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PRODUCTION OF ARTIFICIAL PROTEIN THREADS, FIBERS, FILAMENTS, AND THE LIKE

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This invention relates to the production of artificial protein threads, fibres, filaments and the like, hereinafter generally referred to as threads, and is particularly concerned with the production of spinning solutions of keratin and regenerated keratin threads made from such solutions.

Proposals have already been made for the production of artificial threads from keratinous materials such as are present in wool waste and animal hair, horns and hooves. Such proposals usually consist in dissolving or dispersing the keratin, after suitable pretreatment, in a liquid such as cuprammonium solution, aqueous solutions of urea with or without reducing agents, or aqueous ammonia, caustic soda or sodium sulphide solution, and extruding the solution or dispersion into a coagulant bath, generally an acid bath which contains one or more salts.

It has been proposed to pretreat the keratinous material with oxidising agents. Thus, P. Alexander, R. F. Hudson and M. Fox in "The Biochemical Journal," volume 46, No. 1 (1950) pages 27–32 describe pretreating keratin with oxidising agents including peracetic acid, the keratin so treated being soluble in aqueous caustic soda, ammonium hydroxide and urea solutions. It is believed that the action of peracetic acid is to oxidise and rupture the cystine link in the keratin so that the oxidised product is soluble or dispersible in alkali. The use of peracetic acid as an oxidising agent on a commercial scale, however, is undesirable; the acid itself is corrosive and unpleasant to operatives and in addition the manufacture of the acid from acetic anhydride and hydrogen peroxide is dangerous in that the reaction mixture may explode.

The object of the present invention is to provide an improved oxidative pretreatment of keratin particularly for the manufacture of regenerated keratin fibres.

According to the present invention, a process for the oxidative pretreatment of keratin comprises subjecting the keratin to the action of hydrogen peroxide in the presence of ferrous sulphate and an acid. The preferred acid is sulphuric acid but other acids such as phosphoric acid and acetic acid may also be used. The amounts of hydrated ferrous sulphate and of sulphuric acid used may be from 2 to 20 per cent by weight of the weight of keratin. It is preferred

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to use from 8 to 10 per cent of ferrous sulphate based on the weight of keratin. The amount of acid used should be sufficient to keep the ferrous sulphate in solution; 1 gram per litre of ferrous sulphate usually requires approximately 1 gram per litre of sulphuric acid.

The keratin pretreated according to the invention is readily soluble in dilute alkali and the present invention therefore also includes a process for the production of keratin solutions comprising subjecting the keratin to the action of hydrogen peroxide in the presence of ferrous sulphate and an acid and dissolving the oxidised keratin in an aqueous alkaline solution. The solutions obtained according to the invention may be used directly as spinning solutions in the manufacture of artificial threads; they may also be used as sizes and dispersing agents.

The invention also includes a process for the production of regenerated keratin threads comprising subjecting the keratin to the action of hydrogen peroxide in the presence of ferrous sulphate and an acid, dissolving the oxidised keratin in an aqueous alkaline solution, such as aqueous ammonia or aqueous caustic soda solution, and extruding the solution so obtained into an aqueous coagulant bath containing one or more metal salts known to coagulate proteins; suitable salts are sodium sulphate, magnesium sulphate and aluminium sulphate; mixtures of such salts may also be used. The bath preferably has a pH value between 5.0 and 9.0.

The threads obtained according to the invention may be treated in the manner usual for artificial protein threads, including stretching, hardening, and insolubilising treatments.

The stretching of the threads may be effected by passing the thread between godets, rollers or reels the peripheral speeds of which are adjusted to give the desired amount of stretching; alternatively a pair of tapered rollers may be used. The stretching should usually be at least 50 per cent but is preferably higher, for example from 100 to 300 per cent. Stretching may be effected in air or in the presence of a coagulant bath free or substantially free from hardening agents.

The hardening baths may be any of the usual baths proposed for this purpose with casein threads, for example aqueous formaldehyde either alone or preferably in conjunction with one

or more metal salts such as sodium sulphate, magnesium sulphate, aluminium sulphate, calcium chloride, zinc chloride, basic chromium sulphate and zirconyl sulphate.

The threads after hardening are preferably subjected to an insolubilising treatment as usually applied to protein threads. The preferred insolubilising treatment is that using formaldehyde and sodium bisulphate as described in United States Patent specification No. 2,385,674.

The hardened threads may be subsequently stretched further and then treated in a further hardening bath without allowing them to contract as described in United States Patent specification No. 2,290,789.

The regenerated keratin fibres obtained according to the invention are generally of the alpha configuration as shown by X-ray analysis, and possess a wool-like elasticity.

The present invention is illustrated by the following examples:

Example 1

100 grams of wool waste were stirred at 20° centigrade with 1500 cubic centimetres of 100 volume hydrogen peroxide containing 8 grams of ferrous sulphate ($FeSO_4.7H_2O$) and 9 grams of sulphuric acid per litre. The temperature of the mixture was maintained at 20° centrigrade by external cooling until the reaction subsided. The mixture was allowed to stand at 20° centrigrade for 16 hours. The fibres were separated and washed with water until they were free from the contents of the treating bath. The fibrous product was then stirred for 4 hours with 3 litres of 1.75 per cent aqueous ammonium hydroxide. The liquor was filtered off from a small insoluble residue and clarified by centrifuging in a gravitational field of 1000×g. The clear liquor was then stirred, and sufficient 2 N sulphuric acid added to bring the pH value to 4 so that a creamy white curd was precipitated. The curd was filtered off using a nainsook cloth and pressed free of extraneous liquor. The wet curd was then redissolved by the addition of sufficient concentrated ammonia (sp. gr. 0.88) to raise the pH value to 9.0.

The viscous solution obtained was then centrifuged free from air and other particles and was then extruded into an aqueous solution containing in each litre 450 grams of crystalline magnesium sulphate ($MgSO_4.7H_2O$) and 150 grams of anhydrous sodium sulphate, the pH value of the solution being 7.0. The freshly extruded thread was stretched 200 per cent on tapered rollers with inclined axes with the lower rollers rotating in a solution having the same composition as the coagulant bath.

The threads were then collected on a godet and hardened for 2 hours at 50° centrigrade in a bath containing in each litre 10 grams of formaldehyde, 450 grams of crystalline magnesium sulphate and 150 grams of anhydrous sodium sulphate and then insolubilised by further treatment for 2 hours in a bath at 45° centrigrade containing in each litre 10 grams of formaldehyde, 300 grams of sodium sulphate and 400 grams of sulphuric acid. The threads were then washed in water and dried.

Example 2

100 grams of wool waste were stirred at 20° centrigrade with 600 millilitres of 100 volume hydrogen peroxide containing 2 grams of ferrous sulphate and 10 millilitres of 5 N sulphuric acid. The mixture was stirred for 3 hours with external cooling to keep the temperature about 20° centigrade. The mixture was then diluted with an equal volume of water and, after stirring, allowed to stand for 3 days. The solid material was separated, dissolved and extruded as described in Example 1.

The procedure described in Examples 1 and 2 may be applied to rabbet down to give threads having tensile properties comparable with those of the regenerated wool products of Examples 1 and 2.

What we claim is:

1. A process for the oxidative pretreatment of keratin preparatory to its solution in an aqueous alkaline solvent, which comprises subjecting the keratin to the action of hydrogen peroxide in the presence of ferrous sulphate and an acid chosen from the group consisting of sulphuric acid, phosphoric acid and acetic acid.

2. A process for the oxidative pretreatment of keratin preparatory to its solution in an aqueous alkaline solvent, which comprises subjecting the keratin to the action of hydrogen peroxide in the presence of ferrous sulphate and sulphuric acid.

3. A process for the oxidative pretreatment of keratin preparatory to its solution in an aqueous alkaline solvent, which comprises subjecting the keratin to the action of hydrogen peroxide in the presence of from 2 to 20 per cent by weight of ferrous sulphate and from 2 to 20 per cent by weight of sulphuric acid, both percentages being based on the weight of the keratin.

4. A process for the production of keratin solutions which comprises subjecting the keratin to the action of hydrogen peroxide in the presence of ferrous sulphate and an acid chosen from the group consisting of sulphuric acid, phosphoric acid and acetic acid and dissolving the oxidised keratin in an aqueous alkaline solution.

5. A process for the production of keratin solutions which comprises subjecting the keratin to the action of hydrogen peroxide in the presence of ferrous sulphate and sulphuric acid and dissolving the oxidised keratin in a aqueous alkaline solution.

6. A process for the production of keratin solutions which comprises stirring together keratin and hydrogen peroxide in the presence of from 2 to 20 per cent by weight of ferrous sulphate and from 2 to 20 per cent by weight of sulphuric acid, both percentages being based on the weight of the keratin thereby oxidising the keratin, and dissolving the oxidised keratin in an aqueous alkaline solution.

7. A process for the production of regenerated keratin threads which comprises stirring together keratin and hydrogen peroxide in the presence of ferrous sulphate and an acid chosen from the group consisting of sulphuric acid, phosphoric acid and acetic acid, thereby oxidising the keratin, dissolving the oxidised keratin in an aqueous alkaline solution and extruding the solution so obtained into an aqueous salt bath having a pH value between 5.0 and 9.0.

8. A process for the production of regenerated keratin threads which comprises stirring together keratin and hydrogen peroxide in the presence of ferrous sulphate and sulphuric acid, thereby oxidising the keratin, dissolving the oxidised keratin in an aqueous alkaline solution and extruding the solution so obtained into an aqueous salt bath having a pH value between 5.0 and 9.0.

9. A process for the production of regenerated keratin threads which comprises stirring together

keratin and hydrogen peroxide in the presence of from 2 to 20 per cent by weight of ferrous sulphate and from 2 to 20 per cent by weight of sulphuric acid, both percentages being based on the weight of the keratin, thereby oxidising the keratin, dissolving the oxidised keratin in an aqueous alkaline solution and extruding the solution so obtained into an aqueous salt bath having a pH value between 5.0 and 9.0.

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