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TANNING AGENTS AND PROCESS OF PRODUCING THE SAME

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The present invention relates to new tanning agents and a process of producing the same.

It has been found that tanning agents containing iron obtained by treating albuminous substances with oxidizing agents (for example nitric acid, oxides of nitrogen or oxidizing substances free from nitrogen) in the presence of iron salts have certain drawbacks; they are unstable, difficult to obtain in a concentrated form and difficult to handle.

We have now found that valuable tanning agents containing iron free from the said drawbacks can be obtained by combining iron compounds, in particular iron salts, with soluble albuminous substances including soluble proteinic substances and soluble degradation products thereof which in case of oxidizing degradation have been made in the absence of iron. If albuminous substances or their derivatives or degradation products thereof obtainable with the aid of non-oxidizing proteolytic agents are employed, the tanning composition may be prepared by mixing the albuminous substances with iron compounds and, if desired, heating the mixture. The process may be carried out for example by mixing albumen in the presence of iron salts with non-oxidizing proteolytic agents and, if desired, heating. It is of special advantage first to bring the albuminous components in the absence of iron salts into the form in which they are to be employed together with the iron salts. For example albumen, especially in the case of insoluble albumens, may be first subjected to any desired proteolytic treatment, as for example with acid, alkaline or enzymatic splitting agents or neutral salts having a splitting action, as for example calcium chloride or lithium thiocyanate. Sulphonic acids, especially sulphonic acids having tanning action, may be mentioned for example as agents suitable for carrying out the splitting. The splitting may be carried out under increased pressure. The albumen may also be converted into water-soluble products by the action of ethylene oxide or the like. The resulting albumen degradation products or derivatives may then be mixed with the iron salts in order to obtain the tanning composition.

The tanning material may also be obtained by combining degradation products of albuminous substances or their derivatives, which have been obtained in the absence of iron compounds with the aid of oxidizing agents, as for example nitric acid, nitrous gases or hydrogen peroxide, with iron compounds having a tanning action. When employing albuminous substances obtained by oxidizing degradation, the addition of the iron compounds should be effected after the oxidation while in other cases the iron compounds may be added to the albuminous substances or degradation products thereof before, during or after degradation, if any degradation is effected at all. A preliminary tanning may also be carried out with iron alone and the albuminous substances only added to complete the tanning process. When employing albuminous substances which are adsorbed by the hides, these substances may also be first caused to act on the material to be tanned and then subjected to the action of the iron salts.

If the tanning agent containing iron compounds and albuminous substances contains free acid (for example from the degradation step) it is advantageous to neutralize the acid at least to a far-going degree; the solution may then be evaporated in the usual manner under ordinary or diminished pressure. Acid reacting agents may then be added to the dry products. Non-hygroscopic pulverulent products are thus obtained. Suitable acid reacting agents are for example oxalic acid and alkali metal bisulphates. The products are readily soluble in water and may be directly employed for tanning after being adjusted to the usual acidity and hydrogen ion concentration.

Suitable abluminous substances are for example leather scraps for making glue, leather parings, casein, horn and the like and also their soluble degradation products and derivatives. As iron compounds may be mentioned all iron compounds having tanning action, in particular the water soluble ferric salts.

The tanning with the aid of the tanning agents above described may be combined in any desired manner with other tanning methods; for example leather tanned with the said tanning agents may be further treated with mineral, synthetic organic or vegetable tanning agents or their neutral salts, or the reverse procedure may be followed.

The said tanning agents have an excellent tanning action which in part is superior to that of the known iron tanning agents. Their stability as well as their capacity for being stored and transported is usually very good. Leather prepared with the aid of the said tanning agents shows no plumping when washed.

The following examples will further illustrate the nature of this invention but the invention is not restricted to these examples. The parts are by weight.

Example 1

30 parts of leather scraps for making glue are boiled for 16 hours with 40 parts of 30 per cent sulphuric acid. The undissolved residue is filtered off and the sulphuric acid precipitated as barium sulphate and removed. The filtrate is evaporated to dryness and mixed with 4 parts of anhydrous ferric chloride. A good iron tanning agent is thus obtained.

Example 2

500 parts of soy bean cuttings are boiled with 2000 parts of 25 per cent sulphuric acid for 16 hours, the sulphuric acid then being precipitated as barium sulphate and filtered off. The filtrate is evaporated, about 180 parts of albumen degradation products being obtained as the residue. This is mixed with 360 parts of anhydrous ferric chloride, an excellent iron tanning agent thus being obtained.

Example 3

50 parts of cane sugar molasses, which contains albumen degradation products, are mixed with 35 parts of ferric nitrate, an excellent tanning agent being obtained. Other molasses containing albumen, or similar products, may be used in a similar manner.

Example 4

Pickled unhaired calf pelts are drummed for 6 hours in a bath consisting of 100 per cent of water, 17 per cent of ferric nitrate and 4.5 per cent of calcined sodium carbonate, the percentages being with reference to the weight of unhaired pelts. The tanning is then carried out, 0.5 per cent of protalbic acid being added periodically in small amounts.

Example 5

100 parts of leather scraps for making glue are heated for three hours at 90° C. with 50 parts of nitric acid having a specific gravity of 1.333 and 40 parts of water. After cooling, the whole is neutralized with caustic soda solution and evaporated. The residue is mixed with 75 parts of ferric nitrate. The resulting product is a good iron tanning agent.

Example 6

100 parts of chrome leather scrapings, 500 parts of water and 200 parts of nitric acid of 36° Baumé strength are heated at 90° C. for about three hours. After cooling, 50 parts of anhydrous ferric chloride are added to the reaction mixture, a solution thus being obtained which may be employed as a tanning agent.

If it is desired to prepare products having increased capacity for storage and increased stability, it is preferable to neutralize, for example with sodium carbonate, and if desired to evaporate, before the addition of the ferric chloride.

Example 7

700 parts of chrome leather scrapings containing 65 per cent of water are treated for two hours at 100° C. with 150 parts of sulphuric acid of 66° Baumé strength. The mass is then neutralized with 117 parts of caustic soda and 368 parts of anhydrous ferric chloride are added. The viscous mass obtained possesses an excellent tanning action.

Example 8

100 parts of dry chrome leather scrapings are treated for three hours at 90° C. with 800 parts of 20 per cent sulphuric acid and 162 parts of anhydrous ferric sulphate. The reaction product is neutralized with 635 parts of a 35 per cent sodium hydroxide solution and evaporated to dryness. Each 100 parts of the powder obtained are mixed with 50 parts of sodium bisulphate.

Example 9

5 parts of dry chrome leather scrapings are treated for three hours at 85° C. with 10 parts of an about 53 per cent nitric acid, 8.4 parts of crystallized ferric chloride and 20.4 parts of water then being added. The mass is neutralized with 3.52 parts of a 35 per cent caustic soda solution and evaporated to dryness. Each 100 parts of the dry product obtained are mixed with 50 parts of sodium bisulphate.

What we claim is:

1. The process of producing tanning compounds which comprises degrading an albuminous substance in an aqueous medium, evaporating the solution obtained to dryness and then combining the degradation product with a soluble ferric compound which does not form a precipitate therewith.

2. The process of producing tanning compounds, which comprises degrading an albuminous substance in an aqueous medium with an oxidizing proteolytic agent, evaporating the solution obtained to dryness and then combining the degradation product with a soluble ferric compound which does not form a precipitate therewith.

3. The process of producing tanning compounds, which comprises degrading an albuminous substance in an aqueous medium with a non-oxidizing proteolytic agent, evaporating the solution obtained to dryness and then combining the degradation product with a soluble ferric compound which does not form a precipitate therewith.

4. The process of producing tanning compounds which comprises combining a soluble ferric compound with a soluble albuminous substance which latter is obtained by degradation of a protein by an acid agent, neutralizing the acid agent at least partly, evaporating the mass and adding an acid reacting agent.

5. Tanning materials comprising a soluble albuminous degradation compound obtained by a wet process, excluding oxidation, and by evaporation to dryness, and a soluble ferric compound which does not form a precipitate therewith.

6. Tanning materials comprising a soluble albuminous degradation product obtained by means of a non-oxidizing proteolytic agent in an aqueous medium and evaporation to dryness, and a soluble ferric compound which does not form a precipitate therewith.

7. Tanning materials comprising a soluble albuminous degradation product obtained by wet oxidizing degradation and evaporation to dryness, and a soluble ferric compound added after evaporation and which does not form a precipitate with the said degradation product.

8. Non-hydroscopic tanning materials comprising (1) a soluble ferric compound, (2) a neutralized soluble acid albuminous degradation product which is obtained while avoiding an oxidizing breakdown in the presence of an iron compound and does not form a precipitate with the said ferric compound, and (3) an acid reacting agent.

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