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MANUFACTURE OF IMPROVED FIBROUS MATERIALS AND THE MATERIALS THUS OBTAINED

Ludwig Orthner, Gerhard Balle, and Heinz Schild, Frankfurt am Main, Max-Otto Schürmann, Dormagen, and Karl Brodersen and Matthias Quaedvlieg, Dessau, Germany; vested in the Alien Property Custodian

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The present invention relates to a process of manufacturing artificial fibrous materials and to the materials thus obtained. It is an object of the invention to prepare fibers having an agreeable, soft handle. It is a further object of the invention to impart to the fibers a soft and elastic feel stable to the usual washing operations. The invention especially relates to the process of improving artificial fibrous materials which comprises incorporating in the aqueous spinning solution alkali compounds of sulfonic acid amides containing a saturated aliphatic hydrocarbon radical of at least 8 carbon atoms. In the manufacture of improved artificial filaments from aqueous solutions, e. g. cellulose spinning solutions, such as viscose or cuprammonium solutions of cellulose or protein spinning solutions, alkali compounds are added which are soluble in the said solutions. The alkali compounds are derived from sulfonic acid amides containing a saturated aliphatic hydrocarbon radical of at least 8 carbon atoms. In general the said sulfamides are readily soluble in the alkaline spinning solutions; only in the cases the molecular weight of the sulfamide is extremely high, there is not obtained a clear solution in alkaline fluids, but a suspension or emulsion is formed which may be stabilized by the addition of the usual dispersing agents and which is likewise suitable for the present process. Furthermore, mixtures of sulfamides may be used, for instance mixtures of compounds of high molecular weight and of compounds of lower molecular weight. The aqueous spinning solutions containing alkali compounds of sulfonic acid amides having a saturated aliphatic hydrocarbon radical of at least 8 carbon atoms are spun in the usual way into a known spinning bath containing for instance sulfuric acid and Glauber's salt.

Sulfamides of high molecular weight and their alkali compounds may be prepared in different ways: by transformation of alcohols of high molecular weight into halogen compounds, reaction of the halogen compounds with sodium sulfite to form sulfonic acids and transformation of said acids or their alkali metal salts into the corresponding sulfochlorides or sulfobromides, for instance with phosphorus pentachloride, and transformation of the sulfochlorides with ammonia or primary bases, such as methylamine, ethylamine, butylamine, dodecylamine, cyclohexylamine, aniline, furthermore hydroxyamines, such as ethanolamine, propanolamine, butanolamine or oxethylaniline, into the corresponding sulfonamides. At this synthesis there may likewise be started from alcohols of high molecular weight as they are, for instance, obtained by the reduction of fats and oils, of fatty acids or the like.

Sulfamides of high molecular weight are obtained in a technically especially simple manner by the reaction of sulfochlorides formed by the simultaneous action of chlorine and sulfur dioxide on saturated aliphatic hydrocarbons having at least 8 carbon atoms with ammonia, or amines or hydroxyamines. By the selection of the hydrocarbons or hydrocarbon mixtures serving as starting material, the effect attainable with the sulfamides may be varied to a large extent.

There may be started from hydrocarbons or from mixtures of hydrocarbons which are obtained by fractionating petroleum or from products which are obtained by the hydrogenation of carbon or the reduction of carbon monoxide. These technical products may be freed from any unsaturated portions which may be present, by hydrogenation or refining. The hydrocarbons may be reacted with chlorine and sulfur dioxide with exposure to ultraviolet rays. The hydrocarbons may be used in excess, so that only a part is transformed into products containing chlorine, sulfur and oxygen. The excess of the hydrocarbon may be separated immediately or after the reaction with ammonia or amines.

Sulfamides which are useful for the present process may also be obtained for instance as follows: carboxylic acids having an aliphatic hydrocarbon radical of at least 8 carbon atoms are caused to react with sulfamides containing amino groups, for instance by the condensation of lauric acid with meta-aminobenzene-sulfamide or beta-aminoethane-sulfamide.

The sulfamides herein described may be incorporated in the spinning solutions used for the manufacture of artificial fibers suitably by the addition of an alkaline solution of the sulfamide to the spinning solution, for instance a viscose solution or the solution of cellulose in copper oxide and ammonia. During said operation the solubility or distributability in alkali may be enhanced by the simultaneous use of dispersing agents, such as alcohol-sulfonates, condensation products of carboxylic acids of high molecular weight and amino-sulfonic acids or hydroxy-sulfonic acids or amino-carboxylic acids or hydroxy-carboxylic acids, aromatic sulfonic acids, for instance alkyl-naphthalenesulfonic acids, condensation products from ethylene-oxide and alcohols of high molecular weight, carboxylic acids of

high molecular weight, alkylphenols, alkylcyclohexanols and others. The sulfamide may be added to the spinning solution in any desired phase of its preparation. The alkaline solutions of the sulfamides may also be incorporated without any difficulty to the spinning solutions for casein fibers. The spinning solutions to which the sulfamide has been added are worked up in the usual manner in the usual devices. During the formation or the after-treatment of the threads in the usual acid precipitating bath the sulfamide is separated from its alkaline solution and finely and uniformly subdivided in the thread. During the preparation of casein fibers while simultaneously using sulfamides a reaction of the sulfamide with the formaldehyde moreover probably occurs during the usual hardening operation; a good fixing in the fiber of the substance added is thus attained.

The artificial fibers thus obtained are distinguished by a soft and elastic feel. Owing to the insolubility of the sulfamides in alkali carbonates the incorporated substance imparting softness is not removed from the fiber by the usual washing operations when washing liquids containing sodium carbonate are used. According to the present process artificial fibers are obtained which contain the softening agent not only at the surface; on the contrary, the product imparting softness is uniformly subdivided also in the interior of the fiber. The good subdivision is attained by the fact that the product is present in the spinning solution in the form of a molecular or colloidal solution. If the fiber is formed in the acid spinning bath it is uniformly precipitated in an insoluble form. The softening effect produced is, therefore, more stable than in those cases where the fibers are treated with water-soluble softening agents which are absorbed by the fiber. In that case salts of amines of high molecular weight are frequently used. The free amines are, as is known, insoluble in alkaline spinning solutions and can, therefore, not be incorporated in the same manner as the alkali metal compounds of sulfamides. Furthermore, quaternary ammonium compounds of high molecular weight or other watersoluble bodies are used as softening agents. If the compounds of said kind are already used on spinning it is found that the effect produced is not very resistant to washing operations owing to the solubility in water of the compounds.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto, the parts being by weight:

1. 4000 parts of a viscose solution containing about 5 per cent of cellulose are mixed with a solution in 2N-caustic soda solution of a sulfamide obtained by the simultaneous action of chlorine and sulfur dioxide on a benzine fraction mainly containing saturated aliphatic hydrocarbons and boiling between 240° C and 340° C formed by reduction of carbon monoxide and a subsequent reaction of the aliphatic sulfochlorides formed with ammonia. The solution is spun in known manner into an acid precipitating bath. The fibers obtained are after-treated in the usual manner and dried and are distinguished by an excellent softness and suppleness.

A similar effect is attained by using an aliphatic sulfamide prepared by the simultaneous action of chlorine and sulfur dioxide on a paraffine fraction boiling between 340° C and 380° C and a subsequent reaction with ammonia.

The viscose solutions may also be worked up by a process of spinning by stretching the filament.

2. 100 kilograms of casein are caused to swell at 24° C in 200 liters of water, a mixture of 23 liters of caustic soda solution of 35 per cent strength and 77 liters of water is added and the whole is then diluted with water so as to obtain 550–600 liters of a clear, alkaline casein solution. 5 kilograms of a mixture of sulfamides prepared by the simultaneous action of chlorine and sulfur dioxide on a mixture of paraffine wax formed during the benzine synthesis by the catalytic reduction of carbon monoxide and a subsequent reaction of the sulfochlorides obtained with ammonia is dissolved in 2N-caustic soda solution and the solution is added to the spinning solution. After the solution has been allowed to ripen in the usual manner it is spun into an acid precipitating bath. The filament formed is then hardened in the known manner with formaldehyde. The artificial fibers obtained are distinguished by an agreeable and soft feel.

3. 46 parts of a sulfamide (obtained by the simultaneous action of chlorine and sulfur dioxide on a mixture of hydrogenated hydrocarbons by the reduction of carbon monoxide and boiling between 240° C and 340° C and a subsequent reaction of the sulfochlorides formed with ammonia) are stirred with 9.5 parts of 2N-caustic soda solution, while adding 4.6 parts of the product of the reaction between octadecyl alcohol and 10 mol of ethylene oxide. The whole is diluted with about 300 parts of cold water and stirred into 12700 parts of a solution of 9 per cent strength of cellulose in copper oxide and ammonia. The solution is then spun by a process of spining by stretching the filament so as to obtain artificial silk. The skeins are washed as usual with acid and water, then agitated for 5 minutes in water heated to 65°, centrifuged and dried. The artificial silk thus obtained has a soft feel even without the usual after-treatment with softening agents.

4. 40 parts of a sulfamide (obtained by the simultaneous action of chlorine and sulfur dioxide on a paraffine fraction mainly containing saturated aliphatic hydrocarbons and boiling between 320° C and 380° C and a subsequent reaction of the aliphatic sulfochlorides formed with methylamine) are dissolved in 2N-caustic soda solution. The solution is stirred into 4000 parts of a viscose solution containing about 6 per cent of cellulose. The solution produced is spun in known manner into an acid precipitating bath. The fibers obtained are distinguished, after having been worked up in the usual manner and dried, by a soft and supple feel.

A similar effect is attained by using an aliphatic sulfamide obtained by the simultaneous action of chlorine and sulfur dioxide on the paraffine fraction named above and a subsequent reaction with aniline. The product is suitably dissolved in 1N-caustic soda solution.

5. 4000 parts of a viscose solution containing about 6 per cent of cellulose are mixed with a solution in 2N-caustic soda solution of 8 parts of a sulfamide substantially containing 16 to 18 carbon atoms and obtained by the reaction of a mixture of cetyl alcohol and octadecyl alcohol with thionyl chloride so as to obtain the corresponding chlorides, reaction of the chlorides with sodium sulfite so as to obtain the corresponding sulfonic acid salts, transformation of the sulfonic acid salts with phosphorus pentachloride into the corresponding sulfonic acid chlorides

and finally reaction of the sulfochlorides with ammonia to obtain the corresponding sulfamides. The solution is spun into an acid precipitating bath and worked up as usual. The fibers obtained have a very good softness and suppleness.

6. To 4000 parts of a viscose solution containing about 6 per cent of cellulose there is added an alkaline casein solution prepared by dissolving 40 parts of casein in the corresponding quantity of alkali lye. To the solution thus produced there are added 6 parts of a sulfamide obtained by the simultaneous action of chlorine and sulfur dioxide on a benzine fraction containing saturated aliphatic hydrocarbons and boiling between 230° C and 320° C and the subsequent reaction of the sulfochlorides formed with ammonia. For said purpose the sulfamide is dissolved in 2N-caustic soda solution, while adding 1 per cent of an emulsifying agent, for instance the product of reaction of octadecyl alcohol and 10 mol of ethylene oxide. The spinning solution formed is worked up in the usual manner to obtain fibers which after having been hardened with formaldehyde are distinguished by an agreeable and soft feel.

LUDWIG ORTHNER.
GERHARD BALLE.
HEINZ SCHILD.
MAX-OTTO SCHÜRMANN.
KARL BRODERSEN.
MATTHIAS QUAEDVLIEG.