Sept. 29, 1964 J. L. RILEY 3,151,191

PROCESS OF REGENERATING SPENT SPIN BATH AND
COMPOSITION THEREOF
Filed Aug. 10, 1960

Fig. 1.

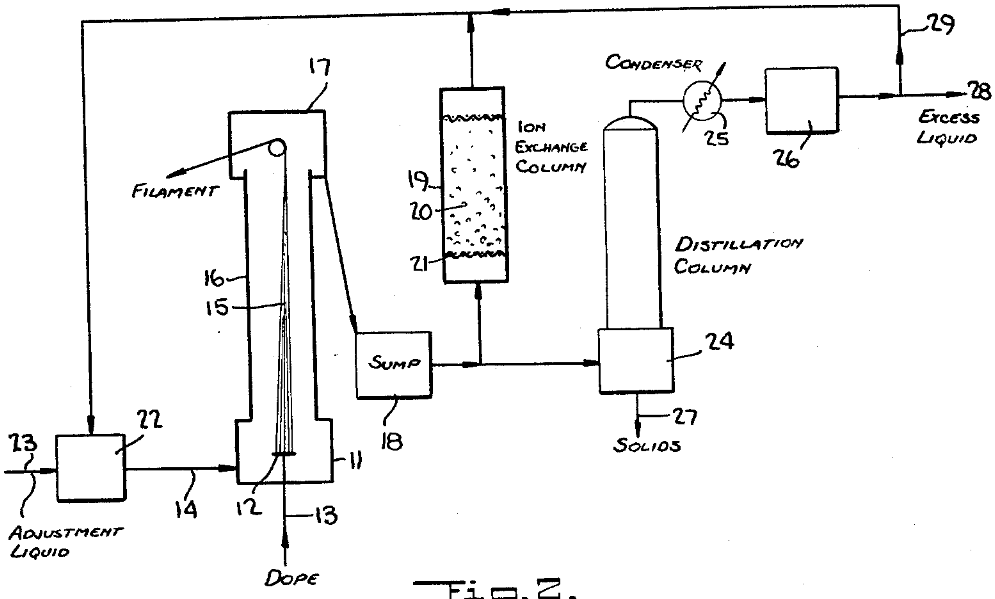
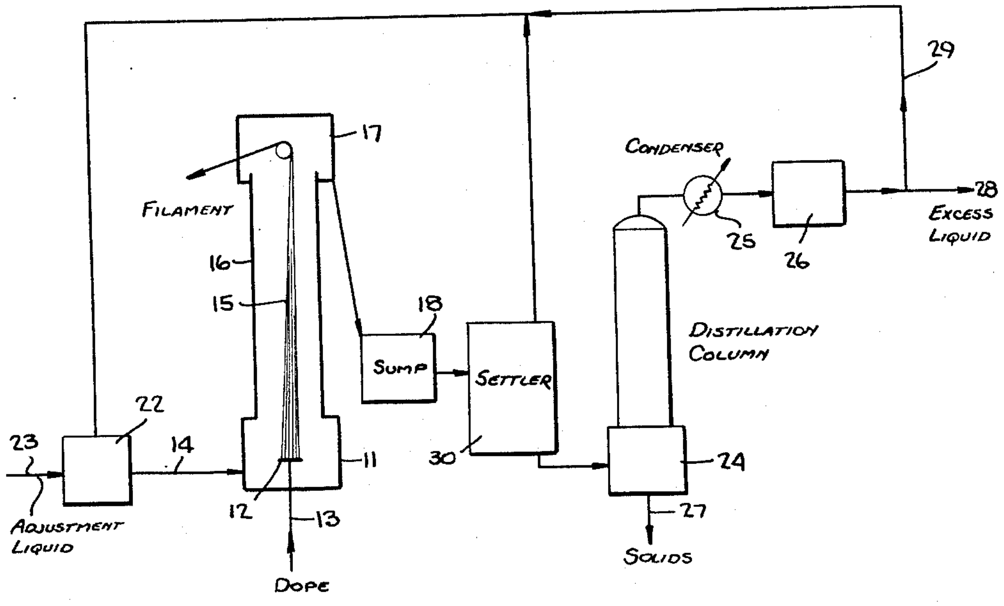


Fig. 2.



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PROCESS OF REGENERATING SPENT SPIN BATH AND COMPOSITION THEREOF

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The present invention relates to a novel spin bath in the wet spinning of cellulose esters to produce shaped structures and to novel processes for the treatment and regeneration of spent spin bath.

In the wet spinning of methylene chloride solutions of cellulose triacetate into methylene chloride-methanol spin baths to form filaments as described in application Serial No. 730,021, now Patent No. 3,057,039, filed April 21, 1958, it has been found that after spinning for some time solids begin depositing on the inside of the equipment so as gradually to change the characteristics of the filaments being spun and eventually requiring shut-down of the apparatus for cleaning when spinning becomes unstable.

It is an object of the present invention to reduce or eliminate the deposition of solids so as to lengthen the duration of stable spinning without interruption.

It is a further object of the invention to provide novel dopes and/or spin baths which will contribute to elimination of the deposits.

Other objects and advantages of the invention will become apparent from the following detailed description and claims in which all parts are by weight and all conductivities are determined at 25° C. unless other specified.

In accordance with one aspect of the invention it has been found that the deposited solids are essentially cellulose triacetate fines of somewhat lower average molecular weight than the filaments and that deposition of such suspended cellulose triacetate in the coagulation apparatus can be reduced if the formula $C^2-7C+10$ has a positive value where C is the conductivity in micromhos of the liquid in which coagulation takes place, i.e. substantially the spent spin bath. When operating within the lower portion of the recited conductivity range, preferably from about 0.3 to 2 micromhos, it has been found surprisingly that the tendency for suspended cellulose triacetate fines to deposit is minimized so that spent bath can be recycled with a minimum amount of treatment other than adjustment of its composition. When operating within the upper portion of the recited conductivity range, preferably from about 100 to 1000 micromhos, it has been found surprisingly that upon standing the spent spin bath will rapidly deposit suspended cellulose triacetate so that the supernatant liquid can be recycled relatively rapidly, after adjustment of its concentration.

The composition of the liquid in which coagulation takes place, whose conductivity is to be controlled according to the present invention, can be computed from a knowledge of the compositions of dope, fresh spin bath and freshly formed filaments and from a knowledge of the mass rates at which the dope and spin bath are supplied and the filaments are withdrawn. While cellulose triacetate, methylene chloride and methanol are all substantially non-conducting, in practice it has been found that the spent spin bath has an appreciable conductivity but one for which $C^2-7C+10$ has a negative value. This conductivity is apparently the result of introduction of ions with the dope or fresh spin bath. The cellulose triacetate always contains some ions introduced from the original cellulose, from the acetylation catalyst, the catalyst neutralization, the water washes, etc. These in part are transferred to the methylene chloride-methanol spin bath which when recycled as fresh spin bath also serves to introduce ions. In addition, there is unavoidably some small amount of water associated with the methanol as well as ionic contaminants in the methylene chloride and methanol introduced either during manfacture or by corrosion of vessels and lines. Even if the fresh spin bath were substantially non-conducting, the liquid in which coagulation takes place may be quite conductive due to the ions introduced with the dope. It is for this reason that the conductivity which is measured is that of the spent spin bath rather than that of the fresh spin bath; in any particular system operating at steady state there will be a definite relationship between the conductivity of the fresh spin bath and of the spent spin bath and, once this relationship has been determined, it may suffice to measure only the conductivity of fresh spin bath or components thereof supplied to the system as make-up.

Reduction in the conductivity of the spent spin bath can generally be accomplished by supplying fresh spin bath having a conductivity of less than about 0.5 micromho, the exact value depending upon the relative feed rates of dope and fresh spin bath. If there is employed a dope having a higher conductivity it will be necessary to compensate by employing fresh spin bath of lower conductivity.

I have found that more conductivity is usually imparted by the dope than by the fresh spin bath. Accordingly, to maintain a low conductivity in the liquid in which coagulation takes place it is usually necessary to treat any removed spent spin bath to lower its conductivity before re-use as fresh spin bath. The reduction in conductivity can be achieved by distillation to separate the substantially non-conductive organic solvents from the water and non-volatile ions. It can also be achieved by electrolysis of the spent spin bath to plate out metallic cations or to evolve as gases oxygen and/or hydrogen present in ionic form. Dialysis or electrodialysis of the spent spin bath with water or other liquid of lower ionic content on the other side of a semi-permeable membrane can also be employed. Because these techniques are slow, or expensive or so inefficient as to necessitate special treatment of the dope as well they are not the preferred treatments for reducing conductivity. The preferred treatment involves contact of the spent spin bath with an ion exchange resin. There can be employed an anion exchange resin or a cation exchange resin or both either in admixture or in succession. Preferably they operate on hydroxyl or hydrogen cycles; as explained hereinafter, however, different ions have different effects on the spent spin bath and accordingly even if the ion exchange resin operated on the sodium cycle it would result in a decrease in conductivity where the principal cations in the spent spin bath are calcium, iron, or the like. The exact amount of resin and the extent of treatment of course depend upon the degree of diminution in conductivity which is desired. Advantageously strong acid or basic resins are preferred such as the cation exchange resin sold under the name Dowex 50WX-8 by the Dow Chemical Co. Natural and/or inorganic ion exchange resins can also be employed. A partial list of suitable cation exchange resins includes sulfonated styrene-divinyl benzene copolymers, phenol-formaldehyde resins, phenol-formaldehyde-sulfite reaction products, sulfonated coal, and the like. A partial list of suitable anion exchange resins includes the reaction product of a tertiary amine with the chloromethylated copolymer of styrene and divinyl benzene, the reaction product of an alkylating agent such as methyl chloride or dimethyl sulfate with an amine-containing resin such as is obtained by reaction of formaldehyde, aniline and ethylene diamine, and the like.

When employing ion exchange resins preferably they are used as particles supported on a screen with spent spin bath flowing upwardly therethrough. This fluidizes the resin, prevents channeling of the spin bath and prevents the resin from functioning as a filter on which the suspended cellulose triacetate particles would settle if flow were downward. The exact particle sizes of ion exchange resins to achieve the desired effect will vary somewhat in dependence upon the shape of the container and the flow rate; generally, however, the particle size of the resins will range from about 0.01 to 0.05 inch and preferably from about 0.02 to 0.03 inch in diameter. The composition of the de-ionized spin bath is then adjusted, advantageously with de-ionized solvents, and it is recycled as fresh spin bath. The cellulose triacetate fines being recycled in the fresh spin bath will generally constitute about 0.02 to 0.5% and preferably about 0.08 to 0.12% of the spin bath. When starting spinning it is possible to commence with distilled spin baths free of cellulose triacetate or there can be employed a spin bath containing cellulose triacetate so that the system will be at steady state substantially from the outset.

In time the cellulose triacetate fines will coat out on the ion exchange resin particles and may reduce their efficiency. Accordingly, it is advantageous to soak the resin periodically in a solvent for cellulose triacetate to clean the particles; this solvent may be evaporated to separate the solvent from the residual cellulose triacetate which may be discarded. The number of ions involved in the reduction of conductivity is so small that the resin can be used for months without regeneration. When the ion exchange resin is being washed or regenerated, flow of spent spin bath can be collected in a reservoir or it may be passed to a second resin arranged in parallel to the first.

The volume of spent spin bath will obviously be greater than the volume of fresh spin bath supplied to the system in a given time interval, due to the solvent introduced from the dope. Accordingly a portion of the spent spin bath is generally withdrawn, advantageously before passage through the ion exchange resin or other conductivity-adjusting means, and may be treated to recover its values. One suitable treatment of this type involves withdrawal of a portion of spent spin bath containing about as much suspended cellulose triacetate fines as are left behind in the spent spin bath per cycle, e.g. if from the dope supplied 10 grams per hour of cellulose triacetate fines would be suspended in the spin bath in addition to the suspended fines introduced in the fresh spin bath, then so much spent spin bath would be withdrawn per hour as would contain 10 grams of suspended cellulose triacetate. This withdrawn portion could be evaporated so as to leave behind the cellulose triacetate fines and the purified distillate could be used either to adjust the composition of the fresh spin bath or to make up additional dope.

If desired, non-ionic peptizing or dispersing agents may be added to the dope or spin bath, fresh or spent, to assist in keeping the cellulose triacetate fines suspended. Representative dispersing agents include the higher fatty acid esters of polyalkylene glycols, e.g. the mono-oleate of polyethylene glycol, blown sperm oil (oleyl esters of palmitic, myristic and stearic acids aerated hot), and the like. These substances are preferably present in from about 0.08 to 0.15% by weight of cellulose triacetate in the dope although as much as 0.5% or even more can be present, if desired.

Where it is desired to keep the conductivity high in an effort to speed up settling of the fines in the withdrawn spent spin bath this can be achieved by use of dopes or spin baths of high conductivity but, to ensure constancy, electrolytes are preferably added to the system in predetermined amounts more or less frequently to compensate for the loss of ions in that portion of the spent spin bath which is withdrawn to reduce the volume of recyled spin bath. The spent spin bath is collected, allowed to settle for about 1 to 4 hours and about 50 to 99% and preferably about 90 to 99% of the spent spin bath is removed from the supernatant liquid and forwarded for recycle as fresh spin bath after adjustment of its composition and volume by addition of solvent and possibly electrolyte. The settling may be effected in a single stage or in a plurality of stages, although care should be taken not to complicate settling by re-dispersing settled solids in supernatant liquid. The separated liquid recycled as fresh spin bath will contain cellulose acetate in about the same proportion as when de-ionized spin bath is employed although the intrinsic viscosity and acetyl value of the cellulose acetate will in this case be much lower due to selective settling out of the material of higher intrinsic viscosity and acetyl value.

From the bottom of the settler thickened spent spin bath high in cellulose triacetate and of higher specific gravity than the supernatant liquid is withdrawn and treated to evaporate the solvents for recovery. The distillation residue is purged from the process. The percentage of the total spent spin bath which is sent to be evaporated in either this embodiment or in the embodiment employing reduction in conductivity will vary and will remove from the cycle cellulose triacetate fines at the same rate new fines are introduced by spinning. This percentage will vary but generally lies between about 1 and 10% and most preferably between about 1 and 4% of the total spent spin bath where settling is employed. Where de-ionization is employed without settling the percentage generally lies below about 25% and preferably below about 15%.

Where the conductivity of the spent spin bath is below about 5 micromhos it is found that its rate of settling in a quiescent settler is so slow as to require excessively large tanks, holding time and quantities of solvent to maintain the continuity of the process. This can be partially cured by subjecting all or much of the spent spin bath to evaporation or filtration but these alternatives are economically almost as undesirable as the use of a large settler.

In accordance with another aspect of the invention it has been found that certain ions are especially effective in accelerating settling, viz. the ions of polyvalent metals and especially cations of metals of Group II of the periodic table, copper, aluminum, chromium, iron, nickel or cobalt. For example, a spent spin bath whose conductivity is raised from 2 micromhos to 10 micromhos by addition of calcium acetate will settle much more rapidly than when the same increase in conductivity is effected by addition of sodium or ammonium acetate. The metal electrolytes can be added in finely divided elemental state, relying on substances in the spent spin bath to oxidize and ionize the metals, e.g. traces of acidic substances reacting with the metals. Conveniently, however, the desired increase in conductivity is achieved by addition of the metals as salts dissolved in the methanol used to keep the composition in balance and added just before the spinning column since metering is thus simplified, mixing is assured and the effect is rapidly realized. Alternatively, addition can occur before or in the settling tank, especially where an appreciable increase in conductivity is to be effected. Of the numerous materials which give satisfactory results the all-around best are calcium acetate and sodium acetate since they are effective in small amounts, greatly accelerate settling, do not liberate a strong acid or volatile weak base upon hydrolysis as occurs with ammonium acetate, generally do not create processing complications and/or are inexpensive. A partial list of other materials which have proven effective includes $FeCl_3$, $CuCl_2$, ammonium acetate, $AlCl_3$, ammonium hydroxide, sodium acetate, $ZnCl_2$, NaCl, ammonium phosphate, $FeSO_4$, $Al_2(SO_4)_3$, Na_2HPO_4, $CuSO_4$, NaOH, CuO, etc., as well as metallic Fe, Cu, Pb, Al and Zn in the form of powder, wire or fine turnings.

The invention has been described with reference to the treatment of spent spin baths obtained by wet spinning methylene chloride solutions of cellulose triacetate into methylene chloride-methanol spin baths. In this basic system, cellulose triacetate has reference to cellulose acetate having fewer than about 0.29 and preferably fewer than about 0.12 free hydroxyl group per anhydroglucose unit of the cellulose molecule, i.e. an acetyl value in excess of about 59% and preferably in excess of about 61% by weight calculated as combined acetic acid. The methylene chloride dope solvent may comprise up to about 20% and preferably about 5 to 15% of a lower alkanol such as methanol although ethanol and isopropanol are almost as good. The composition of the methylene chloride-methanol spin bath will vary in dependence upon its temperature. The methylene chloride concentration is approximately governed by the formula 75¼ minus the spin bath temperature in ° C.±5. Since spinning is usually carried out within the temperature range of about 15 to 45° C., the methylene chloride will generally constitute about 25 to 65% of the weight of the methylene chloride-methanol. The spin bath may also contain small amounts of water. Other halogenated lower alkanes plus other lower alkanols may be substituted although the results are not generally as good. The wet spinning of course may be designed to obtain shaped structures other than filaments, e.g. sheets, etc.

The process can be applied to wet spinning other filament-forming materials into other spin baths in which fines of the filament-forming material become suspended. The filament-forming material could comprise, for example, acetone-soluble secondary cellulose acetate as well as esters of cellulose with one or more organic or inorganic acids such as cellulose acetate-formate, cellulose acetate-propionate, cellulose propionate, cellulose acetate-propionate-butyrate, cellulose acetate-butyrate, cellulose butyrate, cellulose nitrate, and the like, the esters having varying degrees of substitution. The dope solvent and spin bath compositions will of course depend upon the identity of the filament-forming material. Even when operating with a dope of cellulose triacetate in a solvent comprising essentially methylene chloride, spin baths other than methylene chloride-methanol can also be successfully employed such as aqueous solutions containing up to about 15% of methylene chloride and about 45 to 70%, alone or in admixture, of a glycol, a polyglycol or hydroxylated cyclic ether as described in Belgian Patent 571,379, e.g. tetrahydrofurfuryl alcohol, propylene glycol-1,2, 2-methyl-pentanediol-2,4, 3-methyl-pentanediol-2,4, diethylene glycol, triethylene glycol, di-ethyl or di-methyl ether of diethylene glycol, 3-methoxybutanol-1, hexanediol-2,5, etc. The dope may also contain small amounts of these solvents or of a lower alkanol such as methanol or isopropanol.

The invention will be further described with reference to the accompanying drawing wherein:

FIG. 1 is a schematic flow sheet of an apparatus employing ion exchange to reduce conductivity; and

FIG. 2 is a schematic flow sheet of an apparatus employing electrolyte addition to increase conductivity.

Referring now more particularly to the drawing, in FIG. 1 there is shown a spin pot **11** housing a spinnerette **12** to which there is supplied a dope of filament-forming material through pipe **13**. Fresh spin bath is supplied to the spin pot **11** through pipe **14**. The freshly formed filaments **15** and spin bath flow upwardly through spin column **16** into head box **17** from whence the filaments are withdrawn for further processing. Spent spin bath in head box **17** drains into sump **18** from which the major portion of the spent spin bath is caused to flow upwardly through a column **19** in which a mixture of cation and anion exchange particles **20** rests freely between widely-spaced relatively large mesh screens **21**. The deionized liquid leaving the column **19** passes to a composition adjusting tank **22** which feeds pipe **14**. Additional liquid is supplied to tank **22** through line **23** in order to adjust the composition of the effluent from tank **22** to that required for fresh spin bath.

A portion of the effluent from sump **18** is passed to an evaporator **24** in which solvents are withdrawn overhead, condensed at **25** and collected in receiver **26**. The non-volatiles, principally comprising cellulose triacetate, are withdrawn from evaporator **24** at **27** to be discarded, or put to other use. A portion of the distillate in receiver **26** is withdrawn from the system at **28** to be used for making fresh dope or the like and a portion is recycled through pipe **29** to be combined in tank **22** with the effluent from column **19** and the liquid supplied through line **23** in adjusting the composition of fresh spin bath supplied through pipe **14**.

The system shown in FIG. 2 is employed where the conductivity of the spent spin bath is maintained high to accelerate settling. The apparatus is generally the same as in FIG. 1 except that column **19** of FIG. 1 has been replaced by a settler **30** which is fed by gravity with all the liquid from sump **18**. The overflow from settler **30**, relatively light in cellulose triacetate fines, is recycled while the underflow, relatively rich in cellulose triacetate fines, is treated for solvent recovery. Electrolytes may be added to the system along with the liquid introduced at **23**, along with the dope supplied at **13** and/or along with the spent spin bath supplied to settler **30** to accelerate settling and to compensate for the electrolyte lost at **27**. When added to the settler **30**, the electrolyte will be incorporated not only in the recycling portion but also in the underflowing portion which is directly removed from the recirculating system. This seeming waste is countered by the increased rate of settling achieved in settler **30**.

The invention will be further described in the following illustrative examples.

Example I

Using an apparatus such as shown in FIG. 1 there is supplied at **13** at the rate of 30 parts per hour a solution comprising 21.7/70/7.7/0.5/0.1 cellulose triacetate/methylene chloride/methanol/water/dispersing agent; the dispersing agent comprises 60/20/20 mineral oil/blown sperm oil/polyethylene glycol monooleate. 1100 parts per hour of fresh spin bath comprising 38/61.4/0.1/0.5 methylene chloride/methanol/cellulose triacetate/water is supplied at **14**. The conductivity of the dope is 0.07 micromho, of the fresh spin bath 0.4 micromho. The conductivity of the spent spin bath in sump **18** is 1.8 micromhos and 82% of this spent spin bath is passed through column **19** in which there is loosely arranged a mixture of a strong cation exchange resin on the hydrogen cycle (Dowex 21K) and a strong anion exchange resin on the hydroxyl cycle. The conductivity of the liquid leaving the column **19** is 1.8 micromhos and it is forwarded to tank **22** along with 34 parts per hour of methanol supplied at **23** and having a conductivity of 0.3 micromho. Of the 18% of spent spin bath forwarded to evaporator **24**, there is withdrawn at **27** 9 parts per hour of 9/84/5/2 methylene chloride/methanol/cellulose triacetate/water. The distillate in **26** comprises 190 parts per hour of which 28% is purged at **28** and the remainder recycled at **29**; its conductivity is 0.3 micromho. The unaccounted for methylene chloride, methanol and water leave the system along with the cellulose triacetate tow.

Whereas the spinning column remains clear and spinning is stable for long periods of time when practicing the process of this example, if the ion exchange resins are removed from column **19** the conductivity in column **16** (assumed to be the same as in sump **18**) increases to an undesired level and cellulose triacetate fines encrust the spinnerette **12**, clog up column **16**, sump **18**, tank **22** and the associated lines, interfering with spinning and necessitating shut-down.

Example II

Using the apparatus shown in FIG. 2 the same dope as in Example I is fed at the same rate. 1100 parts per hour of fresh spin bath comprising 38.5/61.5 methylene chloride/methanol (excluding its ionic content) is supplied at **14**, having a conductivity of 100 micromhos. The conductivity of the spent spin bath in sump **18** is 101 micromhos. The overflow from settler **30** comprises 1080 parts per hour of 39.4/60.3/0.03 methylene chloride/methanol/cellulose triacetate having a conductivity of 101 micromhos. The underflow from settler **30** comprises 20.3 parts per hour of 38.9/59.6/1.5 methylene chloride/methanol/cellulose triacetate having a conductivity of 101 micromhos. 2.3 parts per hour of 8/77/15 methylene chloride/methanol/cellulose triacetate are withdrawn at **27**. Of the 18 parts per hour of 42.3/57.7 methylene chloride/methanol passing into receiver **26**, 85% is purged at **28** and the remainder is recycled at **29**; its conductivity is negligible. At **23** there is supplied per hour 34 parts of 100% methanol along with 0.0125 part of calcium acetate. The yarn carries off 10 parts per hour of a composition 51/49 methanol/methylene chloride.

Whereas spinning in this manner is stable, if the addition of calcium acetate is terminated the conductivity of the spent spin bath in sump **18** will decrease to an undesired level. There will be inadequate settling in settler **30** and the overflow will contain so much cellulose triacetate that the apparatus will soon become clogged. If a less effective electrolyte than calcium acetate is employed, substantially the same results can be achieved by using more electrolyte and/or longer settling times.

It is to be understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of my invention.

Having described my invention what I desire to secure by Letters Patent is:

1. In the continuous wet extrusion of a cellulose ester, wherein a solution of said cellulose ester is extruded into a spin bath to effect coagulation of said cellulose ester in the form of a shaped structure and said structure and spent spin bath are continuously withdrawn, the improvement which comprises maintaining the conductivity of the liquid in which coagulation takes place at a value ranging between about 0.3 to 2 micromhos.

2. In the continuous wet extrusion of a solution of a cellulose ester wherein a solution of said cellulose ester is extruded into a zone supplied with a spin bath to effect coagulation of said cellulose ester in the form of a shaped structure, said shaped structure and spent spin bath are continuously withdrawn from said zone, and

a portion of the spent spin bath is recycled to said zone, the improvement which comprises treating said recycling portion while continuously in liquid state to effect deionization thereof to a conductivity below almost 2 micromhos.

3. The process set forth in claim 2, wherein deionization is effected by contacting said recycled portion with an ion exchange resin.

4. The process set forth in claim 2, wherein deionization is effected by contacting said recycled portion with an anion exchange resin and a cation exchange resin.

5. The process set forth in claim 2, wherein there is present in said zone a dispersing agent.

6. The process set forth in claim 2, wherein there is present in said zone up to about 0.5% based on the weight of cellulose ester of a non-ionic dispersing agent.

7. In the continuous wet extrusion of a solution of cellulose triacetate wherein a solution of said cellulose triacetate is extruded into a zone supplied with a spin bath to effect coagulation of said cellulose triacetate in the form of a shaped structure, said shaped structure and spent spin bath are continuously withdrawn from said zone, and a portion of the spent spin bath is recycled to said zone, the improvement which comprises removing ions from said recycling portion in an amount such that the conductivity of the liquid in said zone is maintained between about 0.3 to 2 micromhos.

8. The process set forth in claim 7, wherein deionization is effected by contacting said recycled portion with an ion exchange resin.

9. A spin bath comprising a mixture of methylene chloride and methanol of which the methylene chloride constitutes about 25 to 65% by weight, said spin bath having about 0.02 to 0.5% by weight of cellulose triacetate suspended therein and having a conductivity ranging between about 0.3 to 2 micromhos.

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