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[54] **METHOD OF REGENERATING SPINNING BATHS**
11 Claims, No Drawings

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37, 179

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ABSTRACT: Cumene/dimethylformamide/paraffin spinning baths used in the preparation of acrylonitrile copolymer thread are regenerated by (i) admixture with the largely paraffin liquid from the drawing bath (ii) water separation of a fraction of the mixture to give an aqueous dimethylformamide layer and a cumene/paraffin layer and (iii) fractionation of the layers and recombination of the components with a non-separated fraction of the mixture to give the desired spinning bath composition. The paraffins and dimethylformamide not required are recycled to the drawing bath and preparation of the acrylonitrile spinning solution, respectively.

METHOD OF REGENERATING SPINNING BATHS

The invention relates to a method of regenerating spinning baths employed in the manufacture of threads from acrylonitrile polymers or copolymers.

More particularly, the invention relates to regeneration of baths employed in wet spinning methods in which acrylonitrile polymerisates dissolved in dimethylformamide are extruded into coagulating baths comprising cumene and paraffins in addition to a solvent for the polymer, the threads being subsequently drawn in drawing baths essentially comprising paraffins.

As described in a previous Italian Pat. application No. 23652 filed Dec. 7, the 1967 the coagulating baths contain cumene in a concentration exceeding 50%, preferably 60% by weight, and the dimethylformamide concentration ranges between 15% and 35% by weight. The paraffins are linear chain products having 10 to 16 carbon atoms in the molecule, present up to a maximum of 25% by weight.

The concentration of the ingredients of the coagulating bath is maintained as constant as possible during the spinning process.

Thus, in practice, the solution is continuously fed to the coagulating bath, its ingredients at the desired concentration, and a solution is continuously discharged, in which the dimethylformamide concentration exceeds the concentration of the feed solution, though preferably not by more than 3 preferably 2 units percent by weight.

The solution discharged from the coagulating bath has to be regenerated to restore the concentration of the ingredients of the coagulating bath to their feed values and remove in part at least the impurities contained therein.

It has been found that the quantity of impurities should be maintained below 0.1%, preferably 0.05%, by weight, especially when threads of low denier number are being manufactured.

As described in our previous patent application the drawing baths essentially comprise linear chain paraffins having 10 to 16 carbon atoms in the molecule; the word essentially is employed herein to convey that the baths shall at any time contain the paraffins at concentrations exceeding 80%, preferably 90%, by weight, especially when threads of low denier numbers are being manufactured, the balance comprising cumene and dimethylformamide.

In this case the paraffins are preferably actually supplied in a substantially pure condition, a solution being continuously discharged in which paraffin is present in a quantity above 80%, 90%, by weight.

The solution discharged from the drawing bath has likewise to be regenerated in order to remove impurities and restore the paraffin content to its feed values.

It has now been found in accordance with the invention that the baths discharged from the coagulating and drawing steps, though they differ in composition, may be regenerated by a single treatment which will maintain a content of impurities below 0.1, preferably 0.05 % by weight during spinning and at the same time restore the feed solution to the coagulating and drawing baths to their desired composition.

According to the method of the invention the solutions discharged from the coagulating and drawing steps are mixed, a fraction of the mix being treated, as described hereinafter, with a view to removing the impurities therefrom and separately obtaining in a substantially pure condition dimethylformamide, paraffins and cumene.

The constituents separated as above are utilized in part for restoring the untreated mix fraction to a composition such that it can be directly fed to the coagulating step, the balance comprising paraffins and dimethylformamide being utilized after suitable replenishment as feed for the drawing step and as solvent for the polymer, respectively, in forming the spinning solution.

Thus, by the method of the invention the solution discharged from the coagulating bath, comprising cumene, paraffins and dimethylformamide, and of raised concentration of impurities and dimethylformamide with respect to the feed solution, is mixed with the discharge solution from the drawing bath. The latter mainly comprises paraffins and contains impurities, in addition to cumene and dimethylformamide, with respect to the feed.

The solution discharged from the coagulating and drawing steps are of a composition within the above described limits.

A fraction of 5% to 90%, preferably 10% to 50% by weight of the solution resulting from mixing is treated with water in order to effect separation of two layers, one comprising cumene and paraffins, and the other an aqueous solution of the dimethylformamide containing the impurities. The quantity of water added ranges between 0.5 and 10 parts, preferably 1 and 5 parts by weight to 1 part by weight of dimethylformamide contained in the mix.

According tc a preferred embodiment, the water from the thread wash baths is utilized, which has dissolved therein small quantities of dimethylformamide.

Moreover, the fraction which is being regenerated is admixed with the cumene and paraffins which separate by stratifying as the lighter phase in the thread wash baths.

Water is then removed by distillation from the aqueous phase containing the dimethylformamide, the residue being distilled by the thin layer technique, preferably in a Luwa evaporator equipped with scrapers, in order to separate dimethylformamide in a pure condition.

The organic phase is likewise fractioned in order to separate cumene from paraffins.

The cumene resulting from the above-described separation is added in full to a mix fraction which has not undergone any treatment together with a fraction of the dimethylformamide and, if desired, of the paraffins, in order to restore the composition to that of the feed values.

The remaining fraction of the dimethylformamide and paraffins is utilized in forming the spinning solution and feeding the drawing bath, respectively.

The method of the invention, which can be carried out continuously by adopting simple measures, is advantageous by reason of the simplicity of the treatment and the circumstance that a single treatment is sufficient for both the coagulating and drawing baths, which differ considerably in composition.

Moreover, the method recovers the solvent practically in full, so that only very small solvent quantities have to be added as replenishment.

Finally, the above-described treatment will yield the feeds to the coagulation and drawing with the desired concentration, impurities being moreover maintained in the baths at levels such as to ensure satisfactory spinning.

The invention is illustrated by the following Example.

EXAMPLE

An acrylonitrile copolymer containing 8% by weight methylmethacrylate, of a molecular weight of 90,000 measured according to Staudinger is dissolved in dimethylformamide to obtain a spinning solution having a copolymer content of 20% by weight.

4.6 kg./hour spinning solution are extruded, at the bottom of a coagulating bath, through a die having orifices 0.18 mm. in diameter at a linear rate of feed of the spinning solution of about 4.2 meter/min.

The coagulating bath is maintained at a temperature of 50°C. and is of a volume of about 190 liters.

About 142 kg./hour coagulating solution is fed to the bottom of the coagulating bath, the solution comprising 60% cumene, 20% paraffins and 20% by weight dimethylformamide.

Cumene is of the commercial type of a concentration exceeding 99.5% by weight, the paraffins comprising a mixture of the linear chain products having 11 to 14 carbon atoms in the molecule, the average number of carbon atoms in the molecule being 12.2.

The solution discharged from the top of the coagulating bath has a dimethylformamide content of about 22% by weight.

The thread is collected after coagulation at a rate of 10 meter/min. and conveyed to a drawing bath maintained at 115°C.

Eleven kg./hour of the above-described paraffins are charged to the drawing bath, a solution being discharged therefrom comprising in addition to paraffins cumene and dimethylformamide in a quantity of about 5 and 2.5 by weight, respectively.

The thread is drawn 10 times in the drawing bath and subsequently washed in water baths, finally dried. Its thickness is about 2 denier and its toughness about 3 g./denier.

The solutions charged to the coagulating and drawing baths are mixed and a mixture is obtained of 155 kg./hour of the following composition : paraffins 24.7%, dimethylformamide 20.6% and cumene 54.7% by weight.

This mix is admixed with the organic layer separated in the thread wash baths, mainly comprising paraffins with small quantities of cumene. About 40 kg./hour of the resulting mixture is subjected to regeneration by adding thereto 16 kg./hour of the water from the thread wash baths, containing small quantities of dimethylformamide.

Water is separated from the aqueous layer by distillation at reduced pressure, the dimethylformamide being separated in a Luwa thin layer evaporator equipped with scrapers, at a rate of about 8 kg./hour.

The organic layer is likewise distilled at reduced pressure, cumene being recovered at a rate of about 22 kg./hour and paraffins being recovered at a rate of about 10 kg./hour.

The resulting cumene is added in full to the untreated fraction of the mix together with about 55% of the recovered dimethylformamide.

This yields a solution suitable for direct supply to the coagulation.

The remaining dimethylformamide and paraffins as recovered are utilized for forming the spinning solution and as feed to the drawing bath, respectively.

What we claim is:

1. A method of regenerating spinning baths used in the manufacture of acrylonitrile homopolymer or copolymer threads wherein a polymer spinning solution of said homopolymer or copolymer of acrylonitrile in dimethylformamide is extruded into a coagulating bath comprising, by weight, from 15% to 35% dimethylformamide, at least 50% cumene, and up to 25% of linear paraffins having from 10 to 16 carbon atoms, the resulting threads being drawn in baths consisting essentially of said paraffins, said method of regeneration comprising:

a. mixing a first solution discharged from said coagulating bath, said first solution being enriched in dimethylformamide with respect to the initial coagulating bath, with a second solution discharged from said drawing bath, said second solution being enriched in cumene and dimethylformamide with respect to the initial drawing bath, to thereby form a first mixture;

b. separating said first mixture into an untreated portion and a second portion comprising from 10% to 50%, by weight, of said first mixture;

c. treating said second portion with from 0.5 to 10 parts, by weight, based on the weight of said dimethylformamide in said second portion, of water to produce an aqueous layer and an organic layer;

d. recovering said dimethylformamide from said aqueous layer;

e. recovering said cumene and said paraffins from said organic layer;

f. mixing all of the recovered cumene and a portion of said recovered dimethylformamide and, if necessary, a portion of said recovered paraffins with said untreated portion of said first mixture in order to restore said untreated portion of said first mixture to the concentration values of the initial coagulating bath;

g. recycling the resulting mixture to the said coagulating bath;

h. recycling the remaining portion of said recovered paraffins to the drawing bath; and,

i. utilizing the remaining portion of said recovered dimethylformamide to form the acrylonitrile homopolymer or copolymer solution.

2. A method as claimed in claim 1 wherein the cumene percentage in said coagulating bath exceeds 60%, by weight.

3. A method as claimed in claim 1 wherein the drawing baths comprise linear paraffins have 10 to 16 carbon atoms in the molecule in a quantity exceeding 80%, by weight, the balance comprising cumene and dimethylformamide.

4. A method as claimed in claim 3, wherein the quantity of said paraffins in said drawing bath exceeds 90%, by weight.

5. A method as claimed in claim 1 wherein the increase in dimethylformamide content in the coagulating bath between the feed solution and discharge solution is lower than 3 percent by weight.

6. A method as claimed in claim 5, wherein said increase is lower than 2 percent by weight.

A method as claimed in claim 1 wherein the water quantity used to treat said second portion of said first mixture is 1 to 5 parts by weight, based on the weight of dimethylformamide in said second portion.

8. A method as claimed in claim 1 wherein the recovering of dimethylformamide from said aqueous layer is performed by first distilling water from the aqueous layer and then dimethylformamide.

9. A method as claimed in claim 1 wherein said cumene and said paraffins are recovered separately from the organic layer by distillation at reduced pressure.

10. A method as claimed in claim 1 wherein the water utilized to treat said second portion of said first mixture is derived from the thread wash baths used to wash said thread and contains dissolved therein small quantities of dimethylformamide.

11. A method as claimed in claim 10 wherein said second portion of said first mixture is admixed, prior to treatment with water, with an organic layer separated in the thread wash baths, said organic layer consisting essentially of said paraffins with small quantities of cumene.