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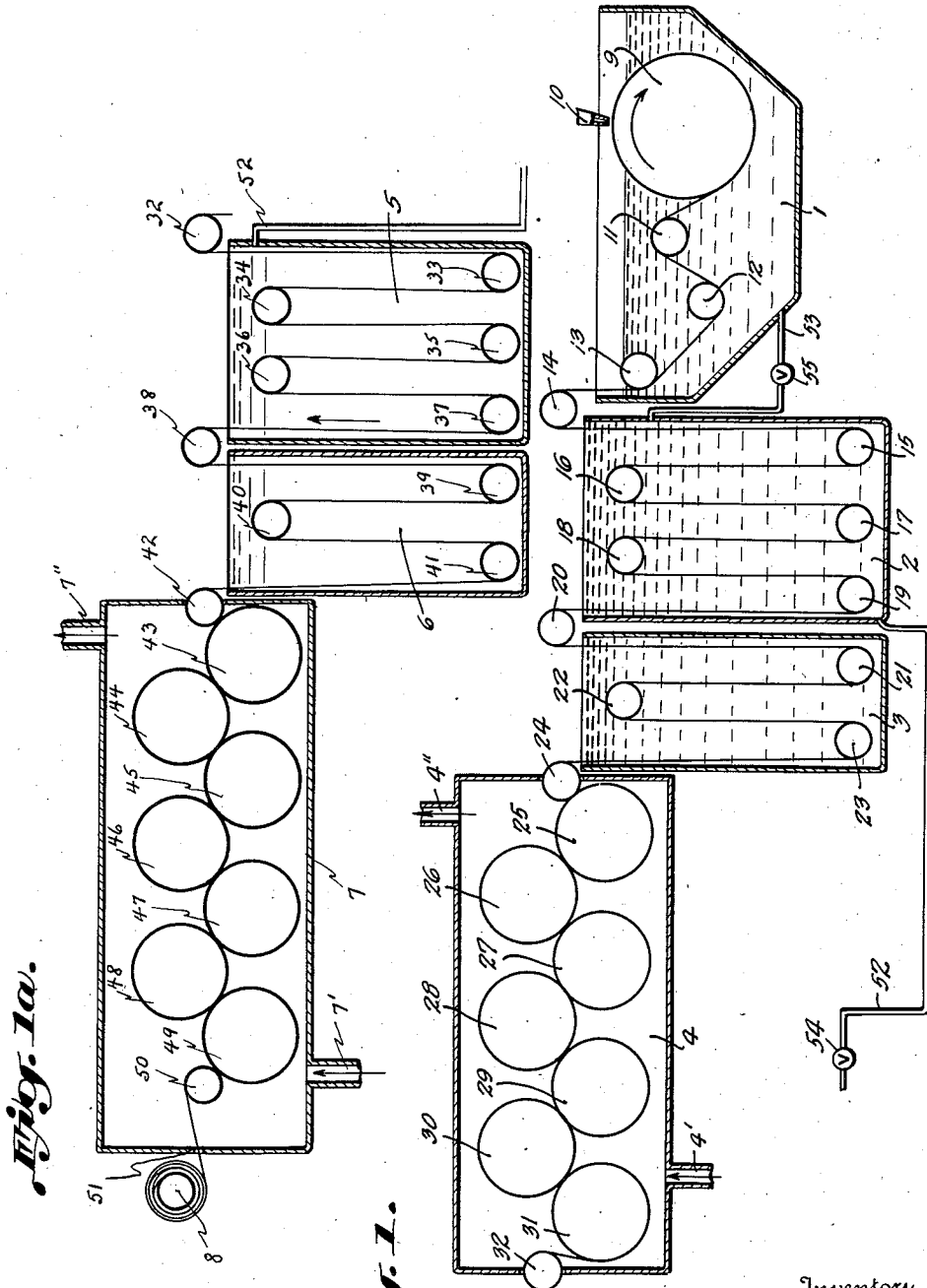


Fig. 1a.

Fig. 1.

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PROCESS FOR THE PRODUCTION OF FOILS
OR FILMS OF CELLULOSE TRIACETATE

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9 Claims. (Cl. 18—57)

The present invention relates to a process and apparatus for the production of foils or films of cellulose triacetate.

In the past, efforts have been made to produce various forms of articles from cellulose triacetate by introducing the acetylated solution into an aqueous solution of acetic acid as a precipitating agent. No practical procedure for producing films or foils by this method has heretofore been discovered. Products of this nature have generally been cloudy or turbid, and at times brittle, and their surfaces have been marked by longitudinal or transverse striations which rendered them unfit for any practical use.

We have discovered that these defects can be avoided by the process to be described below. This process consists essentially in using solutions of cellulose triacetate in which the cellulose triacetate contains at least 59% acetyl, calculated as acetic acid, in combined form, and in which the catalyst has been rendered inactive directly after the termination of acetylation. Furthermore, the precipitating liquid into which the cellulose triacetate is introduced contains not more than 20% and preferably from 7% to 20% of acetic acid. A film produced in this manner, after it has been washed and dried, has a surface which is free from striations and cloudiness. In no other manner can these defects be avoided.

In carrying out the process in practice, solutions of cellulose triacetate which have been primarily stabilized are suitable.

A further feature of the process is that the strength and lustre of the films is considerably increased, if the temperature of the precipitating bath is kept as low as possible, and especially below 30° C. Where very low temperatures are used, a pouring device in the nature of a slotted nozzle is preferably used, because of the tendency of the solution which is being poured to solidify. Since at low temperatures the rate of precipitation is reduced considerably, it is possible for the adjacent cells of the cellulose to arrange themselves in parallel relation throughout the film, this arrangement being essential both for strength and for complete transparency to light. It is especially advantageous to stretch the film during its coagulation.

If the above conditions are observed it is possible to obtain a completely precipitated foil from a solution which contains 10% or more of cellulose triacetate. Solutions of such high concentration produce a foil which has a consider-

able permanence of form so that damage by tearing during the process is avoided.

Further objects and advantages of the invention will appear more fully from the following description particularly when taken in conjunction with the accompanying drawing which forms a part thereof, and which discloses an apparatus for carrying out the invention.

In the drawing:

Fig. 1 shows a portion, diagrammatically and in section, of an apparatus for carrying out the invention.

Fig. 1a shows a continuation of the same device, the right hand side of Fig. 1a corresponding to the left hand side of Fig. 1.

As shown in the drawing, the apparatus comprises a bath 1 of precipitating liquid in which is arranged a roll 9 which extends above the level of the surface of the liquid. A nozzle, such as a slotted nozzle 10, is arranged adjacent the top of the roll 9. Within the bath 1 are arranged idler rolls 11, 12, 13. Washing baths 2 and 3 are arranged as shown in series with the bath 1. A roll 14 is arranged between baths 1 and 2 and a roll 20 between baths 2 and 3. In the bath 2 are arranged idler guide rolls 15, 16, 17, 18, 19 and in the bath 3 guide rolls 21, 22, 23.

The drying device 4 consists of a substantially closed chamber having an inlet 4' and an outlet 4''. In one wall of the drying chamber 4 adjacent the bath 3 is arranged a roll 24 and in the opposite wall a roll 32. Within the chamber are a plurality of guide and pressing rolls 25, 26, 27, 28, 29, 30 and 31.

Next to the drying chamber 4 are arranged a pair of washing baths 5 and 6 (Fig. 1a). Bath 5 is arranged adjacent the roll 32, and between baths 5 and 6 is a roll 38. Within the bath 5 are guide rolls 33, 34, 35, 36, 37 and in the bath 6 are guide rolls 39, 40, 41. 7 represents the second drying chamber having an inlet 7' and an outlet 7'', this being a closed chamber in one wall of which adjacent the bath 6 is arranged a roll 42. Within the chamber are guide rolls 43, 44, 45, 46, 47 and 48, and adjacent the other wall of the chamber is a guide roll 50. Adjacent the outlet slot 51 near the guide roll 50 in the wall of chamber 7 is a take-up roll or reel 8 driven in a suitable manner by a friction clutch.

The use of this arrangement will be clear from the following examples:

Example I

The starting material is an acetylated solu-

tion of cellulose triacetate, the cellulose triacetate containing about 61% acetyl, calculated as acetic acid. This material is produced by the use of suitable quantities of a weak catalyst. The weak catalyst is first neutralized, the excess acetic anhydride is converted into approximately 95% acetic acid, and the solution is stabilized by heating for several hours at 80° C. to 100° C. This solution which contains about 15% cellulose triacetate is filtered and de-aerated. It is then fed to the nozzle 10 so as to be spread in the form of a film on the roll 9. The film so produced is carried by the roll 9 into the bath 1 containing a 7% aqueous solution of acetic acid. If a foil of a thickness of 0.02 mm. is to be formed, the foil should remain on the roll 9 in the bath for a period of about 30 seconds so that it will attain sufficient permanence of form to be removed from the roll 9 without injury. The concentration of the bath may vary up to about 20% acetic acid, but if this limit is exceeded irregularities in the surface of the film and longitudinal striations are likely to be produced. The bath 1 is maintained preferably at room temperature.

After the film passes out of the bath 1 it may be dried or washed in any suitable manner, preferably in the manner described below in connection with the remainder of the apparatus.

Example II

An acetylated solution is produced using from 2% to 5% of sulphuric acid as the acetylation catalyst. The cellulose triacetate in this solution contains about 62.5% acetyl, calculated as acetic acid. The catalyst is neutralized and the excess fatty acid anhydride removed by adding 5% to 10% (calculated on the weight of the solution) of methanol chloride or formic acid. The solution is then filtered and de-aerated, while it is maintained at a temperature between 30° C. to 50° C. to avoid any undesirable increase in the viscosity. The material is expressed through a slotted nozzle, at a pressure of several atmospheres, into a precipitating solution or coagulating bath comprising a 15% solution of acetic acid in water, which is maintained at a temperature of from 0° C. to 5° C. Because the foil is exposed on both sides to the material of the bath, 5 to 10 seconds' contact with the material of the bath coagulates the foil sufficiently so that it may be handled for passage to a further coagulating and washing bath.

With respect to the purposes and advantages of the washing and drying arrangements now to be described, the following features of interest should be noted.

During the process, precaution should be taken to prevent any free inorganic acids, which may be formed through the splitting of easily saponifiable catalyst residues of the cellulose acetate, from passing into the precipitating bath and accumulating therein.

If desired, materials may be added as softening agents to the solution to be poured. These softening agents should be such as will not be dissolved from the material of the freshly poured foil by the precipitating agent. For example, triphenyl phosphate and tributyl phosphate may be added in amounts as high as 100% of the triacetate in the solution. Triacetine, ethyl phthalate, and the like, on the other hand, are easily dissolved by the precipitating bath.

According to the process, we have found that the removal of the last traces of acetic acid from

the foil will be facilitated if the foil is first washed, then dried by heating to a moisture content of about 20% to 50%, then again washed and then dried. This second washing step appears to remove all of the acetic acid.

We have also discovered that although cellulose triacetate in itself is hydrophobic, it possesses the property of taking up water soluble softening agents from other liquids. By adding suitable softening agents to the washing baths, such as glycerin, di-glycerin, or glucose, these agents may be incorporated in the foil before it is dried. The quantity of softening agent may be regulated by varying the concentration of such agent in the washing bath.

A further feature of the invention consists in removing the principal portion of the water contained in the foil, before the final step of drying it by heat, by washing the film with an organic solvent which is easily miscible with water but does not exert a swelling action on the film. Methanol is suitable for this step. When the film is dried in this manner after treatment with methanol no creases caused by shrinkage occur on drying. Even extremely thin foils may be rolled without damage after such a treatment.

Referring now to the drawing, in which the dot and dash lines indicate the path of the film, a film formed and precipitated for example as described above in Example I may pass from the roll 9 over the rolls 11, 12, 13 and 14 into the bath 2. This bath for instance may contain water for washing the film. The foil passing over rolls 15, 16, 17, 18, 19 and 20 then enters the washing bath 3 which may contain either water or an organic liquid such as methanol. The foil then passes over roll 24 into the first drying chamber 4. Air is blown through this chamber into contact with the film on the rolls 25 to 31, and this air escaping through the outlet 41 may be carried to a recovery device for removing any organic liquid therefrom. By regulating the humidity and flow of the air, the amount of drying produced in the drying chamber 4 may be controlled.

The foil then passes out of the chamber over roll 32 to a bath 5 of water in which any residual acid is washed out. After being guided by rolls 33, 34, 35, 36 and 37 through the bath 5 the film passes over roll 38 to a bath 6 in which it is guided by rolls 39, 40 and 41. This bath may contain either water or methanol. When the bath contains water, water soluble softening agents such as glycerin, di-glycerin or glucose may be included and thus introduced into the foil. If the bath contains an organic liquid, it is possible to introduce either dyes which are soluble in alcohol or benzol, or softening agents such as alkyl phosphates or phthalic esters. By varying the concentration of the material and the time the foil remains in the bath the quantity of any material taken up by the foil may be regulated.

The roll 32 may be arranged so as to regulate the width of the film, so that, if shrinkage has occurred in the width of the films during the drying, they will be again expanded before they enter the baths 5 and 6.

The film then passes over roll 42 into the drying chamber 7 which is substantially similar to drying chamber 4, and in this chamber, the film is guided by pressure and guide rolls 43 to 50. The film then passes through the slot 51 to the drum 8 where it is wound up into a roll.

By the inclusion of softening agents or dyes in the material of the bath 6 it is possible to incorporate such materials into the foil just before its

final drying. However, such materials also may be included just before the intermediate drying by introducing them into the bath 3.

It is also desirable to have the precipitating bath and washing baths operate on the counter-current principle. For this purpose the individual washing baths may be connected with each other and with the precipitating bath by conduits, such as for Example 52, 53. These conduits may be provided with manually or automatically regulated valves 54, 55. By passing the water through bath 5, and then through bath 2 to the bath 1, the acetic acid dissolved from the film acts as a precipitating agent in the precipitating bath.

While we have described herein some embodiments of our invention, we wish it to be understood that we do not intend to limit ourselves thereby except within the scope of the appended claims.

We claim:

1. A process for the production of foils or films of cellulose triacetate, comprising forming a film of acetylated solutions of cellulose triacetate, in which the cellulose triacetate has an acetyl content of at least 59%, calculated as acetic acid, and in which the catalyst has been rendered inactive substantially directly after termination of the acetylation, and introducing such film into an aqueous precipitating bath which contains from 7% to 20% of acetic acid, washing out and drying the film thus obtained.

2. A process according to claim 1 in which the temperature of the precipitating bath is below 30° C.

3. A process according to claim 1 in which the acetylated solution contains at least 10% of cellulose triacetate.

4. In a process according to claim 1, the washing out and drying steps consisting of first washing the film, subjecting the film to a partial intermediate drying, further washing the film to remove residual acid therefrom, and then further drying the film.

5. In a process according to claim 1, said washing out step comprising introducing the film into a bath which contains water soluble softening agents, whereby such softening agents are incorporated in the film before it is dried.

6. In a process according to claim 1, said washing out step comprising washing the film with water, and then with an organic liquid miscible with water which does not exert a swelling action on the film.

7. Process according to claim 1 in which said washing out step comprises introducing the film into a bath of water and thereafter into a bath of an organic liquid miscible with water which does not exert a swelling action on the film, said last bath containing a softening agent.

8. Process for the production of foils or films from cellulose triacetate, comprising forming a film of acetylated solutions containing at least 10% of cellulose triacetate, in which the cellulose triacetate has an acetyl content of at least 59% calculated as acetic acid and in which the catalyst has been rendered inactive directly after termination of the acetylation, and introducing such film into an aqueous precipitating bath which contains from 7% to 20% of acetic acid and which is at a temperature of less than 30° C., then introducing the film thus obtained into a washing bath containing water, then partially drying the film, then introducing the film into a second washing bath containing water to remove residual acid therefrom, then introducing the film into a bath of an organic liquid which is soluble in water but which does not exert a swelling action on the film, and then drying the film.

9. A process for the production of foils or films of cellulose triacetate, comprising forming a film of acetylated solutions of cellulose triacetate, in which the cellulose triacetate has an acetyl content of at least 59%, calculated as acetic acid, in which the catalyst has been rendered inactive substantially directly after termination of the acetylation and containing a softening agent which cannot be dissolved out of the film by an aqueous precipitating bath which contains 7% to 20% of acetic acid, and introducing such film into an aqueous precipitating bath which contains from 7% to 20% of acetic acid, washing out and drying the film thus obtained.

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