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PROCESS OF TREATING ANIMAL PELTS

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This invention relates to the treatment of filamentous materials particularly the fur, hair or wool of animal pelts to encase such filamentous portions of the pelt, with or without chemically modifying the parent substance, permanently straighten or permanently curl the said filaments, to impart gloss or finish thereto, or to make the filaments resistant to chemical or to mechanical action. In the present invention the treatment of the filamentous parts of the pelt, namely the fur, hair or wool, is carried out under conditions such that the skin or leathery portions of the pelt are not deteriorated.

The treatment of the filamentous portions of the animal skin or pelt may be carried out in various ways, as by the formation of condensation products with the parent substance of the filaments with properly selected re-agents. The chemical mechanism is analogous to that of synthetic resin formation, but in this manner of proceeding, the active chemical functional groups of the parent substance of the filaments of the skin or pelt act as one of the condensation re-agents, while the other is supplied according to requirements, for producing the desired effect, result or reaction, without materially destroying the physical structure of the filaments themselves. In the case of hair or wool, the pelt is treated with a substance which chemically reacts with the fibre substances of such filaments including the keratin or amino-bearing material of the filament, to form therewith in situ a permanent synthetic resin or resinoid, or condensation products, or the like. In carrying out the treatment of the fur, hair or wool, of the pelt, the leathery portions are coated or impregnated with non-injurious protecting agents which are later either removed or allowed to remain in the leathery portions of the pelt, as desired.

The invention is applicable for the treatment of tanned pelage such for example as that of sheep to permanently straighten the wool and give gloss and finish, all without deterioration of the leather parts of the pelt, so that the treated pelt can be used for making fur garments in imitation of other more expensive furs.

Straightening of the hair, fur or wool parts of the pelt has heretofore been attempted but has not proved to be permanent, the wool again becoming curly or kinky after wetting. Previously to the present invention, efforts were made merely to coat the fibres with greases, waxes or soaps in an attempt to straighten them and keep them straightened, but such coating material had no

permanence, since it merely formed an outer covering on the filaments, an incomplete layer in most cases, and in many instances the leathery portions of the pelt were deteriorated.

Various reactant substances may be used in carrying out the invention, and the following is only one example of the application of the principles in the treatment of tanned pelage such as that of the sheep, or other soft or hard fur, wool or hair to straighten the wool or hair portions of the pelt and impart a high gloss to the hair, fur or wool, and impart to it hydrophobic properties, all without deterioration of the leather parts of the pelt. The gloss of the hair, fur or wool is a function of the straightening. Brilliance, or gloss, is not usually obtainable when super-curling fur, because of the change in light reflecting properties, brought about by the physical structure produced.

Example I

Preliminary treatment and formation of the protective coating and impregnation of the leathery parts of the skin or pelt:

The tanned and dried pelt is optionally first degreased either by washing or by treatment with a hydrocarbon solvent such as petroleum, or benzol, or ethers, or chlorine-substituted hydrocarbons, or with any suitable degreasing or washing agent, after which the pelt may or may not be dried. The pelt is then soaked in water which completely penetrates the leather and serves as a vehicle to draw thereinto, uniformly and gradually a properly selected substance which will penetrate the fibrous structure of the leather, and so coat it as to prevent deleterious contact therewith of re-agents subsequently applied. As an example of such a substance is a water solution of corn syrup, of a concentration of from 50 to 85%. The preliminary treatment with water is customary in tanneries to insure the uniform penetration of the dressing or softening agents, whether the skin has been dehaired or not. In my process, the excess water is removed and then the pelt is thoroughly covered on the side opposite to that of the hair or wool, with a protective impregnant and coating such as a water mixture of an inert or non-reactant material such as above mentioned.

After impregnation of the leather by this protective impregnating and coating solution the pelt is thoroughly dried. The drying is desirable for two reasons: First, because if the leather is impregnated with moisture it will selectively withdraw from the reacting mixture, the most hygro-

scopic constituents, such as mineral acids, to result in destruction of the leather; and second, because it is undesirable, for accuracy to introduce into the impregnating solution any more water than the calculations require. This application of a water solution of corn syrup or other protective agent has for its object the formation of a continuous film on the surface of the leather, as well as within the fibrous structure thereof, to prevent deleterious action of the reagent or re-agents subsequently used. In other words, this application is protective of the leather portions of the skin or pelt. Corn syrup is preferred because of its cheapness and easy availability, but other substances such as glycol-borborate or glyceryl-borborate or similar water-soluble film-forming materials can be used. If desired the protecting of the leather may be done by impregnating and coating the leather of the pelt with any other suitable protecting agent.

Example II

Treatment of the fur, hair or wool portions of the pelt or skin after formation of the protective impregnation and coating on the leather parts of the pelt.

After the tanned pelt is prepared as above, it is treated with a reactant which is prepared as follows: To 60 parts by weight of commercial cresol is added 40 parts of an azeotropic mixture composed of benzol, alcohol and water. The above is saturated with enough hydrogen chloride to give the proper acidity, which may range from 0.1 to 0.4 normal.

Other mineral acids or acid producing substances possessing condensing properties can also be used instead of hydrogen chloride. As an example there may be mentioned sulphuric acid and mixtures of anhydrous aluminum chloride and hydrochloric acid.

As an example there may be used 60 parts of cresol, 8 parts of denatured ethyl alcohol; 40 parts of benzol and 4 parts of concentrated hydrochloric acid. The acid concentration should be carefully balanced, because if too high will destroy the azeotropic mixture, and if too low will slow down the reaction during subsequent treatment of the wool. The hydrochloric or other acid is used as a catalyst and dehydrating agent and may be added in any suitable manner, such as by bubbling hydrogen chloride through the mixture. The above mixture or solution is brought to a temperature approximately within the range of 30 to 55° C., and the previously prepared pelt is submerged in this solution for from 15 to 300 minutes. In the case of sheep pelts treatment at 38° C. for 120 minutes gives good results. During this period the skin may be moved to insure good and uniform contact of the reacting substances with the wool. At the end of the time period the skin is removed from the bath and the excess of treating solution is removed mechanically as by squeezing or centrifuging or by washing with benzol, or other suitable solvent. Some of the impregnating liquid penetrates the fibres themselves and some is only retained by capillary attraction. The latter being undesirable for this process, it is removed, if for no other reason than to avoid waste. After removal of the excess solution the skin is submerged for from 5 to 30 minutes in a solution of commercial formaldehyde having a concentration of about 40% by volume and having a temperature of between about 30 to 60° C. For sheep skin a treatment at 45° C. for 20 minutes gives good results.

At higher temperatures and at a given concentration of reactants, a shorter time of treatment is necessary. It is desirable to bring about the desired changes in the minimum of time, with stronger reactants, but in this regard one is limited by the time required for penetration of the reactant into the fibres. The time of reaction at a given concentration is inversely proportional to temperature. The temperature of reaction for a given time is inversely proportional to concentration of the reactants within certain limits. The treatment must be regulated to the requirements in reference to the perishable parts of the pelage.

I have found that treatment with formaldehyde, after the impregnation, gives a better product. The seeming explanation for this is that some of the amino groups which by now have been rendered active by the hydrochloric acid in the impregnating solution, can be easily made to react with formaldehyde to give rise to the well known condensation products between amines and aldehydes. Furthermore, the formaldehyde under these circumstances reacts with some of the excess of cresol which is adsorbed by the fibre, giving rise to Bakelite-like products.

Similar results can be obtained by carrying out the same reaction at ordinary temperature and pressure for 24 to 72 hours, removing the fibrous materials from the formaldehyde solution and drying them at a temperature of about 100° C. The fibrous materials are then washed to free them of any water soluble substances and dried again.

Of the reacting substances which I have described, cresol in Example II is very useful. However, cresol has only a limited solubility in water but is completely miscible in hydrocarbons and alcohol. On the other hand hydrochloric acid, whose presence is also necessary for the reaction is only slightly soluble in hydrocarbons and in cresol, but is very soluble in water. Therefore, in order to make a homogeneous mixture of hydrochloric acid, hydrocarbon and cresol it is desirable to use a fourth substance termed a homogenizer, which in this instance is alcohol. Between alcohol, benzol, and water a constant boiling point azeotropic mixture is formed which will dissolve hydrochloric acid gas in sufficient amount for the purposes of this invention without suffering a disturbance of equilibrium. However, if the maximum tolerance of this azeotropic mixture for hydrochloric acid gas is exceeded the homogeneity of the mixture is destroyed and it separates into two layers, one composed mainly of hydrochloric acid and water and alcohol, and the other of benzol and alcohol.

The principal object in the preparation of this solution is to have a physically homogeneous mixture, the presence of water and other reactants which are water-non-miscible both being required. For the proper mixing of these non-miscible substances the homogenizer is important. It is therefore necessary to have a liquid capable of dissolving both the catalyzer and the reactants.

To straighten the wool or hair of pelts or skins, it is preferable to carry out the reaction in the presence of an acid catalyst. Thus in Example II the wool portions of the pelt are reacted with a hydroxy-aromatic compound, such as cresol, in the presence of hydrochloric or sulphuric acid. A fine fur like a beaver will not tolerate as high a temperature as a sheep skin, partly because of the thickness of the skin.

The results of the above treatment will be a

straightening of the fur, hair or wool portion of the pelt, with a simultaneous production of high gloss (for straightening).

Example III

Removal of excess reactants and finishing of the skin or pelt:

The skin or pelt treated as in Example II is removed from the treating solution and is washed in running cold water and is then put to soak for a time in a solution containing about one-fourth pound of common salt per gallon with an equal amount of sodium bicarbonate. The running cold water is for the purpose of removing as much as is possible of the formaldehyde. During the treatment with formaldehyde the protection given to the leather with the proper inert material is nullified because these inert materials are soluble in the formaldehyde solution. Where any other protective agent is used, it is removed by any suitable means. The next operation, which is washing, has for its object the removal (as completely as possible) of all entrained substances, which were used during impregnation and during formaldehyde treatment, as well as the complete removal of the inert substance that was used in protecting the leather. Incomplete removal of the above mentioned substances would lead to a severe weakening, if not complete destruction, of the leather during the subsequent heat treatment or combing. The function of salt in this salting solution is to suppress the swelling of the leather, which swelling annuls the effects of tanning. The sodium bicarbonate is used to supply enough potential alkali (without being over-alkaline) to neutralize any hydrochloric acid which might have been retained or adsorbed by leather or fibrous material. After the above soaking which is for the purpose of removing the last traces of acid, the skin is washed with water. This washing is for the purpose of freeing the skin from any salt which has penetrated it from the previous solution and which has been formed at the expense of hydrochloric acid and sodium bicarbonate on the inside of the skin. The general object is to rid the skin of sodium chloride. The skin is then dried and then prepared to be mechanically finished by combing, during which operation the temperature of the wool should be between 70 to 110° C. This heat treatment completes the formation of the resinous or resinoid condensation products which it is the object to produce. The combing operation thus carried out on the dry and chemically modified fibre assists in completing the condensation reactions which had been taking place at lower temperatures.

Example IV

Treatment of the fur, hair or wool portions of tanned pelage such as skins or pelts which have been tanned by oil tanning or formaldehyde tanning is as follows:

The tanned pelt is first degreased and then treated with an agent for protecting the leather portions of the pelt, all as described in Example I. The hair, fur or wool portions of the skin or pelt are then subjected to the action of formaldehyde or formaldehyde producing substances such as hexamethylenetetramine preferably aided by a mild alkaline catalyst such as triethanolamine and operating in an autoclave under pressure preferably at a temperature corresponding to a developed pressure between 20 and 75 pounds. The time of treatment is 30 to 90 minutes. The resulting fur, hair or wool possesses gloss and is

silky and free of "kinks." The thus treated skin or pelt is removed from the autoclave and is washed thoroughly with water as set forth in Example III and may then be dried and heated if desired. Heating will increase polymerization of the formaldehyde treated fur, hair or wool of the pelt which results in some stiffening action. This is an economical way of treating wool pelts and has the advantage that the final product is completely free from odor. In addition the treatment has the effect of rendering the keratinous portions of the fur, hair or wool less susceptible to chemical reaction, when brought in contact with strong alkalies or acids.

Example V

If the wool portion of the pelt is treated with a suitable re-agent, at the proper temperature, in an alkaline medium, for example, acetyl chloride in pyridine, or even glacial acetic acid in pyridine the result will be a wool whose curl has been substantially increased (super curl). In this case, the amino groups of the keratinous material of fibre are acetylated. In such reactions the leather portions of the pelt are, of course, protected by the use of a suitable coating and impregnating agent as set forth in Example I.

The following is an example of the procedure for the formation of the condensation products, around, or to encase, an animal fibre, as distinguished from the utilization of the keratins of the fibre in the formation of such condensation products.

Example VI

The filamentous material, after degreasing by any suitable means, and after treating the leather portions of the pelt with a protective agent, as previously described in Example I, is coated with furfuryl alcohol as for example by dipping. The excess furfuryl alcohol is then allowed to drain off, and the alcohol coated fur, hair or wool is then either exposed to hydrogen chloride or dipped in a solution of hydrochloric acid of any concentration from 5 to 37%. By this process the furfuryl alcohol is transformed into a resinous substance formed in situ, which encases and adheres to the fibre. There is no reaction in this case, between the material of the fibre, and the furfuryl alcohol or hydrochloric acid, and the protective agent in the leather prevents the reactants from damaging the leather portion of the pelt.

Example VII

In the following process for treating animal fibres, the parent substance of the fur, hair or wool fibres reacts with the re-agents, giving rise to a resinoid substance. In this case the skin or pelt is preliminarily treated as in Example I so as to protect the leather portions of the skin or pelt, and is then either coated or, by allowing sufficient time, the fur, hair or wool is impregnated with an aqueous solution of saligenin. The coated or impregnated fibres are then subjected to the action of gaseous ammonia, or are dipped in a water solution of ammonia. The fibres thus treated are dried, and will be found to be either coated without penetration, or its structure will be penetrated by the resinous body, resulting from the reaction. This penetration is to be distinguished from coating without penetration which latter is also a feature of the present invention. Saligenin requires the presence of an alkaline environment in order to be converted into a resinoid. Such an environment

may be furnished by the keratinous substance of the fibres, or by the action of ammonia without reaction with the parent substance of the fibre. The time required for penetration varies with the type of hair, fur or wool fibre of the pelt but can be accomplished within a period of about 72 hours. It is possible, by varying the time, to control the degree of penetration, or entirely to prevent penetration and simply coat the filament.

Furthermore, one of the re-agents used in the formation of saligenin is formaldehyde, and this substance is present in excess or in equilibrium with phenol, in the saligenin reaction products. These two substances, phenol and formaldehyde also react with keratins giving rise to resinous substances, but are prevented from injuring the leather portion of the skin or pelt by the presence of the initially applied protective agent.

The above example also includes the general type in which the fibre is coated by a resinoid formed in situ. Internally it has in its structure resinoid bodies, formed from saligenin, and keratin, the two having reacted to form the resinous substance.

In Example VI, a mineral acid, namely hydrochloric acid was the catalytic agent for the reaction of resinification. In Example VII, a base, namely ammonia was the catalytic agent inducing a similar type of reaction.

In carrying out the present invention, the available reactive groups of the substances comprising the parent material being treated are utilized as starting materials in the formation of resinoid materials. The types of reactions involved depend upon the substance being treated, that is to say, whether it is fur, wool, hair or bristle and may be illustrated by the following examples of resinoid formation: (1) condensation of aromatic amines with aldehydes; (2) condensation of amides and aldehydes; (3) condensation of amino groups linked to carbonyl groups with aldehydes; (4) condensation of amines with hydroxy-aromatic compounds; (5) condensation of aldehydes with hydroxy-aromatic compounds; (6) condensation of amino acids with aldehydes; (7) condensation of proteinic substances with aldehydes; (8) condensation of proteinic substances with hydroxy-aromatic compounds; (9) condensation of aldehydes among themselves; and (10) condensation and polymerization of unsaturated compounds.

In the case where a chemical change of the parent substance of the fibrous material takes place, the change is obtained without destroying the filamentous structure, or form, and thus it is possible to impart to the filaments those desirable properties needed for their intended uses. For instance, in the case of furs, the wool of sheep skin can be converted into a filamentous product hardly distinguishable, by the naked eye, from hair. The invention is applicable for curling as well as straightening, and curling can be carried to a point wherein the final product has a compact felted structure. The fur, hair or wool treatment processes impart to these filaments either stiffness or softness as desired making them resistant to the action of depolymerizing, hydrolytic, or hydrolizing agents. The processes also provide a non-shrinking effect and render the fur, hair or wool resistant to destruction by insects such as moths. In addition it is possible to increase the diameter of the individual filament of the fur, hair or wool.

During the formation of the condensation

product or products in the filament, straightening or curling of the filament is induced, depending upon the reacting medium selected to form the condensation product. The invention is not intended to be limited to the character of the synthetic resin or condensation product which is formed and which changes the character of the filament. In the case of hair or the like, the chemical structure of the keratinous, amino-bearing filamentous material of the fur, hair or wool portions of the skin or pelt is changed.

It is to be understood that, by the practice of the invention herein described the parent substance of the fibre, animal, can be made to in situ react in various degrees with the treating re-agent, or the resinoid substance can be formed in situ without any reaction involving utilization of the substance of the fibre. In some instances there are surface reactions; in some no surface reactions; in some there is a deeper reaction amounting to impenetration and in some the reaction may involve any selected portion of the filament.

In using the expression "in situ" it is the intention to distinguish from the separate making of a resinoid substance and dissolving it by suitable means and then applying it to the fibres, and then subsequently eliminating or removing the solvent by physical or chemical means; as for example, by dissolving a material or synthetic resin in a solvent which is later eliminated by evaporation, or by dissolving this resin or resinoid substance which reacts with that chemical whose reaction product is later broken up by use of a third reagent such for example as rosin soap, precipitated subsequently with an acid producing substance.

This application is a continuation-in-part of my application Serial Number 106,427 filed October 19, 1936.

Obvious variations may be made in the processes herein described without departing from the spirit of the invention claimed.

I claim as my invention:

1. A process of treating fur pelts to modify the fur by resinification of the fur in situ with a resinification agent which is normally capable of deteriorating the leather of the pelts, which comprises forming a protective coating on such leather portions and then treating the fur by reaction with such resinification agent.

2. A process of treating fur pelts to modify the fur by resinification of the fur in situ with a resinification agent which is normally capable of deteriorating the leather of the pelts, which comprises impregnating the leather portions of the pelt with a substance capable of protecting said leather portions from deterioration by the resinification agent and then treating the fur with said resinification agent.

3. The art of processing filamentous covering of the skin of animals which consists in treating the back of a tanned pelt with a water solution of corn syrup, then treating the filaments with a reactant composed of a solvent, a hydroxy-aromatic compound and an acid, then removing excess reactant and treating with an aldehyde, then washing in cold water, and then treating with a solution of sodium chloride and sodium bicarbonate.

4. The art of processing filamentous covering of the skin of animals which consists in protecting the tanned pelt with a chemically inert substance, then treating the filaments with a reactant composed of a solvent, a hydroxy-aromatic com-

pound and a catalyst, then removing excess reactant and treating with formaldehyde, then washing in cold water, and then treating with a solution of sodium chloride and sodium bicarbonate.

5. The art of processing filamentous covering of the skin of animals which consists in treating the back of a tanned and degreased pelt with a water solution of corn syrup, then treating the filaments with a reactant composed of a solvent, cresol and an acid catalyst, said reactant being at a temperature of 35 to 55° C., and the treatment being continued for from 15 to 300 minutes, then removing excess reactant and treating with formaldehyde, having a concentration of about 40% by volume and at a temperature of about 30 to 60° C. for about 5 to 30 minutes, then washing in cold water, then treating with a solution of sodium chloride and sodium bicarbonate for one-half to three hours, then washing, and then drying and combing the filaments with simultaneous

application of heat to the fibres being combed to make them reach a temperature of from 60 to 115° C.

6. A process of treating fur pelts to modify the fur by resinification of the fur in situ with a resinification agent containing an aldehyde, which is normally capable of deteriorating the leather of the pelts, which comprises forming a protective coating on such leather portions, and then treating the fur by reaction with such resinification agent.

7. A process of treating fur pelts to modify the fur by condensation of the fur in situ with a condensation agent which is normally capable of deteriorating the leather of the pelts, which comprises forming a protective coating on such leather portions and then treating the fur by reaction with such condensation agent.

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