Sept. 2, 1941. F. P. ALLES 2,254,200

CELLULOSIC SHEETING

Filed March 1, 1939 2 Sheets-Sheet 1

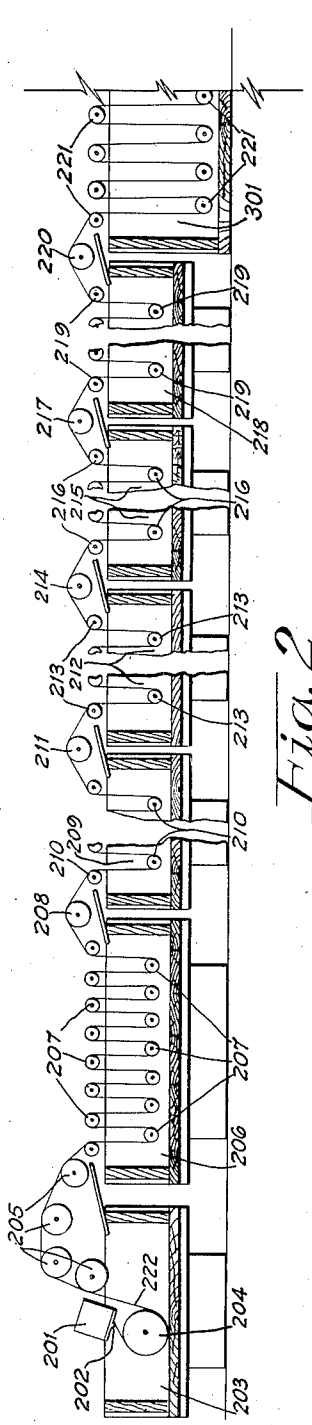


Fig. 2

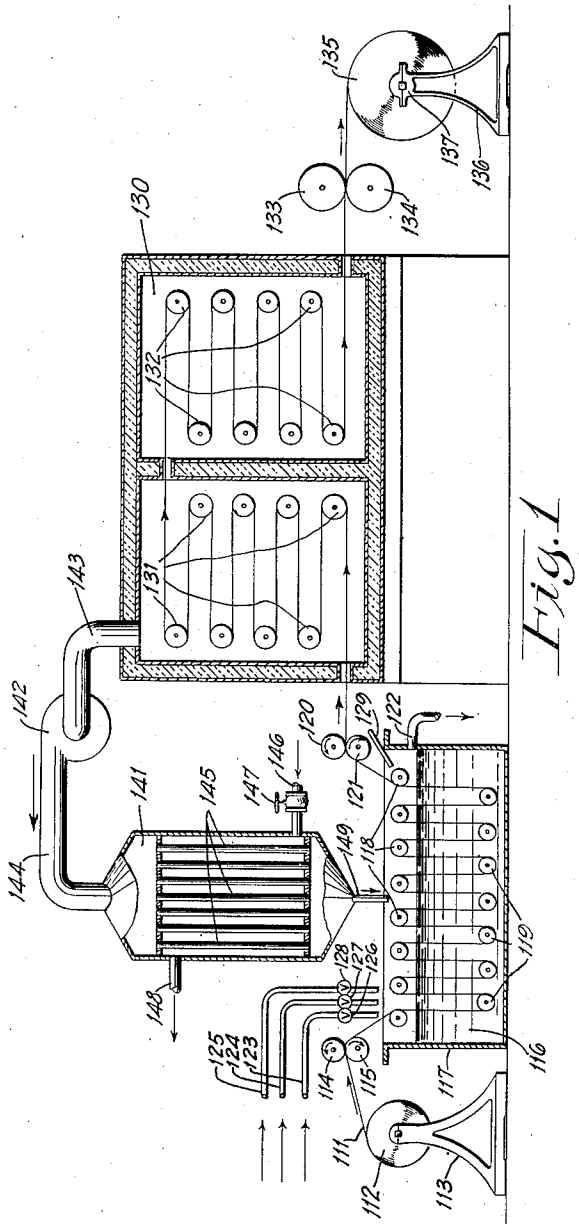


Fig. 1

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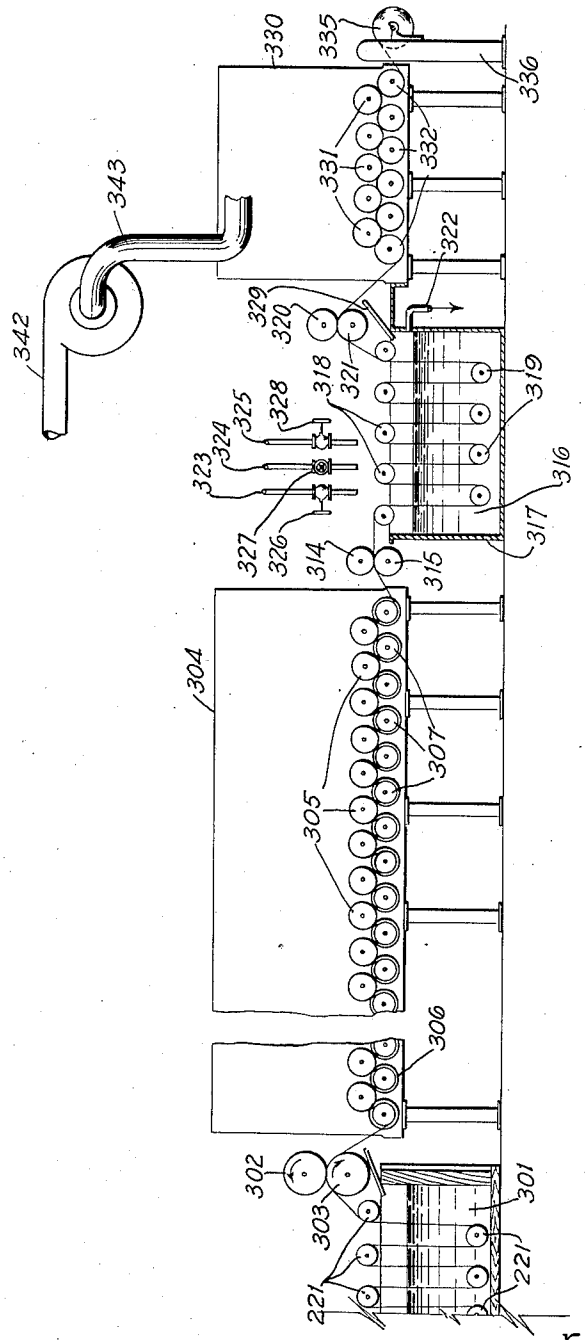


Fig. 3

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Patented Sept. 2, 1941

2,254,200

UNITED STATES PATENT OFFICE

2,254,200

CELLULOSIC SHEETING

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Application March 1, 1939, Serial No. 259,115

17 Claims. (Cl. 18—57)

This invention relates to the treatment of non-fibrous sheets and films which are subject to shrinkage during drying, and more particularly to the preparation of a wrapping material which does not shrink with age. It especially appertains to the treatment of regenerated cellulose sheeting cast from viscose for the purpose of eliminating permanent shrinkage.

In the manufacture of sheets and films of regenerated cellulose, it is customary to cast a film into a coagulating and/or regenerating bath. The film so cast is then treated to prepare it for commercial use. Such treatments, when the film is cast from viscose, ordinarily include desulfuring, bleaching and softening. In carrying out these treatments the coagulated film is generally passed through baths in which the desired result is effected. A washing bath may follow each of the coagulating, desulfuring and bleaching baths, and in some instances an additional regenerating bath and an auxiliary washing bath may be inserted after the bath in which the film is coagulated. Usually the last bath through which the film passes prior to drying is one in which glycerinating (softening) takes place. After passing through the drying apparatus, the film is usually wound up into mill rolls.

Ordinary drying reduces the moisture content of the film (which is ordinarily about 30–40 parts per 10 parts of cellulose as it leaves the softening bath) to about 0.6–0.8 part, which is the usual moisture content of mill roll material. In losing this moisture the film tends to shrink to a great extent, thus diminishing the area of the regenerated cellulose film and producing puckers and wrinkles. In order to prevent puckers, wrinkles and loss of area during the drying process, it is customary to employ a drying apparatus comprising a series of rotating heated rollers over which the film passes, and to keep the film under marked tension during its passage over said rollers.

Film so produced, however, attains its greater area and plane surface at the sacrifice of other desirable properties. Such film suffers a loss in dimensions with age and use. This loss in dimension, or irreversible shrinkage, is commonly referred to in the art as "permanent shrinkage," to distinguish it from reversible changes in dimension which presumably result solely from gain or loss in moisture in or by the sheet. The term "deformation" is ordinarily employed to describe or define the reversible changes in dimensions which a sheet of regenerated cellulose undergoes with changes in its internal moisture content.

The release of internal strains (which at present is believed to be the reason for and to result in permanent shrinkage) takes effect more quickly on increasing the moisture content of the film, but also takes effect during other moisture changes or at constant moisture content.

A method previously proposed for preparing regenerated cellulose film free from permanent shrinkage involves drying the film under tension in the conventional manner until the moisture has been reduced to approximately 6 parts per 10 parts of cellulose (60%), and thereafter completing the drying to the desired extent while supporting the film upon heated rolls at a very low tension so as to allow shrinkage in both machine and transverse directions. The characteristics and advantages of a film free from permanent shrinkage are disclosed in United States Patent No. 2,115,132. Film with a uniform moisture content of not less than 6 parts per 10 parts of cellulose is in a somewhat plastic condition and does not contain internal strains such as would result in permanent shrinkage.

Obviously the aforementioned drying process cannot be applied directly to film already completely dried by ordinary drying methods. In order to utilize such a process for reducing the permanent shrinkage of a previously dried film, it is necessary to remoisten the same to bring it to the strain-free condition, before applying what may for convenience be called the compensating drying treatment. Although remoistening has been accomplished by passing the dry film through a chamber having an atmosphere of relatively high humidity and by passing the dry film through a water bath, neither process is commercially practical, and up to the present time no satisfactory method has been proposed. The first of these procedures is not satisfactory because the time necessary to bring the moisture content up to 6 parts per 10 parts of cellulose is comparatively long in relation to the high speeds obtainable on a drier of the compensating type (even when a relative humidity in the neighborhood of 95% is employed). In the alternative water bath method the film absorbs water so rapidly as it passes through the bath that about 18 parts of moisture per 10 parts of cellulose are taken up before the degree of absorption can be satisfactorily controlled. This amount of moisture is much higher than that required for the removal of strains set up during the drying of the gel structure, and as a re-

sult would, if used, necessitate the use of an undesirably large drier section of a compensating type.

It has been observed that film dried upon the ordinary drier to the extent that the over-all moisture content is approximately 6 parts per 10 parts of cellulose is generally a product in which the moisture is by no means evenly distributed throughout the width of the film. The thinner marginal portions are drier than the relatively thicker central portions, and wide bands or streaks appear in the film. Since the dried film is usually cut into small sections, such as strips, for ultimate use, this lack of uniformity is quite disadvantageous. The said sections may be from portions too dry, so that they exhibit permanent shrinkage or other objectionable characteristics.

This invention has for an object the production of transparent, smooth and glossy regenerated cellulose sheets or films having substantially no permanent shrinkage and being free from wrinkles and other surface irregularities. Another object was to produce regenerated cellulose sheet wrapping tissue having great durability, while being free from puckers and like distortions. A still further object was to produce regenerated cellulose film of any given (definite) moisture content, in which the distribution of the moisture throughout the film is substantially uniform. The production of cellulosic film containing little or no softener and having the aforementioned desirable characteristics, was also an object of the invention. The production of regenerated cellulose film having any desired or given moisture content was yet another object of the invention. A general advance in the art, and other objects which will appear hereinafter, are also contemplated.

It has now been found that a smooth, regenerated cellulose film, exhibiting substantially no permanent shrinkage, can be prepared by subjecting a sheet or film of regenerated cellulose to a treatment in a bath comprising water and a non-aqueous volatile water miscible liquid, such as ethanol, and thereafter drying the sheet or film under tension low enough to permit the film to shrink freely in all directions, but high enough to prevent the formation of unsightly blemishes.

In a preferred embodiment of the invention, regenerated cellulose sheet which has been dried (or which has had its moisture decreased to the extent that it contains not more than 6 parts of moisture for each 10 parts of cellulose) is passed through a bath containing water and ethyl alcohol. Preferably this is done with a bath in which the components are in such proportions that a film or sheet with a moisture content between 60% to 80%, based upon the cellulose content, results. For efficient operation the excess solution is removed from the surface of the film (for example, by means of squeeze rolls, doctor knives or the like) before passing the sheet to the compensating drier, in which it is dried under tension sufficient to prevent the formation of an undesirably irregular surface, but insufficient to prevent free shrinkage in both lengthwise and widthwise directions.

From the following description and specific examples, in which are disclosed certain embodiments of the invention as well as details of what is believed to be the best mode for carrying out the invention, it will be apparent how the foregoing objects and related ends are accomplished. The written description is amplified by the accompanying drawings, in which:

Figure 1 is a side view partly in section of one form of apparatus adapted to the practice of the invention; and

Figures 2 and 3, when placed end to end (Figure 3 following) represent an alternative arrangement for carrying out the invention. In these two figures (2 and 3) a complete film-casting machine, together with the new treating (impregnating) tank and drier combination, are shown.

Similar characters refer to similar parts throughout the drawings.

Referring now to the drawings, Figure 1 shows a dry, regenerated cellulose film 111 being withdrawn from a mill roll 112, which is mounted upon a support 113 in such a manner that it may be readily unwound. The film passes from the mill roll through rollers 114 and 115, which are positively driven in the direction indicated by the arrows thereon, and which have the dual function of withdrawing the film from the mill roll and feeding it to the bath 116. The treating liquid is contained in a suitable tank 117, which also contains a series of upper rolls 118 and a series of lower rolls 119. The film 111, in passing about these rolls 118 and 119, as shown in the drawings, takes up the desired amount of the treating fluid, and thereafter passes up out of the tank between positively driven squeeze rolls 120 and 121, which rotate in the direction of the arrows thereon. These squeeze rolls have a triple function, namely, that of withdrawing the continuous film from the impregnating bath, removing the excess impregnating solution, and feeding the film to a drier.

An overflow line 112 determines the level of the liquid in the tank 117. Feed lines 123, 124 and 125, having valves 126, 127 and 128, respectively, are provided for the purpose of supplying additional materials to the impregnating bath. The separate feeds for the different liquids enable the composition of the bath 116 to be kept constant even though the percentage composition of the mixture returned from the condenser 141 (described later in detail) may be different from that of the bath. The tank 117 is provided with a drain board 129 to return the excess solution from the squeeze rolls 120 and 121 to the impregnating bath.

The wet film (preferably having a moisture content of 40%–100%), after leaving the squeeze rolls 120 and 121, passes into a drier generally indicated at 130. This drier has therein a series of rolls 131 and 132, over which the film passes during its passage through. These rolls may be mounted to rotate freely or may be positively driven. In case they are positively driven suitable arrangements (employing conventional apparatus or the special devices of United States Patent No. 2,115,132) may be made for regulating the speed of the rollers individually so that they may be driven at diminishing speeds toward the end of the drier, if desired. In an alternative form of apparatus the rolls may be of progressively decreasing diameter, so that the film in going from the wet end to the dry end may pass over rollers driven at a decreasing peripheral speed while having a constant angular speed (thereby avoiding a special control for each roller). Each of these arrangements accomplishes the purpose of permitting the film to shrink lengthwise as it is dried. Upon leaving the drier, the film passes through positively driven rolls 133

and 134. These rolls withdraw the film from the drier, and feed it to a wind-up roll 135, mounted on a support 136. The shaft or axis core 137 of the wind-up roll is driven in any desired manner, as for example, by a friction clutch.

The mill roll 112 may be braked to secure even feeding of the material to the pull rolls 114 and 115.

In the various series of pull rolls, namely, 114 and 115, 120 and 121, and 133 and 134, one of the rollers may be journaled to rotate freely instead of being positively driven. In such an arrangement it is preferred to have the upper roll rotate freely.

Since the impregnating (humidifying) bath of this invention contains valuable organic compounds, it is necessary to arrange for their recovery if efficient and economical operation is desired. With this in mind, a recovery apparatus, including a condenser 141 and a suction device 142, are connected to the drier by a vapor removing duct 143. Pipe 144 connects the suction device and the condenser. The condenser illustrated is of the conventional type, having the tubes 145, in which the valuable organic liquid is condensed because of the refrigeration fluid which circulates on the outside thereof. The refrigerating fluid (brine, for example) enters the condenser through a line 146 having a valve 147, and leaves the condenser through line 148. The condensed solvent, or impregnating liquid, drains from the tubes 145 into the bottom of the condenser, from where it flows through pipe 149, back into the tank 117.

Although at present it seems preferable to operate with previously dried film, it is possible to obtain very desirable results with film which has never been dried, for example, a gel film from the wet end of a casting machine. In Figures 2 and 3 there is shown an arrangement for treating such film according to this invention.

In Figure 2 there is shown a casting hopper 201 (of a conventional film-casting machine) having an extrusion orifice 202 in the form of a narrow slit, through which viscose is extruded into a coagulating bath 203. The coagulated film 222 passes around a premier roll 204, and out of the coagulating bath over guide rolls 205, into a washing bath 206. A series of rolls 207 guide the film through this bath. A guide roll 208 passes the film from the washing bath to a desulfuring bath 209, through which it travels about a series of rolls 210. The film thereupon leaves the desulfuring bath, passes over another guide roll 211, into another washing bath 212, in which its course of travel is controlled by rolls 213. After this second washing a guide roll 214 conducts the film into a bleaching bath 215. Rolls 216 provide a suitable lengthening of the course of travel of the film in this bath, and feed the film therefrom to guide roll 217, which conducts it to another washing bath 218. This bath, like the preceding baths, is provided with guide rollers, in this instance indicated by the numerals 219. Upon leaving this washing tank, the film passes over another guide roll 220 on to a series of rolls 221 mounted in a softening bath 301 (see both Figures 2 and 3). Suitable drain board, similar to that shown at 129 in Figure 1, are provided as indicated in the drawings.

From the softening bath (which usually contains glycerin as a softening agent), the film is withdrawn by squeeze rolls 302 and 303. The squeeze rolls remove the excess softening solution and pass the film to a conventional drier 304. In this drier there are a series of freely mounted upper rolls 305 which are driven by means of tires 306 on a series of lower rolls 307. The lower rolls are positively driven, and the tires on the ends thereof serve to space them from the freely mounted rolls 305. This drier does not, in ordinary practice, completely dry the film, but merely reduces its moisture content to about 60% to 100%, based on the cellulose.

The film in this condition passes from the drier through pull rolls 314 and 315, which feed it to an impregnating bath 316 in a tank 317. This bath corresponds to the bath 116 in tank 117 in Figure 1. This tank, like the tank in Figure 1, is provided with lines 323, 324 and 325, having valves 326, 327 and 328, respectively, for the purpose of adding additional liquid to the bath. There are also corresponding squeeze rolls 320 and 321, an overflow 322, and a drain 329. The upper and lower rolls in this tank are indicated by the numerals 318 and 319, respectively. From the rolls 320 and 321 the film passes a drier 330 containing compensating drier rolls of a type previously described. The arrangement of the rolls in this drier follows the arrangement in the drier 304 as to position and mode of operation. Preferably, the upper rolls 331 are driven by positively driven lower rolls 332, but a reversal of this mode of driving may sometimes be convenient. As was the case with the rolls 131 and 132 in Figure 1, these rolls may operate at a constantly decreasing speed. If desired, they may also operate at constant speeds and be of progressively decreasing diameter. In some instances both upper and lower rolls may be positively driven. After leaving the drier 330, the film is wound on a take-up roll 335, mounted on a support 336. A blower 342 removes the vapors from the final drier through a duct 343. The blower passes the vapors to a suitable recovery apparatus, such as that shown in Figure 1, or to some other form of recovery apparatus such as a bed of activated absorbent carbon.

Throughout the specification and claims the parts are given by weight.

Example I

A regenerated cellulose film, which had been dried in the conventional manner known to the art, was run through a bath containing 54% water, 38% ethanol, and 8% glycerol, at such a rate and with such a bath travel that the time of treatment was approximately 15 seconds. Before entering the bath the film, because of its mode of production, contained strains and was not free from permanent shrinkage. After leaving the bath the film was dried at low tension in both the machine and transverse directions, thereby allowing the sheet material to shrink freely. The film thus produced was found to be strain free and to exhibit substantially no permanent shrinkage.

Example II

A film, which had been dried by the method old in the art, containing strains and being capable of permanent shrinkage, was passed through a bath containing 54 parts of water, 38 parts of acetone and 8 parts of glycerol at such a rate that each portion of the film had a bath treatment of approximately 15 seconds. The film was then passed through a drier such as that shown in Figure 1 of the drawings, and dried therein at low tension in both lengthwise and

transverse directions. The tension was of such degree that the sheet was allowed to shrink freely during the drying. The film thus produced when tested was strain free and exhibited practically no permanent shrinkage.

Example III

A web of regenerated cellulose, after desulfuring, bleaching and washing according to processes well known in the art, was impregnated with glycerol to soften the same. It was thereafter partially dried by passing over heated rolls in an atmosphere of dry, warm air in an apparatus such as that disclosed on the left in Figure 3. Other methods of reducing the moisture content of film known to the art have also been satisfactorily employed. The dehydration of the film was continued until the moisture content was approximately 60% (6 parts of moisture per 10 parts of cellulose).

Tests showed that a section of the film from one bead (edge) to the other, having this over-all moisture content, did not have a uniform moisture content across the width of the film. This is generally the case because certain portions of the film are thinner than other portions, and as a result, tend to dry faster. Lack of uniformity is also contributed to on occasion by non-uniform application of heat. It has been found commercially impractical to secure distribution of heat across such drier rolls sufficiently uniform to completely avoid unevenness in drying. A web with an over-all moisture content of approximately 6 parts per 10 parts of cellulose produced as above described may frequently exhibit a range of moisture content between the dry and wet sections of between 7 parts and 3 parts of moisture per 10 parts of cellulose.

The film in the aforementioned stage in the drying cycle was removed from the heated rolls and passed through a tank such as that disclosed at 316 in Figure 3 containing 54 parts by weight of water, 38 parts by weight of ethyl alcohol, and approximately 8 parts of glycerol. The bath travel was so adjusted to the speed at which the web moved that the web was in contact with the solution for approximately 15 seconds. It was then withdrawn through the squeeze rolls, which removed the excess liquid, and passed on to drier rolls of the compensating type described in United States Patent No. 2,115,-132, issued April 26, 1938. While passing over these drier rolls the drying of the film was completed under very much reduced tension. The tension was sufficient to produce a smooth film. The film as it issued from the drier was substantially free from alcohol, and contained approximately 0.6 part of water and 1.4 parts of glycerol per 10 parts of cellulose. The alcohol which evaporated from the film was recovered from the atmosphere of the drier and returned to the treatment bath. Additional water and glycerin were added at the same time to keep the composition of the bath constant. When the film so produced was subjected to changes in humidity, reversible expansion and contraction resulted, but substantially no permanent shrinkage was observed.

Example IV

The water-alcohol-glycerol bath of Example III was replaced with a bath containing 54 parts of water, 38 parts of acetone and 8 parts of glycerol. Production of film in the manner described in Example III was continued, utilizing the new bath. The film so produced was free from permanent shrinkage.

Example V

In another run of the process described in Example III, a bath containing 54 parts of water, 38 parts of a 50–50 diethyl ether-ethyl alcohol mixture and 8 parts of glycerol was substituted for the bath previously described. The resulting film, when subjected to an atmosphere of 95% relative humidity at 35° C., and again returned to approximately ordinary room conditions of 35% relative humidity at 20° C., exhibited a permanent shrinkage of less than 1.0%.

Films in contact with baths such as those described herein very rapidly attain a moisture content suitable for compensating drying to avoid permanent shrinkage.

For safety reasons it is desirable that the bath mixture be such that an explosive gas mixture is not formed in the driers and condensers.

Baths of 60% ethanol-40% water and 50% ethanol-50% water have been used to secure special results. Treating baths containing 54% water give a film meeting the demands of industry for the major portion of regenerated cellulose film used at present.

Although the present invention has for convenience been described in terms of cellulose which has been regenerated from viscose, it will be understood that the procedures are equally applicable to cellulose which has been regenerated from the cuprammonium compound. Films of lowly etherified cellulose, lowly esterified cellulose, gelatin, casein, and the like, which have been produced in aqueous treating media and which therefore contain a large amount of water, the removal of which is necessary before the film is suitable for wrapping tissue, may be similarly processed with desirable results.

Desirable results are obtained by the treatment of film containing an opaquing agent (for example, a pigment such as titanium oxide) by the procedure above described. Other materials which are not clear and transparent may also be processed in accordance with this invention.

The films treated in accordance with the invention, whether clear or not, may be softened in the usual manner with any suitable softener. Glycerol is the most widely used softener, and is generally preferred for regenerated cellulose. Many other softeners which are well known in the art may be employed. Triethanolamine, ethanol-formamide, ammonium-sulfamate, ethylene-glycol, and the like, for example, may be employed with satisfactory results.

Although many water soluble or water miscible materials are available which will accomplish the purposes of this invention, it is preferred to use systems in which the non-aqueous component is readily volatile, particularly along with the water. Liquids boiling below, or not greatly above, the boiling point of water are especially attractive. With the systems described above, the additional component may be removed together with the water under the drying conditions which are encountered in conventional apparatus. Materials such as ethyl alcohol and acetone readily recommend themselves because of their low cost, high volatility and ease of handling. Such compounds as methanol, ethyl-methyl ketones and the like, and their related non-aqueous, volatile and water miscible materials also merit special mention.

The moisture content of the film may be accurately controlled over quite a large range by the

simple adjustment of the concentration or composition of the treating solution. In such a way it is possible to produce not only a film with low permanent shrinkage, but also (by a selection of the proper moisture content for the beginning of the compensating drying process) to produce a film having any desired or predetermined permanent shrinkage factor. Film with a definite permanent shrinkage may have many applications in the art, such as the wrapping of packages subjected to a known slowly varying environment over a long period of time. The present invention furnishes a simple and effective means for producing film of the highest quality for specific uses from film which would otherwise be unsuited to or useless for that purpose. For example, previously prepared film entirely unsuited for wrapping tissue can, by this invention, be converted to a valuable material for that purpose.

The alcohol, for example, will not when used alone relieve the permanent shrinkage strains. It seems to act more as a diluent for the water, thereby preventing the film (which can only take up a certain amount of liquid) taking up more than the desired amount of water.

As previously indicated, regenerated cellulose film with a moisture content of not less than 6 parts per 10 parts of cellulose is somewhat plastic, and if this moisture is uniformly distributed, no permanent shrinkage or internal strain exists. It follows that this is a most satisfactory moisture content at which to release the tension (to the extent that free shrinkage is possible) on the film during drying, and that it is a desirable moisture content at which to release internal strain in previously dried film (in which the permanent shrinkage is to be eliminated).

Some variation from this figure, so far as the release of tension is concerned, particularly on the higher moisture content side, is permissible (if the necessity for additional drier capacity, and other drawbacks mentioned earlier in the specification, are to be neglected). For example, if tension is released at a moisture content of about 18 parts per 10 parts of cellulose, the finished film, after completion of the drying, will not show undue loss in dimensions during drying. If the tension is not released until after the film reaches a moisture content of 4 parts per 10 parts of cellulose, the resulting permanent shrinkage in the finished film is still comparatively low. The preferred ranges may, however, be influenced by the factors in the manufacturing process, such as the kinds of cellulose or pulp used, the speed of drying, the temperature of drying, the amount and character of softener used, etc.

While it is not desired to limit the invention by theories, it is desired to explain it to the fullest possible extent so that it may be better understood. With this object in mind it may be pointed out that it now appears that the results obtained by this invention are due to the fact that film containing 6 parts of moisture per 10 parts of cellulose is sufficiently plastic to allow free adjustment of the cellulose micelles, thereby avoiding strains. The fact that film which is not restrained from shrinking during drying from this point down to the final condition of the film is substantially free from permanent shrinkage, supports this theory. Film dried in the ordinary manner, i. e., with marked tension, and which consequently has not been allowed to equalize or normalize itself during the corresponding period of moisture removal, has strains which are relieved extremely slowly under normal conditions, as manifested by a decrease in dimensions. The further fact that freshly prepared film capable of permanent shrinkage has its strains released when subjected to an atmosphere of 95% relative humidity (which is a very high relative humidity in practice), also supports the theory set out above. An atmosphere of 90% relative humidity brings about a moisture content of approximately 6 parts of moisture per 10 parts of cellulose, based on the weight of the dried film plus softener.

A finished film produced in accordance with this invention, if subjected to an atmosphere of 95% relative humidity and returned to normal conditions, will not have any substantial change in dimensions. Film dried in the ordinary manner and similarly treated, i. e., brought to a moisture equilibrium in an atmosphere of 95% relative humidity, exhibits a considerable loss in dimensions upon being returned to normal conditions.

For the purpose of measuring permanent shrinkage and defining the term "substantially no permanent shrinkage," a method has been evolved for reducing the strains in a finished piece of uncoated film and measuring the resulting changes in dimensions. The method is as follows: A sample of the finished film to be tested is allowed to come to equilibrium with respect to moisture content in an atmosphere of 35% relative humidity at a temperature of 75° F., and the dimensions then measured. The film is next placed in an atmosphere of 95% relative humidity at a temperature of 95° F. for a period of two hours, during which time substantially all of the permanent shrinkage is eliminated, since strains are more quickly relieved at high moisture contents of the film. The film is then subjected to a relative humidity of 0–5% at 95° F. for two hours. Finally, the film is brought back to the atmosphere of 35% relative humidity at 75° F., allowed to come to equilibrium with respect to moisture content, and again measured. The percentage decrease in dimensions between initial and final measurement is the amount of permanent shrinkage in the film. In the ordinary regenerated cellulose films of the prior art it amounted to about 3.5% to 4% in each direction on a rectangular piece of film, or a total of about 8%. For the purposes of this invention the term "substantially no permanent shrinkage" will mean a total permanent shrinkage, including both directions, of less than 2%, and preferably less than 1%.

Film produced in accordance with this invention has many advantages over prior art materials. It has greatly increased durability at average relative humidity and at low relative humidities and at low temperatures. It has superior gloss, thereby enhancing the appearance of the material. It is possible to store film manufactured according to this process for much longer lengths of time than was the case with the prior art materials, due to the fact that the present products do not buckle or exhibit "washboard" effects upon standing. Films of the present invention have much less tendency to stick together or cake under pressure, and elevated humidities, than do the ordinary films heretofore known. A stack of ordinary sheets and a stack of sheets manufactured according to this invention were subjected to relative humidities of 80% and a pressure of 1 pound per square inch. The stack of ordinary sheets stuck

together at the end of four days, while the stack of improved sheets did not stick together until the end of 17 days.

Packages wrapped with the material manufactured according to this invention have much less tendency to distort, buckle and collapse, especially when subjected to high humidity conditions and subsequently returned to normal condition. Laminated materials in which at least one of the plies comprises a sheet or film of regenerated cellulose manufactured according to this invention, for example, a laminated material comprising a sheet of heavy paper surface on one or both sides with an adhering sheet of regenerated cellulose, do not exhibit any appreciable buckling, curling, or wrinkling upon exposure to the atmosphere. Furthermore, the improved film of this invention does not exhibit the substantial gradual decrease in dimensions over a period of time characteristic of the film of the prior art, upon exposure to ordinary normal room atmospheric temperatures, pressures, and humidities.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. In the production of regenerated cellulose film having substantially no permanent shrinkage and which is smooth, glossy and free from wrinkles, the steps of treating a film of regenerated cellulose with an aqueous solution of a water miscible organic liquid of 40%–54% water content until the film contains 40% to 100% moisture, based on the cellulose content, and thereafter drying the treated film while maintaining it under tension sufficient to prevent the formation of wrinkles, puckers and like distortions, but insufficient to prevent free shrinkage in both lengthwise and widthwise directions.

2. The process of claim 1 when the water miscible organic liquid is ethanol.

3. The process of claim 1 when the water miscible organic liquid is a member of the group consisting of ethyl alcohol and acetone.

4. The process of claim 1 when the aqueous solution contains a softener such as glycerol.

5. The process which comprises maintaining a regenerated cellulose film having a moisture content not greater than 60%, based on the cellulose content, and which is not evenly distributed throughout the width thereof in a bath comprising essentially 54% water, 38% ethanol and 8% glycerol for 15 seconds, and thereafter drying the treated film while maintaining it under tension sufficient to prevent the formation of wrinkles, puckers and like distortions, but insufficient to prevent free shrinkage thereof.

6. The process of preparing a regenerated cellulose film having 60% to 80% moisture content, based on the cellulose content, which comprises treating a regenerated cellulose film of less than this water content with a water-water miscible organic liquid composition capable of raising the water content of the film to the desired value and forming a water content equilibrium therewith at the desired value.

7. In the production of regenerated cellulose film having substantially no permanent shrinkage and which is smooth, glossy and free from wrinkles, the steps of treating a film of regenerated cellulose with an aqueous solution of a water miscible organic liquid of 40%–54% water content until the film contains 60% to 80% moisture, based on the cellulose content, and thereafter drying the treated film while maintaining it under tension sufficient to prevent the formation of wrinkles, puckers and like distortions, but insufficient to prevent free shrinkage in both lengthwise and widthwise directions.

8. In the production of regenerated cellulose film having substantially no permanent shrinkage and which is smooth, glossy and free from wrinkles, the steps of treating long lengths of film of regenerated cellulose with an aqueous solution of a water miscible organic liquid of 40%–54% water content until the film contains 40% to 100% moisture, based on the cellulose content, by passing the film through a bath of the treating liquid, and thereafter drying the treated film while maintaining it under tension sufficient to prevent the formation of wrinkles, puckers and like distortions, but insufficient to prevent free shrinkage in both lengthwise and widthwise directions.

9. In the production of regenerated cellulose film having substantially no permanent shrinkage and which is smooth, glossy and free from wrinkles, the steps of treating a film of regenerated cellulose with an aqueous solution of a water miscible organic liquid of 40%–54% water content until the film contains 40% to 100% moisture, based on the cellulose content, and thereafter drying the treated film while maintaining it under tension sufficient to prevent the formation of wrinkles, puckers and like distortions, but insufficient to prevent free shrinkage in both lengthwise and widthwise directions, said water miscible organic liquid boiling below the boiling point of water.

10. In the producton of regenerated cellulose film having low permanent shrinkage and which is smooth, glossy and free from wrinkles, from dry regenerated cellulose film having internal strain and from regenerated cellulose film having a water content not greater than 60% unevenly distributed therein, the steps of treating the said starting material with an aqueous solution of a water miscible organic liquid of 40%–54% water content until the film contains 40% to 100% moisture, based on the cellulose content, to equally distribute the moisture content, and thereafter drying the treated film while maintaining it under tension sufficient to prevent the formation of wrinkles, but insufficient to prevent free shrinkage in both lengthwise and widthwise directions, the said water miscible organic liquid comprising acetone.

11. The process of preparing a regenerated cellulose film having 60% to 80% moisture content, based on the cellulose content, which comprises treating a regenerated cellulose film of less than this water content with a water-water miscible organic liquid composition capable of raising the water content of the film to the desired value and forming a water content equilibrium therewith at the desired value, said water miscible organic liquid boiling below the boiling point of water.

12. In the production of regenerated cellulose film having substantially no permanent shrinkage and which is smooth, glossy and free from wrinkles, the steps of treating a film of regenerated cellulose with an aqueous solution of a water miscible organic liquid of 40%–54% water content until the film contains 60% to 80% moisture, based on the cellulose content, and thereafter drying the treated film while maintaining it

under tension sufficient to prevent the formation of wrinkles, puckers and like distortions, but insufficient to prevent free shrinkage in both lengthwise and widthwise directions, said water miscible organic liquid boiling below the boiling point of water.

13. In the production of regenerated cellulose film having substantially no permanent shrinkage and which is smooth, glossy and free from wrinkles, the steps of treating long lengths of film of regenerated cellulose with an aqueous solution of a water miscible organic liquid of 40%–54% water content until the film contains 40% to 100% moisture, based on the cellulose content, by passing the film through a bath of the treating liquid, and thereafter drying the treated film while maintaining it under tension sufficient to prevent the formation of wrinkles, puckers and like distortions, but insufficient to prevent free shrinkage in both lengthwise and widthwise directions, said water miscible organic liquid boiling below the boiling point of water.

14. The process of preparing a regenerated cellulose film having 60% to 80% moisture content, based on the cellulose content, which comprises treating a regenerated cellulose film of less than this water content with a water-water miscible organic liquid composition capable of raising the water content of the film to the desired value and forming a water content equilibrium therewith at the desired value, said water miscible organic liquid being ethanol.

15. In the production of regenerated cellulose film having substantially no permanent shrinkage and which is smooth, glossy, and free from wrinkles, the steps of treating a film of regenerated cellulose with an aqueous solution of a water miscible organic liquid of 40%–54% water content until the film contains 60% to 80% moisture, based on the cellulose content, and thereafter drying the treated film while maintaining it under tension sufficient to prevent the formation of wrinkles, puckers and like distortions, but insufficient to prevent free shrinkage in both lengthwise and widthwise directions, said water miscible organic liquid being ethanol.

16. In the production of regenerated cellulose film having substantially no permanent shrinkage and which is smooth, glossy and free from wrinkles, the steps of treating long lengths of film of regenerated cellulose with an aqueous solution of a water miscible organic liquid of 40%–54% water content until the film contains 40% to 100% moisture, based on the cellulose content, by passing the film through a bath of the treating liquid, and thereafter drying the treated film while maintaining it under tension sufficient to prevent the formation of wrinkles, puckers and like distortions, but insufficient to prevent free shrinkage in both lengthwise and widthwise directions, said water miscible organic liquid being ethanol.

17. The process of claim 9 when the aqueous solution contains glycerol as a softener.

FRANCIS P. ALLES.

CERTIFICATE OF CORRECTION.

Patent No. 2,254,200. September 2, 1941.

FRANCIS P. ALLES.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 5, second column, line 9, for "90%" read --95%--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 28th day of October, A. D. 1941.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)