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UNHAIRING OF HIDES AND SKINS

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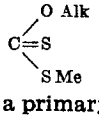
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10 Claims. (Cl. 149—2)

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 a new class of unhairing agents which are suitable for use as unhairing accelerators in unhairing baths containing lime, sodium hydroxide or other alkaline hydrolyzing agents. A further object of the invention is to provide a class of unhairing agents or accelerators which will effect the removal of hair roots as well as hair from hides or skins without damaging the hair or skin. A still further object of the invention is to provide a class of unhairing 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.

We have found that xanthates are excellent unhairing accelerators for baths containing alkaline hydrolyzing agents, and particularly for lime baths. We have tested a large number of xanthates as accelerators for unhairing baths of this type, and they all appear to have a good unhairing action. Some of the higher alkyl xanthates such as the 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 a class comply with all the requirements of the present invention.

The xanthates have the following type formula:



in which Alk may be a primary, secondary or even a tertiary alkyl radical and Me is a positive group capable of forming a salt with the xanthate such as sodium potassium, calcium, ammonium or any other alkali or alkaline earth metal or basic groups such as methylamine, dimethylamine, 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 example 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 contained in this class of compounds that its nucleus will have a strong affinity for fat and will readily penetrate the fat of the hair pockets. It is also evident that the compound will have both a reducing and hydrolyzing action on the disulfide linkages of the keratinous hair roots for it contains the group —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. Accordingly, they fulfill all the conditions necessary for a successful unhairing agent capable of liberating hair at its roots.

The xanthates of the present 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. When so applied, they constitute excellent unhairing accelerators for alkaline unhairing agents such as lime and sodium carbonate, and they may also be used to advantage in admixture with known unhairing accelerators 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 unhaired 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 quantity 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 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.

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.

H_2S: 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	0.5	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_2S 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_2S.
Dimethylamine	do	1	A	A	Bad.
Lime alone	Poor	1	A	A	Sl. amm.

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 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, base on the soak-weight of the sheep skins, and varying amounts of accelerator and water. In some cases kieselguhr was added to increase the stiffness. Sodium ethyl xanthate and xanthate of sucrose 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 possible, 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.

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% $Na_2S_2O_4$.

After 24 hours sodium ethyl xanthate alone gave excellent results in concentrations as low as 3%, while the 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 were used than with sodium sulfide and the wool was less attacked.

Example 3

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_2S	NaOH	Temperature	Unhairing	
				Steer	Goat
Percent	*Percent*	*Percent*	°F.		
----------	1	--------	70	Excellent	Very good.
----------	.75	--------	70	Fair	Fair.
----------	.50	--------	70	----do	Poor.
.30	.75	--------	70	Excellent	Good.
.30	.50	--------	70	----do	Do.
.50	.50	--------	70	----do	Very good.
.50	--------	--------	70	Very good	Good.
.30	.50	.2	70	Excellent	Very good.
.50	--------	.2	70	----do	Do.
.30	.50	--------	85	----do	Do.
30	.50	.2	85	----do	Do.
.50	--------	.2	85	----do	Do.
	Red arsenic				
30	.20	--------	70	----do	Do.
.30	.20	.2	70	----do	Excellent.
.30	.20	--------	85	----do	Do.
.30	.20	.2	85	----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 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 4

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	Hydrosulfite	NaOH	Results		Condition of after 48 hrs.		Plumping
			Steer	Goat	Skin	Hair	
Percent	*Percent*	*Percent*					
----	1	----	Excellent	Very good	A	D	Much.
----	.75	----	Very good	Good	A	C	Do.
----	.50	----	Fair	Fair	A	A	Little.
1	----	----	Excellent	Excellent	A	A	Do.
.75	----	----	do	Very good	A	A	Do.
.50	----	----	Very good	Good	A	A	None.
.40	.10	----	Excellent	Very good	A	A	Little.
.30	.20	----	do	Excellent	A	A	Do.
.20	.30	----	do	Good	A	A	Much.
.40	.10	.2	do	Excellent	A	A	Do.
.30	.20	.2	do	do	A	A	Do.
1	----	.2	do	do	A	A	Do.
.50	----	.2	do	Very good	A	A	Little.
.30	.20	.1	do	Excellent	A	A	Much.
.30	.20	.3	Good	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 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 mixture 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_2) 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 48 hours the results are about the same whether larger or smaller amounts are used.

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 .2 hydrosulfite	Good to excellent	do	Much	A	A
.5 xanthate .5 hydrosulfite	do	do	do	A	B
.25 red arsenic ½% NaOH 1 xanthate—.25 red arsenic ½% 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

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 5

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 Example 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_2+.1% NaOH	Excellent.
.3% xanthate +.2%As_2S_2+.1% NaOH +.2% pancreatin.	Do.
.3% xanthate +.2% $Na_2S_2O_4$ +.1% NaOH	Do.
.3% xanthate +.2% $Na_2S_2O_4$+.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 6

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.

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 sulfite	48		do	do	C
1% sodium hydrosulfite	48		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		Good	Excellent	A
.2% hydrosulfite+.25 NaOH	24	.3% sodium ethyl xanthate	Fair	Good	A
.2% hydrosulfite+.25 NaOH+.3% xanthate.	24		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		Very good	Excellent	A
.3% pancreatin, Na_2CO_3+NH_4Cl (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.

This application is a division of our copending application Serial Number 211,182, filed June 1, 1938.

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 xanthate.

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 xanthate of a monohydric primary alcohol.

3. A method of unhairing hides and skins which comprises contacting them for a sufficient period of time with an aqueous dispersion of an ethyl xanthate.

4. A method of unhairing hides and skins which comprises contacting them for a sufficient period of time with an aqueous dispersion of sodium ethyl xanthate.

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 containing a xanthate together with another unhairing accelerator.

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 containing a xanthate together with red arsenic.

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 containing a xanthate together with a water-soluble hydrosulfide.

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 containing a xanthate together with a proteolytic enzyme.

9. A depilatory composition comprising an alkaline hydrolyzing agent and a xanthate.

10. A depilatory composition comprising lime and a xanthate.

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