Jan. 4, 1944. C. L. HUTCHINSON 2,338,182

REGENERATED CELLULOSIC FILM

Filed Dec. 1, 1939 2 Sheets-Sheet 1

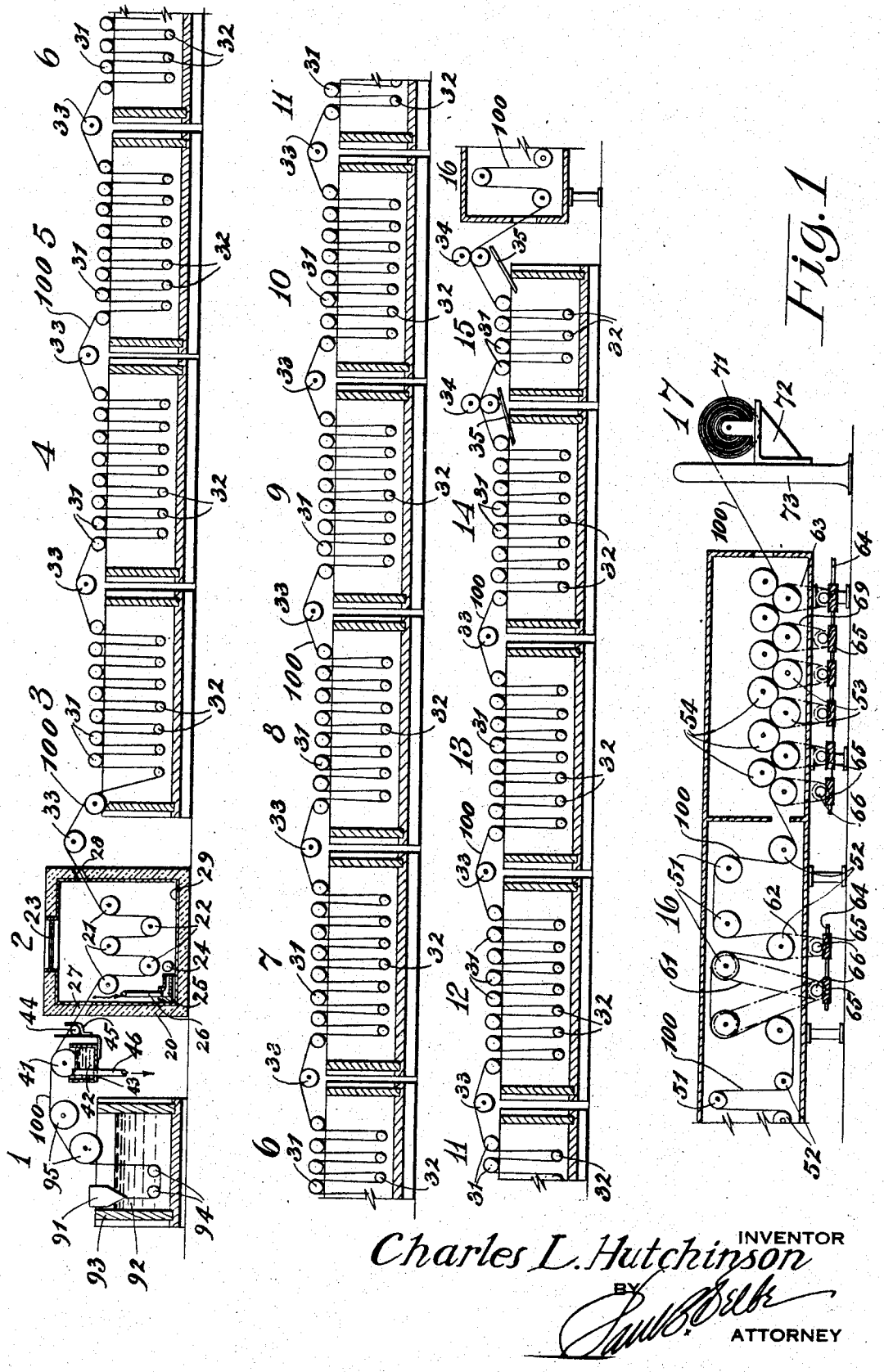


Fig. 1

Charles L. Hutchinson INVENTOR

BY Paul B. Eller

ATTORNEY

Jan. 4, 1944. C. L. HUTCHINSON 2,338,182

REGENERATED CELLULOSIC FILM

Filed Dec. 1, 1939 2 Sheets-Sheet 2

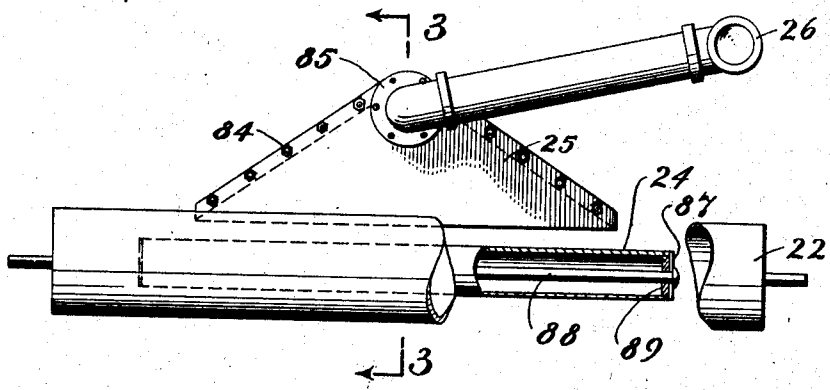
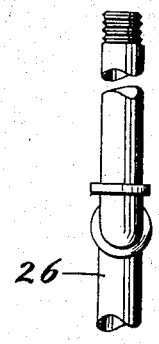


Fig. 2



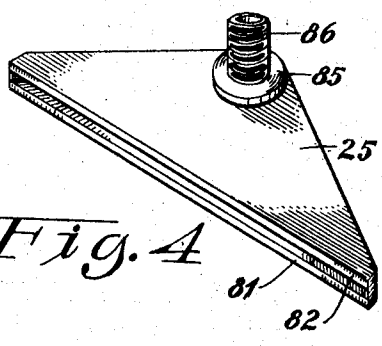


Fig. 4

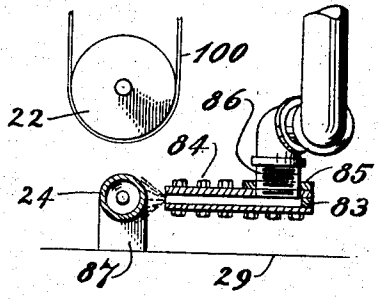


Fig. 3

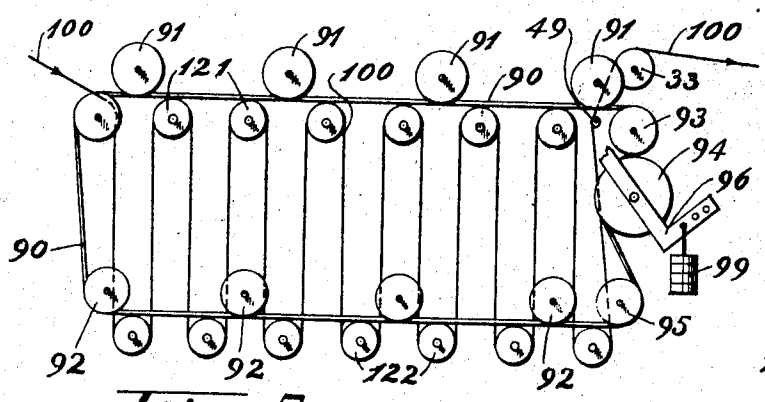


Fig. 5

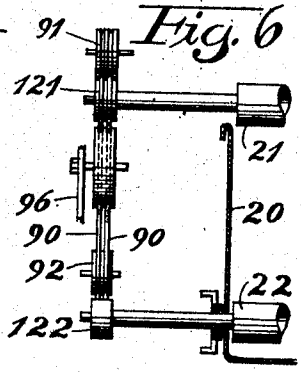


Fig. 6

Charles L. Hutchinson INVENTOR

BY Paul R. Selk

ATTORNEY

Patented Jan. 4, 1944

2,338,182

UNITED STATES PATENT OFFICE

2,338,182

REGENERATED CELLULOSIC FILM

Charles L. Hutchinson, Buffalo, N. Y., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

Application December 1, 1939, Serial No. 307,024

11 Claims. (Cl. 18—57)

This invention relates to regenerated cellulosic film, and more particularly to improvements in regeneration processes whereby regenerated cellulose pellicles having improved transparency, durability and surface characteristics are obtained.

The manufacture of regenerated cellulose film in a continuous manner from viscose is disclosed in United States Patent No. 1,548,864 (Brandenberger). This procedure, which is particularly well suited to a commercial scale operation, in general involves continuous extrusion of a sheet of cellulose xanthate solution (viscose) through a narrow slot directly into a coagulating (and/or regenerating) bath. The extruded web is kept in this bath until it has acquired the mechanical strength necessary to withstand the subsequent treatments which it is to receive.

After the web has become strong enough, it is removed from the coagulating bath and passed through a converting bath which causes the cellulose xanthate to be converted (regenerated) to cellulose. After leaving the converting bath, the web is subjected to a series of treatments such as washing, desulfuring, washing, bleaching (or dyeing, depending upon the use which is to be made of the product), and washing, preferably in the order named. These last mentioned treatments, like the coagulating and converting treatments, are conveniently carried out by passing the continuous web through vats containing the corresponding treating liquid. Variations in the composition of these baths, and the order in which they contact the web, are ordinarily permissible. It is customary to provide for softening the cellulose web by passing it through an aqueous solution of glycerol after it leaves the last washing bath and before it is dried. Usually the cellulosic sheet material is dried by passing it over heated rolls.

It is known that the various physical properties, such as tear resistance, deformational changes with changes in relative humidity, and the like, of cellulose sheet prepared in this manner are anisotropic. Obviously, such nonuniformity is extremely undesirable. In addition to low resistance to tear and the detrimental changes in dimension accompanying the variation in relative humidity, such cellulose sheet material has generally exhibited low durability and presented a surface which was either tacky or which had a tendency to stick to adjacent surfaces when stored under pressure for any length of time. The tendency to stick can be overcome by sizing or coating the surface, but such a procedure detracts from the transparency of the sheets and the ease with which they may be sealed with adhesives. Improvements in durability and like characteristics have been the object of much research.

This invention had for objects the preparation of a superior regenerated cellulose sheet, and the provision of an improved process for the manufacture of regenerated cellulose film and related non-fibrous cellulosic pellicles. A further object was to provide a process for manufacturing cellulosic pellicles having uniform properties in all directions, having improved transparency, having improved durability, and having improved surface characteristics. Still further objects were to provide methods whereby restraining influences could be practically eliminated in the handling of webs of cellulosic material, and whereby the shrinking of gel regenerated cellulose webs could be largely confined to an early stage of the manufacture. Yet further objects were to confine the major portion of cellulosic web shrinkage to the regeneration phase of its process of manufacture, and to effect most of the gel cellulose web shrinkage in a relatively small section of the treating apparatus. A general advance in the art, and other objects which will appear hereinafter, were also contemplated.

It has now been found that the objects of this invention are attained, and that a greatly superior regenerated cellulose sheet material is obtained, by carrying out the regeneration while transporting the web through a gaseous environment by means of supporting rollers or guides which exert no appreciable restraining forces on the web. More specifically, the regeneration is effected by an acid medium at an elevated temperature maintained by the heated gaseous atmosphere. Preferably the regeneration treatment takes place immediately after the coagulated viscose web or related material leaves the coagulation bath (the first stage of coagulation and/or regeneration). The extrusion of the viscose into the coagulating bath, and the treatments subsequent to regeneration, may follow the procedures known to the art. As a result of these operations a remarkably uniform sheet material having many advantages over that heretofore known, results.

From the following description and specific examples, in which are disclosed certain embodiments of the invention as well as details of wnat 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 diagrammatic, side elevation, partly in section, view showing a regenerated cellulose web casting machine;

Figure 2 is a plan view of a portion of the apparatus in section 2 of the casting machine;

Figure 3 is a side view partly in section taken on a line 3—3 in Figure 2;

Figure 4 is a perspective view of the gas distributor illustrated in Figures 2 and 3 and section 2 of Figure 1;

Figure 5 is a side elevation view illustrating a belt drive for the conveyor rollers in section 2 of the casting machine; and

Figure 6 is an end elevation view of the driving mechanism of Figure 5.

Similar characters refer to similar parts throughout the several views.

Referring to Figure 1, the numerals 1 through 17 represent the various sections of a machine for manufacturing regenerated cellulose film from viscose. Section 1 is the section in which the cellulose xanthate solution is coagulated in a continuous manner to form a continuous web. This web, after it has become strong enough to withstand subsequent treatments, is passed into section 2 (the regenerating section) comprising a buttering roll arrangement for treating the coagulated web with regenerating material, and a chamber in which the coagulated and partly regenerated web bearing the regenerating material is subjected to a gaseous environment during further regeneration. In section 3, to which the web next travels, it is given a supplemental and final regenerating treatment, after which it is passed through sections 4 and 5 where it is washed. In section 6 the regenerated and washed web from section 5 is given a desulfuring treatment, after which it is washed as it passes through sections 7 and 8. In passing through section 9 immediately thereafter, the continuous web is bleached. It is then passed consecutively through sections 10, 11, 12 and 13, where it is again washed. In sections 14 and 15 the web is given a softening treatment, after which it passes through a drying section 16 to a wind-up section 17.

In section 1 viscose from a hopper 91 passes, in the form of a sheet, into the coagulating bath 92 in tank 93, where it coagulates into a web 100. The web passes around guides 94 in the coagulating bath, and is then transferred therefrom by rollers 95 to a buttering roll 41 which is rotating in a bath of regenerating material 42 contained in trough 43. The treated web then passes over a guide rod 44 held in bracket 45 on its way to the regeneration chamber 20. A controlled outlet 46 regulates the level of the bath of regenerating material. This outlet comprises a vertically adjustable overflow pipe. After leaving the guide rod 44 the web next passes through slot-like opening 27 in the wall of the regenerating chamber, about upper rollers 21 and lower rollers 22, which convey and guide it through the chamber, and it leaves the chamber through an opening 28. In the chamber 20 there is a nozzle-like device 25 which is supplied with a heated gas (such as steam) through line 26. The gas, upon leaving the nozzle, strikes a spreader device 24 which assists in distributing it through the chamber. A window 23 in the top part of the regenerating chamber permits one to view the operations taking place in the chamber. This window is constructed of some acid-proof material like glass. The chamber also has an acid-proof lining 29.

The regenerated web 100, leaving section 2, passes over the various upper rolls 31, lower guides 32 and transferring guides 33, through the remaining liquid treating sections of the casting machine.

Squeeze rolls 34, following sections 14 and 15, perform the double function of transferring the web and removing excess liquid therefrom. Drainboards 35 return the removed liquid dropping thereon to the corresponding tanks.

After leaving the last treating vat (section 15), the web passes to the drier in section 16, where it passes over the various drying rolls 51, 52, 53 and 54. The rolls 51 are driven by belts indicated at 61, rolls 52 by belts indicated at 62, and the rolls 53 by belts indicated at 63. The belts are driven from a main shaft 64, upon which are mounted worm gears 65. These worm gears turn the meshing gears 66 operating the shaft upon which the belt pulleys are located. The dried web is finally wound into a mill roll 71 (in section 17) upon a core supported upon a bracket 72 attached to an upright 73.

For the purpose of distributing the incoming gas in the regenerating chamber, the fantail steamer 25 and steam expander 24 have been found particularly satisfactory. It is desirable, and sometimes necessary, that the heated steam be applied without turbulence to the cellulosic web. The steamer and associated apparatus are illustrated in considerable detail in Figures 2, 3 and 4. A pipe 26 conducts the treating gas from outside the regenerating chamber 20 to the fantail steamer 25. This pipe line assembly is usually made of some acid-proof material such as convas impregnated with phenol-formaldehyde resin. It is convenient to make it up of a number of jointed sections to facilitate its adjustment and location. The fantail steamer 25 comprises upper and lower plates 81 and 82 bolted together through a spacing element 83 by means of bolts 84. This device is conveniently and satisfactorily fabricated from lead sheets, and for the purpose of strengthening the place of gas entry (and attachment or support) a shoulder 85 and a nipple 86, which also serve to connect the steamer to the line 26, are provided.

It is desirable to construct the steam expander 24 from a lead tube, and convenient to mount this upon end brackets 87 by means of a lead rod 88 and a spacing element 89. In order to show the relation of the parts, a lower roll 22, partly broken away, is shown in Figures 2 and 3.

Instead of having an acid-proof lining 29 (Figure 1, section 2), the chamber 20 may be constructed of acid-proof material throughout.

In order that the web 100 may be free to shrink, it is desirable to have an adjustable and easily regulated drive for the rolls 21 and 22 in section 2 of the casting machine. Such a drive is illustrated in Figures 5 and 6. For the sake of clarity, most of the details of this section, except the conveying rolls 21 and 22 and their driving means, have been omitted. In these figures the web of regenerated cellulose indicated by the numeral 100 passes about the rolls 21 and 22. These rolls have an axis or shaft portion which extends beyond the side of the chamber wall 20.

On the ends of these projecting shafts are located pulleys 121 and 122, which are driven frictionally by a belt device 90. In the species illustrated in Figure 6, the driving belt is made up of a plurality of small belts having trapezoidal cross sections. The belt, which is endless, passes under guide rollers 91, which are adjustable to keep

it against the pulley 121 in frictional drive relationship. The endless belt driving means also passes under guide rollers 92 which press it against pulleys 122 with sufficient force to drive the web guiding rollers 22.

This very light, non-positive frictional type drive is especially suitable for carrying out the present invention. Such a drive permits each roll to follow the passing film or web, and to accommodate itself to the forward motion of the film as well as to any variations introduced by shrinkage within the film. Only sufficient torque is transmitted to each roll to take care of varying friction. As a result, the sheet material, as it passes over any given roll, controls the roll surface speed of that roll. In order to permit shrinkage it is of course necessary to feed the film into the steaming section at a higher rate than that at which it is carried away therefrom. Such regulation is conveniently accomplished by controlling the speed at which the film is transferred from the initial coagulating tank to the steaming section and the speed at which the operations subsequent to the regeneration are performed.

In order to maintain the desired amount of tension in the endless belt means, fixed guide rollers 93 and 95 and pivoted guide roller 94, are provided. The roller 94 is mounted on a pivoted arm 96 which has an extension to receive a weighting means indicated at 99. The weighting means can be varied to cause the roller 94 to press against the endless belt means with the desired force. Since the mounting of the roller 94 is not fixed, any sudden changes in tension are easily taken care of without breaking the belt or otherwise damaging the driving mechanism.

A rod 49 guides the web 100 to the transferring roller 33 in a preferred embodiment of the invention.

Throughout the specification and claims the quantities are given in parts by weight unless otherwise specified.

As a typical example, a sheet of viscose a few feet wide and 0.005 of an inch thick was extruded into an aqueous coagulating bath comprising 13% sulfuric acid and 18% sodium sulfate. The bath was maintained at a temperature of 41° C., and the web passed therethrough at such a rate that each portion remained in contact with the bath for a period of one to four seconds. Some shrinkage took place during this treatment, with the result that the web, as it left the bath, was 89%–99% of the width of the extruded sheet. Upon leaving the coagulating bath the web passed over a buttering roll rotating in 13% sulfuric acid, and was immediately transferred to a steaming chamber, supplied with steam from a source at 15 pounds gauge in sufficient amounts to raise the web to, and maintain it at, a temperature of 70° C. The web was at approximately room temperature as it entered the steam chamber, and was transported therethrough in approximately 12 seconds with a minimum of tension. During this treatment the shrinkage in the machine direction amounted to 7%. The web, after leaving the steaming compartment, was processed in the conventional manner by being passed through the usual treatment baths. There was no machine direction shrinkage between Section 2 and the dryer.

In another embodiment a sheet of viscose a few feet wide and 0.005 inch thick was extruded into an aqueous coagulating bath comprising 18% ammonium sulfate. The bath was maintained at a temperature of 41° C. and the web passed therethrough at such a rate that each portion remained in contact with the bath for a period of 1 to 4 seconds. Some shrinkage took place during this treatment, with the result that the web as it left the bath was 89%–99% of the width of the extruded sheet. Upon leaving the coagulating bath, the web passed over a buttering roll rotating in 13% sulfuric acid and was immediately transferred to a steaming chamber supplied with steam from a source at 15 pounds gauge in sufficient amounts to raise the web to and maintain it at a temperature of 80° C. The web was approximately room temperature as it entered the steam chamber, and was transported therethrough in approximately 12 seconds with a minimum of tension. During this treatment, the shrinkage in the machine direction amounted to 8%. The web passed through the usual treatment baths after leaving the steaming compartment.

In other runs viscose films ranging from 0.003 to 0.009 of an inch in thickness were allowed to remain in coagulating baths of the same composition maintained at 40° C. for from 4 to 20 seconds. Such films were suitably set up and could be transferred from the coagulating bath to the further treating stages. Comparable results were obtained.

The process is applicable to other cellulosic films, pellicles and products of a similar nature, for example, those obtained by regenerating cellulose from a cuprammonium solution.

Various methods of heating the film may be employed. Steam is generally the most convenient in commercial scale operations. Other heated gases, such as air, nitrogen, hydrogen chloride, etc., are also suitable. If desired, the treatment chamber may be heated with radiant heaters, high frequency electric fields, or other methods well known in the art. When heaters of the radiant type are employed, it is advisable to forcibly circulate the gaseous environment (air or the like) over the web and to remove the vapors given off during the process. Ordinary air is a very satisfactory atmosphere in such a modification. Because of their viscosity liquid baths exert a very definite drag upon the cellulosic web as it travels therethrough. The tension upon the web during the regeneration and shrinkage treatments is therefore very desirably reduced when the treating medium in the chamber of section 2 is a gas. A temperature range of 55° C. to 100° C. in the regeneration and shrinkage stages has been found most suitable for atmospheric pressure operations. Temperatures very close to 100° C. (under ordinary normal atmospheric pressure) are preferred. Higher temperatures may be used if the processing chamber is maintained at superatmospheric pressures. Web temperatures high enough to cause desiccation of the same have not been found detrimental.

The amount of shrinkage in section 2 of the casting machine of this invention can be increased by increasing the temperature of the treating fluid applied by the roll 41. For example, with the housing 20 filled with steam at atmospheric pressure and 75° C., a film 0.003 to 0.009 of an inch in thickness, suitably set up for further handling by being cast and held in a coagulating bath consisting of H_2SO_4 13%, Na_2SO_4 18%, H_2O 69% for 4 to 20 seconds (and which has been buttered by the roll 41 with a

regenerating bath of the same composition), has about twice the shrinkage with the treating fluid at 70°–80° C. that it has with the fluid at 40° C.

Shrinkages anywhere from 0% to 12% yield beneficial results in the finished product. A shrinkage in the machine direction of from 8% to 10% is preferred. In the procedures of the prior art there is actually a stretch (which may be as high as 15%) of the film in the casting machine. When excessive shrinkages are permitted, shriveling, with the consequent formation of wrinkles or laps and haze, occur in the dried sheet. Shriveling and haze may be undesirable, and special procedures may be necessary to obviate them—otherwise, there is no upper limit to the amount of shrinkage which can be permitted.

The surface of the finished film produced in the manner above described, is of such a nature as to better resist sticking when subjected to high humidities and pressure over extended periods of time. In addition, the finished product has greater width (based upon the initial width of the viscose sheet) than that obtained by the methods previously used for manufacturing regenerated cellulose pellicles. This results in an increased output per manufacturing unit, a matter of no little economic importance.

As will be apparent from the foregoing considerations, the length of time required for the regeneration-shrinkage treatment may be varied within rather wide limits. Under certain conditions shrinkage takes place quite rapidly, and the "shrinking" section of the casting machine may therefore be comparatively short. The shrinking section must necessarily be longer for a machine operated at higher speeds than for the same machine operated at lower speeds, because the time interval in which the web is under steaming (or equivalent) treatment is decreased as the casting speed is increased (for the particular apparatus set-up in which the distance traveled by the film is not changed).

It may frequently be desirable to have the time of treatment by steaming longer than that actually required for the desired degree of shrinkage in order to more completely remove carbon disulfide and other volatile sulfur compounds. In general, satisfactory results are obtained with treatments for periods within the range of 1 to 20 seconds, depending upon the circumstances.

A certain amount of acid (over that supplied by the bath into which the viscose is cast) is necessary to complete the regeneration of the cellulose. This may be supplied in various ways and by various means, buttering rolls and sprays being preferred.

More than one steam distributor can be used in the chamber **20** if desired. It is convenient to place such expanders under the lower rolls **22**, but other locations and steamers or spargers of other shapes than fan-tail, can be used.

The lower guide members in chamber **20** rotate or remain stationary (see German Patent 567,990). They may have surfaces of glass, stainless steel, hard rubber, soft rubber, phenol formaldehyde resin, and the like. Smooth polished surfaces are most satisfactory.

Slippage of the web over the rotating upper rolls in the chamber **20** can, if desired, be overcome by making knobs thereon or grooves therein.

During the regeneration of the cellulose a large amount of the sulfur present in the cellulose xanthate is released (as the cellulose xanthate is transformed into cellulose) in the form of carbon disulfide and hydrogen sulfide. Most of the remainder becomes colloidal sulfur. The volatile sulfurous compounds are largely driven off by the steaming process. The desirability of having a gas as the treating medium during the regeneration therefore has the double advantage of reducing tension (by eliminating liquid drag) upon the web, and quickly carrying out of the zone of contact (and the machine) the gaseous sulfur compounds and other obnoxious vapors.

The present invention has the advantage of providing in a simple and satisfactory manner for the preshrinkage of the sensitive cellulosic web at the time of regeneration. This is particularly beneficial to the properties of the finished product. It also offers an extremely satisfactory method for obtaining control of many complicated factors in the production of this type of sheet, such as acid and temperature gradients between the center and edge of the film. An adjustment of regeneration at the edge as against the center, to compensate for the thin gauge at present used (because of limitations in certain other portions of the manufacturing process), is permitted. It further permits very careful adjustment of the shrinkage and strain factors, making possible a sheet which has uniform properties in all directions. It combines the effect of regeneration and syneresis into a small controllable section, and thus greatly simplifies the entire process of film manufacture. It causes the contracting of the regenerated cellulose, insofar as it takes place in the wet (that is, up to the drying stage) to be largely effected during the regeneration and in a relatively small section of the casting machine. It is readily adaptable to high speeds of operation, and hence to increased output per manufacturing unit. It also eliminates the disadvantages inherent in processes in which shrinkage is retarded because of the operating difficulties encountered in overcoming the frictional drag of liquid regenerating baths.

The film obtained by this process has more uniform properties in different directions, exhibits less change with atmospheric conditions, and has higher extensibilities (resulting in higher durabilities) than previously obtained.

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 this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. In a process of preparing continuous regenerated cellulose web from viscose, the steps of casting the viscose in web form, coagulating the cast web, coating the coagulated web surface with regenerating material and thereupon allowing it to shrink while passing it through a heated gaseous atmosphere to cause regeneration.

2. In a process of preparing continuous regenerated cellulose web from viscose comprising a sequence consisting of coagulation, regeneration and finishing steps, the step which comprises regenerating the cellulose web while maintaining the web free of appreciable restraining forces whereby the web is permitted to attain the greater part of its shrinkage in the regeneration step.

3. The process of preparing regenerated cellulose web which comprises extruding a sheet of viscose solution, coagulating said solution into a web, regenerating said web in a gaseous atmosphere at temperatures above normal while allow-

ing the web to shrink freely, and thereafter finishing the cellulosic web.

4. The process of claim 1 when the coagulated web is coated with regenerating material having a temperature of 40° to 80° C.

5. In the process of producing regenerated cellulose web of improved transparency and durability, the steps which comprise coagulating viscose to produce a web, coating the coagulated web with cellulose regenerating material, and regenerating the cellulose of the coated coagulated web in a gaseous atmosphere while allowing it to shrink.

6. A process which comprises extruding a thin sheet of viscose into an aqueous coagulating bath, passing the resultant web therethrough at such a rate that the width of the web leaving the coagulating bath is 89%–99% of the width of the extruded sheet, applying a regenerating liquid to the coagulated web after it has left the coagulating bath, passing the said liquid-coated web into a gaseous atmosphere, transporting the web therethrough while regenerating it without stretching it, and thereafter finishing the coagulated and regenerated web.

7. A process which comprises extruding a thin sheet of viscose into an aqueous coagulating bath comprising 13% sulfuric acid and 18% sodium sulfate maintained at a temperature of about 41° C., passing the resultant web therethrough at such a rate that the width of the web leaving the coagulating bath is 89%–99% of the width of the extruded sheet, applying a regenerating liquid consisting of 13% sulfuric acid to the coagulated web after it has left the coagulating bath, passing the said liquid-coated web into a gaseous atmosphere, transporting the web therethrough while regenerating it without stretching it, and thereafter desulfuring, bleaching and drying the web.

8. A process which comprises extruding a thin sheet of viscose into an aqueous coagulating bath comprising 18% ammonium sulfate maintained at a temperature of about 41° C., passing the resultant web therethrough at such a rate that the width of the web leaving the coagulating bath is 89%–99% of the width of the extruded sheet, applying a regenerating liquid consisting of 13% sulfuric acid to the coagulated web after it has left the coagulating bath, passing the said liquid-coated web into a gaseous atmosphere, transporting the web therethrough while regenerating it without stretching it, and thereafter desulfuring, bleaching, softening and drying the web.

9. In the process of producing regenerated cellulose web of improved transparency and durability, the steps which comprise coagulating viscose to produce a web, coating the coagulated web with sulfuric acid, and regenerating the cellulose of the coated coagulated web in a gaseous atmosphere while allowing it to shrink.

10. A process which comprises extruding a thin sheet of viscose into an aqueous coagulating bath, passing the resultant web therethrough at such a rate that the width of the web leaving the coagulating bath is 89%–99% of the width of the extruded sheet, applying sulfuric acid to the coagulated web after it has left the coagulating bath, passing the said liquid-coated web into a gaseous atmosphere, transporting the web therethrough while regenerating it and allowing it to shrink freely, and thereafter finishing the coagulated and regenerated web.

11. A process which comprises extruding a thin sheet of viscose into an aqueous coagulating bath comprising 18% ammonium sulfate maintained at a temperature of about 41° C., passing the resultant web therethrough at such a rate that the width of the web leaving the coagulating bath is 89%–99% of the width of the extruded sheet, applying a regenerating liquid consisting of 13% sulfuric acid to the coagulated web after it has left the coagulating bath, passing the said liquid-coated web into a gaseous atmosphere, transporting the web therethrough while regenerating it and allowing it to shrink freely, and thereafter desulfuring, bleaching, softening and drying the web.

CHARLES L. HUTCHINSON.