Patented Mar. 23, 1937 2,074,336

UNITED STATES PATENT OFFICE

2,074,336

CELLULOSIC PELLICLE AND METHOD FOR PREPARING SAME

Frederick C. King, Buffalo, N. Y., assignor, by mesne assignments, to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application August 18, 1934, Serial No. 740,525

12 Claims. (Cl. 18—57)

This invention relates to cellulosic structures, especially those of pellicular nature. More particularly, it relates to a method for producing flexible and durable cellulosic pellicles by treating the same with softening agents, and the products resulting from such treatment.

In the manufacture of cellulosic pellicles of the type precipitated from aqueous solutions, such as regenerated cellulose pellicles, including sheets or films, caps, bands, continuous tubing, artificial straw and the like, it has long been customary to incorporate into the cellulosic pellicle a softening agent in order to maintain it in a flexible condition. Such cellulosic pellicles, when free from a softening agent, are known to be quite brittle, and while a softener-free pellicle may find certain uses, a softened, and therefore flexible, sheet or film is much more generally useful. Heretofore, as softeners for cellulosic pellicles, the art has applied such substances as ethylene glycol, propylene glycol, diethylene glycol, formamide, glycerol, and the like, but of these, by far the most important is glycerol which has hitherto known no equal as a softening agent for producing flexible, transparent and durable cellulosic pellicles such as those of regenerated cellulose. Despite the numerous advances which have been made in the production and development of cellulosic pellicles, no softening agent has thus far been found which can be successfully applied as a substitute for glycerol without seriously restricting the utility of the product.

Glycerol is obtained commercially primarily as a by-product from the soap industry. As a by-product, the quantity may be limited and hence glycerol is subject to market fluctuations of supply as well as price. The glycols, mentioned above as useful cellulose softeners, are, for the most part, obtained synthetically and consequently they are relatively expensive. For an industry consuming large amounts of these materials, therefore, the development of less expensive equivalents or means for reducing the consumption of expensive materials will lead to marked economies in production.

It is therefore an object of this invention to provide a new and useful method for producing softened cellulosic materials possessing desirable physical properties.

It is a further object of this invention to provide cellulosic materials having a softening agent associated therewith, which softening agent will not interfere with any subsequent treatment of the cellulosic pellicles such as the application of surface coatings, ink, coloring matter, adhesives, or the like.

It is a still further object of this invention to provide a rigid, flexible, transparent, durable cellulosic pellicle, such as a sheet, film or tube of regenerated cellulose, in which the softening agent consists in part of a water soluble nitrogen-containing compound selected from the group consisting of solid amides, compounds containing condensed or heterocyclic nuclei of amide character, and hydroxyalkyl derivatives of ammonia.

Other objects of the invention will appear hereinafter.

By the term "rigidity" or its equivalent, as used herein, is meant that property which is the opposite of limpness, in other words, rigidity in the sense that the pellicle can be advanced in a wrapping machine or similar apparatus without curling, crumpling, or otherwise fouling the machine.

The term "durability" is used to define resistance to shock or rough handling. Thus, for example, bags may be fabricated from the pellicles and filled with some standard material such as a certain weight of dried beans and the package sealed, whereupon the durability may be measured against a known standard by tumbling the package under standard conditions and noting the resistance to breakage of the wrapper.

The objects of this invention can be attained in general by treating a cellulosic pellicle, such as regenerated cellulose, with a mixed softening agent, such as, for example, carbamide and glycerol, removing the excess softening agent therefrom, and drying the pellicle so treated. For convenience, the invention will be described in terms of the use of carbamide in this capacity, but it is to be understood that other substances of the classes mentioned above can also be used and this will be more specifically discussed hereinafter.

As a base, the invention contemplates the use of any cellulosic structure, particularly of pellicular nature such as a sheet or film, artificial straw, cap, band, or continuous tube, such as may be obtained by the coagulation and/or regeneration from an aqueous cellulosic dispersion in accordance with the procedure customary to the art. Thus, the invention comprehends the use of regenerated cellulose pellicles such as may be obtained from the viscose or cuprammonium processes, glycol cellulose, cellulose glycollic acid, lowly esterified or lowly etherified cellulose derivatives where there is only one ether or ester group associated with several cellulose units, and other

cellulosic structures of similar character. Similarly, various types of paper, especially of the "glassine" type may be used as base materials. Sheets of albuminous materials including gelatin, casein, or the like, may also be used. As a matter of convenience, the invention will be described in terms of its application to the softening of regenerated cellulose pellicles such as those sheets or films of regenerated cellulose which are suitable for use as wrapping tissues, it being understood that the scope of the invention includes any of the other bases set forth above and that the invention is equally applicable thereto.

In the manufacture of regenerated cellulose sheets or films, as for example by the viscose process, the cellulosic dispersion is cast through suitable apparatus into coagulating and/or regenerating baths from which it is finally obtained in the form of a continuous cellulosic sheet which is customarily led in a continuous manner through a series of purifying, bleaching and washing operations. Just prior to the drying operation which is also usually continuous and coordinated with the casting operation, the film is passed through a bath containing a softening agent in such concentration that after the excess liquid has been removed from the surface of the sheet by suitable squeeze rolls and the excess moisture removed by passage through the drier, the final sheet can be wound up in a continuous fashion and will contain an appropriate, predetermined amount of softening agent. The commercially available regenerated cellulose film contains approximately 4–8% moisture and depending upon the particular uses to which the product is destined, the softening agent, usually glycerol, may vary from about 8–25%, based on the combined weight of the cellulose and softening agent in the sheet.

Carbamide alone shows some ability to act in the capacity of a softening agent for regenerated cellulose and this property is also a characteristic of the equivalents for carbamide mentioned herein. Carbamide is, however, a solid material at ordinary temperatures and if an attempt is made to add enough carbamide to a regenerated cellulose pellicle to exert satisfactory softening action, the carbamide will crystallize out on the pellicle, causing undesirable opaqueness of the product. The carbamide equivalents mentioned, being solids also at temperatures at which the resulting product may be used, exhibit the same properties.

In accordance with the invention, however, it has been found that carbamide can be used successfully as a softening agent for cellulosic pellicles if it is used in admixture with softening agents of the prior art such as glycerol. Its combination with glycerol, for example, results in improved softening action which is surprisingly greater than would be expected normally from the mere addition of one softening agent to another. While it might be expected that the mixture of two softening agents would result in a softening action intermediate the softening action of either and proportionate to the relative amounts of each, it has been found that a large proportion of carbamide can be used with glycerol to secure highly satisfactory products and by appropriately adjusting the amount of total softener, a regenerated cellulose film containing, for example, a quantity of carbamide and 6% glycerol can be obtained which will have the physical properties and characteristics of a regenerated cellulose pellicle containing about 14% of glycerol alone as a softening agent.

In the preferred embodiment of the invention, a mixed softener comprising the carbamide and glycerol in a ratio of 2:1 can be used to good advantage, but more or less of the carbamide can be used as conditions demand and mixtures containing equal parts of carbamide and glycerol or even smaller amounts of carbamide will be found to serve useful purposes. Since the glycerol is the more expensive, it is obviously advantageous to use as much of the carbamide as is consistent with satisfactory results and it has been found that the preferred ratio of 2 parts carbamide to each part of glycerol offers economic as well as practical advantages.

The control of the relative amounts of carbamide and glycerol which will be deposited in the regenerated cellulose film is rendered simple by virtue of the fact that they are absorbed by the film from the treating bath in approximately the same proportion in which they are found in the bath itself. Thus, for example, if the treating bath contains the carbamide and glycerol in a ratio of 2:1, the final regenerated cellulose film will contain these ingredients in substantially the same ratio.

The total amount of softener in the film is controlled primarily by the total amount of softening agent in the treating bath; the film thickness, rate of passage through the bath temperature of the bath, etc. may also contribute thereto to a certain extent. The regenerated cellulose pellicle, upon reaching the treating bath, is in a highly swollen and hydrated condition and usually the cellulose of the pellicle is associated with 300% or more of water. This highly swollen and wet pellicle, usually referred to as the gel sheet, is impregnated with the treating bath and because of the large amount of water associated with the cellulose, it is apparent that the removal of this water during the drying operation will concentrate the softening agent with respect to the cellulose content of the pellicle. Thus it is that if a regenerated cellulose pellicle containing about 15% total softener is desired as a final product, the concentration of softener in the treating bath will be adjusted to approximately one-third that value, or about 5%. This is true when the softening agents are, like carbamide and glycerol, substantially non-volatile and are not vaporized during the drying operation. It is obvious that if a mixed softener is used, the components of which are appreciably volatile during the drying operation, then the softener concentration in the treating bath must be increased sufficiently to compensate for the loss thereof during the drying step.

The following examples will illustrate the practice of the invention, but it is to be understood that they are in no way limitative of the principles of the invention.

Example I

A sheet or film of gel regenerated cellulose, in which the final dry thickness will be about 0.0009", is immersed in or drawn through an aqueous bath containing a mixture of carbamide and glycerol, the concentrations of the softening agents being adjusted so that the final dried product will contain about 6.3% moisture, 11.8% carbamide and 5.9% glycerol based on the combined weight of cellulose and softener in the film. The sheet or film is allowed to remain in contact with the bath until thoroughly impregnated whereupon it is removed from the bath,

the excess liquid drained off or removed by suitable squeeze rolls, blotters, or the like, when the film can be dried in the usual manner down to the final moisture content indicated above. The final film thus contains about 18% total softener of which about 12% is carbamide, based on the combined weight of cellulose and softener. When tested at a relative humidity of about 35% (24° C.) or even at relative humidities as low as 15–22% at ordinary temperatures, the durability of the film is found to be at least equal to that of a similar regenerated cellulose film softened with about 14% glycerol alone.

Example II

A sheet or continuous film of gel regenerated cellulose such that the final dry thickness will be about 0.0012" is treated in the manner described in Example I, using, however, a treating bath having a composition capable of providing a final film containing about 6.3% moisture, 13.4% carbamide and 6.7% glycerol. In this case the final product will be equal to or better than a similar regenerated cellulose sheet or film bearing 15–16% glycerol alone as softener, insofar as its physical properties are concerned, including transparency, flexibility and durability under varying conditions.

It is to be noted that in the above examples the ratio of carbamide to glycerol in the treating bath is approximately 2:1. It is not necessary to use this preferred ratio in the practice of the invention, but, depending on the properties desired in the final film, more or less glycerol can be combined with the carbamide in the softener mixture. This can be illustrated at least in part by the following examples of treating baths which can be used in the manner described, as in Example I.

Example III

	Percent by weight
Glycerol	2.5
Carbamide	3.75
Water	93.75

Carbamide to glycerol ratio about 1.5:1.

Example IV

	Percent by weight
Glycerol	2.5
Carbamide	2.5
Water	95.0

Carbamide to glycerol ratio about 1:1.

Example V

	Percent by weight
Glycerol	3.1
Carbamide	1.9
Water	95.0

Carbamide to glycerol ration about 0.6:1.

Example VI

	Percent by weight
Glycerol	4.0
Carbamide	1.0
Water	95.0

Carbamide to glycerol ratio about 0.25:1.

Sheets or films of gel regenerated cellulose treated with any of the baths described in Examples III–VI inclusive in accordance with the procedure outlined in Example I will show physical characteristics substantially equal to those of a similar regenerated cellulose sheet treated with a softener bath containing 5% of glycerol alone, (that is, a final film containing about 15% glycerol), especially when the physical properties include transparency, flexibility, rigidity, durability, elongation and the like.

Regenerated cellulose sheets or films softened with mixtures of carbamide and glycerol are always superior in physical characteristics to a similar film provided with a quantity of glycerol alone equivalent to the glycerol in the mixture. They are superior also to a similar film softened by carbamide alone in an amount equivalent to the total mixed softener and they are also surprisingly superior to what might be expected through the use of a mixed softener. The following example will illustrate some of these points.

Example VII

A sheet or continuous film of gel regenerated cellulose similar to that of Example I is treated in the manner described in Example I, using, however, a treating bath of the following approximate composition:

	Percent by weight
Glycerol	2.5
Carbamide	1.9
Water	95.6

The ratio of carbamide to glycerol in this example is approximately 0.76:1. The film obtained will contain total softener in the amount of about 13% based on the combined weight of the cellulose and softener, and it will be superior in its physical properties to a similar regenerated cellulose film which would be obtained by treatment with a bath containing 2.5% glycerol alone, or even a bath containing 4.4% carbamide alone.

All of the above examples have been set forth in terms of a sheet or film of gel regenerated cellulose. Obviously, this is the more practical way of practicing the invention since the softening agent is customarily incorporated into the sheet or film while the latter is in the gel state and during the normal course of manufacture. Obviously, if one desires to impregnate an already dried regenerated cellulose film with a mixed softener of the character described, it is possible to rewet the dried film so as to render it highly swollen whereupon it may be treated with treating baths similar to those described but of composition suitable for obtaining the final product desired. In the same way, any of the sheets set forth as equivalent to regenerated cellulose sheets can be substituted in the specific examples.

The following example illustrates the method employed when a relatively volatile cellulose softener is admixed with carbamide and compensation is made for loss during the drying operation.

Example VIII

A sheet or continuous film of gel regenerated cellulose such that the final dry thickness will be about 0.0009", is immersed in or passed through a treating bath of the following approximate composition:

	Percent by weight
Carbamide	2.88
Ethylene glycol	4.32
Water	92.80

In this bath the ratio of carbamide to ethylene glycol is about 1:1.5. The film is treated as described in Example I and yields a final product containing about 6.3% moisture, 11.5% of carbamide and 11.5% of ethylene glycol. The ratio of carbamide to ethylene glycol in the dried film is thus about 1:1, the amount of ethylene glycol

having been decreased by loss during the drying operation. The dried film is subsequently provided with a surface coating which may be of any type desired. Thus, for example, it may be provided with a moistureproofing coating which may conveniently contain a cellulose derivative, a plasticizer, a resin or blending agent, and a moistureproofing agent such as a wax or wax-like material. The surface coating in this case serves the double purpose of providing a moistureproof product and of preventing loss by evaporation of the relatively volatile ethylene glycol. Even when tested under such drastic conditions as described in Example I, the product is transparent, flexible and more durable than a similar film softened with 15% glycerol alone or 23% carbamide alone. In this example, if carbamide alone were used as the softener in amount equal to the total mixed softener, the product would be very hazy because of the crystallization of the carbamide. This undesirable effect is avoided by using the mixed softener.

It is obvious that in the above examples the concentration of total softening agent in the treating bath may be suitably varied according to the base being treated in order that the final product will have the appropriate amount of softener.

The major portion of the discussion and the specific examples have been limited to the use of carbamide as a softening agent to which glycerol may be added. The invention, however, is not limited to carbamide, but includes numerous other substances of the type to be described hereinafter. Obviously, to serve as an equivalent for carbamide, a substance must be soluble in water; preferably it should possess a normally low vapor pressure in order that it may not be lost in appreciable quantities during the drying operation; it should be substantially odorless and lack of taste is desirable unless the softened pellicle is provided with a surface coating, in which case a certain amount of characteristic taste can be tolerated, for the coating will seal the softener into the base pellicle. It is, of course, possible to use a substance which has a slightly sweet taste, or at any rate one which is no more objectionable from the odor and taste viewpoint than glycerol itself which is an acceptable softener when used alone. The softener should be such that when incorporated into the pellicle it will be substantially clear and colorless and approximately neutral.

It has been found that substances capable of fulfilling the requirements of the invention include those which may be selected from the group consisting of solid, water-soluble amides, compounds containing condensed and/or heterocyclic nuclei of amide character, and hydroxyalkyl derivatives of ammonia. As specific substances belonging to the first classification may be mentioned acetamide, glycol amide, oxamide, succinamide, monomethyl carbamide, p-phenytyl carbamide and the like. As substances which may be considered as falling in the second classification may be mentioned cyanuric acid, melamine, hexamethylenetetramine and p-toluene sulfonamide. As representative members of the third class may be mentioned triethanolamine and homologues thereof such as tripropanol- or tributanolamine. As substances which may be considered as falling in more than one of the classes mentioned we may include dicyandiamide and thiocarbamide.

The invention has also been described in terms of the use of glycerol in combination with carbamide or its equivalents. It is to be understood that other similar cellulose softeners may be substituted for the glycerol and among those may be mentioned ethylene glycol, diethylene glycol, triethylene glycol, formamide, and other substances known to the art as softeners for cellulose structures.

It is also to be understood that various mixtures of the newly described softening agents may be employed with single softeners of the prior art or with mixtures of the latter, depending upon the type of final film desired and the purposes for which the film is to be used.

If a colored cellulosic pellicle is desired, it may be obtained in any of the ways commonly known in the art including the passage of the sheet or film through a bath containing a suitable dyestuff. If desired, the dyestuff may be added to the bath used for introducing the softening agent. In the same way, after the film has been treated with the softening agent, it may be subjected to any of the customary after-treatments such as sizing or coating, or the like, which may be customarily given to cellulosic pellicles of the type described in just the same manner that a glycerol softened regenerated cellulose film, for example, may be treated.

The instant invention offers numerous advantages over the prior art means for softening cellulosic pellicles. Since the newly described softening agents are substantially solid substances at ordinary temperatures, the control of concentrations used for treating baths is greatly simplified. Because of their crystalline nature, the softening agents are available in highly purified condition and, consequently, improve the quality of the final product. They can be obtained synthetically at a very low cost in comparison to the cost of known softeners, and they are available in unlimited quantity independent of a natural source. The invention, operated in its preferred form and using a mixture of carbamide and glycerol in the ratio of 2:1 enables the manufacturer to effect considerable economies, for example, in the softening of regenerated cellulose film because of the considerably lower cost of the carbamide as compared with the glycerol. The use of the newly described softening agents results in a product having improved physical characteristics, particularly improved transparency, flexibility, durability and the like.

The mixed softener set forth by this invention has been described in terms of its use in connection with the softening of cellulosic pellicles, but it should be understood that such mixed softeners are useful in other roles such as those normally played by such substances as glycerol.

Since it is obvious that various changes and modifications may be made in the above description without departing from the nature and spirit thereof, it is to be understood that the invention is not to be limited thereto except as set forth in the appended claims.

I claim:—

1. In a method for the production of transparent, flexible, durable pellicles the steps comprising forming a thin pellicle from an aqueous alkaline cellulosic dispersion and coagulating the same in an acid coagulating bath, and treating said pellicle with a solution containing, as a softener for said pellicle, a water-soluble amide

which is solid at room temperature and a substance taken from the group consisting of glycerol, ethylene glycol, diethylene glycol and triethylene glycol.

2. In a method for the production of transparent, flexible, durable pellicles, the steps comprising forming a thin regenerated cellulose pellicle from an aqueous cellulosic dispersion, and treating said pellicle with a solution containing, as a softener for said pellicle, a water-soluble amide which is solid at room temperature and a substance taken from the group consisting of glycerol, ethylene glycol, diethylene glycol and triethylene glycol.

3. In a method for the production of transparent, flexible, durable pellicles, the steps comprising forming a thin pellicle from an aqueous alkaline cellulosic dispersion and coagulating the same in an acid coagulating bath, and treating said pellicle with a solution containing, as a softener for said pellicle, a water-soluble amide which is solid at room temperature and glycerol.

4. In a method for the production of transparent, flexible, durable pellicles, the steps comprising forming a thin pellicle from an aqueous alkaline cellulosic dispersion and coagulating the same in an acid coagulating bath, and treating said pellicle with a solution containing, as a softener for said pellicle, carbamide and a substance taken from the group consisting of glycerol, ethylene glycol, diethylene glycol, and triethylene glycol.

5. In a method for the production of transparent, flexible, durable pellicles, the steps comprising forming a thin pellicle from an aqueous alkaline cellulosic dispersion and coagulating the same in an acid coagulating bath, and treating said pellicle with a solution containing, as a softener for said pellicle, carbamide and glycerol.

6. In a method for the production of transparent, flexible, durable pellicles, the steps comprising forming a thin regenerated cellulose pellicle from an aqueous cellulosic dispersion, and treating said pellicle with a solution containing, as a softener for said pellicle, carbamide and glycerol.

7. A flexible, durable, transparent cellulosic pellicle produced from an aqueous alkaline cellulosic dispersion and coagulated in an acid coagulating bath, containing a softener therefor composed of a water-soluble amide which is solid at room temperature and a substance taken from the group consisting of glycerol, ethylene glycol, diethylene glycol, and triethylene glycol.

8. A flexible, durable, transparent cellulosic pellicle produced from an aqueous cellulosic dispersion, comprising a regenerated cellulose base and a softener therefor composed of a water-soluble amide which is solid at room temperature and a substance taken from the group consisting of glycerol, ethylene glycol, diethylene glycol, and triethylene glycol.

9. A flexible, durable, transparent cellulosic pellicle produced from an aqueous alkaline cellulosic dispersion and coagulated in an acid coagulating bath, containing a softener therefor composed of a water-soluble amide which is solid at room temperature and glycerol.

10. A flexible, durable, transparent cellulosic pellicle produced from an aqueous alkaline cellulosic dispersion and coagulated in an acid coagulating bath containing a softener therefor composed of carbamide and a substance taken from the group consisting of glycerol, ethylene glycol, diethylene glycol and triethylene glycol.

11. A flexible, durable, transparent cellulosic pellicle produced from an aqueous alkaline cellulosic dispersion and coagulated in an acid coagulating bath containing a softener therefor composed of carbamide and glycerol.

12. A flexible, durable, cellulosic structure produced from an aqueous alkaline cellulosic dispersion and coagulated in an acid coagulating bath containing a softener therefor composed of a solid amide and a substance taken from the group consisting of glycerol, ethylene glycol, diethylene glycol, and triethylene glycol.

FREDERICK C. KING.