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PROCESS FOR THE UNHAIRING OF SKINS AND HIDES WITH PERACIDS OR THEIR SALTS

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3 Claims

ABSTRACT OF THE DISCLOSURE

Hair bearing skins and hides are treated with an aqueous solution of a peracid or salt to degrade the hair and render it soluble in aqueous neutral salts, and weak to strongly acting alkaline acting salts and bases.

The present invention relates to a process for unhairing skins and hides with oxidizing agents which renders possible a reduction in the time required for the unhairing considerably, as well as, a dissolution of the hair to biologically degradable products.

It is known that skins and hides can be unhaird with oxidizing agents such as chlorine dioxide in an acid pH range. However, several serious drawbacks are connected therewith, such as, for example, the disagreeable and health debilitating chlorine and chlorine dioxide fumes and, furthermore, the strong attack on the collagen which occurs, causing a reduction in tear strength of the leather produced from the treated skins and hides, whereas the attack of chlorine dioxide on the keratin of the hair only proceeds rather slowly. A further disadvantage is the danger in handling sodium chlorite, usually employed as source of the chlorine dioxide, as a concentrated solution or as a dry substance, as negligence may give rise to explosions and fire.

It furthermore is known that leather may be bleached with percompounds, such as, for instance, peracetic acid. However, such bleaching was applied to skins or hides which had already been unhaird by other methods.

The object of the present invention is to provide a process for unhairing skins and hides with oxidizing agents which renders it possible to effect a substantial reduction in the time required for the unhairing operation and thereby to avoid the aforementioned disadvantages and which also renders it possible to dissolve the hair to provide biologically degradable products.

According to the invention it was found that this object can be achieved when the skins and hides to be unhaird are first subjected to the action of peracids or their salts and then subjected to an aftertreatment with neutral salts or weak or strong alkaline acting salts or bases. Expediently such after treatment is carried out with aqueous solutions of, for instance, ammonium sulfate, trisodium phosphate, disodium phosphate, ammonium carbonate, sodium bicarbonate, sodium carbonate, potassium carbonate, borax or ammonia. The after treatment serves to dissolve the tough partially oxidized hair and renders them such that the decomposition products can easily be removed by rinsing with water.

A substantial advantage of the process according to the invention is that the unhaird hides and skins are simultaneously bleached so that after the unhairing pure white unhaird hides are obtained which are exceptionally suited for aniline dyeing.

The process according to the invention renders it possible to reduce the time required for dissolving of the hair carried by skins and hides considerably. With the

previously employed treatment with chlorine dioxide reaction periods of about 20–26 hours were required. However, with the present treatment with peracids or their salts combined with the above described aftertreatment, the reaction period required, for example, with monopersulfuric acid (H_2SO_5 , Caro's acid) or its salts is 3–15 hours and with peracetic acid about 2–8 hours. Poisonous health debilitating fumes such as are apt to occur with unhairing treatments with ClO_2 do not occur in the process according to the invention. Precise times for the duration of the preliminary treatment of the skins or hides to be unhaird with the peracids or their salts cannot be given as this depends upon the type and condition of the skins and hides treated, as well as the concentrations involved. The time when the preliminary oxidative treatment has been of sufficient duration is easily determined by removal of a sample of the treated skins or hides and testing the solubility of the hair in the aqueous salt or base solution to be employed in the after treatment. The quantity of salt or base in the aqueous solution employed for the aftertreatment, for example, can be between 0.5 and 4% by weight with reference to the hides.

The time required for the unhairing of long haired hides can be reduced by subjecting such hides to a preliminary mechanical or chemical (for instance, with Na_2S enzyme) unhairing treatment before it is subjected to the treatment according to the invention.

Monopersulfuric acid and its equivalent water soluble salts and peracetic acid have been found particularly suited as the oxidizing percompounds employed in the first stage of the process according to the invention.

Permonosulfuric acid and its salts as well as peracetic acid only attack the keratin of the hair and degrade it by oxidation. The skin pigments are simultaneously bleached so that with proper treatment pure white unhaird skins and hides are obtained and the yield of uniformly dyeable leather is increased. It, furthermore, is noteworthy that the skins and hides do not swell during the treatment with peracetic acid, and permonosulfuric acid or its salts so that a smooth and firm grained leather can be obtained.

When the aftertreatment is carried out with aqueous solutions of neutral salts, dissolution of the hair is effected but no swelling of the skins or hides is effected. When aqueous solutions of weak or strongly alkaline acting salts or bases are used for the aftertreatment, dissolution of the hair is again effected but in addition such aftertreatment permits a weak short swelling of the skins and hides which is controlled by the duration of such aftertreatment. Such swelling is desired under certain circumstances to obtain a leather having a soft hand.

The following examples will serve to illustrate the process of the invention.

EXAMPLE 1

1000 kg. of hides or skins (cowhides, calfskins, sheepskins or goatskins) were fleshed and treated in a drum rotating at 2–5 r.p.m. with 50–100% by weight, with reference to the skins or hides treated, of aqueous 5–15% Caro's acid. After the hair had been sufficiently attacked and the skins and hides bleached, the skins and hides were drained, rinsed with water and then treated in the drum with 1000 liters of a 4% by weight of an aqueous solution of sodium carbonate for 1 hour.

The oxidation products of the hair were water soluble and biologically degradable. After rinsing the skins and hides were pickled and tanned.

The time required for the preliminary treatment with Caro's acid depended upon the hides and skins treated and the concentration employed. It varied between 5 and 15 hours.

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EXAMPLE 2

1000 kg. of softened and fleshed cowhides were treated with 50–200% by weight of an aqueous liquor with reference to the hides treated, containing 0.5–5% (pH 2–5.5) or peracetic acid in a slowly rotating drum. After three hours the attack on the hair was such that they dissolve after drawing off the original liquor and rinsing with water when treated for 1 hour with 1000 liters of a 4% by weight aqueous solution of $(\text{NH}_4)_2\text{SO}_4$. After rinsing and removal of any oxidizing agent eventually still present by reduction the unhaird hides which were smooth and pure white were pickled and tanned. Similar results were obtained when the $(\text{NH}_4)_2\text{SO}_4$ solution employed was replaced by analogous aqueous NaHCO_3 or Na_2CO_3 solutions.

We claim:

1. A method of unhairing hair bearing cowhides, calfskins, sheepskins or goatskins comprising contacting such skins or hides with an aqueous solution of an oxidizing agent selected from the group consisting of permonosulfuric acid and peracetic acid and their water soluble salts until the hair borne by said skins or hides is sufficiently degraded that it is rendered soluble upon treatment with an aqueous solution of a salt selected from the group consisting of aqueous solutions of ammonium sul-

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fate, trisodium phosphate, disodium phosphate, ammonium carbonate, sodium bicarbonate, sodium carbonate, potassium carbonate, borax and ammonia.

2. The method of claim 1 in which said per acid is 5–15% by weight of permonosulfuric acid.

3. The method of claim 1 in which said per acid is 0.5 to 5% by weight of per acetic acid.

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