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SPIN BATH TREATMENT

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This invention relates to the production of regenerated cellulose filaments by the viscose process, and relates more particularly to the treatment of the spin baths employed for the precipitation of said regenerated cellulose materials whereby regenerated cellulose materials of improved color may be obtained.

In the production of artificial filaments by the viscose process, cellulose is treated with sodium hydroxide to convert it to alkali cellulose, the alkali cellulose reacted with carbon bisulfide to form cellulose xanthate and the cellulose xanthate then dissolved in aqueous sodium hydroxide to yield a spinning solution which is extruded through a spinneret into an acid spin bath where it coagulates or sets to form cellulose filaments. The acid spin bath employed usually comprises a 10-12% aqueous solution of sulfuric acid containing about 18-24% sodium sulfate and a small amount of zinc sulfate. In commercial spinning operations, the spin bath is normally circulated in a closed system. The bath is made up originally in one part of the system, pumped to the spin bath troughs into which the viscose solution is extruded, then sent to a make-up zone where it is brought up to the desired strength, filtered and the recharged spin bath recirculated to that part of the system where the actual spinning is effected. Due to the corrosive nature of the sulfuric acid spin bath solution, the entire circulation system is usually lined with a material, such as lead, for example, which is strongly resistant to corrosion.

Although lead is so highly advantageous as an acid-resistant structural material that its use is practically universal, the presence of lead in contact with the acid spin bath permits the latter to pick up varying amounts of soluble lead compounds. In turn, the cellulose materials coagulated in lead-containing spin baths also pick up the lead compounds present and, when the amount of lead in the spin bath is above a certain minimum concentration, the cellulose materials coagulated in the spin bath tend to become badly discolored. While certain special washing procedures are effective in removing at least some of the discoloration, these washing operations represent an additional and appreciable item in the cost of production. Since it has been firmly established that the presence of excessive amounts of lead in the spin bath is responsible for the discoloration which has been observed in cellulose materials coagulated in such baths, the removal of the lead or a reduction in the quantity of lead present to a non-discoloring concen-

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tration appears to be essential if special washing procedures are to be eliminated. While several methods for the elimination or reductions of lead in spin baths have been proposed, they are, however, either ineffective or else unsatisfactory for commercial application.

It is, therefore, an important object of this invention to provide an efficient and economical process for the treatment of spin baths employed in the production of cellulose materials by the viscose process and circulating in contact with lead whereby the lead content of said spin baths may be reduced to an innocuous concentration.

Another object of this invention is to effect a reduction in the amount of lead present in viscose process spin baths to a non-discoloring concentration by a continuous treatment of the coagulating spin bath employed while the same is being circulated and fortified for reuse.

A further object of this invention is the provision of a process for the treatment of lead-containing spin baths employed in the production of cellulose materials by the viscose process whereby the lead is separated from the spin bath in the form of a precipitate which may be readily filtered from the spin bath during recirculation.

Other objects of this invention will appear from the following detailed description.

I have found that the lead present in contaminated sulfuric acid spin baths employed for the production of cellulose materials by the viscose process may be readily removed or at least the amount present reduced to a non-discoloring concentration by co-precipitating the lead from solution by the addition to said solution of a compound of an alkaline earth metal. Upon addition of an alkaline earth metal compound to the sulfuric acid spin bath, said alkaline earth metal precipitates therefrom as the corresponding sulfate. The precipitation of said alkaline earth metal sulfate from solution causes a coprecipitation whereby the lead sulfate present coprecipitates with the alkaline earth metal sulfate. By adding a sufficient amount of the alkaline earth metal compound to the spin bath as the same is circulated, the amount of lead present may be readily reduced to a non-discoloring concentration. After the addition of the alkaline earth metal compound, the spin bath may then be filtered, brought up to strength and then reused for the further production of cellulose materials without any danger of producing discolored materials due to an excessive concentration of lead in the spin bath.

Examples of alkaline earth metal compounds

which may be employed in carrying out my novel process for the reduction of lead in spin baths are the compounds of barium or strontium, for example. Preferably, the soluble compounds of alkaline earth metals are employed. Thus, as suitable compounds which may be added to the spin bath in accordance with my novel process to effect a reduction in the lead content of said spin bath, there may be mentioned barium chloride, barium hydroxide, barium oxide, strontium nitrate, strontium chloride and strontium acetate. These compounds may be added alone or in admixture with each other. A suspension of the insoluble barium carbonate may also be employed.

The amount of the soluble alkaline earth metal salt added to the spin bath may vary depending upon the amount of lead in the spin bath and the extent to which it is desired to reduce the amount of lead in said spin bath. The lead in the spin bath normally amounts to from about 4 to about 16 parts or more per million on the weight of the spin bath after the bath has been in use for several months and an equilibrium has been reached. The addition to the spin bath of 1 to 50 parts, preferably 1 to 15, per million by weight of soluble barium or strontium compounds effectively reduces the lead content of the bath to as little as 0.3 parts per million on the weight of the spin bath. Optimum results are obtained employing soluble barium compounds, particularly barium chloride or barium hydroxide, as the precipitating agent in the removal of lead from the spin bath.

To be effective in removing lead from the spin bath as a coprecipitate with the alkaline earth metal sulfate precipitate formed upon addition of an alkaline earth metal compound to the spin bath, the alkaline earth metal compound must be added under such conditions as to result in the formation of a very finely divided dispersion of the corresponding sulfate. The very finely divided sulfate precipitate is then permitted to settle in the spin bath for a sufficient time to allow the colloidal particles to agglomerate. The precipitation of the alkaline earth metal sulfate in finely divided form, followed by settling, allows the desired mixed crystal formation of lead sulfate and alkaline earth metal sulfate to take place. The mixed crystal formation causes a coprecipitation of lead sulfate from the spin bath, which reduces the amount of lead sulfate in the spin bath to below its normal solubility. Preferably, the spin bath is maintained at a temperature of 40 to 55° C. during the addition of the soluble salt whereby the initial colloidal precipitation takes place. Settling may be conveniently achieved by providing a baffled chamber of relatively large volume which permits the precipitate to be trapped by the baffles and the supernatant liquid continuously drawn off and recirculated.

In order further to illustrate my invention, but without being limited thereto, the following examples are given:

Example I

An aqueous spin bath of a total volume of about 1,000 gallons containing about 12% by weight of sulfuric acid, 20% sodium sulfate and 0.9% by weight of zinc sulfate is continuously circulated at the rate of approximately 6.33 gals. per minute through a closed lead-lined system at a temperature of 50° C. and is employed for producing cellulose filaments by continuously extruding therein a suitable viscose solution employing the usual multi-hole spinneret. After effecting the

coagulation of the viscose solution with the production of regenerated cellulose filaments, the spin bath is filtered through a sand filter, refortified to the optimum sulfuric acid, sodium sulfate and zinc sulfate content and recirculated to effect further coagulation of the viscose solution extruded therinto. After circulation for 72 hours with the production of about 280 pounds of regenerated cellulose yarn, the spin bath is found to contain lead in an equilibrium amount of about 6.7 parts per million on the weight of the spin bath. The soluble lead compounds are picked up by the coagulating filaments and cause an appreciable amount of discoloration on the filaments. Only a part of the discoloration can be removed by washing. The yarn spun through said spin bath contains approximately 150 parts per million of lead. After the lead content of said spin bath has reached an equilibrium value, a 25% by weight solution of barium chloride is continuously added to the spin bath as it leaves the zone wherein the coagulation of the filaments takes place, said addition being in an amount of about 5.3 cc. per minute. After the addition is continued for 48 hours, the concentration of the barium chloride solution added is reduced to 12.5% by weight and the addition made at a rate of about 10.6 cc. per minute. After 24 hours, the concentration of the solution added is reduced to 6.25% and the rate of addition held to about 21 cc. per minute. The absolute rate of addition of barium chloride is maintained substantially constant at about 40 to 50 parts per million by weight on the weight of the spin bath circulated through the system. The addition of the 6.25% by weight solution is continued at about 21 cc. per minute for about 1 week and at that time the lead content of the bath is found to be stabilized at about 0.6 parts per million. The spin bath is allowed to settle after the barium chloride addition and any of the agglomerated barium sulfate precipitate remaining in the supernatant liquid is continuously filtered from the spin bath as the same is circulated through the system. The color of the yarn obtained when the lead content of the spin bath is held to 0.6 part by weight per million parts of spin bath is found to be substantially improved by the removal of the lead and special washing procedures may be entirely eliminated without any substantial effect on yarn color.

Example II

An aqueous spin bath of total volume of about 53,000 gallons, containing approximately 10% by weight of sulphuric acid, 22% by weight of sodium sulfate and .9% by weight of zinc sulfate, is continuously circulated through a closed lead-lined system at a circulating rate of approximately 1200 gallons per minute. This spin bath is employed for producing viscose yarn by continuously extruding therein a suitable viscose solution employing the usual multi-hole spinneret. After effecting the coagulation of the viscose solution with the production of regenerated filaments, the spin bath, filtered through a sand filter is refortified to the optimum sulfuric acid, sodium sulfate and zinc sulfate content and recirculated to effect further coagulation of the viscose solution extruded therinto. On reaching equilibrium with the lead-lined system, this spin bath is found to contain 15 p. p. m. of lead. The lead compounds are picked up by the coagulating filaments and cause an appreciable amount of discoloration. After the normal type

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of yarn purification, the yarn contains approximately 13 p. p. m. lead.

To this spin bath which contains an equilibrium concentration of 15 p. p. m. of lead is added a 5% solution of barium hydroxide, maintained at 40° C. at the rate of approximately 15 p. p. m., based on the quantity of spin bath circulated through the system. The barium hydroxide is added under conditions of violent agitation. During the first 12 hours, 132 pounds of barium hydroxide are added. This reduces the lead content of the spin bath from 15 p. p. m. to 6 p. p. m. During the next 12 hour period, 87 pounds of barium hydroxide are added at the rate of approximately 10 p. p. m. on the weight of the spin bath circulated. This results in a reduction in the lead content of the spin bath to 2 p. p. m. During the next 12 hour period, 66 pounds of barium hydroxide are added at the rate of approximately 7½ p. p. m. on the weight of the spin bath circulated. Then for 12 hours the barium hydroxide addition is maintained at 5 p. p. m., which results in a reduction of the lead content of the spin bath to approximately 2.5 p. p. m. The addition of barium hydroxide is then reduced to approximately 2.5 p. p. m., based on the weight of the spin bath circulated, and maintained at this level for 16 days, at the end of which time the lead content of the spin bath is found to be reduced to approximately 1.2 p. p. m. The addition of barium hydroxide is increased to 3.75 p. p. m. for 6 days, then reduced to 1.25 p. p. m. for 20 days. By the end of this period the lead content of the spin bath reached a value of less than 0.5 p. p. m. The yarn spun through the spin bath containing this low concentration of lead is found to contain approximately 4 p. p. m. of lead and does not exhibit the discoloration characteristic of yarns spun through spin baths containing several p. p. m. of lead.

Example III

An aqueous spin bath of a total volume of about 74,000 gallons, containing approximately 12% by weight of sulfuric acid, 20% of sodium sulfate and 0.9% of zinc sulfate, is continuously circulated through a closed lead-lined system at a rate of approximately 4300 gallons p. m. This spin bath is employed as described in Example II.

To this spin bath, now containing an equilibrium concentration of 7 p. p. m. of lead, is added a 5% solution of barium hydroxide, maintained at 40° C. at the rate of 2.5 p. p. m., based on the quantity of spin bath circulated through the system. The barium hydroxide is added under conditions of violent agitation. During the first 12 hours the lead content of the spin bath is reduced to 2 p. p. m. The addition of barium hydroxide is then increased to 5 p. p. m., and maintained at approximately this concentration for 16 days. By this time, the lead content of the spin bath is found to be reduced to less than 0.5 p. p. m. The addition of barium hydroxide is then reduced to 2.5 p. p. m. and maintained at this level for several days. The lead content of the spin bath remains less than 0.5 p. p. m. The marked discoloration characteristics of the yarn, spun prior to the addition of barium hydroxide to the spin bath disappears by the time the lead content of the spin bath is below 1 p. p. m.

Example IV

Employing a 5% aqueous solution of strontium

nitrate as the precipitating agent, the addition to the spin bath of 50 parts of strontium nitrate per million by weight reduces the lead content to about 3 parts or less per million.

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 a process for the production of regenerated cellulose wherein viscose spinning solution is extruded into a spin bath comprising an aqueous solution of sulfuric acid, sodium sulfate and zinc sulfate for coagulating said spinning solution, in which process the spin bath is circulated through and outside the coagulating zone thereby coming into contact with metallic lead equipment, causing said spin bath to become contaminated with lead, the improvement which comprises adding an alkaline earth metal compound, which reacts with said spin bath to produce an alkaline earth metal sulfate, to said circulating spin bath, at a point removed from the coagulating zone and under such conditions as to produce an alkaline earth metal sulfate in finely divided form which precipitates and causes the co-precipitation of the lead sulfate in said spin bath, and removing the precipitate whereby the amount of lead contaminant is diminished and the tendency of the regenerated cellulose to discolor is reduced.

2. The process of claim 1 in which the alkaline earth metal of the alkaline earth metal compound is selected from the group consisting of strontium and barium.

3. Process of claim 1 in which the amount of the alkaline earth metal compound added to the spin bath is 1 to 50 parts per million based on the weight of the spin bath.

4. In a process for the production of regenerated cellulose wherein viscose spinning solution is extruded into a spin bath comprising an aqueous solution of sulfuric acid, sodium sulfate and zinc sulfate for coagulating said spinning solution, in which process the spin bath is continuously circulated through and outside the coagulating zone thereby coming into contact with metallic lead equipment, causing said spin bath to become contaminated with lead, the improvement which comprises adding with agitation to said circulating spin bath, at a point removed from the coagulating zone, an alkaline earth metal compound which reacts with said spin bath to produce an alkaline earth metal sulfate which precipitates in finely divided form and causes the co-precipitation of the lead sulfate in said spin bath, and removing the precipitate whereby the amount of lead contaminant is diminished and the tendency of the regenerated cellulose to discolor is reduced.

5. The process of claim 4 in which the alkaline earth metal of the alkaline earth metal compound is selected from the group consisting of strontium and barium.

6. Process of claim 4 in which the amount of the alkaline earth metal compound added to the spin bath is 1 to 50 parts per million based on the weight of the spin bath.

7. Process according to claim 4 in which the alkaline earth metal compound is barium hydroxide.

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8. Process according to claim 4 in which the alkaline earth metal compound is barium chloride.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,547,111	Finn -----	July 21, 1925
1,689,036	Leiss -----	Oct. 23, 1928
2,326,592	Wicker -----	Aug. 10, 1944

8

FOREIGN PATENTS

Number	Country	Date
366,429	Great Britain -----	Feb. 4, 1932

OTHER REFERENCES

Journal American Chemical Society, vol. 60, 1938, pages 197-201.