Cl 106

Published Apr. 27, 1943

Serial No. 386,770

ALIEN PROPERTY CUSTODIAN

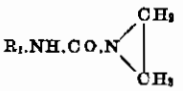
PROCESS OF IMPROVING CASEIN FIBERS AND THE MATERIAL THUS OBTAINED

Herbert Bestian, Joseph Nüsslein and Werner Asch, Frankfurt am Main, Germany; vested in the Alien Property Custodian

No Drawing. Application filed April 4, 1941

The present invention relates to a process of improving casein fibers and to the material thus obtained.

We have found that artificial casein fibers may be improved in many respects by treating them with compounds of the general formulae:



or

R_1 and R_2 standing for aliphatic or isocyclic radicals or with compounds of the above-mentioned types substituted in the ethylene group of the ethylene imine nucleus by hydrocarbon radicals.

The said compounds are obtained by reacting aliphatic or isocyclic monoisocyanates or diisocyanates as e. g. ethyl-monoisocyanate, chloroethyl-monoisocyanate, undecyl - monoisocyanate, pentadecyl-monoisocyanate, octodecyl - monoisocyanate, phenyl - monoisocyanate, cyclohexyl-monoisocyanate, tetramethylene - diisocyanate, hexamethylene - diisocyanate, octomethylene-diisocyanate, para - cyclohexylene - diisocyanate, meta-cyclohexylene-diisocyanate, meta - phenylene-diisocyanate, with ethylene-imine or substitution products thereof, such as phenyl-ethylene-imine, methyl - ethylene-imine, dimethyl-ethylene-imine, ethyl-ethylene-imine, dodecyl-ethylene-imine, cyclohexyl-ethylene-imine.

A great number of urea derivatives suitable for the process of the present invention are named in the co-pending U. S. applications Serial No. 322.031 and Serial No. 322.032, both filed March 2, 1940, in the name of Herbert Bestian. They are colorless, very reactive compounds which, owing to their urea structure, possess a more or less good solubility in water.

It is an object of the present invention to improve casein fibrous materials by impregnating them with urea derivatives of the constitution defined above. By casein fibrous materials there are understood all synthetic fibrous materials prepared from natural albuminous substances, such as casein in the proper sense, e. g. milk casein or other albuminous substances of animal origin, such as fish albumin. Further there may be used albuminous substances of vegetable origin, such as albumin from soy beans.

It is immaterial for the present invention which process of manufacture has been performed in the production of fibrous materials from the albuminous substances of animal or vegetable origin. There may also be used mixtures of fibers of different origin or mixtures of casein fibrous materials with other textile fibers, such as wool, real silk, artificial silk or staple fibers from regenerated cellulose or cellulose acetate. Moreover, there may be used fibrous material which has been subjected to a pre-treatment, for instance with tanning compounds, such as natural or artificial tanning agents, aldehydes, aluminum salts or zirconium salts and the like. According to their solubility the compounds may be used during the impregnation from an aqueous solution or from an aqueous suspension or emulsion; solutions in organic solvents may, however, also be used. The urea derivatives may be used alone or in mixture with other compounds suitable for hardening albumin, for instance aldehydes or metal compounds, such as basic aluminium compounds or zirconium compounds. The treatment may be performed directly after the production of the fiber or at a later stage of its being worked up, for instance at the finished spun goods or the tissue.

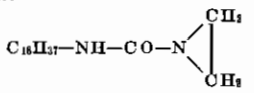
By the treatment with the urea derivatives the properties of the casein fibrous material are considerably improved. The fibrous material becomes resistant to stressings of all kinds, particularly to wet treatments, such as washing, fulling, dyeing while boiling in an acid or a feebly alkaline liquor and the like. By the treatment according to the invention there is also produced an improved resistance to stressings in practical use. Whereas for instance the non-treated fibrous material when being wet-treated in the heat, for instance in washing, agglutinates and in consequence thereof has a hard feel after having been dried, the treated fibrous material keeps its original softness and suppleness and does not show any agglutination of the individual fibers. The natural tint is by no means impaired by treating the material with the ureae named so that the fibrous material treated may be dyed just as wool in any desired tint.

It is especially remarkable that not only the resistance of the fibrous material to wet-treatment is improved but that moreover the resistance to tearing in the dry and above all in the wet state of the fiber is considerably increased. By the treatment of the dyed fibrous material the fastness to wet processing of the dyeings is in many cases much improved. The dyed fibrous substances treated according to the present in-

vention may, therefore, still be subjected to other wet improving processes, for instance to a treatment with water-repellent agents without having to fear any action on the dyeings.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto;

(1.) 100 grams of finished casein fibers are treated as follows with 20 per cent of a compound of the formula:

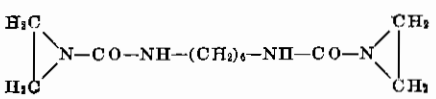


the volume of liquor being 1:50: the material is introduced into a liquor of 40°C; the temperature is raised in the course of half an hour to 70°C and the material is then treated for 1 hour at 70°C, centrifuged, hanged up for half an hour, rinsed and dried.

The suppleness of the fiber is entirely maintained. The resistance to tearing in the dry state is increased by about 20 per cent to 30 per cent. The resistance to tearing in the wet state amounts to about 50 per cent to 60 per cent of the resistance to tearing in the dry state, whereas the resistance to tearing in the wet state of the non-treated fibers amounts to at most 10 per cent of the resistanee to tearing in the dry state. This improvement of the fiber is not decreased by an alkaline treatment during the washing or fulling process. On dyeing the fibers while boiling in an acid bath the fibers remain open and do not agglutinate, whereas the non-treated fiber is completely agglutinated on dyeing while boiling; after drying it has a hard feel.

The derivative of urea named is obtained from octodecyl-isocyanate and ethylene-imine by the reaction in an indifferent organic solvent or in water. With the same good success they may be replaced by the ureae obtained by the reaction of ethylene-imine or 1.2-propylene-imine with dodecyl-isocyanate or cyclohexyl-isocyanate.

(2.) 100 grams of finished casein fibers are treated as described in Example 1 with 20 per cent of the urea of the following formula:



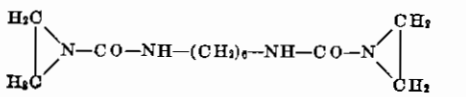
the volume of liquor being 1:50. There is obtained a fiber which as regards its properties is improved in a manner similar to that of Example 1. The treatment may also be carried through in alcohol instead of water.

The derivative of urea is obtained by the reaction of 1.6-hexamethylene-diisocyanate with 2 mols of ethylene imine in an indifferent organic solvent or in water. The urea obtained from meta-phenylene-diisocyanate and ethylene-imine may be used with the same good success.

(3.) 100 grams of finished fibers obtained by spinning a solution of 50 per cent of cellulose xanthogenate and 50 per cent of fish albumen (compare Hiltner and Mecheels, Meliand "Textilberichte," 1938, page 1) are treated according to the prescriptions given in example 1 with 20 per cent of the urea derivative mentioned in example 2, the volume of liquor being 1:50.

The fiber maintains its entire suppleness. The resistance to tearing in the dry and wet state is increased by 10 to 15 per cent by the treatment described. This improvement of the fiber is not diminished by an alkaline treatment, such as washing and fulling or by overdyeing it, while boiling.

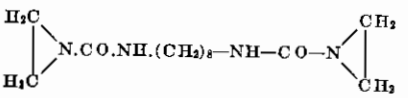
(4.) 100 grams of casein fibers (obtained by the precipitation of casein solutions in acid baths with or without the addition of alcohol or other organic solvents, with or without an after-treatment with formaldehyde or another adehyde, in the form of an endless fiber or cut into a certain staple length) are treated as follows with 20 grams of a compond of the formula:



the volume of liquor being 1:50: The material is introduced into the liquor heated to 40°C. The temperature is raised in the course of half an hour to 70°C. The material is then treated for half an hour at 70°C, centrifuged, hanged up for half an hour, rinsed and dried.

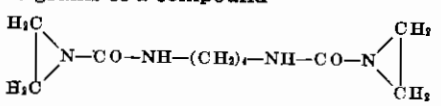
The complete suppleness of the fiber is maintained. Its resistance to tearing in the dry state is increased by 20 per cent. In the wet state the slipping of the fiber is strongly reduced by its after-treatment, whereby the resistance to wet-processing is improved by about 40 to 50 per cent. By washing it in an alkaline bath of 80°C, the treated fiber is not influenced, whereas most of the non-treated fiber is dissolved. By a subsequent dyeing process, while boiling, in an acid bath, the fiber remains open, does not agglutinate and, after having been dried, shows a soft feel, whereas the non-treated fiber firmly agglutinates and is hard after having been dried.

(5.) 100 grams of albumin fibers from soy beans (obtained in a manner analogous to that of the casein fibers from albumin of soy beans as starting material) are treated with 20 grams of a compound of the formula:



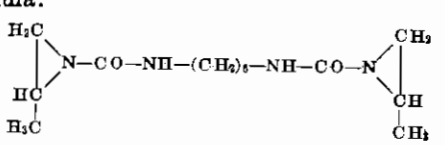
The method of operating and the effect obtained are the same as in the preceding example.

(6.) 100 grams of fish albumen (prepared in a manner analogous to that of casein fibers from fish albumen as starting material) are treated with 20 grams of a compound



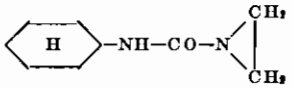
The same method of operating is applied as in example 4 and the effect obtained is likewise the same as that of example 4.

(7.) 100 grams of a mixed fabric consisting of wool and casein fiber in the proportion of 50:50 are treated in the manner described in example 4 with 20 grams of a compound of the formula:



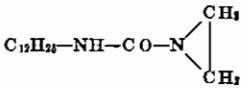
The mixed fabric treated has a somewhat harder feel, possesses an essentially higher resistance to tearing in the wet state and is more resistant to washing in an alkaline bath than the non-treated fabric. On dyeing while boiling, the casein fiber does not stick together with the wool and after drying, the soft feel is maintained, whereas the non-treated good becomes hard.

(8.) 100 grams of a mixed fabric from silk and albumin fibers from soy beans in a proportion of 40:60 are treated with 20 grams of a compound of the formula:



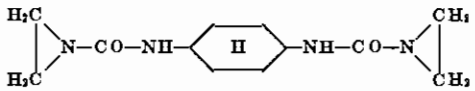
The method of operating and the effect produced are the same as those of example 7.

(9.) 100 grams of a fiber consisting of 40 per cent of fish albumin and 60 per cent of cellulose spun together from a bath (compare Hiltner and Mecheels, Melliand "Textilberichte," 1938, page 1) are treated with 20 grams of a compound of the formula:



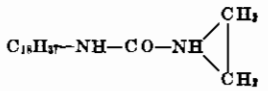
The same method of operating is applied as in example 4 and the effect produced is likewise the same as that of example 4.

(10.) 100 grams of a mixed fabric from albumin fibers from soy beans and wool in the proportion of 60:40 are treated with 20 grams of a compound of the formula:



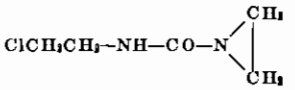
while operating in the manner described in example 7; the effect produced is the same as that of example 7.

(11.) 100 grams of a mixed fabric from casein fibers and artificial silk staple fiber from viscose in the proportion of 70:30 are treated with 20 grams of a compound of the formula



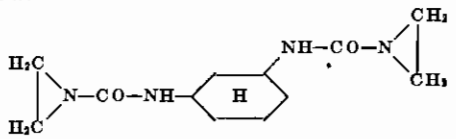
Method of operating and effect produced are those of example 7.

(12.) 100 grams of a mixed fabric from casein fibers and artificial silk staple fiber from acetate in the proportion of 80:20 are treated with 20 grams of a compound of the formula:



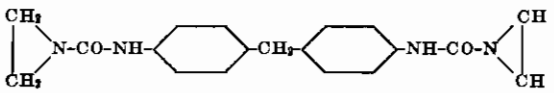
The same method of operating is applied as in example 7 and the same effect as in the said example is obtained.

(13.) 100 grams of a mixed fabric of 40 per cent of casein fiber and 60 per cent of cotton are treated with 20 grams of a compound of the formula:



The material is treated as it is described in example 7 and the same effect is obtained.

(14.) 100 grams of finished casein fibers are treated as follows with 20 per cent of a mixture consisting of 65 per cent of N-octadecyl-N'.N'-ethylene-urea and 35 per cent of the urea of the formula:



the volume of liquor being 1:50: the material is introduced into the liquor of 40°C. The temperature is raised in the course of half an hour to 70°C and the material is then treated for 1 hour at 70°C, centrifuged, hanged up for half an hour, rinsed and dried.

The effect produced is the same as that described in Example 1.

HERBERT BESTIAN.
JOSEPH NÜSSLEIN.
WERNER ASCH.