Patented Aug. 24, 1943 2,327,760

UNITED STATES PATENT OFFICE

2,327,760

FIBROUS MATERIALS

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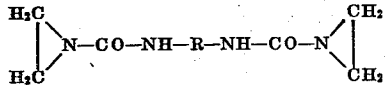
No Drawing. Application July 19, 1941, Serial No. 403,232. In Germany July 19, 1940

18 Claims. (Cl. 8—116)

The present invention relates to fibrous materials. More particularly it relates to a process of improving the properties of cellulosic fibrous material and to the products thus obtained.

We have found that the wearing strength and the other properties for the practical use of fibrous materials from natural or regenerated cellulose or mixtures containing such fibrous material may be improved to a large extent by treating them with a member of the group consisting of compounds of the general formula:



wherein R stands for a member of the group consisting of aliphatic and carbocyclic radicals, and the derivatives of said compounds, wherein at least one hydrogen atom of the nuclear bound ethylene group is substituted by a hydrocarbon radical.

By such a treatment a number of properties of the fibrous material are simultaneously improved which are of importance for the practical use of the material. For instance the tensile strength of regenerated cellulose in the dry or wet condition is remarkably enhanced. This improvement of the tensile strength is not decreased even by the usual washing operations, whereas the resistance to tearing in the dry and wet state of non-treated regenerated cellulose is diminished by a repeated washing. Textile fibers have, as is known, the tendency of swelling in the wet state. This property is particularly marked with fibers of regenerated cellulose, a broadening of the cross section and in consequence thereof a closing of the pores of the tissue being due to said swelling. By treating the fibrous material with the derivatives of di-urea named above a considerable reduction of the swelling property is attained and the spaces in the tissues are well maintained when the material becomes wet; in consequence thereof the permeability to air so important from the hygienic point of view is hardly impaired. Contrary to a non-treated material, a tissue which has been treated according to the present invention has only a slight tendency of shrinking on washing it in an aqueous liquor. The resistance to crumbling of the tissue is, therefore, considerably enhanced.

There exist a series of fibrous materials which, when being rubbed in the wet state, have the characteristic that the singular fibers split into very fine fibrils and the material becomes downy. This phenomenon is particularly evident with staple fibers from viscose which were subjected to an extensive after-stretching, furthermore with artificial silk and staple fiber which were prepared according to a process of spinning by stretching; said process consists in stretching the fibers in a slowly coagulating spinning bath before hardening the threads. The phenomenon just named may produce an undesirable and a disadvantageous effect particularly if, for instance, during a dyeing process the tissue is subjected to a scraping or rubbing or if the finished textile material is rubbed on washing. The optic behaviour of the surface of the material is altered due to the split single fibers and a whitish shimmer is produced which may give the impression of an uneven dyeing, especially in those cases where fabrics uniformly dyed in dark shades are concerned. By treating the fibrous material according to the present invention said drawback has been satisfactorily overcome.

It must furthermore be emphasized that by the treatment herein described the resistance to creasing of the fibrous material is considerably improved. Owing to the good resistance to washing of the impregnation the improvement of the resistance to creasing is evident even after a repeated washing.

As already stated above, the fibrous goods show, when being wet, a reduced swelling power. Moreover, there is simultaneously observed that the impregnated material distinctly possesses water-repellent properties. By the treatment according to the present invention it is attained that the fibrous goods are only difficultly wetted by the action of moisture. In case the material has become wet due to a prolonged action of water, it takes up only a small portion of water owing to the reduced swelling power; it, therefore, can rapidly be dried again.

Gloss and embossed effects produced by calendering on textile goods disappear, as is known, more or less completely, when the material becomes wet; if, before the calendering, the material is impregnated with the derivatives of di-urea named and subsequently subjected to a heat treatment, the effects are retained not only after a treatment with water, but even after one washing operation or after a repeated washing with a aqueous soap liquor or the solution of another washing agent, even if the material is simultaneously subjected to a mechanical treatment. By a moist or dry ironing of the washed goods, the embossed or glossy patterns do not disappear. What is said above about cal-

endering of tissues holds also true when fibers are given a form, for instance, by curling.

The treatment described herein ends in the surprising result that the cellulose material is improved in various respects for the practical use. The resistance to tearing and creasing and the water-repellent properties are enhanced; the tendency of splitting, shrinking and swelling is diminished. The impregnation described may be carried out with fibrous goods consisting of pure cellulose; but mixed fibrous materials from natural or regenerated cellulose and other vegetable, animal or synthetic fibrous materials may be subjected to the said treatment.

The monomeric starting compounds may be obtained by reaction of aliphatic, cycloaliphatic, aromatic and araliphatic diisocyanates with ethylene imine or the homologues thereof. For instance the following compounds may be named: aliphatic diisocyanates with a straight and a branched carbon chain, for instance ethylene-1.2-diisocyanate, propylene - 1.3 - diisocyanate, butylene - 1.4 - diisocyanate, hexamethylene-1.6-diisocyanate, octamethylene - 1.8 - diisocyanate, decamethylene-1.10-diisocyanate, trimethylpentylene-1.5-diisocyanate, 2-methyl-butylene-1.4-diisocyanate, or the like. The carbon chain of the aliphatic diisocyanates may be interrupted once or severel times by heteroatoms, for instance oxygen, sulfur or nitrogen.

Furthermore there are useful cycloaliphatic diisocyanates, for instance cyclohexylene-1.4-diisocyanate, cyclohexylene-1.3-diisocyanate, cyclohyxylene - 1.2 - diisocyanate, dicyclohexylene-4.4'-diisocyanate, dicyclohexylene-methane-4.4'-diisocyanate and others; aromatic and araliphatic diisocyanates, for instance para- and meta - phenylene - diisocyanate, tolylene-diisocyanates, xylene - diisocyanates, diphenylene - methane-4.4'-diisocyanate, and the methyl homologues thereof, diphenyl - 4.4' - diisocyanate, para-xylene - ω - ω' - diisocyanate, 2-chloro-1.4-xylene-α-ω'diisocyanate or the like.

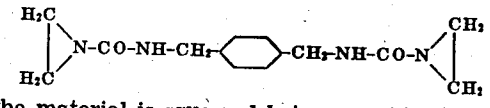
The ethylene group of the ethyleneimine radicals may be substituted by aliphatic or isocyclic radicals, hydrocarbon radicals, for instance methyl, ethyl, propyl, butyl, decyl, benzyl, phenyl and others.

The ethylene ureae may be used alone or in mixture with each other. According to the solubility of the compounds, the impregnation may be performed in aqueous solutions or suspensions. They may be operated with dilute or with concentrated liquors. For instance a quantity of 10–200 grams per liter of the derivatives of diurea may be used, but with inferior concentrations a distinct improvement of the properties of the material treated is also attained. The impregnation may be carried out at room temperature or at a raised temperature, if necessary in the presence of wetting agents. The impregnating devices suitable for the present purpose are for instance a foulard, a washer-jigger, a boiling and crabbing machine. After the impregnation, the material is squeezed or centrifuged and then dried. For this purpose the material is suitably heated to an elevated temperature, if necessary after a previous drying at a low temperature.

The diethylene-ureae may also be used together with monoethylene-urea, as they are prepared by condensation of monoiso-cyanic acid esters with ethyleneimine and the homologues thereof. Furthermore they may be used in combination with other adjuvants for the textile industry, for instance with the usual hydrophobing agents and softening agents or dressing agents, such as polyvinyl alcohol, sodium polyacrylate, ammonium poly-methacrylate, water-soluble salts of interpolymerization products from vinyl compounds, for instance vinyl chloride, vinyl acetate, styrene, or the like, and maleic acid or the anhydride thereof; furthermore interpolymerization products, the one component of which is acrylic acid or crotonic acid; starch, cellulose-glycolic ether acid, condensation products from urea or melamine and formaldehyde, and the like. The treatment with the diureae named may also be carried through in combination with a treatment with formaldehyde.

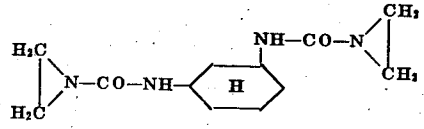
The following examples serve to illustrate the invention, but they are not intended to limit it thereto;

1. A fabric of stable fiber from viscose is impregnated at 30° C. in a liquor containing per liter 50–100 grams of the diurea of the following formula:



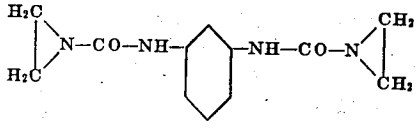
The material is squeezed between rubber rollers so that the tissue still contains 100 per cent of liquor. The material is then dried at 50° C. and the dried tissue is further heated for 20 minutes at 140° C. The impregnated tissue shows an improvement of the resistance to tearing in the dry and wet state which remains unaltered even after a three-times washing (the fabric was washed for 20 minutes at 90° C. with 5 grams of soap per liter of water).

2. A fabric of spun rayon is impregnated at 30° C. in a liquor containing per liter 150 grams of the diurea of the following formula:



The material is thoroughly squeezed between rubber rollers so that the tissue still contains 100 per cent of liquor. The material is then dried at 50° C. and the dried tissue is further heated for 20 minutes at 140° C. The tissue thus obtained is substantially resistant to creasing. The resistance to creasing is substantially retained even after a three times washing (the material was washed for 20 minutes at 90° C. with 5 grams of soap per liter of water).

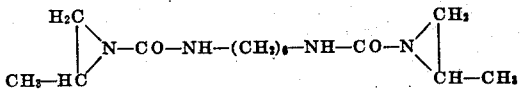
3. A fabric of cotton or staple fiber from viscose is impregnated at 30° C. in a liquor containing per liter 100 grams of the diurea of the following formula:



The material is squeezed between rubber rollers so that it still contains 100 per cent of liquor. The fabric is then preliminarily dried at 50° C. and finally calendered at 120° C. with application of a pressure of the rollers of 10,000 kilograms. The fabric is further heated for half an hour at 125° C. A stamping is produced which is resistant to washing and boiling.

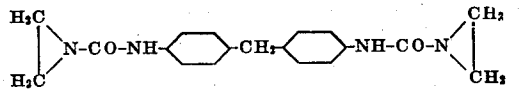
4. A fabric of staple fiber from viscose is impregnated at 30° C. with a liquor containing per

liter 100 grams of the diurea of the following formula:



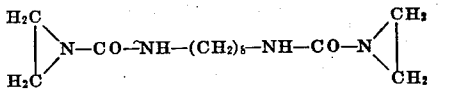
The material is squeezed, dried and further baked for half an hour at 130° C. A tissue is thus obtained which, contrary to the non-treated fabric, has only an insignificant swelling power in water or dilute alkalies and which, on washing, no longer shrinks, i. e., the fabric is resistant to shrinking.

5. A tissue of staple fiber from viscose is impregnated at 25° C. in a liquor containing in suspension per liter 10 grams of the diurea of the following formula:



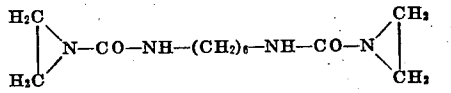
The fabric is squeezed, pre-dried at 80° C. and then further heated for 20 minutes at 140° C. The tissue thus treated shows a strongly hydrophobic character which is retained even when the tissue treated is washed.

6. A cotton fabric is impregnated at 40° C.–50° C. in a liquor containing per liter 50 grams of the diurea of the following formula:



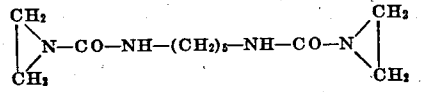
The material is squeezed, pre-dried for as short a time as possible and then passed at 120° C. through a calender for producing gloss. The fabric is then heated for 20 minutes at 140° C. By this treatment a glossy luster is produced on the cotton fabric which is fast to washing.

7. A fabric of staple fiber from viscose is impregnated at 30° C. in a liquor containing per liter 100 grams of the diurea of the following formula:



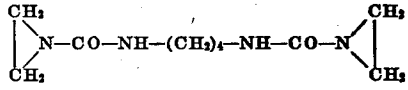
and 10 grams of octadecyl-N'-N'-ethylene-urea. The material is squeezed and, after a pre-drying at 80° C., heated for 30 minutes at 120° C. The tissue thus obtained is distinguished, contrary to the non-treated tissue, by an agreeable and a soft touch, by a considerably improved resistance to tearing in the wet and dry state, by an essential reduction of the swelling power of the individual fibers, by a substantial resistance to creasing and shrinking and by its highly hydrophobic character. The effects produced possess an excellent resistance to washing and fulling. Instead of 10 grams of N-octadecyl-N'.N'-ethylene-urea there may be used 10 grams of stearic acid methylolamide.

8. A fabric of staple fiber prepared from viscose or according to the ammoniacal copper oxide process is impregnated at 40° C. in a liquor containing per liter of water 120 grams of dimethylol-urea, 25 grams of diethylene urea of the formula:



and furthermore 3 grams of glycolic acid. The fabric is centrifuged or squeezed, dried and then heated for 20 minutes at 120° C. In comparison to non-treated material the tissue treated has, besides other improved properties, an improved resistance to creasing; the impregnation remains permanently fast to washing and boiling for 15 minutes with 5 grams of soap and 2 grams of sodium carbonate per liter of water.

9. Staple fiber obtained from ammoniacal copper oxide spinning solution by spinning in water, subsequently hardening it in dilute sulfuric acid and further treating it in the usual manner, is dried at about 40° C. and soaked with an aqueous solution of 50 grams of the compound



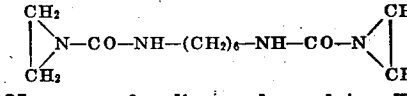
per liter of liquor. The fiber is centrifuged, dried in a current of air at 80° C.–90° C. and then heated for 10 minutes to 130° C.–140° C. When compared with the non-treated fibers the fibers treated as herein described are 200 times more resistant to splitting when they are subjected to mechanical stress in the wet state.

10. Spun rayon is soaked, after having been cut, with a solution of 25 grams of hexamethylene-diethylene-urea per liter of water, vigorously squeezed and carefully dried at a temperature of about 50° C. The artificial silk staple fiber is then curled by pressing it with grooved rollers and the curled fibers are hardened by subsequently heating them for 15 minutes to 120° C. The curling thus obtained is fast to washing.

11. Artificial silk staple fiber prepared according to the ammoniacal copper oxide process is treated in a bath containing per liter of water 50 grams of tetra-methylene-diethylene-urea and 10 grams of stearyl-ethylene-urea. The fibers are centrifuged, carefully dried and then curled by stamping at a temperature of 130° C. between rollers provided with a pattern. The fibers are subsequently heated for 5 minutes at 130° C. A curled staple fiber is obtained which is not brittle. The curling is resistant to washing with soap.

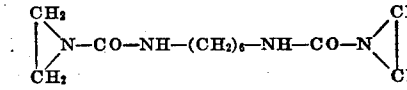
12. A viscose artificial silk yarn is twisted and wound in this state on perforated bobbins. The artificial silk is then impregnated with a solution of 30 grams of hexamethylene-diethylene-urea per liter of water, and carefully dried on the bobbins. The yarn is then twisted again in a twister and finally heated for half an hour to 110° C. A curling resistant to washing is obtained.

13. A fabric of viscose staple fiber is impregnated at 25° C. in a liquor containing per liter 50 grams of the diurea of the following formula:



and 25 grams of sodium polyacrylate. The fabric is squeezed, pre-dried at 80° C. and then subsequently heated for 20 minutes at 130° C. The tissue thus obtained has a finish fast to washing and is distinguished, in comparison with the non-treated material, by an agreeable feel, a small swelling power and an improved resistance to tearing, scraping and rubbing in the wet state.

14. A fabric of viscose staple fiber is impregnated at 25° C. in a liquor containing per liter 50 grams of the diurea of the following formula:

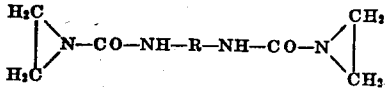


and 30 grams of the ammonium salt of an inter-

polymerization product of equal parts of vinyl-methyl-ether and maleic anhydride. The fabric is squeezed, pre-dried at 80° C. and then subsequently heated for half an hour at 120° C. The fabric thus treated has a finish resistant to washing and an improved resistance to scraping and rubbing.

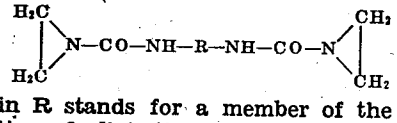
We claim:

1. The process of improving the properties of cellulose fibrous material which comprises impregnating the material with a member of the group consisting of compounds of the general formula:



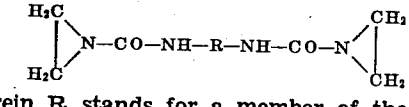
wherein R stands for a member of the group consisting of aliphatic and carbocyclic radicals, and the derivatives of the said compounds, wherein at least one hydrogen atom of the nuclear bound ethylene group is substituted by a hydrocarbon radical, and subsequently drying and baking the impregnated material in order to simultaneously enhance tensile strength, crease-resistance, hydrophobic properties and to diminish the tendency to splitting, shrinking and swelling of the cellulose material.

2. The process of preventing the tendency of splitting of cellulose fibers which become downy when used, especially on rubbing in a wet condition which comprises impregnating the material with a member of the group consisting of compounds of the general formula:



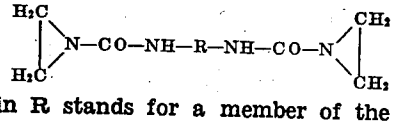
wherein R stands for a member of the group consisting of aliphatic and carbocyclic radicals, and the derivatives of the said compounds, wherein at least one hydrogen atom of the nuclear bound ethylene group is substituted by a hydrocarbon radical, and subsequently drying and baking the impregnated material.

3. The process of producing gloss and embossing effects fast to washing on fibrous material containing cellulose which comprises impregnating the material with a member of the group consisting of compounds of the general formula:



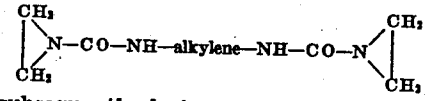
wherein R stands for a member of the group consisting of aliphatic and carbocyclic radicals, and the derivatives of the said compounds, wherein at least one hydrogen atom of the nuclear bound ethylene group is substituted by a hydrocarbon radical drying the impregnated material at a moderate temperature for a short time, calendering and subsequently heating the formed material.

4. The process of improving the properties of cellulose fibrous material which comprises impregnating the material in combination with the usual dressing agents with a member of the group consisting of compounds of the general formula:



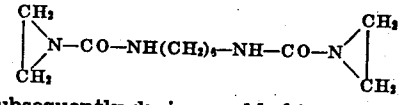
wherein R stands for a member of the group consisting of aliphatic and carbocyclic radicals, and the derivatives of the said compounds, wherein at least one hydrogen atom of the nuclear bound ethylene group is substituted by a hydrocarbon radical, and subsequently drying and baking the impregnated material.

5. The process of improving the properties of cellulose fibrous material which comprises impregnating the material with an alkylene diethylene urea having the general formula:



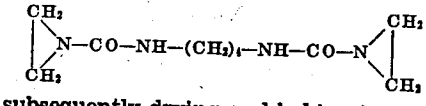
and subsequently drying and baking the impregnated material.

6. The process of improving the properties of cellulose fibrous material which comprises impregnating the material with hexamethylene diethylene urea of the formula:



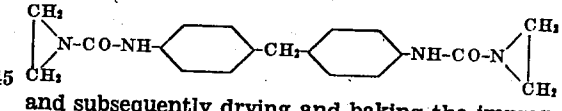
and subsequently drying and baking the impregnated material.

7. The process of improving the properties of cellulose fibrous material which comprises impregnating the material with tetramethylene diethylene urea of the formula:



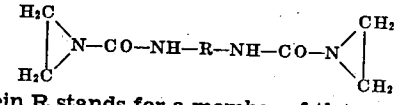
and subsequently drying and baking the impregnated material.

8. The process of improving the properties of cellulose fibrous material which comprises impregnating the material with the product of the formula:



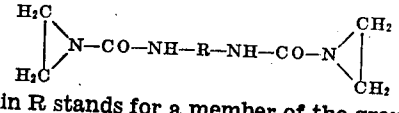
and subsequently drying and baking the impregnated material.

9. Cellulose fibrous material having enhanced tensile strength, crease resistance, hydrophobic properties and diminished tendency to splitting, shrinking and swelling obtained by impregnation with a member of the group consisting of compounds of the general formula:



wherein R stands for a member of the group consisting of aliphatic and carbocyclic radicals, and the derivatives of the said compounds, wherein at least one hydrocarbon atom of the nuclear bound ethylene group is substituted by a hydrocarbon radical drying and baking the impregnated material.

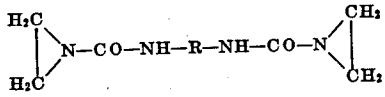
10. Cellulose fibers having the tendency to become downy in their usual condition, impregnated with a member of the group consisting of compounds of the general formula:



wherein R stands for a member of the group consisting of aliphatic and carbocyclic radicals, and the derivatives of the said compounds, wherein at

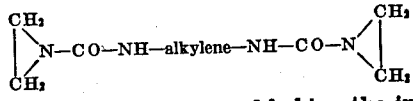
least one hydrocarbon atom of the nuclear bound ethylene group is substituted by a hydrocarbon radical, said fibers being dried and baked after impregnation, the treated material having no tendency to split.

11. Glossy and embossed fibrous materials containing cellulose obtained by impregnating the material with a member of the group consisting of compounds of the general formula:



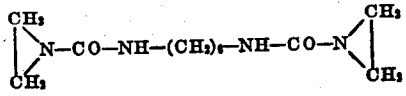
wherein R stands for a member of the group consisting of aliphatic and carbocyclic radicals, and the derivatives of the said compounds, wherein at least one hydrocarbon atom of the nuclear bound ethylene group is substituted by a hydrocarbon radical, and after previously drying, calendering and heating.

12. Cellulose fibrous material obtained by impregnating with an alkylene diethylene urea having the general formula:



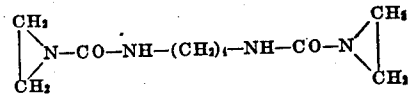
and subsequently drying and baking the impregnated material.

13. Cellulose fibrous material obtained by impregnating with hexamethylene diethylene urea of the formula:



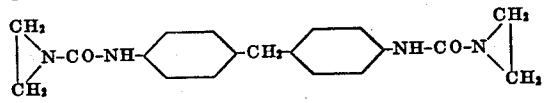
and subsequently drying and baking the impregnated material.

14. Cellulose fibrous material obtained by impregnating with tetramethylene diethylene urea of the formula:



and subsequently drying and baking the impregnated material.

15. Cellulose fibrous material obtained by impregnating with the product of the formula



and subsequently drying and baking the impregnated material.

16. The process as defined in claim 1 wherein the baking takes place at a temperature ranging from about 120 to 140° C.

17. The process as defined in claim 2 wherein the baking takes place at a temperature ranging from about 120 to about 140° C.

18. The compounds as defined in claim 9 wherein the baking takes place at a temperature ranging from about 120 to about 140° C.

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