanthate and hydrosulfite gave

48 hours the results are about the same whether larger or smaller amounts are used.

With 0.5% sodium hydroxide the skins plumped too much and did not unhair as well as with less. There was little difference between 0.1 and 0.2% of sodium hydroxide. Apparently it is best to add enough caustic soda to obtain the highest degree of alkalinity without excessively plumping the hides or skins, and this amount may vary greatly depending on the amount of lime, agitation and type of skin used.

EXAMPLE 6

The unhairing agents of the present invention

may also be used in unhairing processes employing proteolytic enzymes such as pancreatin, and papain. When so used they produce a cleaner and finer grain and increase the efficiency of the unhairing process.

Tests were made on steer hides using the procedure and type of lime bath described in Ex-

ample 1 and a temperature of 30° C. The enzyme preparations were first suspended in a small amount of water and then added to the lime liquors containing the accelerators.

Table of results

Accelerator combination	Unhairing
5% xanthate	Good.
5% xanthate+.2% pancreatin	Very good.
3% xanthate+.2% As_2S_3 +.1% NaOH	Excellent.
3% xanthate+.2% As_2S_3 +.1% NaOH+.2% pancreatin	Do.
3% xanthate+.2% $\text{Na}_2\text{S}_2\text{O}_4$ +.1% NaOH	Do.
3% xanthate+.2% $\text{Na}_2\text{S}_2\text{O}_4$ +.1% NaOH+.2% pancreatin	Do.

Tests of sodium ethyl xanthate were also made in solutions containing sodium carbonate and ammonium chloride, but no lime, adjusted to a pH between 8 and 9 and a temperature of 30° C. 0.5% of the xanthate and 0.2% of pancreatin were added to these solutions and the unhairing action was noted. It was rated as "very good".

EXAMPLE 7

Another field of application of the unhairing agents of the present invention is their use prior to or subsequent to other unhairing accelerators. For example, it is possible to avoid the severe action of such accelerators as sodium sulfide and sodium hydrosulfite on the hair and grain of the skins by immersing them for only a short time in limes containing these materials and then finishing the unhairing in a lime bath containing a xanthate, an ester or salt of dithiocarbamic acid, or any of the other unhairing agents or accelerators which we have described as being included within the scope of the invention.

Unhairing tests were made on steer hide according to this procedure using the methods outlined in Example 1 with 8% lime and 400% water in both unhairing baths except in the bath containing sodium carbonate and ammonium chloride, where no lime was used.

Table of results

I bath	Hrs.	II bath	Unhairing		Cond. hair
			24 hrs.	48 hrs.	
1% sodium sulfide	8	.5% sodium ethyl xanthate	Good	Excellent	B.
1% sodium hydrosulfite	8	.5% sodium ethyl xanthate	do.	do.	B.
1% red arsenic	8	.5% sodium ethyl xanthate	do.	do.	A.
1% sodium sulfide	48	do.	do.	do.	C.
1% sodium hydrosulfite	48	do.	do.	do.	D.
.5% red arsenic+.25 NaOH	24	.3% sodium ethyl xanthate	Fair	Very good	A.
.5% red arsenic+.25 NaOH+.3% xanthate	48	do.	Good	Excellent	A.
.2% hydrosulfite+.25 NaOH	24	.3% sodium ethyl xanthate	Fair	Good	A.
.2% hydrosulfite+.25 NaOH+.3% xanthate	24	do.	Good	Excellent	A.
.2% hydrosulfite+.25 NaOH+.3% xanthate	24	.3% pancreatin	do.	Very good	A.
.2% hydrosulfite, .25% NaOH, .3% xanthate, .3% pancreatin	48	do.	Very good	Excellent	A.
.3% pancreatin, Na_2CO_3 +HNCl (pH 8.5)	24	.2% hydrosulfite, .25% NaOH, .3% xanthate	Poor	Good	A.

Sodium hydrosulfite and sodium sulfide alone attacked the hair very seriously after 24 and 48 hours unhairing. The hair was not attacked, or only slightly so, when the treatment with these agents was short and followed by a final unhairing with sodium xanthate. Separate pretreatment with small quantities of sodium hydrosulfite, red arsenic and caustic soda, followed by a treatment with xanthate, did not give as good results as when these agents were all together from the start.

Pancreatin also gave better results when used

in conjunction with the xanthate and the other agents than when used either prior to or following these agents.

In the foregoing examples various methods of application of our unhairing agents have been illustrated. The first two examples illustrate the action of a number of xanthates and other derivatives of carbon bisulfide in simple lime solutions while the remaining examples are intended to show how many of these substances may be employed in other fields of application. Accordingly it should be understood that whenever a xanthate or any other specific unhairing agent of the present invention is specified in these latter examples it is intended to be illustrative of the compounds described in Examples 1 and 2, and that any of the compounds specified in Examples 1 and 2 can be substituted for those used in the subsequent examples.

What we claim is:

1. A method of unhairing hides and skins which comprises contacting them for a sufficient period of time with an unhairing composition comprising an aqueous dispersion of a non-swelling compound containing in chemical combination at least one group capable of disrupting the disulfide linkages of keratin and at least one fat-solvent group containing an atom of carbon directly linked to an atom of sulfur.

2. A method of unhairing hides and skins which comprises contacting them for a sufficient period of time with an unhairing composition comprising an aqueous dispersion of a non-swelling compound containing in chemical combination at least one group capable of disrupting the disulfide linkages of keratin and at least one fat-solvent group containing an atom of carbon doubly linked to an atom of sulfur.

3. A method of unhairing hides and skins which comprises contacting them for a sufficient period of time with an unhairing composition comprising an aqueous dispersion of a non-swelling compound containing in chemical com-

bination at least one group capable of disrupting the disulfide linkages of keratin and at least one fat-solvent group containing an atom of carbon directly linked to two atoms of sulfur.

4. A method of unhairing hides and skins which comprises contacting them for a sufficient period of time with an unhairing composition comprising an aqueous dispersion of a non-swelling compound containing in chemical combination at least one group capable of disrupting the disulfide linkages of keratin and at least one fat-solvent group containing an atom of car-

bon directly linked to an atom of sulfur and also directly linked to an atom of oxygen.

5. A method of unhairing hides and skins which comprises contacting them for a sufficient period of time with an unhairing composition comprising an aqueous dispersion of a non-swelling compound containing in chemical combination at least one group capable of disrupting the disulfide linkages of keratin and at least one fat-solvent group containing an atom of carbon directly linked to an atom of sulfur and also linked through an oxygen atom to an alcohol or phenol group.

6. A method of unhairing hides and skins which comprises contacting them for a sufficient period of time with an unhairing composition comprising an aqueous dispersion of a compound selected from the group consisting of esters of thiocarbamic acid and salts and esters of dithiocarbamic acid.

7. A method of unhairing hides and skins which comprises contacting them for a sufficient period of time with an unhairing composition comprising an aqueous dispersion of a compound selected from the group consisting of ester salts of thiocarbamic acid and salts of trithio- and tetrathiocarbamic acids.

8. A method of unhairing hides and skins which comprises contacting them for a sufficient period of time with an unhairing composition comprising an aqueous dispersion of a compound selected from the group consisting of salts and ester salts of thiolcarbamic acid.

9. A depilatory composition comprising an alkaline hydrolyzing agent and a non-swelling compound containing in chemical combination a group capable of disrupting the disulfide linkages of keratin and a fat-solvent group containing an atom of carbon directly linked to an atom of sulfur.

10. A depilatory composition comprising an alkaline hydrolyzing agent and a non-swelling compound containing in chemical combination a group capable of disrupting the disulfide linkages of keratin and a fat-solvent group containing an atom of carbon doubly linked to an atom of sulfur.

11. A depilatory composition comprising an alkaline hydrolyzing agent and non-swelling compound containing in chemical combination a group capable of disrupting the disulfide linkages of keratin and a fat-solvent group containing an atom of carbon directly linked to two atoms of sulfur.

12. A depilatory composition comprising an alkaline hydrolyzing agent and a non-swelling compound containing in chemical combination a group capable of disrupting the disulfide linkages of keratin and a fat-solvent group containing an atom of carbon directly linked to an atom of sulfur and also directly linked to an atom of oxygen.

13. A method of unhairing hides and skins which comprises contacting them for a sufficient period of time with an unhairing composition comprising an aqueous dispersion of a compound having the formula



in which Z is a member of the group consisting of sulfur and oxygen, Pos is a member of the class consisting of salt-forming and ester-forming groups, and X is a member of the known class of keratin-splitting groups consisting of S—Me

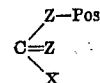
and NR₁R₂, in which Me is a salt-forming group and R₁ and R₂ are hydrogen or positive groups capable of forming a substituted amide.

14. A method of unhairing hides and skins which comprises contacting them for a sufficient period of time with an unhairing composition comprising an alkaline hydrolyzing agent and an aqueous dispersion of a compound having the formula



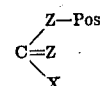
in which Z is a member of the group consisting of sulfur and oxygen, Pos is a member of the class consisting of salt-forming and ester-forming groups, and X is a member of the known class of keratin-splitting groups consisting of S—Me and NR₁R₂, in which Me is a salt-forming group and R₁ and R₂ are hydrogen or positive groups capable of forming a substituted amide.

15. A method of unhairing hides and skins which comprises contacting them for a sufficient period of time with a lime suspension which also contains an aqueous dispersion of a compound having the formula



in which Z is a member of the group consisting of sulfur and oxygen, Pos is a member of the class consisting of salt-forming and ester-forming groups, and X is a member of the known class of keratin-splitting groups consisting of S—Me and NR₁R₂, in which Me is a salt-forming group, and R₁ and R₂ are hydrogen or positive groups capable of forming a substituted amide.

16. A method of unhairing hides and skins which comprises contacting them for a sufficient period of time with an unhairing composition comprising an alkaline hydrolyzing agent, a compound having the formula



in which Z is a member of the group consisting of sulfur and oxygen, Pos is a member of the class consisting of salt-forming and ester-forming groups, and X is a member of the known class of keratin-splitting groups consisting of S—Me and NR₁R₂, in which Me is a salt-forming group and R₁ and R₂ are hydrogen or positive groups capable of forming a substituted amide, and another unhairing agent.

17. A depilatory composition comprising an alkaline hydrolyzing agent and a compound having the formula



in which Z is a member of the group consisting of sulfur and oxygen, Pos is a member of the class consisting of salt-forming and ester-forming groups, and X is a member of the known class of keratin-splitting groups consisting of E—Me and NR₁R₂, in which Me is a salt-forming group and R₁ and R₂ are hydrogen or positive groups capable of forming a substituted amide.

ALPHONS O. JAEGER.
RICHARD HERRLINGER.

CERTIFICATE OF CORRECTION.

9

Patent No. 2,169,147.

August 8, 1939.

ALPHONS O. JAEGER, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 25, for the word "its" first occurrence, read it; page 5, first column, line 16, in the table, for "dimethymine" read dimethylamine; page 6, second column, line 30, in the table, last column thereof, under the sub-heading "Hair" for "A" read B; line 54, in the table, last column thereof, for "Plumbing" read Plumping; page 7, first column, line 13, third last line of the table, for "2%" read .2%; line 61, in the table, for " HN_4Cl " read NH_4Cl ; and second column, line 10, for "many" read any; page 8, first column, line 26, claim 7, for "thiocarbamic" read thiocarbonic; line 27, same claim, for "tetrathiocarbamic" read tetrathiocarbonic; and second column, line 67, claim 17, for "E—Me" read S—Me; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 26th day of September, A. D. 1939.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.