

## UNITED STATES PATENT OFFICE

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## PROCESS OF UNHAIRING HIDES OR SKINS

Harold G. Turley, Moorestown, N. J., and Wallace Windus, Bristol, Pa., assignors to Röhm & Haas Company, Philadelphia, Pa.

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This invention relates to a process of unhairing hides or skins by the use of mercaptans or those organic compounds containing or yielding a mercaptan or thiol group ( $-SH$ ) when employed with alkaline solutions such as now used for the removal of hair, fur or wool.

The object of our invention is to complete the process of unhairing hides or skins in a shorter time than is ordinarily necessary and yet accomplish the unhairing process without creating or leaving any deleterious effect upon the hide or skin and with or without hair recovery depending upon the amount and nature of the above compounds. Another object is to use compounds, which may be solid or liquid, that can be obtained in a high degree of purity.

Various processes are used for bringing about the removal of hair from animal skins. In general, the skin is first soaked in water or a dilute solution of some chemical. After proper soaking, the skin is placed in an unhairing solution or painted with an unhairing paste. The materials used vary in composition, but that most widely used consists of a saturated solution of calcium hydroxide containing excess lime. It is well known that many inorganic sulfides, notably the sulfides of sodium and arsenic, will hasten the unhairing action of lime and the two named are extensively used for this purpose. A very rapid method of unhairing is carried out by destroying the hair with alkali sulfides alone. Hair may also be loosened by the so-called "sweating" process, in which the skins are placed in a warm, humid room until the bacterial enzymes loosen the hair. Proteolytic enzymes may also be used to loosen the hair, usually after a suitable alkaline treatment of the hide or skin. Recently, the use of amines in conjunction with lime, has been patented for accelerating depilation.

We have found (1) that the addition to the lime or other alkaline unhairing solution of certain organic chemical substances that may be considered as derived from hydrogen sulfide by the replacement of one of the hydrogen atoms by a suitable organic group or radical has a marked effect in reducing the time required for unhairing.

(2) that the addition to the lime or other unhairing solution of certain organic chemical substances that may be considered as derived from hydrogen sulfide by the replacement of the two hydrogen atoms by suitable organic groups or radicals, which, however, are unstable in the presence of alkali, even in the cold, and give the type of compound stated in (1), has a marked effect in reducing the time required for unhairing.

Our invention refers to and includes:

(1) Aliphatic mercaptans, primary, secondary and tertiary, with one or more  $-SH$  groups, such as, methyl, ethyl, butyl, hexyl, cetyl, sec. hexyl, tertiary butyl mercaptans, and dithioglycol.

(2) Aliphatic mercaptans containing other groups in the molecule, such as, thioglycollic acid, cysteine,  $-thiol-$   $-butoxydiethyl$  ether, and reduced glutathione.

(3) Alicyclic mercaptans, such as, cyclohexyl mercaptan.

(4) Heterocyclic mercaptans, in which the thiol group is attached to an aliphatic side chain, such as furfuryl mercaptan.

(5) Aromatic mercaptans, in which the thiol group is attached to the aliphatic part of the molecule, such as, benzyl mercaptan.

(6) Organic sulfides which give rise to a thiol group ( $-SH$ ) by an internal rearrangement, that is by tautomerism, such as, thioacetamide and thiosemicarbazide.

(7) Organic sulfides in which the molecule has been so modified as to cause the liberation of a mercaptan in the presence of an alkali, such as, methylisothiurea sulfate and benzylisothiurea hydrochloride.

(8) Compounds of those described in (1) to (6) with sodium or any other alkali or alkaline earth metal, such as, sodium methyl mercaptide, potassium benzyl mercaptide, calcium butyl mercaptide.

(9) Mixtures of any of the above.

Since these foregoing compounds are generally used in alkali or alkaline earth solutions, it is obvious that the alkali and alkaline earth salts or mercaptides of these compounds are also included.

In place of lime suspensions, solutions of caustic soda may also be employed.

Further, unhairing may be obtained by immersing hides or skins in a solution of the sodium or any other alkali and also alkaline earth metal compounds of the substances described in (1) to (6) above. Such compounds include sodium methyl mercaptide, potassium benzyl mercaptide, and calcium butyl mercaptide.

Alternatively, the above described compounds can be mixed together with lime or other suitable alkaline unhairing materials to form a paste which may be applied to the skins. After contact for several hours, the hair or wool may then be readily removed by hand or some suitable mechanical treatment.

These illustrations are merely specific examples of the types of compounds that may be employed

and we do not limit ourselves to these specific compounds, they being given simply to describe our invention clearly.

We have found the following aromatic mercaptans to have no unhairing properties when used with lime or with caustic soda, viz., thio-phenol, p-thiocresol, thiosalicylic acid, thio-naphthol, p-chlorothiophenol, and p-nitrothiophenol; and also such compounds as methyl sulfide, propyl sulfide, amyl sulfide, methyl disulfide, ethyl disulfide, and cystine do not accelerate the unhairing action of alkalies unless they belong to group (6) above.

#### Examples

1. When 200 g. of a soaked, cured calf skins, 1000 g. of water, 20 g. of hydrated lime and 5 g. of ethyl mercaptan are placed together, hair loosening and hair damage results within a few hours. In one day the hair is pulped and can be rubbed off.
  2. When 200 g. of soaked, cured calf skin, 1000 g. of water, 20 g. of hydrated lime and 2 g. of ethyl mercaptan are placed together, good hair slippage is obtained in two days with little or no hair damage.
  3. When 200 g. of soaked, cured calf skin, 1000 g. of water, 20 g. of hydrated lime and 1 g. of ethyl mercaptan are placed together, a good hair loosening is obtained in two days. The hair slips well in three days and is not damaged.
  4. When 100 g. of soaked, cured calf skin, 500 g. of water, 4 g. of caustic soda and 1 g. of ethyl mercaptan are placed together, a good hair slip is obtained in two days, with hair damage.
  5. When 180 g. of soaked, cured calf skin, 900 g. of water, 18 g. of lime and 2.7 g. of butyl mercaptan are placed together, the hair is damaged and can be rubbed off readily within two days.
  6. When 200 g. of soaked, cured calf skin, 1000 g. of water, 8 g. of caustic soda and 3.8 g. of normal hexyl mercaptan are placed together, hair pulping takes place in a few hours. It can be rubbed off in one day.
  7. When 100 g. of calf skin, 500 g. of water, 4 g. of caustic soda and 2.8 g. of cetyl mercaptan are placed together, the hair is noticeably looser and damaged in a few hours. The hair is pulped and can be removed in one day.
  8. When 200 g. of soaked, cured kid skin, 100 g. of water, 20 g. of lime and 5 g. of butylcarbitol mercaptan ( $C_4H_9OCH_2CH_2OCH_2CH_2SH$ ) are placed together, a hair loosening, with a good slip, is obtained in one day, with no hair damage.
  9. When 100 g. of soaked, cured, wet-salted calf skin, 500 g. of water, 10 g. of lime and 1.9 g. of secondary hexyl mercaptan are placed together, hair damage results within a few hours. After two days, there is a good hair slip and the fine hairs are quite loose.
  10. When 700 g. of soaked, cured calf skin, 3500 g. of water, 70 g. of lime, and 10 g. of tertiary butyl mercaptan are placed together, a hair loosening is obtained in one day. The slip is fairly good in two days, but the compound is less active than the other simple aliphatic mercaptans tested.
  11. When 100 g. of soaked, cured calf skin, 500 g. of water, 10 g. of lime and 2.54 g. of cysteine hydrochloride are placed together, a good slip is obtained in one day, with no hair damage. In two days the slip is very good and the fine hairs are very well loosened.
  12. When 200 g. of soaked, cured calf skin, 1000 g. of water, 20 g. of lime and 1.5 g. of dithioglycol are placed together, a good hair slip with hair damage is obtained in a few hours.
  13. When 100 g. of soaked, cured calf skin, 500 g. of water, 10 g. of lime (or 4 g. of caustic soda) and 1.9 g. of cyclohexyl mercaptan are placed together, hair loosening and pulping are noticeable in a few hours.
  14. When 100 g. of soaked, cured calf skin, 500 g. of water, 10 g. of lime and 1.9 g. of furfuryl mercaptan are placed together, a good hair slip is obtained in two days.
  15. When 200 g. of soaked, cured calf skin, 1000 g. of water, 20 g. of lime (or 8 g. of caustic soda) and 4 g. of benzyl mercaptan are placed together, hair loosening and pulping are noticeable in a few hours.
  16. When a mixture consisting of 300 cc. of water, 60 g. of lime and 30 g. of benzyl mercaptan are painted on a sheep skin, the wool can be removed in a few hours.
  17. When 100 g. of soaked, cured calf skin, 500 g. of water, 10 g. of lime (or 4 g. of caustic soda) and 1.3 g. of thiosemicarbazide are placed together, good hair slippage is obtained in two days with no hair damage.
  18. When 100 g. of soaked, cured calf skin, 500 g. of water, 10 g. of lime (or 4 g. of caustic soda) and 4.5 g. of methylisothiourrea sulfate are placed together, good hair slippage is obtained in two days with little or no hair damage.
  19. When 100 g. of soaked, cured calf skin, 500 g. of water, and 2.4 g. of sodium benzyl mercaptide are placed together, a good hair slip with damage is obtained in a few hours.
- It is understood that the above examples are merely illustrative and are in no way to limit the invention, the scope of which is limited only by the claims which follow.
- What we claim is:
1. In the process of unhairing hides and skins the step which comprises immersing them in a solution of any known alkaline unhairing agent to which has been added an organic compound containing the sulphydryl ( $-SH$ ) group.
  2. In the process of unhairing hides and skins the step which comprises immersing them in a solution of any known alkaline unhairing agent to which has been added an organic compound containing a sulphydryl ( $-SH$ ) group attached to an aliphatic carbon atom.
  3. In the process of unhairing hides and skins the step which comprises immersing them in a solution of any known alkaline unhairing agent to which has been added an aliphatic primary mercaptan.
  4. In the process of unhairing hides and skins the step which comprises immersing them in a solution of any known alkaline unhairing agent to which has been added an aliphatic secondary mercaptan.
  5. In the process of unhairing hides and skins the step which comprises immersing them in a solution of any known alkaline unhairing agent to which has been added an aliphatic poly mercaptan.
  6. In the process of unhairing hides and skins the step which comprises immersing them in a solution of any known alkaline unhairing agent to which has been added an aliphatic mercaptan in which the unhairing properties of the thiol group have not been modified by substituents in the molecule.
  7. In the process of unhairing hides and skins the step which comprises immersing them in a solution of any known alkaline unhairing agent

to which has been added an organic sulfide which, under these conditions, gives rise to a mercaptan by an internal rearrangement.

5 8. In the process of unhairing hides and skins the step which comprises immersing them in a solution of any known alkaline unhairing agent to which has been added an organic sulfide in which the molecule has been so modified as to cause the liberation of a mercaptan in the presence of the alkali.

10 9. In the process of unhairing hides and skins the step which comprises immersing them in a solution of any known alkaline unhairing agent to which has been added an alicyclic compound containing the sulfhydryl ( $-SH$ ) group in the ring.

15 10. In the process of unhairing hides and skins the step which comprises immersing them in a solution containing the alkali or alkaline earth metal compound of an organic compound containing the thiol group.

20 11. In the process of unhairing hides and skins the step which comprises immersing them in a solution containing an alkali or alkaline earth aliphatic mercaptide the sulphhydryl group of which is attached to the aliphatic carbon atom.

12. In the process of unhairing hides and skins the step which comprises immersing them in a solution containing an alkali or alkaline earth primary aliphatic mercaptide.

13. In the process of unhairing hides and skins the step which comprises immersing them in a solution containing an alkali or alkaline earth secondary aliphatic mercaptide. 80

14. In the process of unhairing hides and skins the step which comprises immersing them in a solution containing an alkali or alkaline earth aliphatic poly mercaptide. 85

15. In the process of unhairing hides and skins the step which comprises immersing them in a solution containing an alkali or alkaline earth mercaptide in which the unhairing properties of the thiol group have not been modified by substituents in the molecule. 90

16. In the process of unhairing hides and skins the step which comprises immersing them in a solution containing an alkali or alkaline earth mercaptide of an alicyclic compound containing the sulfhydryl ( $-SH$ ) group in the ring. 95

HAROLD G. TURLEY. 100  
WALLACE WINDUS.

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