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REENFORCED HYDRATED CELLULOSE
CONTAINER

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The present invention is concerned primarily with the preparation and utilization of a unitary, or unitary appearing, partially transparent body of an unmodified and modified cellulosic material, or the combination of a structural and structureless cellulose body as a container for products intended for human consumption and is related to my co-pending applications, "Method of treating fibrous material", Ser. No. 442,443, filed April 7, 1930, which is now Patent Number 1,829,702, dated October 27, 1931; "Reinforced hydrated cellulose from nitrocellulose", Ser. No. 511,114, filed January 24, 1931; "Reinforced hydrated cellulose from acetylcellulose", Ser. No. 511,113, filed January 24, 1931; "Reinforced hydrated cellulose from viscose", Ser. No. 511,452, filed January 26, 1931.

This invention relates to improvements in methods of treating vegetable fibrous material and the products obtained therefrom, especially in connection with the treatment of those types of fibrous material prepared from, or having the characteristics of those fibers known as mitzumata, kodzu, gampi and by other names, and other similar plants and types of plants and of fibers obtained therefrom, with soluble organic sulfur derivatives of cellulose, as viscose (alkali salt of xanthated cellulose) which soluble derivative is subsequently regenerated, with the formation of a regenerated cellulose product, which forms a unitary, translucent body or compound with the above stated fibers, irrespective of whether said fibers are in the individual state, loosely commingled, or in the matted aggregate condition, and the employment of the finished product as a wrapper case container or casing for the storage and preservation of edible products, either animal or vegetable.

It is well known that so-called regenerated celluloses, in general, readily absorb moisture. In this condition the tensile strength and other desirable physical properties are materially impaired, and this disadvantage of such regenerated celluloses has heretofore materially narrowed the scope of their technical usefulness, for example, in such arts as the sausage casing industry, as a substitute for the natural gut of animals now used for this purpose.

One of the objects of this invention is to so reinforce, fortify and strengthen this regenerated cellulose material or membrane that its tensile strength, resistance to rupture, and other valuable characteristics are considerably augmented, both in the dry and moist condition, without at the same time materially detracting from the valu-

able properties of the regenerated cellulose, and in so doing not only to increase its usefulness in arts in which it may now be employed, but to extend its usefulness to arts in which, up to the present, it has not been used to any considerable extent.

As typical of the organic esters of cellulose containing sulfur, this invention is limited to the use of the esters of cellulose with the xanthic acid radical, the so-called cellulose xanthates or sulfocarbonates, in which the cellulose has been esterified under such conditions as to be soluble in, or miscible with, weak alkali metal hydroxides in aqueous solution, and not incompatible with softeners, as now used in the cellulose xanthate or viscose art.

Another object of my invention is to combine in a pellucid, or semi-transparent, unitary-appearing layer of indeterminate dimensions as to thickness, length and width, fibers as above stated, in their individual fibrous condition, or when agglomerated, agglutinated, or aggregated, or in the form of sheets containing a multiplicity of the fibers and made by ways now known, the fibers being either in an untreated, undyed, partially dyed or dyed condition, with a xanthated cellulose in solution or viscose which is afterwards regenerated, suitably by acid treatment, resulting in the formation as the finished preparation of a cellulose material not hydrated and cellulose in a more or less hydrated condition, the two classes of materials being united to a uniformly appearing unitary body or sheet. If the cellulosic fibers are dyed, it is to be understood that said fibers may all be dyed one color or shade, or of two or more colors or shades to produce new and novel effects. The coloring matter used, of course, must not be deleteriously affected by the chemicals employed in the subsequent operations.

Another object of this invention is the preparation of cylindrical, rectangular or other shaped lengths, of uniform or varying diameter or length, of fibers of the nature specified, in the individual, matted or agglomerated condition, undyed, dyed or otherwise colored or modified in properties and in appearance, treated, coated or impregnated with viscose, which is regenerated to form a combined layer or body of unmodified or fibrous cellulose and of cellulose which has been modified in its chemical and physical characteristics.

Hydrated cellulose, being inert, and substantially permanently stable, is especially advantageous in comparison with protective coatings of the cellulose esters which heretofore have been

proposed for this purpose, certain of which may undergo slow decomposition and form undesirable decomposition products.

The finished material has to a high degree the desirable properties of natural gut, in strength, elasticity, flexibility, pliability and porosity, and like natural animal membranes, possesses the unique property of high expansion in the moistened condition and contraction when dried. It has also been found to satisfactorily meet the exacting requirements of casings when smoking, curing, and boiling processes are involved.

The casings made by my process of the present invention have increased tensile strength even in the wetted condition. In case of a break or tear, because of this fibrous base or intermediary reinforcing layer, further progress of any break or tear is retarded, and its area restricted.

The product of this invention therefore, is especially practicable for use in a tubular or other shaped container for foods intended for human consumption, altho it is to be understood that the material comprising a normal and a modified cellulose material may be used for receiving and preserving substances of a non-edible nature, or, in fact, wherever and whenever a container or material with properties of natural gut and other animal membranes is required, irrespective of the nature of the material contained therein.

The well known abnormal strength of the class of fibers comprehended in this invention, their suppleness, ready permeability by means of cellulose xanthate in the dissolved condition or viscose, and their pliability and other valuable physical characteristics in the impregnated state, when combined with a cellulosic material neutral in reaction, having inherent strength, expansibility and contractility of a high degree, produces a combination of desirable physical characteristics and chemical deportment highly advantageous in those technical arts such as the sausage casing industry, wherein relatively high tensile strength, a well defined porosity, high expansibility and contractility, indestructibility, insolubility in water and all known volatile solvents or solvent combinations without change, are valuable desiderata.

Another object of this invention is the production of capsules or casings, tubular or otherwise, neutral and diaphanous, especially applicable as containers for edible products or for products not intended for human consumption, simulating animal membrane in appearance, properties and usefulness, and having the desired tensile strength, flexibility, pliability and porosity, and the ability to undergo relatively high expansibility and contractility under normal methods of commercial application without rupturing or substantial loss in strength.

In contradistinction to natural or animal membranes which have been proposed and used for the temporary preservation of food products, the classes of fibers enumerated herein, when homogeneously impregnated and covered with a body of stable regenerated cellulosic material as herein described, are antiseptic and aseptic, not prone to deterioration from normal atmospheric influences, and are especially applicable for this purpose by virtue of its physical characteristics as enumerated herein.

If an imprint is to be placed on the finished article, said imprint may be made upon the cellulose fibrous matrix or sub-structure before the application of the viscose, or upon the regenerated cellulose layer. At any stage of the process,

the sheets, film or layer, may be corrugated, embossed or otherwise given a surface pattern.

By virtue of the opalescence and translucency of the cellulosic fibers, the finished integument, layer, sheet or film is never wholly transparent, although the degree of translucency and nearness to transparency may be varied within wide limits as will be readily understood by those conversant with the art to which this invention appertains. If it is desired to more nearly approach transparency, the fibrous material may be mercerized or otherwise treated chemically or its opalescence may be diminished by treatment with oils or oleaginous mixtures, before the viscose is applied thereto and thereon; or the opalescence may be diminished in other ways.

The major portion of cellulose xanthate prepared at the present time is for viscose rayon production. In the viscose solution, during the ageing or ripening process, the usual free alkali content is 6%-7% NaOH. It has been found that this amount of alkali is prone to soften the fibers comprehended in this invention to the extent that it is difficult to coat and impregnate them in the matted or fibrous-condition. I therefore prefer to use a viscose solution for this purpose which contains therein a minimum of free alkali, about 3% having been found satisfactory. It is also essential for best results that after the close of the xanthation period in viscose formation, great pains be taken to remove the free or uncombined carbon bisulfide.

The material produced by the present invention may be prepared by first impregnating or depositing on and in a vegetable fibrous structure a suitable organic sulfur-containing ester of cellulose which is soluble in water and in diluted solutions of alkali metal salts, and then regenerating the cellulose or group contained therein, or else by admixing the suitable fibers in individual pulp form, with the sulfur-containing cellulose ester in solution and then regenerating the cellulose by removing the acidic radical formerly attached to the cellulosic portion.

While specifically the vegetable fibers used in the present invention may be prepared from the plants mitzumata, kodzu (koso) and gampi (ganpi) being plants of the Edgeworthia, Broussonetia and Wilkstroemia families respectively, and it is to be understood that any other fibers having similar characteristics may be employed for this purpose within the limitations of this invention.

Fibers from these plants, comprise relatively long thin cells of great suppleness and strength, and are little affected, comparatively speaking, by the chemicals and solutions used in carrying this invention into effect.

In carrying my invention into effect, the following two general examples indicate two of the preferred methods of practicing the same, but it is to be understood that these two examples are merely given for illustrative purposes and may be varied within comparatively wide limits.

Example I.—A mat or sheet of cellulosic fibers of the nature above referred to such as Yoshino or Japanese "cobweb" paper in sheet or roll form, and of any desired width and thickness is immersed in—a so-called viscose solution containing the equivalent of about 6% cellulose, and about 3% sodium hydroxide,—the solution being of relatively low viscosity and suitably at the temperature of the room. Where the viscose solution is kept at 20° C. and lower, there is less softening of the fibers than when a higher temperature dur-

ing immersion is resorted to. Better results are also obtained by subjecting the viscose solution to a vacuum treatment for an hour or longer in order to remove the major portion of the air bubbles and dissolved air in the solution.

If it is desired to strengthen the fibrous base before applying thereto the viscose solution, this may be accomplished in several ways, the fibrous base may be superficially acetylated or nitrated or otherwise esterified and the ester radical removed by hydrolysis. The fibrous portion may also be strengthened by applying thereto a dilute cellulose ester solution in a non-aqueous, volatile solvent or solvent combination, leaving a deposit of the cellulose ester, from which the acid radical may be removed by hydrolysis before the application of the viscose solution. In practice I have obtained excellent results by spraying the fibrous cellulose with a solution of cellulose acetate as by an air brush or airspray, and have found that with the comparatively small amount of cellulose acetate required, it is unnecessary to remove the acetic acid by a separate de-esterification treatment.

However, I may submit the sheet thus superficially coated with the cellulose ester to a saponifying treatment, to remove the acetic acid therefrom before submitting the sheet to impregnation with viscose solution.

After applying the viscose solution to the fibrous sheet, the latter is immediately immersed in a warm, acid setting bath, similar in composition to that used in the viscose rayon industry, I having found a bath consisting primarily of 10%–12% sulfuric acid and at a temperature of about 42° C. satisfactory for the purpose. After immersion in the hydrolyzing bath it is expedient to allow the sheet to stand for some time to ensure uniform and complete penetration of acid and neutralization of alkali and regeneration of the cellulose. The translucent, milky appearing sheet is next washed until neutral, immersed in an alkali metal sulfide bath at about 45° C. and containing 10–12 grams sodium sulfide per liter to remove the sulfur contained therein, and washed free from sulfur. If it is desired to impart added suppleness and flexibility, the sheet may be immersed in an appropriate solution such as one of glycerol, glycol, glucose or other similar material, and the excess moisture removed in any convenient manner.

If it is desired that the final sheet shall be more nearly transparent, the sheet of matted fibers may be subjected to a preliminary chemical treatment as by a mercerizing bath under carefully regulated conditions in order to guard against softening and disintegration of the sheet, the reactants removed, and the sheet deprived of extraneous moisture. Or the sheet may be rendered translucent by other treatment prior to impregnation with viscose solution.

If a colored effect is sought, the fibrous cellulose may be colored before impregnation, or coloring matter may be dissolved in the aqueous alkali used to bring the xanthated cellulose into solution, or the hydrated cellulose may be dyed. The coloring material may comprise dyestuffs, lakes or pigments or a mixture of soluble and insoluble color may be employed.

Example II.—A suitable amount of loose, not matted fiber, of the class comprehended in this invention, depending upon the ratio of fibers to regenerated cellulose desired in the finished product, is intermingled or stirred with the desired amount of viscose solution of the characteristics

desired. When the fibers are uniformly disseminated in the syrupy mixture, the liquid is poured on a smooth surface and then immersed in a setting bath as heretofore indicated, or the mixture is cast upon a movable hard smooth surface and then precipitated. The amount of total solids deposited upon a given area will depend primarily upon the percentage of non-evaporable solids in the viscose solution and the viscosity of the same.

In certain cases, and where especial effects are to be obtained, the matted fibrous base mentioned in Example I may be used, and the solution of viscose with individual fibers admixed therewith as outlined in Example II, may be substituted for the plain viscose solution indicated in Example I.

If it is desired to form the finished article in a tubular or other closed form, a tube may be formed in any suitable way, as for instance, by slipping the fibrous portion over a hollow mandrel and then immersing mandrel and contents in the viscose solution as above indicated, or if the fibers are in the loose condition in the viscose solution, they may be deposited on a mandrel or other suitable form, and the viscose coagulated by precipitation as has been outlined.

Having now described my invention which is the production of a non-transparent film comprising a structural and structureless cellulosic body, or the combining of a normal cellulose with modified cellulose devoid of organic acid radical, and in what manner the same may be performed, what I claim as new, and desire to secure by Letters Patent is:—

1. The method of producing a container for edible products comprising, lightly impregnating a long-fibered material in tubular form with a dilute acetylated cellulose dissolved in a non-aqueous solution, evaporating the volatile solvent, then homogeneously impregnating and covering the stiffened tube with a solution of viscose containing about 3% free alkali-metal hydroxide, immersing said tube in an acid precipitating bath, washing free from reacting chemicals and allowing to dry whereby a tube is formed in which the fibers serve as a reinforcing structure.

2. The method of producing a container for edible products which comprises, lightly impregnating a long-fibered material in tubular form with a dilute acetated cellulose dissolved in a non-aqueous solution, evaporating the volatile solvent, impregnating the tube with a solution of viscose to homogeneously impregnate and cover the tube, immersing the tube in an acid precipitating bath, washing free from reacting chemicals, and allowing to dry whereby a tube is formed in which the fibers serve as a reinforcing structure.

3. The method of producing a container for edible products which comprises, treating a long-fibered material in tubular form with a solution of xanthated cellulose having a minimum content of free alkali to homogeneously impregnate and cover the tube and regenerating the xanthated cellulose to form an impregnation of regenerated cellulose in and on the fibrous base whereby a tube is formed in which the fibers serve as a reinforcing structure.

4. The method of treating a fibrous base prepared from mizumata, kodzu, gampi or other similar plants which comprises impregnating the base with a viscose solution to homogeneously impregnate and cover the same and then substantially or completely regenerating the cellulose as an insoluble film with the fibrous base as a reinforcing layer.

5 5. The method of producing a casing for edible products which comprises treating a tube of fibrous material prepared from mitzumata, kodzu, gampi or other similar plants with a viscose solution to homogeneously impregnate and cover the same and then regenerating the cellulose as an insoluble tubular film with the fibrous base as a reinforcing layer.

10 6. The method of forming a casing for meat and other edible products which comprises applying a viscose solution to a tissue-like sheet of matted, long-fibered cellulose to homogeneously impregnate and cover the same and regenerating the cellulose to form a film having said fibrous sheet as an intermediate reinforcing layer.

15 7. The method of forming a casing for sausages and other edible products which comprises treating a tube of matted long-fibered cellulose with a viscose solution to cover and homogeneously impregnate the same and subsequently regenerating the cellulose to form a tubular film having said fibrous sheet as a reinforcing layer.

20 8. The method of forming a casing for sausages and other edible products which comprises forming a tissue-like sheet of matted cellulose fibers prepared from mitzumata, kodzu, gampi or other similar plants, applying a viscose solution thereto to homogeneously impregnate and cover the same, and regenerating and drying the cellulose to form a film having said fibrous sheet as a reinforcing layer.

25 9. The method of forming a container or casing for meat and other edible products which comprises immersing long-fibered tissue paper in a viscose solution containing about 6% cellulose to homogeneously impregnate and cover the same, then immersing the paper and applied viscose coating in a suitable setting bath, and washing and drying the resulting product, thereby forming a film-like casing with said paper as a reinforcing layer.

30 10. The method of forming a container or casing for meat and other edible products which comprises immersing long-fibered tissue paper in a viscose solution containing about 6% cellulose to homogeneously impregnate and cover the same, then immersing the paper and applied viscose coating in a suitable setting bath, washing the resulting product, applying a softening agent thereto and drying it, thereby forming a film-like casing having said paper as a reinforcing layer.

35 11. A method of producing a material having the properties of a synthetic gut which comprises mixing vegetable fibers as such with viscose to homogeneously impregnate and cover the fibers, forming the mixture to produce a film, and subjecting the film to the action of a setting bath and subsequently washing and drying the resulting

film, said fibers serving as an intermediate reinforcing structure.

40 12. The method of producing a casing for meat and other edible products having properties simulating those of a natural casing which comprises mixing vegetable fibers as such with viscose solution to homogeneously impregnate and cover the fibers, forming the mixture to produce a tubular film, subjecting the tubular film to the action of a suitable setting and regenerating bath and drying the resulting product, thereby forming a tubular film of regenerated viscose united with the fibers in which the fibers serve as a reinforcing structure.

45 13. The method of preparing a thin sheet of material suitable for use as casings which comprises treating long-fibered cellulose material with viscose to homogeneously impregnate and cover the same and regenerating cellulose from the viscose to provide a regenerated cellulose sheet having an intermediary reinforcing structure of fibers.

50 14. The method of preparing a thin sheet of material suitable for use as casings which comprises treating fibers obtained from mitzumata, kodzu, gampi or other similar plants with viscose to homogeneously impregnate and cover the same and regenerating cellulose from the viscose to provide a regenerated cellulose sheet having an intermediary reinforcing structure of fibers.

55 15. The method of preparing a thin sheet of material in tubular form suitable for use as casings which comprises forming a tissue of long-fiber cellulose material into a tube and treating said tube of cellulose material with viscose to homogeneously impregnate and cover the same and regenerating cellulose from the viscose to provide a tube of regenerated cellulose sheet material having an intermediary reinforcing structure of fibers.

60 16. As a casing, a tubular film composed of regenerated cellulose reinforced by tissue-like long-fibered cellulose material prepared from the process which comprises, treating long-fibered cellulose with viscose to homogeneously impregnate and cover the same and regenerating cellulose from the viscose to provide the regenerated cellulose sheet having the intermediary reinforcing structure of fibers.

65 17. As a new article of manufacture, a film composed of regenerated cellulose reinforced by tissue-like long-fibered cellulose material prepared from the process which comprises, treating long-fibered cellulose with viscose to homogeneously impregnate and cover the same and regenerating cellulose from the viscose to provide the regenerated cellulose sheet having the intermediary reinforcing structure of fibers.

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