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MANUFACTURE OF TEXTILE MATERIALS

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This invention relates to the manufacture of textile materials, and in particular to the manufacture of filamentary materials, i. e. single filaments, multi-filament yarns, tow, bristles and the like, having a basis of a purely synthetic substance and possessing good dimensional stability at elevated temperatures.

In accordance with the present invention we produce filamentary material by extruding and solidifying by the removal of solvent an acetone solution of an acetone-soluble copolymer of vinylidene chloride and acrylonitrile containing 20–50% by weight of acrylonitrile, stretch the material by 300–2000% of its initial length while it is at a temperature above 120° C., set the stretched material by heating it to 150° C. or higher while maintaining it under a tension sufficient to prevent shrinkage, and then heat the set material to 150° C. or higher while allowing it to shrink freely or to a controlled degree.

The copolymer from which the filamentary material is made preferably contains 25–50%, and especially 40–48%, by weight of acrylonitrile, and in order that it shall be soluble in acetone it is necessary that the unit structures derived from the respective monomers should be fairly regularly distributed throughout the polymer chain. Copolymers satisfying this condition may be made for example by copolymerising vinylidene chloride and acrylonitrile in an aqueous medium in which the monomers are emulsified or suspended, the amount of water present at the beginning of the process being between 5 and 10 times the total weight of the two monomers. The water preferably contains a small amount of an emulsifying agent, for instance an anion-active surface-acting agent such as a salt of a sulphated long chain fatty alcohol, and also a polymerisation catalyst, preferably a water-soluble compound capable of forming free radicals, especially ammonium or an alkali metal persulphate. The polymerisation may be carried out at temperatures a little above room temperature, for example at about 35°–50° C., but other temperatures can be used; naturally the lower the temperature the slower is the reaction.

The filamentary material is preferably made by extruding a solution of the copolymer in acetone into an evaporative atmosphere for example a current of air. The acetone may be substantially pure, or it may contain a small proportion, e. g. up to a total of 7.5%, of water and/or an alcohol of boiling point below 120° C., especially

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methyl, ethyl or isopropyl alcohol. Commercial acetone containing about 2–5% of water may be used, with or without a small quantity of an alcohol of boiling point below 120° C. The concentration of the copolymer in the solution is preferably about 18%–32%, the precise concentration being so chosen as to give a suitable spinning viscosity at the temperature at which the solution is to be extruded. The solution may with advantage be made by vigorously mixing the solvent and the copolymer in a mixing machine, preferably a Werner-Pfleiderer mixer or other machine having a kneading action. The solution may be extruded into a counter-current or a co-current stream of air or other evaporative medium. The spinning solution and the evaporative medium may be at or near the temperature of their surroundings, say at 20°–27° C., but higher spinning speeds and more stable spinning become possible if either or both are at a higher temperature, especially about 60°–80° C.

After leaving the spinning cell in which it is formed, the filamentary material may if desired be given a quick wash with water in order to reduce its content of residual acetone. For example the material, after leaving the cell, may be passed through a short bath of water before it is wound up or passed directly to a stretching device in accordance with the invention.

The subsequent stretching of the filamentary material is preferably carried out at a temperature between about 150° and 200° C., and especially about 175°–195° C. For example the material may be stretched while or immediately after passing over a smooth heated surface, which may be stationary or may be the surface of a rotating roll or the like, and which is kept at a suitable temperature by any appropriate heating means; or the material may be heated by means of an inert fluid, for instance hot air, steam or hot water under pressure, a mineral oil, a glycol or glycerol, or by radiation. The best results are usually obtained by stretching the filamentary material to between 500% and 1000% of its initial length.

Following the stretching, the filamentary material is set or annealed by heating it at approximately constant length to a temperature which is preferably between about 150° and 190° C., and especially about 165°–190° C. For example, the material may be wound tightly on a bobbin or other rigid support, which may then be immersed in a heating liquid at the desired tem-

perature; or the material may be treated as a running yarn or the like, for example by causing it to pass one or more times round an internally heated roll or rolls, or round a roll or rolls immersed in a heating fluid. If the filamentary material is to be heated by any means involving direct contact with a heating fluid, there may be used one of the fluids specified above in connection with the stretching step. Quite a short treatment is sufficient to set the material, and indeed is to be preferred; for instance at temperatures between about 165° and 190° C. 2–5 minutes is usually sufficient, while even at temperatures down to about 150° C. 10 minutes will suffice.

The set filamentary material is then heated under little or no tension to a temperature of at least 150° C. for about 2 minutes or more; if the greatest possible degree of thermal stability is required the material may be heated either to the setting temperature or a higher temperature up to about 195° or 200° C., or to a temperature not more than about 25° C. below the setting temperature (but always at least 150° C.) preferably for about 3–7 minutes. For example, if setting has been carried out at 190° C., the material may be subsequently heated to 170°–195° C. During this step the material may either be allowed to shrink freely, or it may be subjected to a degree of tension such that the shrinkage is controlled, but preferably amounts to at least half of the shrinkage under free conditions. The material may be heated by methods similar to those described for the stretching and setting steps, apart from the imposition of tension; thus if the material is to be heated in package form, the package should be so wound or supported as to allow the desired degree of shrinkage to take place; similarly if the material is treated as a running yarn or the like, the take-up rate should be suitably lower than the feed rate.

Although in forming the filamentary material in the process of the present invention it is preferred to use a dry spinning method as described above, satisfactory filamentary material can also be obtained, though as a rule more slowly, by wet spinning, by extruding the spinning solution in the form of filaments into an aqueous coagulating bath, which may with advantage contain a swelling agent for the copolymer; thus for example the bath may contain acetone or another lower aliphatic ketone in concentration substantially below that necessary to dissolve the copolymer, but sufficiently high to exert a swelling effect, or it may contain suitable inorganic water-soluble substances, for example water-soluble metal thiocyanates. The material may be stretched to a considerable extent during the spinning, for instance by passing the freshly coagulated, but not yet hardened, material round stretching rolls situated just outside the coagulating bath.

The method of making synthetic filamentary material which has been described possesses a number of advantages. For instance, it is found that the particular copolymers employed dissolve very readily in acetone even at room temperatures, in contrast to some prior commercial copolymers containing acrylonitrile which have to be heated with acetone above its normal boiling point and under pressure if they are to be dissolved quickly and satisfactorily. Furthermore, the copolymers can be obtained substantially colourless, and articles made from them have little tendency to develop colour on being heated even to quite high temperatures. The invention makes it possible to obtain without difficulty filamentary materials such as yarns having a very high degree of dimensional stability; for example, typical products of the new process when heated to 150° C. will shrink by about 2% at the most, yet these same products have tenacities up to about 3 grams per denier and extensions at break up to about 18%.

In spite of the exceptional and unexpected colour-stability of the copolymers, it may sometimes be found that a certain degree of darkening takes place at very high temperatures, e. g. temperatures in the neighbourhood of 190°–200° C. Any such tendency may be greatly reduced or even eliminated by incorporating in the filamentary material a substance capable of acting as a stabiliser, for example a substance which when incorporated in polyvinylidene compounds acts as an anti-oxidant and/or is capable of taking up hydrogen chloride and chlorine. Examples of suitable stabilisers are certain compounds of lead, zinc, tin and other metals, for instance lead orthosilicate, phthalate, stearate or naphthenate, zinc stearate or naphthenate, dibutyl tin laurate, stearate or naphthenate, dialkyl di-alkoxy compounds of tin such as dibutyl dibutoxy tin, calcium acetoacetate and stearate, cadmium 2-ethyl-hexoate, barium stearate, mixtures of cadmium and barium salts, and strontium naphthenate; other stabilisers include epoxides, e. g. epoxy-propyl ethers of bis-phenols such as 4,4'-bis - (2,3 - epoxypropoxy) - diphenyl, endomethylene tetrahydrophthalic acid, 1,1'-diphenyl-diethyl ether, maleic acid and derivatives thereof, butyro-lactone, 2,3,5-trichloro-2'-hydroxy-benzophenone, 2,2'-di-hydroxy-benzophenone, alkaline earth metal salts of chlorinated hydroxy-benzophenones, phenyl salicylate (salol) and alkyl-phenyl salicylates such as t-butyl-salol. Quite a small proportion of stabiliser is sufficient, e. g. 0.1–2% of the weight of the copolymer. The stabiliser may be incorporated at any convenient stage; for example it may be added to the spinning solution, or it may be present during the actual formation of the copolymer.

The invention is illustrated by the following examples. The "parts" given are parts by weight.

Example I

110 parts of vinylidene chloride, 90 parts of acrylonitrile, 500 parts of water and 10 parts of "Teepol X" (registered trade-mark) (an aqueous solution containing about 20% of sodium secondary octadecyl sulphate, about 6% of sodium sulphate and about 6% of secondary octadecyl alcohol) and 1 part of ammonium persulphate, were introduced under nitrogen into a stainless steel autoclave provided with a stirrer. The stirrer was started, and the temperature kept at 40° C. for 22 hours. The resulting emulsion was broken by adding sodium chloride, and the coagulated copolymer washed free from electrolyte. The product was a copolymer containing 45% by weight of acrylonitrile and 55% by weight of vinylidene chloride, soluble in cold acetone to give a clear solution.

22 parts of the copolymer were mixed in a Werner-Pfleiderer mixer with 71.5 parts of acetone (100%), 3.7 parts of methylated spirit and 2.8 parts of water until a clear solution had been formed. This solution was heated to about 75° C. and extruded downwardly, through a jet having 60 holes each of 0.05 mm. diameter, into an upwardly flowing air stream at room tempera-

ture. Spinning was stable, even at relatively high speeds. The filaments produced were formed into a yarn with a low degree of twist which was first stretched at 180° C. by 600% of its length, and then heated at constant length for 3 minutes at 185° C. The yarn was then heated without tension to 185° C. for 5 minutes, whereupon it shrank by about 7–9%. The shrunk yarn had a tenacity of 3.1 grams/denier and an extension at break of 17%, and it could be heated to 150° C. without suffering more than a negligible degree of further shrinkage.

Example II

A yarn having similar properties was made from a copolymer having an acrylonitrile content of 43% by weight and a vinylidene chloride content of 57% by weight, by spinning under the same conditions as in Example I, stretching by about 900% at 185° C., setting by heating the stretched yarn to 180° C. for 3 minutes without allowing it to shrink, and finally heating the yarn without tension to about 190° C. for 5 minutes.

While Examples I and II illustrate the manufacture of yarns under conditions falling within the ranges which have been found most satisfactory, especially as regards spinning stability and general ease of operation, yarns having useful properties can also be made under conditions falling somewhat outside these preferred ranges, as illustrated by Example III.

Example III

100 parts of vinylidene chloride and 100 parts of acrylonitrile were copolymerised in 600 parts of water by the method described in Example I. The product was a copolymer containing 48% by weight of acrylonitrile and 52% by weight of vinylidene chloride, which dissolved in cold acetone to give a clear solution.

A 25% solution of the copolymer in acetone was made up and extruded downwardly into an upwardly flowing stream of air through a jet having 60 holes each of 0.05 mm. diameter. The temperature of the solution and the air was either 25° C. or, for more rapid spinning, 40° C. The filaments produced were formed into a yarn with a low degree of twist, and the yarn was stretched at 140° C. by 720% of its length, and then wound tightly on a rigid support and heated for 3 minutes at 220° C. The yarn was then heated without tension to 200° C. for 5 minutes, whereupon it shrank by about 12%. The shrunk yarn had a tenacity of 2.7 grams/denier and an extension at break of 18%.

Another bobbin of the stretched yarn was heated to 200° C. for 10 minutes, and the yarn then heated without tension to 150° C. for 5 minutes. The product had a tenacity of 3.0 grams/denier and an extension at break of 15%.

In the processes of all the examples there may with advantage be incorporated in the copolymer one or more of the stabilisers listed above, for example dibutyl tin laurate in amount about 1% of the weight of the copolymer.

Having described our invention, what we desire to secure by Letters Patent is:

1. Process for the manufacture of artificial textile materials of a purely synthetic substance and characterized by having a high degree of dimensional stability at temperatures above 150° C., which comprises forming filamentary material of an acetone-soluble copolymer of acrylonitrile and vinylidene chloride containing 40 to 48% of acrylonitrile by extruding an acetone solution of

the copolymer and removing acetone from the extruded solution, stretching the material by 500 to 1000% of its length at a temperature of 175° to 195° C., setting the stretched material by heating it at constant length to a temperature of 165° to 190° C., and then heating the material under a tension insufficient to prevent shrinkage to a temperature which is in all cases above 150° C. and, subject to this limitation, is between a level 25° C. below the setting temperature and 195° C.

2. Process for the manufacture of artificial textile materials of a purely synthetic substance and characterized by having a high degree of dimensional stability at temperatures above 150° C., which comprises forming filamentary material of an acetone-soluble copolymer of acrylonitrile and vinylidene chloride containing 40 to 48% of acrylonitrile by extruding an acetone solution of the copolymer and removing acetone from the extruded solution, stretching the material by 500 to 1000% of its length at a temperature of 175° to 195° C., setting the stretched material by heating it at constant length to a temperature of 165° to 190° C. for 2 to 5 minutes, and then heating the material for 3 to 7 minutes under a tension insufficient to prevent shrinkage to a temperature which is in all cases above 150° C. and, subject to this limitation, is between a level 25° C. below the setting temperature and 195° C.

3. Process for the manufacture of artificial textile materials of a purely synthetic substance and characterized by having a high degree of dimensional stability at temperatures above 150° C., which comprises forming filamentary material of an acetone-soluble copolymer of acrylonitrile and vinylidene chloride containing 40 to 48% of acrylonitrile by extruding an acetone solution of the copolymer and removing acetone from the extruded solution by evaporation, stretching the material by 500 to 1000% of its length at a temperature of 175° to 195° C., setting the stretched material by heating it at constant length to a temperature of 165° to 190° C., and then heating the material under a tension insufficient to prevent shrinkage to a temperature which is in all cases above 150° C. and, subject to this limitation, is between a level 25° C. below the setting temperature and 195° C.

4. Process for the manufacture of artificial textile materials of a purely synthetic substance and characterized by having a high degree of dimensional stability at temperatures above 150° C., which comprises forming filamentary material of an acetone-soluble copolymer of acrylonitrile and vinylidene chloride containing 40 to 48% of acrylonitrile by extruding an acetone solution of the copolymer and removing acetone from the extruded solution by evaporation, stretching the material by 500 to 1000% of its length at a temperature of 175° to 195° C., setting the stretched material by heating it at constant length to a temperature of 165° to 190° C. for 2 to 5 minutes, and then heating the material for 3 to 7 minutes under a tension insufficient to prevent shrinkage to a temperature which is in all cases above 150° C. and, subject to this limitation, is between a level 25° C. below the setting temperature and 195° C.

5. Process for the manufacture of artificial textile materials of a purely synthetic substance and characterized by having a high degree of dimensional stability at temperatures above 150° C., which comprises forming filamentary material of an acetone-soluble copolymer of acrylonitrile

and vinylidene chloride containing 40 to 48% of acrylonitrile by extruding an acetone solution of the copolymer and removing acetone from the extruded solution by evaporation, stretching the material by 500 to 1000% of its length at a temperature of 175° to 195° C., setting the stretched material by heating it at constant length to a temperature of 165° to 190° C. for 2 to 5 minutes, and then heating the material for 3 to 7 minutes under a tension insufficient to prevent shrinkage to a temperature of 170° to 195° C.

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