June 29, 1926. 1,590,595

T. A. HILL

MANUFACTURE OF CELLULOSE

Original Filed May 26, 1920 3 Sheets-Sheet 1

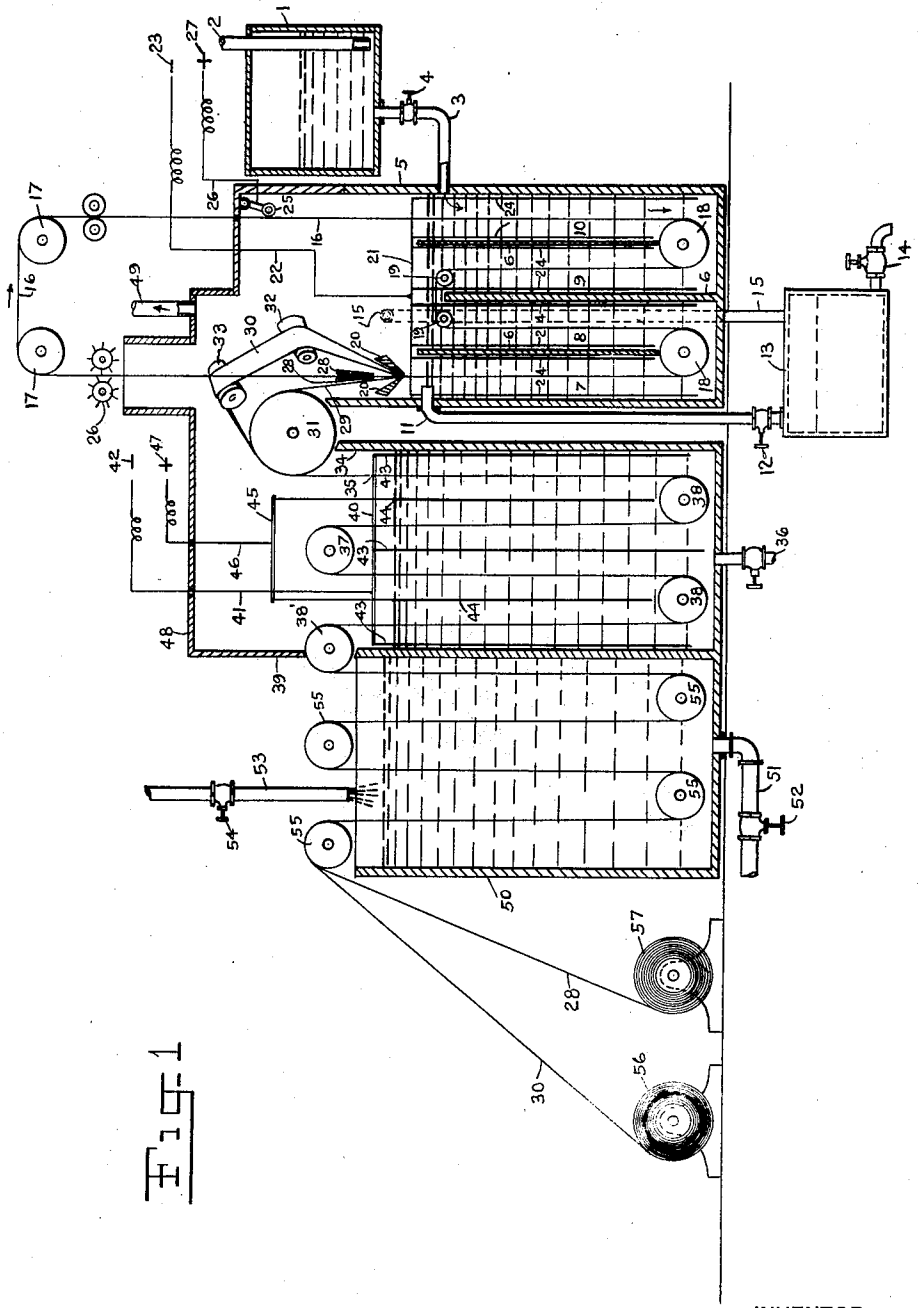


Fig. 1

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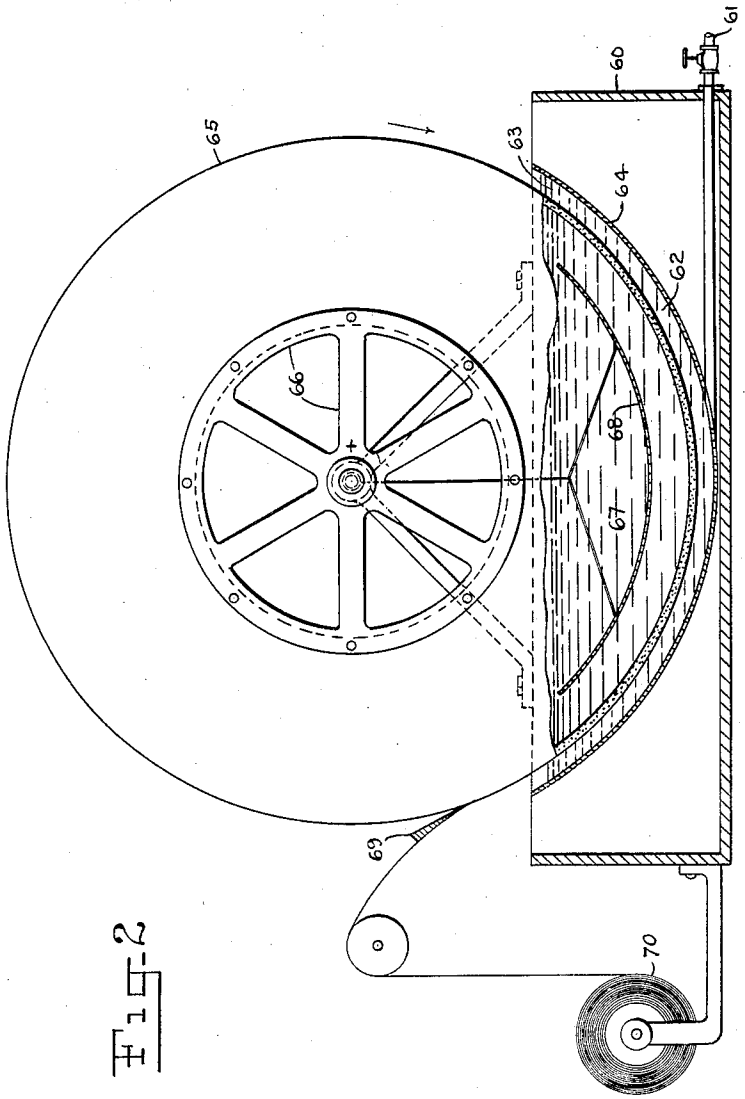


Fig. 2

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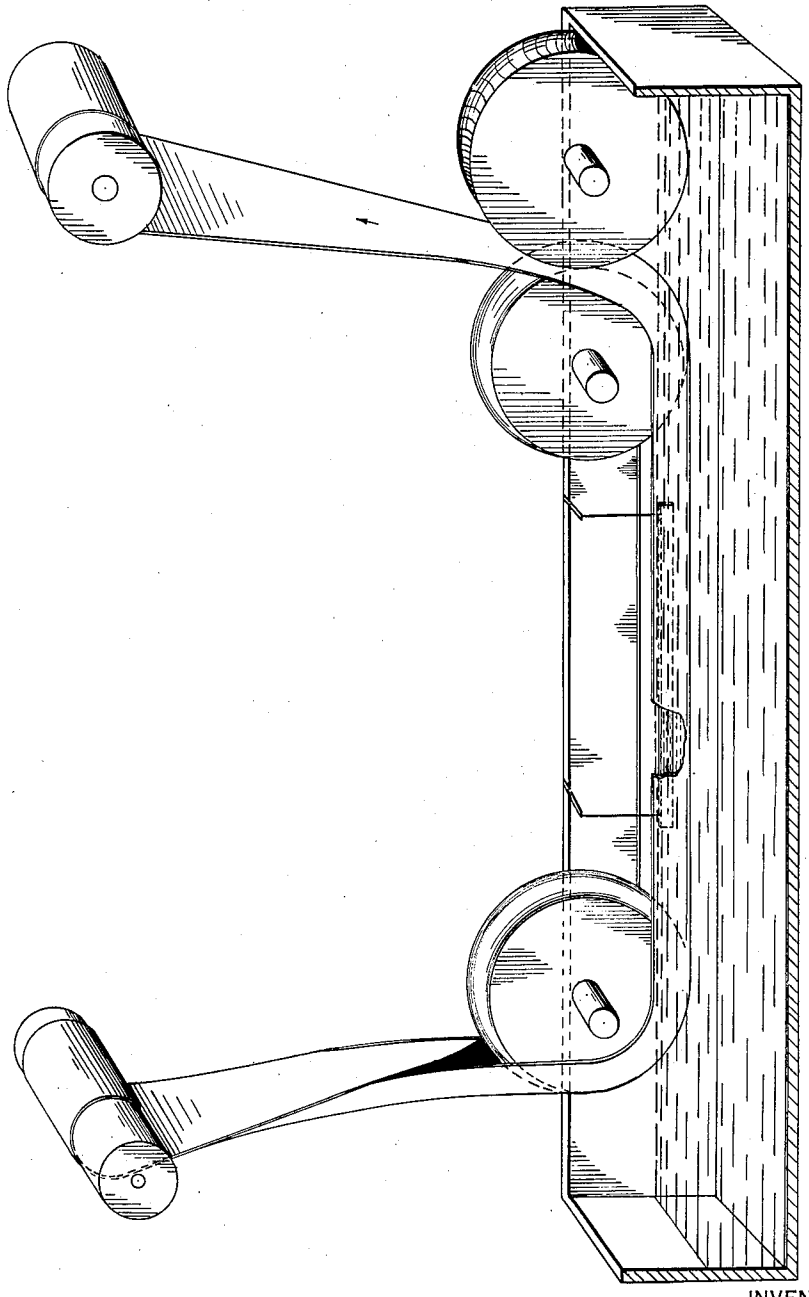


Fig 5-3

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UNITED STATES PATENT OFFICE.

THOMAS A. HILL, OF BROOKLYN, NEW YORK, ASSIGNOR TO TAYLOR LABORATORIES INC., OF NEW YORK, N. Y., A CORPORATION OF NEW YORK.

MANUFACTURE OF CELLULOSE.

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My invention relates to improvements in the manufacture of cellulose products and is more particularly illustrated and described hereinafter in its application to the production of cellulose films and similar articles, the apparatus described having particular reference to films or ribbons made from organic material, such as cellulose dissolved in solvents containing a metal such as cupro ammonia solution or zinc chloride and from which solutions the organic material is deposited in a solid state upon an anode and the metallic solution-element deposited on a cathode by means of a suitable electrical current.

In carrying out my invention, I prefer to pass a metallic belt through an electrical field in a suitable bath the belt constituting the anode upon which the organic material is deposited while the metallic solvent constituent is deposited upon a suitable cathode or cathodes. By this arrangement a continuous film may be produced and its thickness may be governed according to the thickness or density of the solution. Where the belt serves as the anode, the organic material should remain in contact therewith until the last traces of metal have been removed from it. In the apparatus hereinafter described, a suitable belt, not necessarily of great length and preferably of platinum, or platinum plated is caused to pass continuously through a container filled with say for instance, cellulose dissolved in cupro ammonia. By suitable connections this belt which forms the anode carries an electrical current which passes through it and through the cellulose solution or bath to the suitably located cathodes upon which the metallic constituent is deposited. In a preferred form of apparatus, both belt and cellulose solution are moved through the tank or container in the same direction. The electrical current causes the deposition of cellulose upon the belt in a gradually increasing thickness from the point of its first immersion and the cellulose solution is correspondingly reduced in cellulose content and a proportionate amount of solution metal is deposited on the cathodes from which it must be evident that the thickness and density of the deposited film depends upon several factors each of which may be brought fully and conveniently under control of the operator, i. e., the speed of the belt, the time of contact between the belt and cellulose solution, rate of flow of cellulose solution relative to speed of belt with a consequent variation in strength of the cellulose solution at any point in the tank, and the amount of current passing during any interval of time, etc. In practice, these factors may be so regulated that as the belt emerges from the tank it is coated with a predetermined thickness of cellulose which may then be stripped from the belt in a condition permitting it to be subjected to further operations, or if desired, before stripping it can be scraped to remove surplus adhering material. It may be then passed through a second electrolytic bath, washed, and passed on for further treatment. The cellulose solution reduced in strength by the amount of cellulose deposited from it on the belt, may also be removed, its cellulose content increased such as by methods herein later described, and the concentrated solution returned to the tank. The cathodes may be removed from time to time and the metal which is deposited thereon may be used for the preparation of new cellulose solution. This method it will be observed permits of perfect control of the film thickness and manipulation. It materially reduces the length and cost of the belt (important in some cases where platinum is used) and its subsequent upkeep. The arrangement of the apparatus hereinafter described allows for coating the belt on both sides where this is desired, thereby doubling the output per square foot of one side of belt surface, or where a wheel is employed for casting or flowing the material as in other well known processes. Numerous other advantages will be apparent hereinafter.

In the accompanying drawing, I have illustrated in Fig. 1 longitudinal section, several tanks and other apparatus so associated as to embody an application of my invention. Fig. 2 illustrates modifications, and Fig. 3 is a similar view to Fig. 2 showing other modifications.

1 indicates a closed tank provided with a

supply pipe 2 and an outlet 3 provided with a suitable control valve 4. The pipe 3 enters the side of the tank 5 which may be provided with a series of partitions, or walls 6, dividing the tank into several divisions 7, 8, 9 and 10, as shown, so that liquid flowing from the pipe 3 must pass successively through these chambers and finally out of the upper part of the division or compartment 7 of the chamber by way of the overflow pipe 11 which may be provided with a suitable valve such as 12. This overflow enters another tank 13 provided with a draw-off cock 14 and a vent pipe 15 as shown.

An endless belt or carrier 16 which may be made of a suitable copper alloy heavily platinum-plated or preferably of pure platinum, is suitably driven upon the overhead rollers 17, enters the tank 5 passing through the centres of the compartments 7 to 10 inclusive as shown, being guided and positioned by the rollers 18 in said tank 5 and the small rollers 19. The upper peripheries of the rollers 18 practically contact with the lower extremities of the partitions 6 but a suitable space is left between the lower sides or peripheries of the rollers and the bottom of the tank 5 as shown, so that the liquid may pass freely from one compartment to another from below the lower rollers 18 and over the tops of the upper rollers 19. 20 indicates adjustable soft-edged scrapers adjacent both sides of the belt as it emerges from the tank 5 and serves to remove any adhering material from the film of cellulose deposited upon the belt.

21 indicates a suitable bus-bar or electrical rail connected by the wire 22 to the negative source of electricity 23, and from this bus-bar are suspended a series of copper or other metallic plates 24 so that at least two of them are in each of the compartments 7 to 10 inclusive parallel to and equally distant from the belt 16 and extending downwardly in the tank 10 practically as far as the belt 16. The trolley or rolling contact 25 is connected by a wire 26 to the positive terminal 27 of the same electrical source. Any suitable motive power may be applied to the drive pulley 17 and a pair of brushes, scrapers or other suitable apparatus may be employed as indicated at 26 for cleaning the belt after the film has been stripped therefrom.

In operation, the tank 5 is filled with any desired cellulose solution, such as cuproammonia, nickel ammonia, zinc chloride, etc. Having filled the tank 5 to the level of the outlet pipe 11, the tank 1 is now filled with the same kind of solution, the control valve 4 is opened and a flow of liquid is established through the tank 5, outlet pipe 11, and into the dilute solution tank 13. The belt 16 is now started in the direction indicated by the arrow and preferably in a direction parallel with the flow of the cellulose solution and the electric current is turned on. Cellulose will immediately begin to deposit on each side of the belt, becoming thicker and thicker as the belt progresses through the tank 5, the cellulose solution becoming weaker in like proportion, from the point of immersion of the belt in the first compartment to the point of its leaving in the last compartment. It will be apparent that any variation in the amount of current passed, the speed of the belt through the solution, or the speed of the solution through the tank, will have a corresponding effect on the thickness or quality of the cellulose deposited on the belt and that these factors may be kept under the control of the operator by any well known means. It may be preferable to run the belt rather slowly and to run the solution slightly slower than the belt in order to remove the largest practical amount of cellulose from it before permitting it to flow to the dilute solution in the tank 13. It is unnecessary however to remove all of the cellulose from the solution and it is preferable to keep the solution at a more or less uniform condition and to regenerate it either by constant inflow of new solution and outflow of partly exhausted solution or by periodic replenishment as may be found preferable according to the particular uses and type of appartus employed.

After the belt 16 has received the desired thickness of cellulose on both faces, and after the soft-edged scrapers 20 have removed the surplus adhering material from the film thus formed, and have removed or wiped off adhering solution, all of which returns to the tank 5, the belt now passes between the hard-edged scrapers or strippers 28 which separate the films 29—30 from the belt 16, the film 29 passing over the roller 31 directly, and the film 30 passing over the rollers 32—33 which take it out of the path of the returning belt 16 as shown, both films entering the next tank 34 at 35 as shown. This tank 34 is fitted with a suitable outlet valve 36 and a series of guide rollers 37—38. The films pass under and over these rollers traversing the liquid in the tank 34 vertically several times, a slight tension being placed upon the films by means of a driven roller 38′ placed in the outer wall 39. 40 indicates a suitable bus-bar connected by the wire 41 to the negative electrical terminal 42, and 43 are the cathodes suspended therefrom. 44 are the anodes suspended from the bus-bar 45 connected by a wire 46 to the positive terminal 47. The tanks 5—34 are covered by a common hood 48 for collecting the vapors which may be drawn off by suction and recovered by way of the outlet 49.

The tank 34 is filled with any solution adapted to remove electrolytically any remaining traces of the metallic solution con-

stituent which may adhere to or be contained in the films or ribbons 29—30. This solution may be a dilute acid such as nitric or sulphuric acid or it may be a normally metallic salt. For some purposes, such as film making, it is preferable to employ a solution of ammonium nitrate as the ultimate product of this salt under electrolysis is ammonia which by this process is drawn off through the vent pipe 49 and recovered with the ammonia released from the tank 5 when cupro or nickel ammonia solutions of cellulose are employed. The arrangement of anodes and cathodes is such that current passing from one to the other must pass not only through the solution but through the films 28—30 also. During treatment and passage through the tank 34 the last trace of metal is removed from the films which now pass over the roll 38 to a wash tank 50. This wash tank is provided with an outlet 51 and valve 52 therefor and with an inlet pipe 53 and valve 54 therefor by means of which a constant flow of liquid is maintained through the tank thereby removing all traces of ammonia or other gases and foreign matter. From the tank 50, the films which pass over the rollers 55 may now be wound upon the reels 56—57 under slight tension, which reels may be removed from time to time as completed. The film thus made is pure cellulose, quite tough and elastic and of a white translucent appearance owing to its content of water. It is however in a suitable condition for further desired operations.

The dilute cellulose solution flowing into the tank 13 is drawn off from time to time, regenerated and returned to the tank 1 for passage through the tank 5. In the case of a cupro ammonia solution, for instance, the liquid in the tank 13 contains cellulose, copper, ammonia and an undue amount of water. This solution may be first cooled, then saturated with ammonia gas after which hydrated cupric-oxide may be added to saturation and finally any desired grade of cellulose also to saturation. The solution may then be filtered, and if desired returned to tank 1, the ammonia and copper used having been obtained largely by recovery from the previous electrolytic action in tanks 5 and 34.

The cellulose films upon the reels 56—57 may now be passed over a series of hot rolls if desired and dried. Film thus made can be produced with glass-like transparency and of high tensile strength. It can be adapted to a variety of purposes. It may be be cut or otherwise formed in grains, nitrated with a mixture of nitric and sulphuric acids, washed, stabilized and dried and an excellent smokeless powder produced without the use of a volatile solvent. By treatment while still slightly moist with a hot solution of nitric acid of about 80% concentration, a material is obtained rather low in nitrogen content but still decidedly soluble in volatile solvents and of value as a waterproof coating for varnish and the like.

For the production of photographic films, a preferred method of treatment is to protect one side of the film by means of a coating of paraffine or by close contact with a revolving drum, and while thus protected to pass the film slowly and continuously through any desired nitrating bath of nitric and sulphuric acid. By this means the surface exposed to the acid is nitrated to any desired depth, the depth of nitrating being controlled by the speed of the film or by the degree of concentration of the acid mixture. The film is now passed through a water bath, the protective coating stripped or otherwise removed (when used) and the film is passed through an electric field between electrodes immersed in a dilute alkaline solution by which means the last traces of acid are readily removed or decomposed. The film is again washed in hot running water and may be dried on hot rolls. It is now passed through a volatile solvent such as acetone or amyl-acetate, the non-nitrated side being protected by a drum and the nitrated side gelatinated to the full depth of nitration. The film is now drawn through a drying chamber and the volatile solvent removed. At this stage the product consists of a tough cellulose-like, waterproof backing gradually merging into a non-nitrated water-absorbing facing. The facing is now impregnated with any desired light-sensitive salts, passed through boiling water to improve the sensitiveness if desired and finally dried. All of the above operations are continuous, and where space is available the reels 56—57 may be dispensed with and the above operations carried on immediately after the film leaves the roller 55.

The product obtained by these operations compares more than favorably with the present celluloid films. It is cheaper to manufacture and the cost of plant is much less. It is very much slower burning, and is not explosive as practically half of it is unnitrated and the fact that the light-sensitive material, silver for instance, is deposited directly in the film itself instead of being merely coated on the outside, effectually prevents scratching or peeling off with the consequent production of light streaks, etc. upon the projection on a screen. The silver deposited being of a considerable depth, approximately .002 of an inch in place of only .0004 of an inch as in present films, permits of a scratch five times as deep as with the present films, and a correspondingly increase of life of the film. Tracing, blue print material, etc., made of this material

are superior and cost but little more. They are oil and moisture-proof, are transparent and may be printed one from another quite readily.

In case it is desired to produce an elastic or flexible condition such as may be required for artificial leather, the film after leaving the roll 55 on the wash tank 50 may be led through a solution of glycerine and water, say about thirty per cent (30%) glycerine for about a half hour preferably maintained at a temperature of say about 220° Fahrenheit. This forms a glyceride of cellulose which leaves the film non-hydroscopic under atmospheric conditions. It has also been found that asbestos may be dissolved in the cupro ammonia solution and may be treated much the same as the cotton above referred to, and of course various other materials may be employed according to requirements.

In the modification shown in Fig. 2, the electrolytic tank is indicated by reference character 60 with drain-off 61 leading to the electrolytic chamber 62 wherein the electrolyte 63 is carried. 64 indicates a copper strip which may be placed at the bottom of the electrolyte and connected to the negative terminal of the electrical circuit forming the cathode element. 65 indicates a suitable wheel preferably of porous material such as porous cups are made of, and is hollow with an opening at the centre as shown at 66 and is preferably provided with glass ends, through which a dilute acid such as nitric or sulphuric acid may be introduced, or a normally metallic salt, or it may be preferable to employ a solution of ammonium nitrate, the same being indicated by reference character 67. 68 indicates an electrode preferably of platinum connected to the positive terminal of said electrical circuit and suspended as shown, so that the distance between the periphery of the wheel 65 and the two electrodes are preferably fairly equal throughout the tank. The wheel may now be rotated slowly and the film of pure cellulose which accumulates on the periphery is readily removed by the scraper 69 and may be wound around the reel as indicated at 70, or if desired the porous element 65 may remain stationary and a suitable belt may be drawn around the lower periphery of the same through the electrolyte to take the film, and the belt and film may then be separated as indicated at 20—28 in Fig. 1. Of course the anode 68 may be made of carbon or any other suitable material. One of the objects being to prevent any of the metal which is to be taken out of the electrolyte from passing through the porous diaphragm or wheel as the case may be. Where a belt is passed through the electrolyte to receive the cellulose it is of course preferable to have it of a material other than the metal of the electrolyte, and where a suitable flexible porous belt is used it is only necessary to have a guide therefor in order to separate the electrolyte and the anode solution such as ammonium nitrate. The cathode 64 may of course be preferably a strip of metal such as copper laid in the bottom of the electrolytic bath as shown in Fig. 2 so as to conform to the diaphragm or partition 65 separating the electrolyte from the anode solution. Of course where a porous drum is used as in Fig. 2 the ends of the drum are coated preferably with paraffine so that the current passes only through the rim or periphery forming a uniform flat ribbon-like film. It will also be observed that if a finely woven or otherwise formed belt of wool, camel's hair filtered cloth, or other suitable material not soluble in the electrolytes used, is passed around the periphery of the porous drum where it is immersed in the tank, that the film of cellulose will be formed thereon instead of on the drum and may be readily removed therefrom as shown in Fig. 1. In fact, instead of using a wool belt, a strip or ribbon of cellulose itself may be washed in a dilute solution of sulphuric acid, thus rendering it insoluble in the electrolytes though sufficiently porous to allow for the passage of the current therethrough, and the pure cellulose will be deposited thereupon and may be readily removed therefrom as aforesaid. Another method is shown in Fig. 3 wherein an outer tank carrying the cupro ammonia cellulose electrolyte is provided with a pair of convex pulleys carrying a suitable belt such as wool which in turn carries a nitro ammonia solution with an anode therein, and a cathode in the outside electrolyte, it being understood that both electrolytes are maintained at the same level. The current passes through the belt leaving the pure cellulose thereon to be removed as aforesaid, while the copper from the cellulose accumulates upon the cathode.

Of course it will be understood that various modifications may be made in the proportions and combinations of ingredients and in the construction and arrangement of parts and in the mode of procedure without departing from the spirit of the invention as claimed.

I claim:

1. The method of producing a cellulose film consisting in passing an anode carrying the film through an electrolytic cellulose solution containing a cathode.

2. The method of producing films consisting in passing an anode carrier for the film through an electrolytic solution of organic material containing a cathode, thereby depositing organic material on the anode to form the film.

3. The method which consists in passing

an electrode carrier through an electrolytic solution of organic material, thereby electrolytically depositing organic material from said solution on the electrode carrier to form the film as the carrier passes through the electrolyte.

4. The method which consists in passing an electrode carrier through an electrolytic solution of organic material, thereby electrolytically depositing organic material from said solution on the electrode carrier to form the film as the carrier passes through the electrolyte, and regulating the electrolytic deposit by varying the relative strength of the electrical current with reference to the speed of movement.

5. The method which consists in passing an anode carrier through an electrolytic solution of cellulosic material containing a cathode, thereby electrolytically depositing a layer of cellulose from said solution on the anode carrier as the carrier passes through the solution.

6. The method which consists in passing an anode carrier through an electrolytic solution of cellulosic material containing a cathode, thereby electrolytically depositing a layer of cellulose from said solution on the anode carrier as the carrier passes through the solution, and regulating the electrolytic deposit by varying the relative strength of the electrical current with reference to the speed of movement.

7. In an apparatus of the class described, the combination of an electrolytic cell containing an electrolyte having therein organic material in solution, and an electrode carrier passing through the electrolyte in the cell as electrolysis proceeds.

8. In an apparatus of the class described, the combination of an electrolytic cell containing an electrolyte having therein cellulosic material in solution, a metallic belt passing through the solution in said cell, said belt being connected to the positive terminal of a source of electrical current, and a fixed cathode in the solution in the cell.

9. In an apparatus of the class described, the combination of an electrolytic cell containing an electrolyte having a cellulosic material in solution, an anode carrier passing through the solution in the cell, and a fixed cathode in the cell.

In testimony whereof I hereunto affix my signature.

THOMAS A. HILL.