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ANIMALIZING TEXTILE PRODUCT

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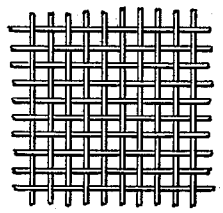

TEXTILE MATERIAL CONTAINING FINELY DISTRIBUTED THEREIN THE RESINOUS PRODUCT OF A JOINT POLYMERIZATION OF 1.) AN ALKYLENE IMINE 2.) CARBON DISULFIDE, CARBONYL SULFIDE, THIOPHOSGENE OR SULFUR CHLORIDE AND 3.) AN ARYLTHIOCYANATE OR ARYLISOTHIOCYANATE.

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ANIMALIZING TEXTILE PRODUCT

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This invention relates to a process of producing artificial fibers, films, foils, ribbons and the like materials capable of being dyed by acid wool dyestuffs.

In our prior application Ser. No. 223,010 filed August 4, 1938, of which the present application is a continuation in part, we have disclosed a method of animalizing artificial fibers by incorporating therein the product of the joint polymerization of an alkylene imine and an arylisocyanate or arylisothiocyanate.

In a prior application filed by us together with Karl Kösslinger, Ser. No. 182,250 we have disclosed animalizing of textile materials by incorporating therein resinous condensation or polymerization products of carbon disulfide and ethyleneimine.

In our co-pending application of even date Ser. No. 284,244 filed July 13, 1939 we have disclosed a new type of synthetic resins which are derived from alkylene imines, carbon disulfide and arylisocyanates or arylisothiocyanates by joint polymerization.

It is an object of the present invention to provide a process by which artificial textile materials capable of being dyed with acid wool dyestuffs in the same manner as wool may be obtained.

A further object is the provision of artificial fibers, threads and the like textile materials, which consist of cellulose hydrate, cellulose acetate or a similar film- or fiber-forming polymer and which contain dispersed therein an addition of a basic artificial resin.

A further object resides in the provision of artificial fibers, which may be dyed by acid wool dyestuffs with a fastness to light and washing, which equals that of wool and which exceeds that of all the animalized fibers hitherto in use.

Still further objects of the invention will become apparent from the detailed specification following hereinafter.

The single figure illustrates a fabric of a conventional form with legends to indicate the improvement of this invention.

We have now found that improved animalizing agents are obtained by jointly polymerizing carbon disulfide or any of the above-named substituents therefor, a cyclic imine and an aromatic isocyanate or an isothiocyanate.

As cyclic imines the following polymerizable imines having a three-membered ring are named as examples: ethylene imine, N-methylethylene imine, N-phenylethyleneimine, propyleneimine, N - propylethyleneimine, N - benzylethyleneimine, butyleneimine, and polymers of these alkyleneimines.

As isocyanates phenylisocyanate may be mentioned, further phenylisothiocyanate, benzylisocyanate, naphthylisocyanate and the corresponding isothiocyanates.

The proportions of the constituents of the resin may vary within wide limits. There should be present at least 5 per cent as the smallest addition of one component and not more than 60 per cent of the single further component, for instance 10 to 50 per cent of carbon disulfide of the weight of the two other resin components may be present.

The polymerization is preferably carried out as follows: carbon disulfide or carbonyl sulfide or thiophosgene or sulfur chloride is added drop by drop to a solution of the alkyleneimine. The temperature during this reaction should not rise about 80 to 100° C. since in that case the reaction products are no longer uniform. The preferred temperature is around 40 to 50° C. The polymerizate obtained from the sulfur compound and the alkyleneimine is allowed to stand for a certain period which may be a few hours or a couple of days. This condensation- or polymerization product is then reacted with an arylisocyanate preferably in an amount that the resultant solution is neutral. The solution obtained polymerizes spontaneously by standing for a certain time. However, the polymerization may be accelerated by acid or basic catalysts or by heating. Products of high degree of polymerization are obtained by heating the resin for a longer period after it has been separated from the solution. Alternatively carbon disulfide may be first condensed with phenylisocyanate and then the ethyleneimine added to complete the polymerization.

The resins according to this invention have a distinctly basic character. They are stable against acid and alkaline liquids and absorb acid dyestuffs eagerly.

We have found that these products are especially useful for animalizing textile materials which are per se incapable of being dyed by acid dyes in the same manner as animal fibers. (The term "animalizing" means imparting to vegetable and artificial fibers such as cotton and rayon the dyeing properties of animal fibers such as wool and silk. For the use of this term compare British Patents Nos. 501,595, 501,804, and 493,509.) The process is carried out by incorporating the insoluble resinous compositions in the spinning solutions in finely subdivided form for instance in the form of an emulsion and spinning the fibers

from this solution. However, it is also possible to impregnate textile fibers such as cotton with a solution of the resins, pressing and drying the same. The incorporation into the spinning solution is preferably carried out as follows: The resin is dissolved in a solvent therefor and this solution is added to the spinning solution for instance to a viscose solution. Preferably solvents are selected which are immiscible with the solvent of the fiber-forming polymer so that the resinous solution can be emulsified in the spinning solution. This may be facilitated with the aid of emulsifying agents.

In the case of solutions of organic polymers in organic solvents the animalizing agent may be dissolved in the organic solvent for the fiber-forming polymer or it may be emulsified in the spinning solution as above.

The following solutions of fiber-forming polymers which are suited for the production of animalized fibers may be mentioned by way of example: viscose solutions, cuprammonia cellulose solutions, cellulose ester solutions, cellulose ether solutions, solutions of vinyl resins.

As already pointed out the artificial fibers or the cotton fibers may be impregnated with the animalizing agent in the form of filaments, yarns, threads, fabrics, etc. After drying such textiles contain a certain amount of the polymerization products according to the invention and acquire exactly the same affinity towards wool dyestuffs and chrome dyestuffs as wool. The fastness of the dyeings thereon against washing and light is likewise not inferior to those on wool owing to the insolubility and chemical resistance of the polymerization products.

The following examples serve to illustrate the invention:

Example 1

To a solution of 500 cc. of ethyleneimine (98 per cent strength) in 1000 cc. of benzene there are added by drops at 40° C. 100 cc. of carbon disulfide (=1/5 mol calculated on the ethyleneimine). This polymerizate is allowed to stand for 14 days and then 250 cc. of it are allowed to react with so much phenylisocyanate at 40° C. that the solution is neutral (testing with phenolphthalein). The consumption of phenylisocyanate differs according to the degree of polymerization and may be about 60–100 cc. This animalizing solution is again allowed to stand for 24 hours at room temperature for the purpose of further polymerization. Of this finished solution 150 cc. are added to 5 liters of viscose and the whole is well emulsified. After de-aeration the viscose is spun. The corresponding proportion of animalizing solution may alternatively be added to the spinning solution on its way to the spinning nozzle. The animalized threads have a strong affinity for acid wool dyestuffs, very good fastness to washing and especially good fastness to light in the case of after-chroming dyestuffs.

Example 2

To a mixture of 400 cc. of benzene and 100 cc. of carbon disulfide there are added gradually 125 cc. of phenylisocyanate. There are then added cautiously drop by drop at 40° C. in a reflux apparatus 100 cc. of ethyleneimine (98 per cent strength).

The condensation product is allowed to stand for 72 hours for further polymerization. Of this animalizing solution 100 cc. are stirred into 5 liters of viscose, which is then spun. The fibers dyed with wool dyestuffs, for instance metachrome Red 5 G, Anthralan Yellow, Supramine Red B, Chrome Yellow A, fast Mordant Blue B, exhibit very good fastness to washing and perspiration. The fastness to light of the fibers is very good, especially in the case of after-chroming and meta-chrome dyestuffs.

Example 3

To a solution of 200 cc. of benzene and 100 cc. of ethyleneimine (98 per cent strength) are added at 40° C. through a dropping funnel 100 cc. of carbon disulfide. The solution is allowed to stand for 24 hours and then at 40° C. 125 cc. of phenylisocyanate are added by drops. The resinous polymerizate is left for 24 hours at room temperature for further polymerization. It is soluble in ethylenechlorhydrin and in benzylalcohol. 100 cc. of the animalizing solution dissolved in a little benzyl alcohol are thoroughly emulsified in 5 liters of viscose and the mass is spun in known manner. Finished threads have a strong affinity for acid wool dyestuffs. After dyeing they are thoroughly fast to washing. The fastness to light of the fibers dyed with after-chroming dyestuffs is very good.

Example 4

To a solution of 500 cc. of ethyleneimine (98 per cent strength) in 1000 cc. of benzene are added by drops at 40° C., 50 cc. of carbon disulfide. The polymerizate is allowed to stand for 8 days and then caused to react at 40° C. with 400 cc. of phenylisothiocyanate. The resin thus obtained is further polymerized at room temperature for 4 days after 5 cc. of glacial acetic acid have been added. 100 cc. of the finished polymerization product is emulsified in viscose and the mass is spun.

Example 5

150 cc. of N-benzylethyleneimine in 300 cc. of benzene are cautiously caused to react at 40° C. with 50 cc. of carbon disulfide. The whole is allowed to stand for 24 hours at room temperature and then at 40° C. and under reflux there are added 60 cc. of α-naphthylisocyanate. The resin solution thus obtained is allowed to stand for 3 days while warm for polymerization and may then be used for animalizing fibers. For example, cotton fabric may be saturated with a benzene solution of the artificial resin, then squeezed between calender rollers and dried. If desired, the resin is used in the form of an aqueous emulsion for preparing the fabric.

In the foregoing examples carbon disulfide may be replaced by the above-named sulfur compounds, while ethyleneimine may be replaced by any of the above-named alkyleneimines, and phenylisocyanate by any of the above-named isocyanates.

We claim:

1. Textile materials capable of being dyed with acid wool dyestuffs in the same manner as wool, comprising a film- or fiber-forming organic polymer incapable per se of being dyed by acid dyes, said film- or fiber-forming polymer containing finely distributed therein the resinous product of a joint polymerization of the following three resin components: 1. an alkylene imine, 2. a sulfur compound selected from the group consisting of carbondisulfide, carbonyl sulfide, thiophosgene and sulfur chloride, and 3. a compound selected from the group consisting of arylthiocyanates and arylisothiocyanates.

2. Textile materials capable of being dyed by acid wool dyestuffs in the same manner as wool,

comprising a film- or fiber-forming organic polymer incapable per se of being dyed by acid dyes, said film- or fiber-forming polymer containing finely distributed therein the resinous product of a joint polymerization of the following three resin components: 1. ethyleneimine, 2. carbon disulfide, and 3. phenylisocyanate.

3. Textile materials capable of being dyed by acid wool dyestuffs in the same manner as wool comprising cellulose hydrate and finely dispersed therein the resinous product of the joint polymerization of the following three resin constituents: 1. ethyleneimine, 2. carbondisulfide, and 3. phenylisocyanate.

4. Textile materials capable of being dyed by acid wool dyestuffs in the same manner as wool comprising cotton fibers impregnated with the resinous product of the joint polymerization of the following three constituents: 1. ethyleneimine, 2. carbondisulfide, and 3. phenylisocyanate.

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