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PROCESS OF TREATING FILAMENTOUS MATERIALS

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This invention relates to the treatment of filamentous materials, animal or vegetable, natural or artificial from natural or synthetic products, including the skins of animals commonly known as furs, hair or wool, to encase the filaments without chemically modifying the parent substance, or to chemically modify such substance, to either permanently straighten or permanently curl the filaments, or to impart gloss or finish, or to make them resistant to chemical or to mechanical action.

A very important phase of my invention is 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 case, the active chemical functional groups of the parent substance of the filaments 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 filament itself.

In the case of hair or wool, I treat with a substance which chemically reacts with the fibre substances of the hair, including the keratin or amino-bearing material of the filament, to form therewith a permanent synthetic resin or resinoid, or condensation product, or the like.

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 so that the treated pelt can be used for making fur garments in imitation of other more expensive furs. Such straightening has heretofore been attempted but has not proved to be permanent, the wool again becoming curly or kinky after wetting. Previously to my invention efforts were made to merely coat the fibres in an attempt to straighten them and keep them straightened, but the coating material had no permanence, since it merely formed an outer covering on the filaments, an incomplete layer in most cases.

The value of bristles in brush making depends upon their stiffness or rigidity. Those bristles which are stiffest, are therefore the most marketable, and are used for tooth brushes, hair brushes, clothes brushes, etc. I have found it possible by my process to so treat bristles as to increase their rigidity and to make marketable those which are today considered of inferior quality or as useless. Thus, by the use of my invention the inferior grades of bristles can be given the qualities of those of the finest natural product.

Hairs or similar fibrous materials are strongly attacked, even to the extent of being dissolved, by strong alkalies like caustic soda. I have found that by treatment of these fibrous materials in accordance with my invention, it is possible to make them generally more resistant to certain chemicals or to make them much less vulnerable to such action.

The following filamentous substances can be treated by the practice of my invention: animal products or products derived therefrom including hair, wool, silk, etc.; artificial products, such as filamentous materials produced from collagen or its derivatives such as those made from glue, gelatin, as well as from casein, isinglass, etc.; and filamentous materials derived from protein substances, such as catgut, etc.; also vegetable products, or products derived therefrom including natural fibres such as hemp, manila, jute, etc.; also roots, such as are used in the manufacture of brushes; and artificial vegetable filaments made from cellulose or cellulose hydrate etc.

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, hair or bristles, to straighten the wool or hair and impart a high gloss to it, and impart to it hydrophobic properties. The gloss 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 1

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 water mixture of an inert or nonreactant material such as above mentioned.

After impregnation of the leather by this 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 hygroscopic constituents, such as mineral acids, to result in destruction of the leather; and second, because I do not want to introduce into the impregnating solution any more water than the calculations require. This application of a water solution of corn syrup has for its object to form 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. Corn syrup is used because of its cheapness and easy availability, but other substances such as glycol-boriborate or glyceryl-bori-borate or similar water-soluble film-forming materials can be used

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 I mention sulphuric acid and mixtures of anhydrous aluminum chloride and hydrochloric acid.

As an example I use 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 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 mcehanically 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 is undesirable for this process and should be 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 twenty 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.

The skin is then removed from this last mentioned bath and is washed in running cold water and is then put to soak for a sufficient length of 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. 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 2

The following is especially recommended for loose wool, bristles, or hair and consists in subjecting the degreased fibre 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 wool possesses gloss and is silky and free of "kinks." The wool is removed from the autoclave and is washed thoroughly with water and then dried and heated if desired. Heating will increase polymerization which results in further stiffening. This is an economical way of treating wool and has the advantage that the final product is completely free from odor. The last process, though most suitable for loose wool, can also be applied to tanned pelage, provided that a special tanning process such as oil tanning or formaldehyde tanning has been used. Both processes are applicable to hair or bristles, in which case the effect sought is not to straighten or impart lustre, since these two properties are already inherent in the product or material, but to make the keratin of which they are formed less susceptible to chemical reaction, when brought in contact with strong alkalies or acids. This process is particularly advantageous for the treatment of bristles used in the manufacture of brushes.

The above process is applicable to loose wool or hair, or bristles. Where shorn wool is being treated the time of processing or the concentration of reagents can be somewhat increased, since there is no tanned skin structure to be preserved. Higher mechanical resistance, and improvement in other mechanical properties, such as rigidity, is obtained by additional polymerization. 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 given in Example 1, cresol which is illustrative of hydroxy-aromatic compounds is useful in my invention. Cresol has only a limited solubility in water but is completely miscible in hydrocarbons and alcohol. Hydrochloric acid whose presence is also necessary for the reaction is 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 which may be termed a homogenizer. This homogenizer in this instance is alcohol. Between alcohol, benzol, and water constant boiling point mixtures are formed of which the azeotropic mixture is an illustration. This azeotropic mixture 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 is required and the presence of some other reactants which are water-non-miscible is also required. For the proper mixing of these non-miscible substances a 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 I may carry out the reaction in the presence of an acid catalyst. For example, I react the wool with a hydroxy-aromatic compound, such as cresol, in the presence of hydrochloric or sulphuric acid. If loose wool is being treated somewhat higher temperatures than those required for the treatment of pelage can be used without deleterious effects on the wool. 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 wool with a simultaneous production of high gloss (for straightening). If the wool, mentioned above, 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.

My process may be applied to sheep wool to condition it for use in the manufacture of rugs giving the wool a gloss which is permanent, and also permanently straightening it, which conditions are not destroyed by water wetting. My treatment also renders the wool moth proof. The invention therefore also includes the treatment of tanned sheep pelage for permanently modifying the chemical structure of the filaments.

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 3

The filamentous material after degreasing by any suitable means, as previously described, is coated with furfuryl alcohol as for example by dipping, and then allowing the excess of the alcohol to drain off. The alcohol coated fibre 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 apparently is no reaction in this case, between the material of the fibre, and the furfuryl alcohol or hydrochloric acid.

Example 4

In the following process for treating animal fibres, the parent substance of the fibre reacts with the re-agents, giving rise to a resinoid substance. In this case; first either coat, or by allowing sufficient time impregnate the animal fibres with an aqueous solution of saligenin. The coated or impregnated fibres are then subjected to the action of gaseous ammonia, or are dipped in liquid ammonia. The fibres thus treated are dried. The resulting fibre will be either coated without penetration, or its structure will be penetrated by the resinous body, resultant from the

reaction. This penetration is to be distinguished from coating without penetration which latter is also a feature of my invention. A saligenin to be converted into a resinoid, requires the presence of an alkaline environment. 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 fibre 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 to entirely 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.

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 3, a mineral acid, hydrochloric acid was the catalytic agent for the reaction of resinification. In Example 4, a base, ammonia was the catalytic agent inducing a similar type of reaction. In the case of vegetable fibres, if they are treated as in Example 3, or as in Example 4, a definite change in the physical properties of the fibre results, due to the formation in situ of resinous bodies.

In carrying out the present invention I utilize the available reactive groups of the substances comprising the parent material being treated, as starting materials in the formation of resinoid materials. The types of reactions involved depends upon the substance being treated, that is to say, whether it is wool, hair, bristle, silk, glue, gelatine, hemp, manila, jute, etc., and are 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 I am enabled 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. In the case of loose animal filamentous materials such as hair, bristles or wool, my process imparts to them either stiffness or softness making them resistant to the action of depolymerizing, hydrolytic, or hydrolizing agents. I am also able to produce products which are non-shrinkable by the action of washing, and which are indestructible by insects. I am also able to increase the diameter of the filament.

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.

In using the expression "in situ" I mean to distinguish from the separate making of a resinoid substance and dissolving it by suitable means and then applying it to the fibers, 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.

It is understood that, by the practice of my invention the parent substance of the fibre, animal or vegetable, can be made to 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 impregnation; and in some the reaction may involve any selected portion of the filament. I also treat materials of the above nature, animal or vegetable, after they have been woven into cloth, and my intention is to cover by claims the application of my invention to the treatment of woven goods, as well as the treatment of filaments whatever form they may be in.

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. The process of unkinking natural wool which comprises subjecting the same to the action of the type of substances of the group consisting of cresol and aldehyde in the presence of acid medium.

2. The process of unkinking natural wool which comprises subjecting the same to the action of cresol in the presence of an acid reacting substance.

3. Fur the hair of which is combined with formaldehyde, thereby being rendered waterproof and straight instead of kinky.

4. The process of unkinking natural wool which comprises subjecting the same to the action of formaldehyde in an acid medium.

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