

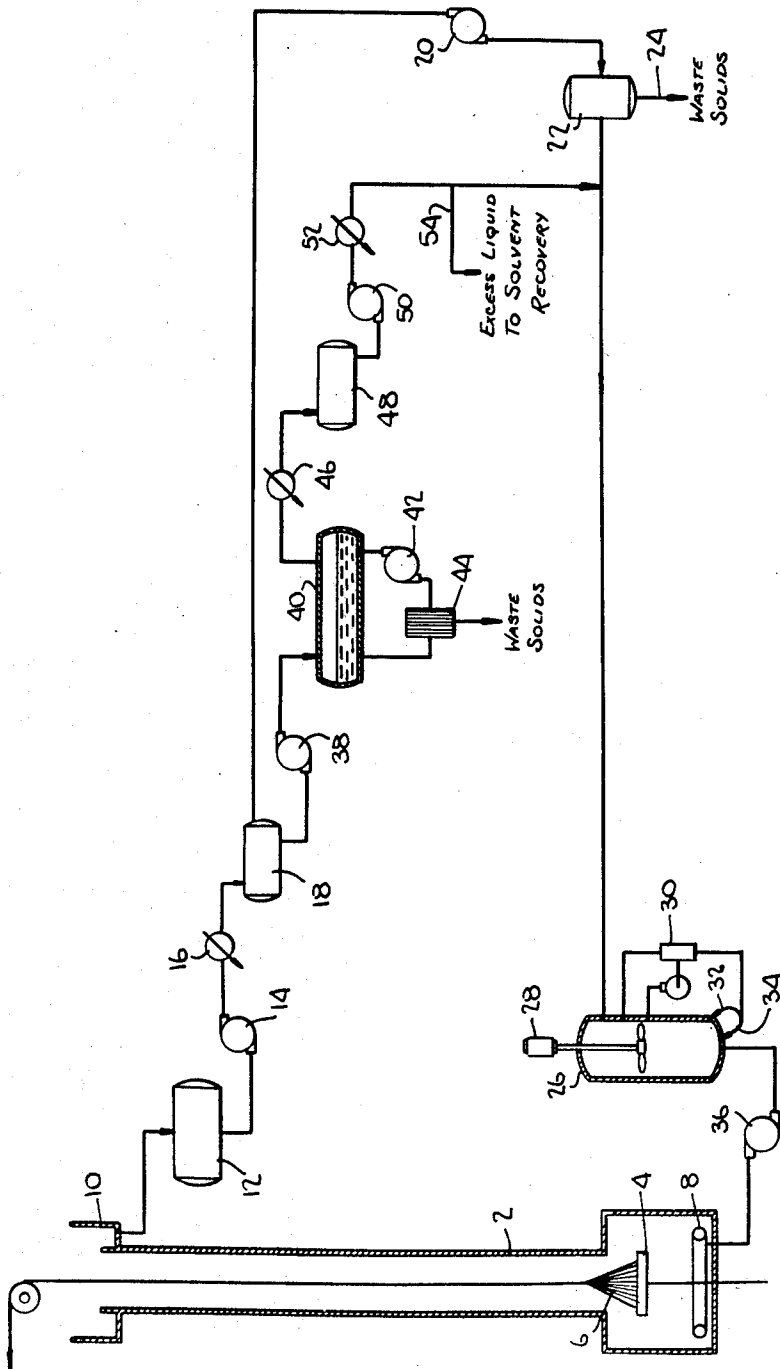
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SPIN BATH

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SPIN BATH

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The present invention relates to the recovery of spent spin bath from a wet spinning process.

In the preparation of filamentary material one process which has found widespread use involves extrusion of a solution of filament-forming material through the apertures of a device known as a spinning jet into a liquid in which the filament-forming material is insoluble thereby coagulating or precipitating it as filaments. The filaments are continuously withdrawn as formed. The solvent from the initial solution will build up in the non-solvent coagulant and to maintain this at a constant value it becomes necessary continuously to withdraw spent coagulant, replacing it with fresh coagulant.

To render the process economical it is usually necessary to recover some or all of the components of the spent coagulant bath. This is especially desirable when working with organic solvents which may be inflammable or toxic and thus could not readily be discarded.

In application Serial No. 638,414, filed February 5, 1957 in the name of Jesse L. Riley there is described a process for wet spinning solutions of organic acid esters of cellulose in solvents comprising halogenated hydrocarbons such as methylene chloride into a coagulant bath containing a lower aliphatic alcohol as non-solvent for the cellulose ester. The spent coagulant accordingly comprises halogenated hydrocarbon, lower aliphatic alcohol and a small amount of cellulose ester some of which is dissolved and some suspended in the liquid mixture.

It is an object of the present invention to process such a spent spin bath for re-use of the solvents.

It is a further object of the invention to separate from the spent spin bath any suspended solids contained therein.

Other objects and advantages will become apparent from the following detailed description and claims taken in conjunction with the accompanying schematic flow sheet.

In accordance with one aspect of the present invention, the spent coagulant bath, generally containing some suspended filament-forming material, is subdivided into a major portion and a minor portion. The minor portion is distilled to recover the volatiles and to separate therefrom non-volatiles such as filament-forming material. The major portion has its composition adjusted and is recycled as fresh coagulant bath.

The subdivision of the spent coagulant bath into two portions advantageously is effected by a procedure such as settling to produce fractions or strata of different densities and contents of filament-forming materials. Advantageously, this is preceded by cooling the spent coagulant bath to precipitate some of the filament-forming material contained therein. That one of the fractions which has a lower content of filament-forming material may be further treated to reduce its content of filament-forming material, as by additional settling, centrifugation, addition of nonsolvent for the filament-forming material, distillation or preferably filtration and is then recycled to the wet-spinning process after its composition has been suitably adjusted. The fraction of high solids content is distilled and the distillate is recovered for re-use, either as fresh coagulant bath after adjustment of its composition or as a portion of the liquid used to form the dope of filament-forming material.

By operating in accordance with the invention and

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cooling the spent spin bath some of the filament-forming material dissolved therein is precipitated out so that the regenerated spin bath at higher temperature will not be saturated with respect to filament-forming material and will be capable of dissolving some of the low molecular weight fines produced in spinning which, were they not dissolved, would clog the spinning column and spin pot or would precipitate on the filaments as a lint during subsequent processing.

The novel process is especially useful in combination with the wet-spinning process described in the above-identified Riley application Serial No. 638,414 wherein the solvent of the extruded solution comprises at least about 85% by weight of a halogenated alkane such as methylene chloride and up to about 15% by weight of one or more alkanols such as methanol, ethanol, isopropanol, propanol, butanol, or the like. Small amounts of water will not interfere.

The coagulant bath may comprise the same classes of liquids as the solution of filament-forming material except that the concentration of alkanol, which is a non-solvent for organic acid esters of cellulose, is much greater. It has been found that when the concentration of methylene chloride in the alcoholic coagulant bath, C, is related to its temperature in degrees centigrade, T, by the equation $C=75\frac{1}{2}-T\pm 5$ the tenacity and elongation of the resultant filament will both simultaneously be higher than if the concentration is increased or decreased beyond the value according to the equation. The temperature generally ranges from about 15 to 45° C. which means the methylene chloride concentration generally ranges between about 25 and 65%.

The organic acid ester of cellulose filament-forming material can be the acetate, propionate, butyrate, acetate-formate, acetate-propionate, acetate-butyrate, or the like. Preferably it contains fewer than about 0.29 free hydroxyl groups per anhydroglucose unit, e.g. cellulose acetate having an acetyl value of at least about 59% by weight calculated as combined acetic acid and hereinafter referred to as cellulose triacetate.

The invention will be further described with reference to the accompanying flow sheet illustrating a recovery process for a spent coagulant bath comprising methylene chloride, methanol, and small amounts of water and cellulose triacetate. All proportions are by weight unless otherwise specified.

A wet spinning apparatus 2, comprising a spin pot and an upwardly extending column, is provided with a dope of cellulose triacetate in 91/9 methylene chloride/methanol which is extruded through a spinnerette 4 to form a tow or bundle of filaments 6 upon contact with methylene chloride/methanol coagulant supplied through a sparger 8. The filaments are drawn out of the spinning column while the spent coagulant bath overflows the column into a headbox 10 from whence it drains into a holding tank 12. The spent coagulant bath is at 32° C. and comprises 44% methylene chloride, 55% methanol, 1% water and 0.1% cellulose triacetate. The spent coagulant bath from holding tank 12 is pumped by pump 14 through a cooler 16 where its temperature is reduced to about 27° C. The cool bath enters a settler 18. A major proportion of the material supplied to settler 18, e.g. about 75 to 98% and preferably about 95%, overflows and is pumped by a pump 20 through a filter 22. The composition of the liquid supplied to filter 22 is 44% methylene chloride, 55% methanol, 1% water and 0.085% cellulose triacetate. One tenth of the cellulose triacetate is withdrawn at 24 with 500 times its weight of liquid carried along; this may be discarded or employed in any desired manner. The filtrate is conveyed to a mixing vessel 26 provided with an agitator 28 and a density monitor 30 which controls addition of methylene chloride

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through 32 and/or methanol through 34 to bring the composition of the liquid within vessel 26 (as determined by its density) to the value required in order to be recycled by pump 36 to sparger 8 as fresh coagulant bath, e.g. 43% methylene chloride, 56% methanol, 1% water and 0.08% cellulose triacetate, or as the solvent for preparing fresh dope for extrusion.

About 5% of the material supplied to settler 18 is underflow comprising 44% of methylene chloride, 55% methanol, 1% water and 0.4% cellulose triacetate, and is pumped by pump 38 to a heated evaporator 40 containing solution whose composition is 9% methylene chloride, 80% methanol, 10% water and 1% cellulose triacetate and whose temperature is 65° C. Solution from evaporator 40 is continuously pumped at 42 through a filter 44 which removes cellulose triacetate to prevent its build-up in the evaporator. The cellulose triacetate-free distillate from the evaporator is condensed at 46 into receiver 48, its composition being 44.6% methylene chloride, 54.5% methanol and 0.9% water. The liquid from receiver 48 is pumped at 50 through a cooler 52 to merge with the filtrate from filter 22, both moving on to vessel 26.

During extrusion, to the coagulant bath there is continuously being added filament-forming dope rich in methylene chloride. Accordingly, the spent coagulant bath is richer in methylene chloride than the fresh bath and it is generally necessary to supply methanol to vessel 26 through 34. To compensate for this increase in the amount of liquid in the system, a portion of the liquid leaving cooler 52 is withdrawn at 54 and passed to a solvent recovery system (not shown) for separation and use in making up fresh dope. While some liquid could be withdrawn at any point, the point chosen ensures that no solids will be carried into the solvent recovery system.

In accordance with another feature of the invention, the filter 22 is of the type employing stones or similar elements as the surface on which the cellulose triacetate is deposited. Periodically it is necessary to backwash the filter to remove the cellulose triacetate from the stones. Whereas it is the usual practice to employ filtrate as the backwashing liquid, in accordance with another aspect of the invention the backwashing may be carried out with distilled liquid, preferably liquid as at 54, since this permits removal of the cellulose triacetate both by washing and by dissolution; by contrast, the filtrate leaving filter 22 is already saturated with cellulose triacetate and could not function to clean by dissolution. In the event it is not desired to interrupt the process when backwashing, a second filter 22 may be provided in "parallel," one being cleaned while the other operates.

From the foregoing description it can be seen that the bulk of the spent coagulant bath is not subjected to distillation and is filtered in highly efficient, inexpensive manner since it contains relatively little cellulose triacetate. Only a small proportion of the coagulant bath, containing much solids, is distilled.

The exact proportions and temperatures obviously can be varied, depending upon the extrusion temperature, the composition of the fresh coagulant bath, the relative volumetric rates of feed of dope and of fresh coagulant to the extrusion apparatus, the chemical composition of the film-forming material and the solvent and non-solvent of the dope and of the coagulant bath, etc.

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

Having described our invention, what we desire to secure by Letters Patent is:

1. The process for the regeneration of fresh coagulant bath from spent coagulant bath containing filament-forming material, a solvent for the filament-forming material and a non-solvent for the filament-forming material, which comprises causing said spent coagulant bath

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to stratify, withdrawing a stratum relatively low in filament-forming material and adjusting the composition of said stratum to produce fresh coagulant bath.

2. The process set forth in claim 1, wherein adjustment of the composition of said stratum is effected by addition of said non-solvent until attainment of a predetermined density.

3. The process set forth in claim 1, wherein said filament-forming material is a cellulose organic acid ester having fewer than 0.29 free hydroxyl group per anhydroglucose unit, said solvent comprises a halogenated hydrocarbon, and said non-solvent comprises a lower aliphatic alcohol.

4. The process for the regeneration of fresh coagulant bath from spent coagulant bath containing cellulose triacetate, methylene chloride and methanol, which comprises causing said spent coagulant bath to stratify, withdrawing a stratum relatively low in cellulose triacetate, and adjusting the composition of said stratum to produce fresh coagulant bath.

5. The process for the regeneration of fresh coagulant bath from spent coagulant bath containing filament-forming material, a solvent for the filament-forming material and a non-solvent for the filament-forming material, which comprises causing said spent coagulant bath to stratify, withdrawing a stratum relatively high in filament-forming material, and distilling said withdrawn stratum to recover the volatiles contained therein.

6. The process set forth in claim 5, wherein said spent coagulant bath is cooled prior to stratification.

7. The process for the regeneration of fresh coagulant bath from spent coagulant bath containing cellulose triacetate, methylene chloride and methanol, which comprises causing said spent coagulant bath to stratify, withdrawing said withdrawn stratum to a body of distilland from which methylene chloride and methanol distillate is boiled off, said body of distilland being filtered to remove cellulose triacetate, and adjusting the composition of the distillate to produce fresh coagulant bath.

8. The process for the regeneration of fresh coagulant bath from spent coagulant bath containing filament-forming material, a solvent for the filament-forming material and a non-solvent for the filament-forming material, which comprises causing said spent coagulant bath to stratify, withdrawing a first stratum relatively low in filament-forming material and comprising a major proportion of the spent coagulant bath, filtering said first stratum, withdrawing from the stratified spent coagulant bath a second stratum relatively high in filament-forming material and comprising a minor proportion of the spent coagulant bath, distilling said second stratum, combining the filtrate from said first stratum and the distillate from said second stratum, and adjusting the composition to produce fresh coagulant bath.

9. The process set forth in claim 8, wherein adjustment of the composition of said stratum is effected by addition of said non-solvent until attainment of a predetermined density, and including the step of withdrawing a portion of the distillate prior to combination with the filtrate from the second stratum.

10. The process for the regeneration of fresh coagulant bath from spent coagulant bath containing cellulose triacetate, methylene chloride and methanol, which comprises cooling said spent coagulating bath, causing said spent coagulant bath to stratify, withdrawing a first stratum relatively low in cellulose triacetate and comprising a major proportion of the spent coagulant bath, filtering said first stratum, withdrawing from the stratified spent coagulant a second stratum relatively high in cellulose triacetate and comprising a minor proportion of the spent coagulant bath, adding said withdrawn second stratum to a body of distilland from which methylene chloride and methanol distillate is boiled off, said body of distilland being filtered to remove cellulose triacetate, withdrawing a portion of the distillate and combining the

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balance with the filtrate from said first stratum, and adding methanol to the composition to produce fresh coagulant bath.

11. The process for the regeneration of fresh coagulant bath from spent coagulant bath containing filament-forming material, a solvent for the filament-forming material and a non-solvent for the filament-forming material, which comprises withdrawing a minor portion of said spent coagulant bath, distilling said minor portion, separating filament-forming material from the distilland, withdrawing a major portion of said spent coagulant bath, and without distillation adjusting the composition of said major portion to produce fresh coagulant bath.

12. In combination, a wet spinning apparatus including means for supplying a dope of filament-forming material to a body of coagulant bath to form filaments, means for separating spent coagulant bath from said wet spinning apparatus into a plurality of strata, means for withdrawing one of said strata relatively low in filament-forming material, means for adjusting the composition of said one stratum, and means for recycling said composition-adjusted stratum to said wet spinning apparatus as regenerated coagulant bath.

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13. A combination according to claim 12, including means for withdrawing from said spent coagulant bath another stratum relatively rich in filament-forming material, means for distilling said other stratum to evaporate the volatiles therein, means to separate from said other stratum non-volatile filament-forming material contained therein, and means for condensing said evaporated volatiles.

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