

# UNITED STATES PATENT OFFICE

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## UNHAIRING PROCESS

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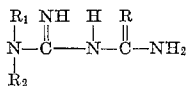
This invention relates to the unhairing of hides and skins, which is a preliminary step in their conversion into leather. More specifically, the invention relates to a new class of unhairing accelerators for use in conjunction with aqueous dispersions of alkaline hydrolyzing agents which have previously been used for unhairing purposes.

The conventional method of unhairing hides and skins is to immerse them in a bath containing lime, sodium hydroxide or other alkaline hydrolyzing agents, or in the case of sheepskins, to subject them to the action of these agents in the form of an aqueous paste. It has been known for many years that the addition to these baths of small amounts of water-soluble inorganic sulfides such as arsenic sulfide, sodium sulfide, cadmium sulfide and the like will speed up the unhairing action, and accordingly these substances are known as unhairing accelerators.

More recent developments in the field of unhairing accelerators have suggested the replacement of the inorganic sulfides by organic compounds which might be expected to have a milder action on the hair and skin. One of the first of these was the discovery of McLaughlin, based upon the examination of mellow limes, that certain of the lower aliphatic amines such as dimethylamine would accelerate hair slippage when added to lime suspensions. This was followed by the work of Turley and Windus, who showed that aliphatic mercaptans or mercaptides would operate as powerful unhairing accelerators, but that organic sulfides and thiophenols are inactive for this purpose.

I have now discovered a further class of organic nitrogen bases which are good unhairing accelerators when used in unhairing baths or dispersions containing an alkaline hydrolyzing agent such as lime or caustic soda. This class consists of the closely related compounds, biguanide and guanylthiourea and their alkyl or aryl substitution products.

The members of the class in question may be defined as compounds of the formula



in which either or both  $R_1$  and  $R_2$  are hydrogen or alkyl or aryl groups and  $R$  is sulfur or a :NH group. These compounds may be present in the unhairing bath or composition in the form of their free bases or in the form of salts.

Typical examples of compounds included with-

in the scope of the invention, as defined by the above formula, are biguanide itself and its salts, mono- and diethyl biguanide, mono- and dimethyl biguanide, and other alkyl substituted biguanides such as the mono- and dibutyl, mono- and diamyl compounds and the like and the corresponding unsubstituted and substituted guanylthioureas. Mixtures of these compounds may also be used, as well as mixtures of one or more of them with other substances. For example, one method of making thiourea produces a mixture of thiourea and guanylthiourea which may be added as such to unhairing baths.

Similarly, mixtures containing biguanide and resulting from special methods of preparation may be used as unhairing accelerators. When dicyandiamide is fused with ammonium salts a mixture of biguanide and guanidine salts is obtained which mixture is an excellent unhairing accelerator. Similarly, when dicyandiamide is heated with aqueous ammonia and copper sulfate at about 105° C. a mixture is obtained containing a pink copper salt of biguanide. This salt may be decomposed with an acid such as sulfuric acid or it may be treated with hydrogen sulfide; in the first case an acid biguanide salt such as the sulfate is obtained while in the latter case the neutral salt is produced. When an aliphatic amine such as dimethyl amine is substituted for ammonia in the foregoing process dimethyl biguanide is obtained.

The invention will be described in greater detail in conjunction with the following specific examples. It should be understood, however, that these examples are given primarily for purposes of illustration and that the invention in its broader aspects is limited only by the scope of the claims appended hereto.

### Example 1

Green salted steerhides were soaked in water for 24 hours and washed in running water for ½ hour, after which they were fleshed and suspended in an unhairing bath containing 400% water, 10% calcium hydroxide and 1.5% of biguanide, based on the weight of the soaked skins.

The hides were agitated in the bath for three minutes once every 12 hours, and were tested for ease of hair removal at the end of 24 hours and again at the end of 48 hours. After 24 hours the long hair was loose, and after 48 hours the skins unhaird easily on the unhairing machine with only a small amount of fine hair remaining.

Similar results were obtained when biguanide

sulfate was substituted for the free biguanide, although a larger amount of this material was necessary by reason of its higher molecular weight.

5 *Example 2*

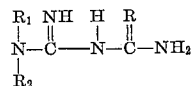
10 Dried goatskins were soaked for 24 hours, washed, and again soaked for an additional 24 hour period. They were then suspended in an unhairing bath similar to the bath of Example 1 but containing 2% of guanylthiourea instead of the biguanide. After 48 hours the hair was loose and after 72 hours a good hair slippage was obtainable and the skins unhaird easily. No damage to the hair was noticeable and a clean skin of good grain was obtained.

15 *Example 3*

20 The procedure of Example 1 was repeated using diethyl biguanide instead of biguanide as the accelerator. After 48 hours the skins could be unhaird easily on the unhairing machine.

What I claim is:

1. A method of unhairing hides and skins which comprises contacting them with an unhairing composition comprising an alkaline hydrolyzing agent and an unhairing accelerator of the formula 5



10 in which either or both  $R_1$  and  $R_2$  are hydrogen or alkyl or aryl groups and  $R$  is a sulfur atom or a :NH group.

2. A method of unhairing hides and skins which comprises contacting them with an unhairing composition comprising an alkaline hydrolyzing agent and biguanide. 15

3. A method of unhairing hides and skins which comprises contacting them with an unhairing composition comprising an alkaline hydrolyzing agent and guanylthiourea. 20

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