

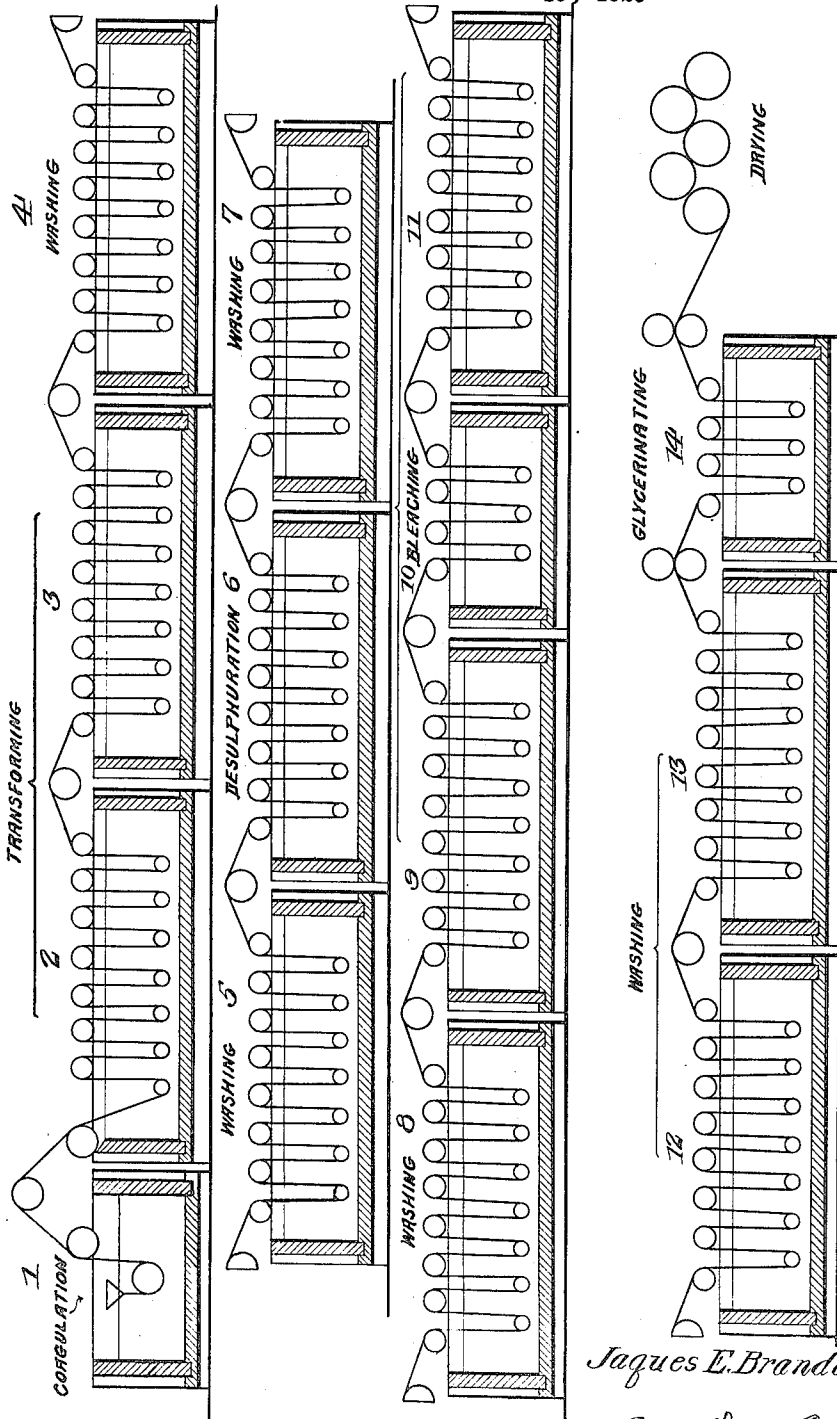
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MANUFACTURE OF VISCOSE FILMS, ETC

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MANUFACTURE OF VISCOSE FILMS, ETC.

Application filed June 19, 1923. Serial No. 646,478.

To all whom it may concern:

Be it known that I, JAQUES EDWIN BRANDENBERGER, a citizen of Switzerland, residing at Neuilly-sur-Seine, France, have invented certain new and useful Improvements in the Manufacture of Viscose Films, Etc., of which the following is a specification.

The object of this invention is to provide a process of manufacturing, in a continuous manner, cellulose strips, films, and the like derived from aqueous solutions of sodium cellulose xanthate generally termed "viscose".

The expression "in a continuous manner", is intended to indicate that the operation is conducted in such a way that the liquid viscose, running uninterruptedly into a coagulating bath, is transformed without any interruption into a finished product: strips, films, etc., consisting of regenerated cellulose obtained from sodium cellulose xanthate.

In certain former processes of making film, the xanthate solution was subjected to the coagulating action of a bath composed of an aqueous solution of ammonium sulphate or of other salts endowed with coagulating properties. The film so obtained was then treated by means of various successive baths for the purpose, first, of purifying it by means of an aqueous solution of sodium chloride, then of causing the xanthate to be transformed into cellulose under the action of a mineral acid, and lastly of washing it first with cold and next with hot water.

The present invention consists of a new process for manufacturing in a continuous manner threads, filaments, strips, films, tubes, etc., starting from viscose. Its essential difference from the one hitherto used—mention of which is to be found above—lies in this; that after the sodium cellulose xanthate has been coagulated in the first bath, its transformation into cellulose by means of a mineral acid follows immediately in the next bath, and the regenerated cellulose is then subjected to the action of certain baths, as will be explained later, for the purpose of purifying, bleaching, dyeing, glycerinizing, etc.

In the following description, there will be discussed, for convenience, the application of the present process to the manufacture of films, which films are obtained by extruding viscose in the form of a sheet from

a slotted hopper and allowing it to pass into the first coagulating bath; if it is desired to obtain threads, films, strips, tubes, etc., it would be necessary to use instead of the slotted hopper, a suitable device containing apertures through which the viscose is extruded, which apertures are adapted to make the kind of product desired.

In manufacturing film the viscose or solution of sodium cellulose xanthate as it issues from the slotted extruding hopper passes into a suitable coagulating bath. The film so formed then travels, in a continuous manner, through a series of vats wherein it is supported by suitable guide rollers, the successive vats containing baths adapted for subsequent operations.

There is no occasion to emphasize the mechanical features of the apparatus; and as regards the progress of the film through the various vats, the drawing which has been appended hereto is merely intended to indicate the sequence of baths and thus facilitate an understanding of the description, the actual invention being primarily limited to the process.

On issuing from the first or coagulating bath, the film passes through a converting bath which causes the cellulose xanthate to be converted to cellulose; next the film is subjected either to cold or to hot water washing and then to the action of a desulphuring bath; thereafter, the film is subjected to a second washing in either hot or cold water, at any rate hot at first, and finally is subjected to the action of either a bleaching or a dyeing bath. After this last operation, the film is successively washed in running water, squeezed, put through a glycerine bath and ultimately dried either immediately or later.

Reference will again be made to each one of the various aforementioned operations, specifying the operating method and the characteristics for and of every one of them; the accompanying drawing showing diagrammatically the complete process as carried out in the successive vats which are indicated by reference numerals in regular order.

Vat 1: coagulation.—Coagulation of the sodium cellulose xanthate is effected, as in former processes, by means of a bath containing, for instance, an aqueous solution of sulphate of ammonia; I can also utilize aqueous solutions containing either a mix-

ture of sulphate of ammonia and an acid, or a mixture of sulphate of ammonia and a base, or bisulphate of soda or sulphate of soda with an acid added thereto, or magnesium sulphate or zinc sulphate; furthermore I may utilize any two normal sulphates in combination.

When I use an acid coagulating bath or a bath containing bisulphates, I find that in this coagulating bath the xanthate immediately becomes partly transformed into cellulose.

The composition (proportion of constituents) of the coagulating bath actually used is determined by a number of factors, viz, the temperature of this bath, the degree to which the viscose has matured or ripened, the composition of the viscose, the thickness of the film desired and the duration of contact of the viscose with the coagulating solution, which is determined by length of travel in the bath and machine speed.

There are, for instance, certain working conditions which hold good for all the following explanations and to which the example given will refer.

I will assume that the working speed is 25 meters per minute, and that the film to be obtained is to weigh from 25 to 30 grams per square meter.

Under these conditions, and utilizing in the first bath as a coagulating solution a mixture of sodium sulphate and sulphuric acid, the best results are obtained with the following proportions, viz: 10 grams of sodium sulphate and 10 grams of sulphuric acid per 100 cubic centimeters, the film remaining in the coagulating bath for about 35 seconds.

Vats 2 and 3: transforming bath.—This bath, which is designed to effect the transformation of the xanthate into cellulose and which is utilized immediately after coagulation and previous to all other operations, consists of an aqueous solution of a mineral acid such as, for instance, hydrochloric acid, sulphuric acid etc.

Under the aforesaid conditions (speed 25 meters per minute, film weight 25 to 30 grams per square meter) good results are obtained with a bath containing about $4\frac{1}{2}$ grams of sulphuric acid in 100 cubic centimeters of water, with a contact-duration of about 35 seconds.

Vats 4 and 5: washing.—On issuing from the transforming bath, the film is subjected to a cold or hot water washing to remove acid and salts. The film after acid treatment is opaque and white. If the washing is thorough, the film becomes somewhat transparent, but it still contains a certain amount of sulphur which makes it somewhat opaque. This sulphur may be removed, however, by means of the desulphuring bath.

Vat 6: desulphuring.—The desulphuring

bath consists either of a hot aqueous solution of sodium sulphide, the temperature of which may be as high as 100° C., or of a solution of caustic soda or of a solution of both or of any other body or substance endowed with desulphuring properties.

The composition of this bath depends on the same factors as those already mentioned. There may be used, for instance, under the aforesaid conditions, a solution of about 0.4 gram or 0.5 gram of caustic soda for about 100 cubic centimeters of water, and the film may be allowed 15 seconds contact with the bath.

Vats 7 and 8: washing.—After desulphuration, the film is subjected to a washing with water in two vats. This washing is preferably effected hot, at any rate in the first vat, and at as high temperature as possible, even up to 100° C. The desulphuring agent which is carried over with the film is in fact of an alkaline nature and therefore very difficult to remove with cold water. The hot washing may, if desired, be followed by a cold water washing.

Vats 9, 10 and 11: bleaching.—This operation may be carried out in various ways. One method consists in treating the film in the first step by means of a bath composed of an aqueous solution of sodium hypochlorite, or of hypochlorite of lime containing a proportion of available chlorine amounting to from about 0.4 gram to 0.8 gram per 100 cubic centimeters, and then by means of a second bath (vat 11) composed of an aqueous solution of a mineral acid such as hydrochloric or sulphuric acid, for instance; in this case, the film passes from vat 9 directly to vat 11 without entering vat 10 which becomes useless.

Another method involves the following:

The film is subjected successively to the action of a bath composed of a solution of sodium hypochlorite in vat 9, to a very brief cold water washing in vat 10 and to the action of a mineral acid in vat 11.

Still another operating method which may be used consists in treating the film with a solution of chlorine in water, the maximum concentration of which should be about 0.3 gram of chlorine in 100 cubic centimeters of water. Part of the dissolved chlorine becomes transformed under the action of water into hydrochloric acid which imparts to the bath the required acidity.

Vats 12 and 13: washing.—After bleaching by means of any one of the above-described methods, the film is subjected to a washing in rapidly running water. This washing may be effected hot or cold, or even in two different baths, one hot and the other cold, with about 15 seconds stay in each bath.

Vat 14: glycerine bath.—After washing, the film is subjected to a squeezing action

between two smooth presser rollers, and is then treated in a glycerine bath. The purpose of this treatment is to impart the required pliancy to the cellulose film.

5 With the assumed speed of 25 meters per minute, the film has a length of time of immersion in the glycerine bath of about eight seconds, and the concentration of the glycerine bath is determined by the use for
10 which the film is intended. This concentration is greater when it is intended to make a more pliable film, and less when it is intended to make a less pliable film, but ordinarily the concentration is maintained so
15 that the specific gravity of the glycerine solution is between 1.009 and 1.012.

After this treatment, the film may be squeezed and then placed in a suitable drying apparatus to dry.

20 If a colored film is desired, the above described bleaching step may, of course, be replaced by a suitable dyeing treatment, without the other operations being modified in any way. The dyeing baths should have the
25 same composition as those used for dyeing cotton, artificial silk or any other cellulosic fiber, in so-called continuous dyeing apparatus, the colors usually used for this purpose being the so-called "direct" colors. Dye-
30 ing may also be effected at the same time as desulphurization by adding to the desulphuring bath coloring materials such as the so-called "sulphur" colors. It is also
35 to be clearly understood that viscose may be used which has been colored previous to coagulation either by means of sulphur colors or of any other coloring materials that will dissolve in viscose without decomposing.
40 No claims are contained in the present case for the dyeing step, however, as such claims form the subject matter of a divisional application No. 708,316, filed April 22, 1924.

45 It is to be understood that the process applies equally to the case where inert substances such as barium sulphate, kaolin, etc., have been introduced into the viscose.

I claim as my invention:

50 1. A process for the continuous manufacture of cellulose films and the like, comprising the steps of coagulating an aqueous solution of sodium cellulose xanthate; passing the coagulated product through a transforming bath consisting of an aqueous solution of sulphuric acid containing about
55 4.5 grams of sulphuric acid per 100 cubic centimeters of water, and allowing the product to remain about 35 seconds in such bath; desulphuring the transformed product; and then bleaching, glycerinating and drying
60 the same.

2. A process for the continuous manufacture of cellulose films and the like, comprising the steps of coagulating an aqueous solution of sodium cellulose xanthate; passing the coagulated product through an aqueous
65 mineral acid solution to transform it into cellulose; washing the transformed product with caustic soda to desulphur it; and then bleaching, glycerinating and drying the same. 70

3. A process for the continuous manufacture of cellulose films and the like, comprising the steps of coagulating an aqueous solution of sodium cellulose xanthate; passing the coagulated product through an aqueous
75 mineral acid solution to transform it into cellulose; washing the transformed product with an aqueous solution of caustic soda containing about 0.5 gram of caustic soda per
80 100 cubic centimeters of water to desulphur it, and maintaining said product in such solution for about 15 seconds; and then bleaching, glycerinating and drying the desulphured product.

4. A process for the continuous manufacture of cellulose films and the like, comprising the steps of coagulating an aqueous solution of sodium cellulose xanthate by introducing it into an aqueous mixture of sodium
85 sulphate and sulphuric acid; transforming the coagulated product into cellulose by passing it through an aqueous sulphuric acid solution; washing the transformed product with caustic soda to desulphur it; then bleaching
90 the product by treating it first with an aqueous solution of sodium hypochlorite and then with an aqueous mineral acid solution; washing the bleached product with running water; and then glycerinating and
95 drying the same. 100

5. A process for the continuous manufacture of cellulose films and the like, comprising the steps of coagulating an aqueous solution of sodium cellulose xanthate
105 by introducing it into an aqueous mixture of sodium sulphate and sulphuric acid; transforming the coagulated product into cellulose by passing it through an aqueous sulphuric acid solution; washing the transformed product with caustic
110 soda to desulphur it; then bleaching the product by treating it first with an aqueous solution of sodium hypochlorite and then with an aqueous mineral acid solution, with a short washing between the two treatments; 115
washing the bleached product with running water; and then glycerinating and drying the same.

In testimony whereof I affix my signature.

JAQUES EDWIN BRANDENBERGER.