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SPINNING SOLUTION AND A PROCESS OF MAKING IT

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18 Claims. (Cl. 106—166)

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The present invention relates to the production of viscose rayon of diminished luster and it provides a new and improved viscose spinning solution for use in the production of such rayon as well as a process by which this spinning solution may be produced.

It has heretofore been the practice to produce viscose rayon of dull luster by one of several different methods. According to one method, a pigment, such as titanium dioxide, is incorporated in the spinning solution. This method is fairly effective in producing yarns of reduced luster, but for yarn of very low luster, the quantity of pigment required is such that the yarn is weakened appreciably and the solution has an abrasive action on the spinning orifice. In addition, as is well known, yarns delustered by pigments regain their luster upon being dyed to a dark color since the pigment has little effect upon the smoothness of the filament surface.

According to another method, it has been proposed to incorporate various oils and fats in viscose spinning solutions. Refined mineral oil for example may be used as the delusterant. However, such oil dispersions in viscose tend to agglomerate and produce breaks or weak spots in the filament. Pine oil may be used to overcome this disadvantage but it delusters only partially and, furthermore, it has a persistent residual odor which is difficult to remove. Both mineral and pine oil impart a slightly yellowish cast to rayon.

Now, in accordance with the present invention, it has been found that the above-mentioned difficulties may be obviated and that viscose rayon of diminished luster may be produced by incorporating in a viscose spinning solution, a delusterant and as a dispersing agent therefor, a suitable amount of a reaction product of an alkylene oxide and an unsaturated or hydroxy terpene, or mixtures of such terpenes, which has been produced by the reaction of at least three moles of the alkylene oxide per mole of the terpene.

The terpene derivatives which are employed as dispersing agents in accordance with the present invention and a method by which they may be produced are described in my copending application Serial No. 494,394, filed on July 12, 1943 (now Patent No. 2,440,093), for "Terpene derivatives and method of producing the same." In general, the method by which these terpene derivatives are produced comprises admixing a suitable amount of an alkaline catalyst with an unsaturated terpene, a hydroxy terpene, or mixture thereof, and placing the mixture in an autoclave which is then heated to a temperature of about 125° C. to about 150° C. to initiate the reaction, and gradually introducing into the autoclave, a

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suitable amount of an alkylene oxide to form a reaction product in which at least three moles of alkylene oxide per mole of terpene are reacted. The compounds having from three to seven moles of alkylene oxide per mole of terpene provide optimum water-dispersability of the delusterants in the viscose.

Upon completion of the above-mentioned reaction, or prior thereto, as indicated by a drop to atmospheric pressure, and by a rapid decrease in temperature, the introduction of the alkylene oxide into the terpene, hydroxy terpene, or terpene mixture, in the autoclave is terminated and the autoclave is permitted to cool to a temperature of approximately 90° C. and the contents of the autoclave are then discharged into a suitable receptacle and permitted to cool to room temperature.

A suitable quantity of the above product, say from about .02% to about .2%, by weight, based on the weight of the viscose to which it is added, is mixed with a suitable delusterant, such as a pigment like titanium dioxide, or a mineral oil, in a colloid mill with sufficient water to form a finely divided dispersion, and the dispersion is then added to a viscose spinning solution and mixed therewith in a tank provided with means for agitation of the contents thereof.

After mixing, the viscose solution may be filtered or otherwise treated by conventional means to remove foreign matter therefrom preparatory to spinning the viscose into suitable filaments or yarn. Rayon produced by the above-described method is uniformly dull in appearance and has the delusterant pigment or oil evenly distributed therein, thus providing rayon of uniform tensile strength.

The following specific examples, in which the parts are given by weight, will serve to illustrate and explain the present invention.

Example 1

60 parts of the reaction product produced by reacting 510 parts of alpha-terpineol with 1020 parts of ethylene oxide, in the presence of an alkaline catalyst, at a temperature of 105° C. to 147° C., and at a maximum pressure of 120 pounds per square inch, during a period of about three hours, is dispersed in 800 parts of white mineral oil having a Saybolt viscosity of 80 to 90 at 100° F. by warming the materials together at a temperature of 60° C. The mixture is then stirred into a slurry of 1250 parts of water and 400 parts of titanium dioxide. The entire mixture is then milled in a colloid mill provided with recirculating means, at a setting of .0014 inch between the rotor and stator of the mill. 315 parts of the

resulting mixture is added to 5000 parts of a viscose spinning solution and stirred for fifteen minutes with a laboratory stirrer. Observation of particle size may be made after the solution has been permitted to stand overnight under a vacuum of 27 inches of mercury and at a temperature of 16° C. Samples taken from the top of the solution when examined microscopically, using an oil-immersion lens and 900 magnifications are found to have the pigment and oil present therein in a finely divided and uniformly dispersed condition. In uniformity of dispersion and particle size of delusterant, the viscose solution containing my improved dispersing agents is found to be superior to a viscose solution containing the same delusterants, but in which one of the usual dispersing agents is employed.

Example 2

600 parts of terpenyl ethylene glycol ether and 600 parts of technical grade alpha-terpineol are admixed with 5 parts of solid sodium hydroxide catalyst by triturating the materials. This mixture is placed in an autoclave which is heated to an initial reaction temperature of 130° C. Then 700 parts of ethylene oxide are gradually introduced into the autoclave during a period of about one hour, while agitating the autoclave, and during this period the temperature of the autoclave is permitted to increase to 149° C. The reaction is controlled to permit a maximum pressure during the reaction of about 100 pounds per square inch, and upon completion of the reaction, the pressure decreased to zero gauge. The reaction product is a straw-colored, fairly viscous oily liquid, having a specific gravity of 1.011 at 25° C. and a refractive index of 1.4760. The product is easily dispersible in either refined mineral oil having a Saybolt viscosity of 80 to 100, or in water, and it is soluble in alcohol.

One part of the above dispersing agent is stirred into 10 parts of mineral oil having a Saybolt viscosity of about 85. Then 3000 parts of water are placed in a tank provided with stirring means and 1.8 parts of titanium dioxide are added to the water and mixed therewith by stirring. Then the mineral oil containing the dispersing agent is poured into the water-titanium dioxide mixture. The entire mixture is then passed through a colloid mill to further comminute the oil and titanium dioxide particles and globules, respectively. The resulting dispersion is then added to a standard viscose mixer containing 2500 parts of viscose solution and stirred therewith for a period of one hour. After mixing, the material is passed through a filter press and air is removed therefrom by vacuum, employing the customary procedure. Particle size measurements are then made using a microscope equipped with an oil-immersion lens and at 970 magnifications and showed an average oil globule size of two microns and an average particle size of one micron for the titanium dioxide particles.

The dispersing agent described above is particularly effective in emulsifying oil as well as dispersing titanium dioxide pigment.

Example 3

910 parts of commercial pine oil consisting of a mixture of terpene alcohols and terpene hydrocarbons is admixed with 5 parts of solid sodium hydroxide catalyst by triturating the materials. This mixture is placed in an autoclave provided with heating and agitating means, and heated to an initial reaction temperature of about 136° C. Then 970 parts of ethylene oxide are gradually introduced into the autoclave during a period of about one and a half hours, while agitating the autoclave, and during this period the temperature of the autoclave is permitted to increase to a maximum of about 193° C. The reaction is controlled so that a maximum pressure of about 180 pounds per square inch is attained during the reaction, and upon completion of the reaction, the pressure decreased to zero gauge. The reaction product is a soft, greasy solid, easily dispersible in either oil or water, and soluble in alcohol.

60 parts of the above-described dispersing agent is mixed with 800 parts of refined mineral oil by warming and stirring the materials together. This mixture is then added to a colloid mill containing 400 parts of titanium dioxide and 1250 parts of water and milled together for about one minute with recirculation. 31.3 parts of the dispersion thus formed is stirred into 5000 parts of viscose solution with a laboratory stirrer for about fifteen minutes. After mixing, the material is passed through a filter press and air is removed therefrom by vacuum, employing the customary procedure. The mixture is permitted to stand overnight and samples are removed from the top and from the middle of the container. Particle size measurements are then made using a microscope equipped with an oil-immersion lens and at 970 magnifications and showed no difference in uniformity of dispersion or in particle size between the samples taken from the top and from the middle of the container. The maximum size of the oil globules is two and a half microns and the average size is one and a fourth microns. The maximum size of titanium dioxide particles is one and a half microns and the average size is .75 micron.

In dispersing mixtures of delusterants for rayon such as titanium dioxide, which is capable of being wetted more readily by hydrophilic than by hydrophobic substances, and refined mineral oil which is extremely hydrophobic in character, it is advantageous in obtaining a finely divided dispersion of these delusterants to employ a mixture of the dispersing agents made in accordance with my above-mentioned copending application, said mixture consisting of approximately equal proportions by weight of the products made according to Examples 1 and 4 of said application.

After viscose containing delusterants and my improved dispersing agents has been spun in the usual manner into a coagulating bath, it is customary to wash it with hot water to remove acid and other coagulating material from the yarn. This washing operation also substantially entirely removes the dispersing agent but leaves the delusterant fixed in the yarn.

Dispersing agents utilized in the present invention, to be most effective for dispersing delusterants in viscose, should be produced by the reaction of at least three moles of alkylene oxide per mole of terpene compound. Preferably, however, from four to seven moles of alkylene oxide per mole of terpene compound are necessary to provide maximum water-dispersibility of the final reaction product.

While the invention has been described in detail with specific examples, such examples are illustrative and are not given as limitations, since other modifications within the spirit and scope of the invention will be apparent to those skilled in the art. Hence, the invention is to be understood as limited only as indicated, in the appended

claims, in which the intent is to set forth all the novelty over the prior art.

I claim:

1. As a spinning solution for use in the production of low luster filaments, a viscose solution containing a delusterant and as a dispersing agent from about .02% to about .2%, by weight, of the reaction product of one mole of a terpene selected from the group consisting of unsaturated and hydroxy terpenes reacted with at least three moles of an alkylene oxide.

2. As a spinning solution for use in the production of low luster filaments, a viscose solution containing a delusterant and as a dispersing agent from about .02% to about .2%, by weight, of the reaction product of one mole of a mixture of unsaturated terpenes and at least three moles of an alkylene oxide.

3. As a spinning solution for use in the production of low luster filaments, a viscose solution containing a delusterant and as a dispersing agent from about .02% to about .2%, by weight, of the reaction product of one mole of a hydroxy terpene reacted with at least three moles of an alkylene oxide.

4. As a spinning solution for use in the production of low luster filaments, a viscose solution containing a delusterant and as a dispersing agent the reaction product formed by reacting at least three moles of an alkylene oxide per mole of a terpene selected from the group consisting of unsaturated and hydroxy terpenes.

5. As a spinning solution for use in the production of low luster filaments, a viscose solution containing a delusterant and as a dispersing agent the reaction product formed by reacting at least three moles of ethylene oxide per mole of a terpene selected from the group consisting of unsaturated and hydroxy terpenes.

6. As a spinning solution for use in the production of low luster filaments, a viscose solution containing a delusterant and as a dispersing agent the reaction product formed by reacting at least three moles of propylene oxide per mole of a terpene selected from the group consisting of unsaturated and hydroxy terpenes.

7. As a spinning solution for use in the production of low luster filaments, a viscose solution containing a delusterant and as a dispersing agent the reaction product formed by the reaction of one mole of a hydroxy terpene and at least three moles of ethylene oxide.

8. As a spinning solution for use in the production of low luster filaments, a viscose solution containing a delusterant and as a dispersing agent from about .02% to about .2%, by weight, of the reaction product formed by reacting one mole of alpha-terpineol and at least three moles of ethylene oxide.

9. A a spinning solution for use in the production of low luster filaments, a viscose solution containing a delusterant and as a dispersing agent from about .02% to about .2%, by weight, of the reaction product formed by reacting one mole of a mixture of hydroxy terpenes and at least three moles of an alkylene oxide.

10. As a spinning solution for use in the production of low luster filaments, a viscose solution containing a delusterant and as a dispersing agent from about .02% to about .2%, by weight, of the reaction product formed by reacting one mole of a mixture of terpenyl ethylene glycol ether and alpha-terpineol with at least three moles of an alkylene oxide.

11. As a spinning solution for use in the production of low luster filaments, a viscose solution containing a delusterant and as a dispersing agent from about .02% to about .2%, by weight, of the reaction product formed by reacting one mole of pine oil with at least three moles of ethylene oxide.

12. As a spinning solution for use in the production of low luster filaments, a viscose solution containing a delusterant and as a dispersing agent from about .02% to about .2%, by weight, of the reaction product formed by reacting an unsaturated terpene with from three to seven moles of an alkylene oxide.

13. As a spinning solution for use in the production of low luster filaments, a viscose solution containing a delusterant and as a dispersing agent from about .02% to about .2%, by weight, of the reaction product formed by reacting from three to seven moles of an alkylene oxide per mole of a hydroxy terpene.

14. As a spinning solution for use in the production of low luster filaments, a viscose solution containing a delusterant and as a dispersing agent from about .02% to about .2%, by weight, of the reaction product formed by reacting from three to seven moles of an alkylene oxide with a mole of a mixture of hydroxy terpenes.

15. A process for the production of viscose rayon of diminished luster which comprises incorporating in a viscose spinning solution, a delusterant and as a dispersing agent from about .02% to about .2%, by weight, of a reaction product formed by reacting one mole of a terpene selected from the group consisting of unsaturated and hydroxy terpenes with at least three moles of an alkylene oxide.

16. A process for the production of viscose rayon of diminished luster which comprises incorporating in a viscose spinning solution, a delusterant and as a dispersing agent from about .02% to about .2%, by weight, of a reaction product formed by reacting one mole of a mixture of unsaturated terpenes with at least three moles of an alkylene oxide.

17. A process for the production of viscose rayon of diminished luster which comprises incorporating in a viscose spinning solution, an aqueous dispersion comprising a delusterant and as a dispersing agent from about .02% to about .2%, by weight, based on the final spinning solution, of a reaction product formed by reacting an unsaturated terpene with an alkylene oxide in the proportion of at least three moles of alkylene oxide per mole of the terpene.

18. A process for the production of viscose rayon of diminished luster which comprises incorporating in a viscose spinning solution, an aqueous dispersion comprising a delusterant and from about .02% to about .2%, by weight based on the final spinning solution, of a reaction product formed by reacting one mole of a hydroxy terpene with at least three moles of an alkylene oxide.

WILLIAM O. ISRAEL.

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The following references are of record in the file of this patent:

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Certificate of Correction

Patent No. 2,440,094. April 20, 1948.

WILLIAM O. ISRAEL

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 5, line 60, claim 9, for "A a" read *As a*; column 6, line 41, claim 16, for ",02%" read *.02%*; line 58, claim 18, after the word "and" insert *as a dispersing agent*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 6th day of July, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.