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PROCESS OF CARROTING

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This invention relates to the treating of animal fibres and the like, such as fur or wool, and pertains particularly to the process of carroting the same, and the present application constitutes a continuation in part of application Serial Number 34,299, filed August 1, 1935.

The present method used almost exclusively for the carroting of fur involves the use of the mercury salt, mercury nitrate. This salt in solution is applied with a brush or by the use of a carroting machine to the fur or fur fibre while intact with the skin and these skins are dried either by heat or at normal room temperature with a resultant volatilization of a certain amount of mercury. In this treatment of the fur or similar fibre and in the subsequent operations for the manufacture of the fur felt body which is to be formed into hats or other objects, a great health hazard exists for those persons who have to carry out the various steps or operations necessary in the felting of the fibre and the subsequent treatment of the same.

The present invention has for its primary object to provide a process for the carroting of animal fur fibre and the like, whereby the same will be affected in the same way as by the use of mercury nitrate solution so that the desired felting properties are imparted thereto, without using poisonous substances or substances which will have a detrimental effect upon persons required to handle or work with the felt or upon users of the felt material after the same is made up into hats or other bodies.

Another object of the invention is to impart to the fur and hair fibre the same properties that are characteristic of the "mercury carrot" without the use of mercury nitrate.

A still further object of the invention is to provide a process which in addition to imparting the desired felting qualities to the fur, hair fibre or wool, will not cause the same to deteriorate after a long period of time; may be used upon white fur without causing the same to discolor; will facilitate the quick wetting down and fast shrinking of the fur and hair fibre in the starting of felting as well as in the sizing; will cause the fur and hair fibre to take an even color without showing an underground or under cast when placed in a dye bath, and will cause the fur and hair fibre to form a stronger, tighter, and more even felt than can be manufactured under present processes.

Felting is confined to those fibres, the surfaces of which are covered with a sheath of scales like shingles on a roof. When a miscellany of such

fibres are worked together, these scales or serrations interlock and hold the fibres together. While with some fibres, such interlocking and felting is easily accomplished, as with wool fibre, certain other animal fibres have the serrations less prominent and the fibre can only be caused to cling together and felt after the scales are stiffened, hardened and rendered prominent by certain chemical reagents. It is significant that the chemical or carroting agents most effective in rendering the fur or hair fibre suitable for felting are protein coagulants. I do not wish to be limited to any particular theory or explanation as to why this remarkable and commercially valuable result is obtained.

The protein coagulants which I have discovered to be entirely effective for carroting purposes and which avoid the objection to the use of mercury nitrate and other mercury solutions, are phosphotungstic acid and phosphomolybdic acid, soluble salts and esters of the same, and derivatives thereof such as chloro-phosphotungstic and chloro-phosphomolybdic acids, aceto-phosphotungstic and aceto-phosphomolybdic acids. These products possess an enhanced felting action and are without poisonous properties and if left on fur or like fibre show no particular deteriorating action or any objectionable effect upon the health of the user. They also exceed mercuric nitrate in protein coagulating power.

The coagulants may be used either alone or in combination with one another, or in conjunction with hydrolytic agents such as inorganic acids having a pH value lower than 3.0 or a combination of organic acids and inorganic acids in which the pH of the mixture is lower than 3.0 and such a combination may be made up with such acids as citric acid, oxalic acid, tartaric acid, nitric acid, sulphuric acid, hydrochloric acid, hydrobromic acid and perchloric acid and these may be used with or without hydrogen peroxide or equivalent agents. Briefly, the method involves a simultaneous solubilization and hydrolysis of fur fibres with a protein coagulation action. The joint and paradoxical action sharpens and develops the serrations or scales so as to permit of an interlocking of the component fibres of the mix.

As previously set forth, the protein coagulants which I have found most satisfactory are phosphotungstic and phosphomolybdic acids and soluble salts and esters of the same, and the derivatives of the acids. The hydrolytic agents employed with these coagulants are those yielding,

under the conditions of the carroting operation, pH values lower than 3.0 or higher than 13.0. This includes the acids named for the lower pH range and the hydroxides of sodium or potassium in the upper.

With the protein precipitants and the hydrolytic agents named, there is a third class of chemical agents employed which are oxidizers, such as hydrogen peroxide.

Owing to the variations between the different types of fur fibres and the climatic conditions, that is, high or low humidity and temperatures, those skilled in the art will understand that it is desirable to use solutions of various strengths to obtain the best felting results, also illustrative embodiments of the compositions which may be used, using the substances specified, will be set forth.

As an example, a solution may be employed comprising 40 ounces by volume of water having dissolved therein one ounce by weight of phosphotungstic acid with $4\frac{1}{2}$ ounces by volume of nitric acid 40° Baumé, or the same solution may be made substituting an equivalent amount of phosphomolybdic acid. In place of the nitric acid either hydrochloric or sulphuric acids or some combination of the same may be substituted or the nitric acid may be partially replaced by some combination of the same, so long as the pH of the mixture is lower than 3.0.

To either of the two solutions specified may be added 2 ounces by volume of 100 volume hydrogen peroxide and in place of the HNO_3 , HCl or H_2SO_4 may be used, with or without H_2O_2 .

As an example for the use of hydrolytic agents having a pH higher than 13.0, I may take 40 volumes of water in which is dissolved 3 ounces of sodium or potassium hydroxide, 1 ounce of either the tungsto or molybdo-phosphoric acid and 1 fluid ounce of hydrogen peroxide. The deleterious effect of the caustic alkali may be reduced or inhibited by the addition of $1\frac{1}{2}$ fluid ounces of glycerine or diethylene glycol without affecting adversely the carroting action of the alkali.

As an illustration of a satisfactory carroting solution using molybdo-chlorophosphoric acid, the following may be given. 2 ounces of molybdo-chlorophosphoric acid are dissolved in 40 ounces of water and to this is added 4 ounces of hydrochloric acid and $\frac{1}{2}$ ounce of perchloric acid. This solution very effectively carrots the fur and the same results may be obtained by substituting tungsto-chlorophosphoric acid or the corresponding aceto derivatives of either of the acids mentioned, using the same proportions.

As an illustration of a soluble ester which may be used, the phosphotungstate ester of oleic acid may be given. This ester is both water and acid soluble and it may be substituted for the phosphotungstic acid given in the example set forth, wherein this acid is described as used in association with nitric acid. The phosphotungstate ester of oleic acid possesses the additional virtue of being a penetrating agent and in consequence assures more rapid and complete penetration of the carroting components into the fur.

Most aliphatic and aromatic acids, alcohols and aldehydes will react with phosphotungstic acid and with phosphomolybdic salts to form esters, and these operate in much the same way as the unesterified acids, providing they possess the requisite solubility. These esters, in the majority of cases, can be solubilized by sulfonation without in any way destroying the potency of the phosphotungstic or phosphomolybdic acids. As

an illustration, when lauryl alcohol, an example of an aliphatic alcohol, is treated with concentrated phospho- or phosphochloro- or phosphoacetotungstic or molybdic acids, an ester results which possesses the same carroting potency as the unesterified acids. Those of the esters which are insoluble may be rendered soluble by esterifying in the presence of 98% sulphuric acid.

As an example of some of the esters which may be employed as substitutes for the phosphotungstic acid, in the example previously referred to, there may cited

The acid sodium salt of laurylphosphotungstic acid,

The acid ammonium salt of benzostearophosphomolybdic acid,

The acid potassium salt of naphthostearophosphotungstic acid,

The sulpho ester of oleochlorophosphotungstic acid.

Aromatic alcohols, aldehydes or halides react with phospho derivatives in much the same way as the lauryl alcohol. The solubilization of the resultant esters frequently requires or necessitates a subsequent sulfonation operation. This may be accomplished by conventional sulfonation procedures.

Examples of some of the soluble salts of phosphotungstic and phosphomolybdic acids which are suitable, are

Sodium hydrogen phosphotungstate

Potassium hydrogen phosphomolybdate

Ammonium hydrogen chlorophosphotungstate.

From the foregoing it will be readily seen that there is herein provided a composition and process of preparing fur or similar material which attains the objects of the invention and avoids the undesirable features of the processes at present employed in addition to including additional practical and useful advantages.

It is to be understood that the invention is not to be limited by the examples set forth but that various changes or modifications may be made in the same so long as such modifications constitute no material departure from the invention as expressed in the appended claims. It is also to be understood that the process of applying the carroting material to the fur or like fibres may be carried on while the fur is still on the skin or it may be carried on after the fur or like fibres have been removed from the skins or pieces.

What is claimed is:

1. The process of carroting animal fur fibres and the like for felting, which comprises treating the same with a solution containing a protein coagulant selected from the class consisting of phosphotungstic and phosphomolybdic acids in an amount sufficient to carrot the fibres, and an alkali in an amount in the solution to give to the same a pH value more than 13.0.

2. The improvement in the art of carroting which consists in subjecting animal fur fibres and the like to the action of a solution of a compound selected from the group consisting of molybdo-chloro-phosphoric, molybdo-aceto-phosphoric, tungsto-chloro-phosphoric and tungsto-aceto-phosphoric acids their soluble salts and esters, in an amount sufficient to carrot the fibre.

3. The process of carroting animal fur fibres and the like for felting, which comprises treating the same with a solution containing an acid selected from the group consisting of molybdo-chloro-, molybdo-aceto-, tungsto-chloro-, and

tungsto-aceto-phosphoric acids, in an amount sufficient to carrot the fibres, and a hydrolytic agent giving to the solution a pH value outside the limits 3.0 and 13.0.

5 4. The process of carroting animal fur fibres and the like for felting, which consists in treating the fibres with a solution containing an acid selected from the group consisting of tungsto-
10 aceto-, tungsto-chloro-phosphoric molybdo-aceto-, and molybdo-chloro-phosphoric acids, in an amount sufficient to carrot the fibres, and a hydrolytic agent selected from the group consisting of nitric, hydrochloric, perchloric, hydrobromic and sulphuric acids in an amount sufficient to
15 yield in the carroting solution a pH lower than 3.0.

5 5. The process of carroting animal fur fibres and the like for felting, which consists in treating the fibres with a solution containing a compound selected from the group consisting of aromatic and aliphatic esters of phosphomolybdic acid, in an amount sufficient to carrot the fibre.

20 6. The process of carroting animal fur fibres and the like for felting, which consists in treating the fibres with a solution containing a compound selected from the group consisting of aromatic and aliphatic esters of phosphomolybdic acid, in an amount sufficient to carrot the fibre and a hydrolytic agent yielding in the solution
25 a pH value outside the limits 3.0 and 13.0.

30 7. The process of carroting animal hair for felt making, which comprises treating the same with a solution containing a protein coagulant selected from the group consisting of phosphotungstic and phosphomolybdic acid, their soluble salts and esters in an amount sufficient to carrot the hair.

35 8. The process of carroting animal hair for felt making, which comprises treating the same with a solution containing a protein coagulant selected from the group consisting of phosphotungstic and phosphomolybdic acids in an amount sufficient to carrot the hair and an acid yielding in the solution a pH value lower than 3.

40 9. The process of carroting animal hair for felt making, which comprises treating the same with a solution containing phosphotungstic acid in

an amount sufficient to carrot the hair, and a hydrolytic agent selected from the group consisting of nitric acid, perchloric acid, hydrochloric acid, sulphuric acid and hydrobromic acid, the hydrolytic agent being in an amount sufficient
5 to yield in the solution a pH lower than 3.0.

10 10. The process of carroting animal hair for felt making, which comprises treating the hair with the solution containing phosphomolybdic acid in an amount sufficient to carrot the hair, and nitric acid in an amount sufficient to yield
15 in the solution a pH lower than 3.0.

11. The process of carroting animal hair for felt making, which comprises treating the hair with a solution containing phosphomolybdic acid in an amount sufficient to carrot the hair, nitric acid, and hydrogen peroxide, the nitric acid being in an amount sufficient to yield in the solution a pH lower than 3.0.

12. The process of carroting animal hair for felt making, which comprises treating the hair with a solution containing a phosphotungstic acid in an amount sufficient to carrot the hair and nitric acid in an amount to yield in the solution a pH lower than 3.0.

13. The process of carroting animal hair for felt making, which comprises treating the hair with a solution containing phosphotungstic acid in an amount sufficient to carrot the hair, nitric acid, and hydrogen peroxide, the nitric acid being in an amount sufficient to yield in the solution a pH lower than 3.0.

14. The process of carroting animal hair for felt making, which comprises treating the hair with a solution containing one of the soluble salts of the acids selected from the group consisting of phosphotungstic acid and phosphomolybdic acid in an amount sufficient to carrot the hair.

15. The process of carroting animal hair for felt making, which comprises treating the hair with a solution containing one of the soluble esters of salts of the acids selected from the group consisting of phosphotungstic and phosphomolybdic acids in an amount sufficient to carrot the hair.

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