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CELLULOSE TREATMENT PROCESS

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This invention relates to new derivatives of cellulose and is a continuation-in-part of our copending applications Serial No. 168,084, filed October 8, 1937 (now U. S. Patent No. 2,284,895) and Serial No. 275,539, filed May 24, 1939 (now U. S. Patent No. 2,284,896).

This invention has an object a process for preparing new cellulose derivatives and novel cellulosic materials. Another object is a process for preparing new cellulosic materials of desirable wet and dry strength. A further object is the preparation of such materials of high resilience. A still further object comprises the improved cellulosic materials thus obtained. Other objects will appear hereinafter.

These objects are accomplished by the following invention wherein new cellulosic materials are prepared by impregnating a cellulosic material with an organic compound having a plurality of $-N=C=X$ groups, wherein X is a chalcogen of atomic weight not greater than 33, and heating the impregnated material.

The more detailed practice of the invention is illustrated by the following examples, wherein parts given are by weight. There are of course many forms of the invention other than these specific embodiments.

EXAMPLE I

Skeins of ordinary bright unfinished viscose rayon yarn are wet with water and dried by solvent interchange with methanol and benzene. This drying procedure consists in thoroughly washing the water out of the yarn with methanol and then washing the methanol out with dry benzene. The skeins of dry swollen yarn are immersed for 10 minutes in dry benzene containing in solution 10% of hexamethylene diisocyanate by weight. They are centrifuged to remove excess solution, dried at room temperature for 45 minutes, baked for one hour in an oven at 140–145° C., washed with a 0.25% soap-0.1% sodium carbonate solution at 70° C. for two minutes, rinsed, and dried. The gain in weight of the yarn due to reaction with hexamethylene diisocyanate is 5.1%. The secondary swelling of the yarn is lowered 15% by this treatment. This is attributed to the formation of a cellulose urethane having a plurality of cellulose nuclei linked by hexamethylene bis-urethane linkages.

Secondary swelling is measured by wetting weighed skeins (conditioned at 50% R. H. and 25° C. before weighing) of untreated and treated yarn with water, centrifuging them together, and weighing each in a closed container to determine the amount of water retained. The untreated

yarn usually retains about an equal weight of water. "Secondary swelling" is the term used to express the amount of water retained by the treated yarn after it has been centrifuged compared with the amount retained by the untreated yarn. It is expressed on a percentage basis.

Secondary swelling is a measure of the sensitivity of yarn to water. Although the secondary swelling of viscose rayon can be lowered somewhat by treatment with mono $-N=C=X$ compounds, such agents are much less effective than are the poly $-N=C=X$ compounds.

EXAMPLE II

There is described in U. S. Patent 2,249,745 a new crimped viscose rayon yarn. This new yarn is produced by the extrusion of viscose into a coagulating bath having a rapid coagulating action and a slow, or no, regenerating action, with a velocity of extrusion at least four times the velocity of drawoff. The streams of viscose issuing from the spinneret into the coagulating bath under the afore-mentioned conditions spontaneously assume a final crimped form which persists as a permanent structural characteristic in the filaments. The resulting yarn is composed of substantially non-crenulated filaments having an inherent and substantially permanent crimp, the crimp in the several filaments of the yarn being out of phase with each other. The filaments exhibit substantially no orientation in the direction of the fiber axis.

Skeins of the above crimped viscose rayon yarn are wet with water and dried by solvent interchange with methanol and benzene as described in Example I. They are then immersed for one hour in a boiling (133–140° C.) 2% solution of hexamethylene diisocyanate in xylene (1 part of yarn to 14 parts of solution), rinsed with benzene, dried, washed with a 0.25% soap-0.1% sodium carbonate solution at 70° C. for two minutes, rinsed and dried. The gain in weight of the yarn due to reaction with hexamethylene diisocyanate is 14.6%. The yarn contains 2.32% nitrogen. The yarn compares as follows with untreated crimped viscose rayon yarn with regard to important physical properties.

Dry breaking strength	Increased 5%
Wet breaking strength	Increased 66%
Secondary swelling	Decreased 43%

In feel the yarn is much more resilient and wool-like than the untreated yarn, particularly when it is wet. The yarn to which no treatment has been applied, or which has merely been treated with a monoisocyanate like hexyl isocyanate,

temporarily loses its crimp when it is wet with water. Yarn treated with hexamethylene diisocyanate by this process, however, retains a substantial proportion of its crimp even when it is wet with water.

In Table I, below, yarn prepared by the process of U. S. Patent 2,249,745 and treated with hexamethylene diisocyanate is compared with the same yarn similarly treated with phenyl isocyanate. Both of these isocyanates have six carbons in the non-isocyanate portion of the molecule.

Table I

Agent	Per cent nitrogen in yarn	Change in wet strength per cent relative to control
Hexamethylene di-isocyanate.....	2.3	+66
Phenyl isocyanate.....	1.0	-5

This comparison strikingly illustrates the marked differences between mono- and poly- —N=C=X compounds. The data in the table are obtained with 2500 denier-100 filament yarn which had been wet with water and dried by solvent interchange with methanol and benzene as in Example I. One sample of the yarn was immersed for one hour in boiling xylene containing 3% phenyl isocyanate. Another sample was immersed for one hour in boiling xylene containing 2% hexamethylene diisocyanate. The difference in the effect of the mono- and di-isocyanates is attributed to the cross linking of a plurality of cellulose molecules by the diisocyanate with the formation of hexamethylene bis-urethane linkages.

EXAMPLE III

Skeins of regenerated cellulose yarn made by the process of U. S. Patent 2,249,745 are wet with water and dried by solvent interchange with methanol and benzene as described in Example I. They are immersed for 15 minutes in dry benzene containing in solution 10% of m-phenylene diisocyanate by weight. They are then centrifuged to remove excess solution, dried at room temperature, baked for one hour in an oven at 140–145° C., washed with a warm 0.25% soap-0.1% sodium carbonate solution at 70° C. for two minutes, rinsed and dried. The gain in weight of the yarn due to reaction with the diisocyanate is 15.6%. The treated yarn shows a 12% increase in dry strength and a 5% increase in wet strength in comparison with an untreated control. It retains a substantial proportion of its crimp even when it is wet with water.

EXAMPLE IV

Skeins of viscose rayon yarn prepared by the process of U. S. Patent 2,249,745 are wet with water and dried by solvent interchange with methanol and benzene as in Example I. They are then treated with hexamethylene diisocyanate by the procedure of Example I. The gain in weight of the yarn due to reaction with hexamethylene diisocyanate is 13.1%. The resultant yarn compares as follows with the original untreated yarn with regard to important physical properties.

Dry breaking strength..... Increased 17%
Wet breaking strength..... Increased 108%
Secondary swelling..... Decreased 76%

This treated yarn is similar in feel and behavior when wet to that of Example II.

EXAMPLE V

Skeins of ordinary bright unfinished viscose rayon yarn are prepared and treated with hexamethylene diisocyanate by the procedure of Example II. The gain in weight of the yarn due to reaction with hexamethylene diisocyanate is 4.9%. The secondary swelling of the yarn is lowered 17% by this treatment.

EXAMPLE VI

Five parts decamethylene diisothiocyanate is emulsified in 15 parts of a 3% aqueous soap solution. Five parts cotton voile fabric is thoroughly wet out in this emulsion and wrung to a weight of 9 parts. Half of this fabric is dried over night at 95–100° C. and the other half 45 minutes at 125° C. Each half is then rinsed with water and dried. Both pieces of voile, although of open weave, are very water-repellent and support drops of water without wetting even after repeated washing with acetone or soap.

While the process of the present invention is of particular value in its application to regenerated cellulose yarn which treatment represents a preferred modification, the invention is applicable to cellulosic material in general, e. g., any of the forms of natural cellulose, including cotton, wood pulp, linen, and ramie, in the form of floors, yarns, fabrics, or paper as well as regenerated cellulose, including films, fibers, filaments, yarns, and fabrics. The regenerated cellulose materials may be prepared by any of the known procedures, for example, by the viscose process, the cuprammonium process, or by hydrolysis of cellulose esters. The cellulose may contain modifying agents such as plasticizers, pigments, proteins, oils, dyes and resins.

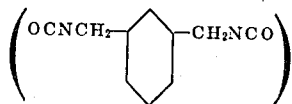
Although it is not necessary to dry the cellulose before treatment with the poly —N=C=X compound, it is preferable to do so to avoid loss of the treating agent through reaction with water. Furthermore, although it is not necessary to first wet the cellulose with water or other swelling agent therefor and then dry it by solvent interchange, such a pretreatment is highly desirable since it leaves the cellulose in a swollen, much more reactive condition than does simple air drying. Cellulose prepared in this way for treatment is more readily penetrated by an agent which is applied in a hydrocarbon solvent, since such solvents do not swell cellulose.

In the process of this invention, the cellulose is treated with an organic compound having a plurality of —N=C=X groups, wherein X is a chalcogen of atomic weight less than 33. Of these, the diisocyanates and diisothiocyanates in general are most useful in the practice of this invention and form a preferred subclass because of their ease of preparation, low cost, reactivity, etc. Additional examples of this subclass are: polymethylene diisocyanates and diisothiocyanates, such as ethylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, etc.; the corresponding diisothiocyanates; alkylene diisocyanates and diisothiocyanates, such as propylene-1,2-diisocyanate, butylene-1,2-diisocyanate, butylene-1,3-diisocyanate and butylene-1,3-diisothiocyanate; alkylidene diisocyanates and diisothiocyanates, such as ethylidene diisocyanate $(\text{CH}_3\text{CH}(\text{NCO})_2)$, and heptylidene diisothiocy-

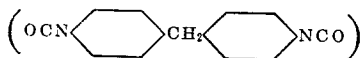
anate ($\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{NCS})_2$); cycloalkylene diisocyanates and diisothiocyanates, such as cyclopentylene-1,3-diisocyanate, cyclohexylene-1,4-diisocyanate, and cyclohexylene-1,2-diisothiocyanate; aromatic diisocyanates and diisothiocyanates, such as m-phenylene diisocyanate, p-phenylene diisocyanate, 1-methylphenylene-2,4-diisocyanate, naphthylene-1,4-diisocyanates, o,o'-tolane diisocyanate, diphenyl-4,4'-diisothiocyanate, m-phenylene diisothiocyanate, and p-phenylene diisothiocyanate; aliphatic-aromatic diisocyanates or diisothiocyanates, such as xylylene-1,4-diisocyanate



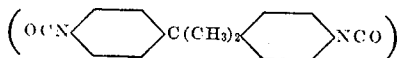
xylylene-1,3-diisocyanate



4,4'-diphenylenemethane diisocyanate



4,4'-diphenylene propane diisocyanate



and xylylene-1,4-diisothiocyanate



and diisocyanates and diisothiocyanates containing hetero-atoms, such as $\text{SCNCH}_2\text{OCH}_2\text{NCS}$, $\text{SCNCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{NCS}$, and



and acyl diisocyanates and diisothiocyanates such as suberyl, pimelyl, azelalyl, brassyl isocyanates and isothiocyanates. In fact, any diisocyanate, diisothiocyanate, or mixed isocyanate-isothiocyanate of the general formula XCNRNCX , in which X is oxygen or sulfur and R is a divalent organic radical, will react with the cellulose to give improved products according to the present invention. This invention is not, however, limited to di ---N=C=X compounds since organic compounds having a higher number of ---N=C=X groups may be employed including 1,2,4-benzene triisothiocyanate and butane-1,2,2-triisocyanate, as well as the isothiocyanic or isocyanic esters of castor oil or hexahydro castor oil (glyceryl tris-hydroxy-stearate). The treatment of crimped viscose rayon yarn with diisocyanates having a bivalent hydrocarbon radical of six carbons between the two isocyanate groups is particularly preferred.

It will be noted from the examples that the new cellulose derivatives of this invention contain nitrogen. The products are believed to have a plurality of cellulose nuclei united through urethane (or thiourethane) linkages by the organic radical of the diisocyanate (or diisothiocyanate).

The treatment involves bringing the cellulose and poly ---N=C=X compound into contact with each other under such conditions that they will react with each other uniformly and to the desired extent in a convenient length of time. Preparation of the cellulose as described above facilitates thorough impregnation of the cellulose.

In order to control better the degree of formation of the new cellulose derivative, the poly

---N=C=X compound is preferably applied from a solution in an inert solvent, although if the poly ---N=C=X compound is a liquid, it may be applied as such. The solvent should preferably be anhydrous to avoid loss of agent and should be free of active hydrogen atoms, altho this is not absolutely necessary as is shown by Example VI. Hydrocarbons such as benzene, toluene, xylene, or petroleum fractions are preferred solvents. Halogenated hydrocarbons, ethers, and tertiary amines may also be used. Tertiary amines, pyridine for example, are useful where a solvent which will swell cellulose is desired to facilitate reaction.

Various procedures may be used for applying the poly ---N=C=X compound to the cellulose. One is illustrated by Example II and another by Example I. The former is particularly useful where uniformity of treatment is desired. It involves immersion of the cellulose in a hot solution of the poly ---N=C=X compound. Uniformity of treatment is favored by the uniform heating obtained by this procedure. The degree of new cellulose derivative formation increases with the reactivity of the poly ---N=C=X compound, its concentration, the ratio of solution to cellulose, the temperature of the solution, and the duration of the treatment. The concentration may vary from 0.5% or less to 90% or more, although in most cases a concentration of from 1 to 10% is preferred. Sufficient solution must be used to cover the cellulose completely. Although poly ---N=C=X compounds react with cellulose at room temperature, such a long time is required to obtain the degree of modification usually desired, that use of higher temperatures, 80-170° C., is much preferred. For this reason, the solvent used should possess a boiling point above 80° C., although it is possible to use a lower boiling solvent if the treatment is carried out under pressure. At temperatures above 170° C. the cellulose is likely to be damaged to an undesirable extent, particularly if the treatment is prolonged beyond a few minutes. A range of 120-150° C. is usually preferred. In most cases treatment for from 16-60 minutes at 120-150° C. will be sufficient to bring about the desired reaction. The exact conditions of time, temperature, and concentration can best be determined for each particular poly ---N=C=X compound and type of cellulose by a preliminary experiment. The poly ---N=C=O compounds as a class react much more rapidly than the poly ---N=C=S compounds.

The treating procedure illustrated by Example I involves impregnation of the cellulose with the poly ---N=C=X compound in a volatile inert solvent followed by evaporation of the solvent and a heat treatment. This procedure is most satisfactory when the poly ---N=C=X compound has a low enough vapor pressure to remain in contact with the cellulose during the heat treatment. Application of the poly ---N=C=X compound from a solvent facilitates control of the quantity of treating agent in contact with the cellulose during the heat treatment, and, consequently, the degree of modification obtained. The solvent may be evaporated at room temperature or higher temperatures, preferably in dry, warm, circulating air. The heat treatment, during which the reaction between the poly ---N=C=X compound and the cellulose takes place, is preferably carried out in an oven provided with a mechanism for efficiently circulating the heated air; the uniformity of heating

and, therefore, the uniformity of the treatment are much better when the air in the oven is circulated. Heating temperatures of from 120-170° C. are preferred, although lower temperatures may be used if the heating period is prolonged. Treatments at higher temperatures are likely to damage the cellulose and should not be extended beyond a few minutes.

Other treating procedures may of course be used. For example, the cellulose may be exposed to hot vapors of the poly $-N=C=X$ compound or, if the cellulose is in the form of yarn, it may be impregnated with the poly $-N=C=X$ compound and passed through a bath of hot molten metal to bring about reaction. In the latter case, higher temperatures, 200° C. for example, may be satisfactory if the yarn is passed so rapidly through the bath that the heating period lasts only a few seconds.

The expression "cellulosic material" is used to include cellulose both natural and regenerated, but not cellulose ethers or esters, most of which are essentially hydrophobic in nature as contrasted with the essentially hydrophilic cellulose.

The term "chalcogen" is defined by the Committee of the International Union of Chemistry for the Reform of Inorganic Chemical Nomenclature in its Rules for Naming Inorganic Compounds at J. Am. Chem. Soc. 63, 892, column 1, lines 9-11 (April, 1941) as follows:

"the elements oxygen, sulfur, selenium, and tellurium may be called 'chalcogens' and their compounds 'chalcogenides.'"

The above description and examples are intended to be illustrative only. Any modification of or variation therefrom which conforms to the spirit of the invention is intended to be included within the scope of the claims.

What is claimed is:

1. Process for the preparation of new cellulose derivatives which comprises heating a cellulosic material with an organic compound having plurality of $-N=C=X$ groups, wherein X is a chalcogen of atomic weight not greater than 33.

2. Process for the preparation of new cellulose derivatives which comprises impregnating a cellulosic material with a solution, in an inert solvent, of an organic compound having a plurality of $-N=C=X$ groups, wherein X is a chalcogen of atomic weight not greater than 33, and baking the impregnated material.

3. Process for the preparation of new cellulose derivatives which comprises heating a cellulosic material in a solution, in an inert solvent, of an organic compound having a plurality of $-N=C=X$ groups, wherein X is a chalcogen of atomic weight not greater than 33.

4. Process which comprises impregnating viscose rayon with a solution, in an inert solvent, of an organic compound having a plurality of $-N=C=X$ groups, wherein X is a chalcogen of

atomic weight not greater than 33, and baking the impregnated material.

5. Process which comprises impregnating a crimped viscose rayon yarn with a solution, in an inert solvent, of an organic compound having a plurality of $-N=C=X$ groups, wherein X is a chalcogen of atomic weight not greater than 33, and baking the impregnated material.

6. Process which comprises impregnating a cotton fabric with a dispersion of an organic compound having a plurality of $-N=C=X$ groups, wherein X is a chalcogen of atomic weight not greater than 33, and baking the impregnated material.

7. Process which comprises impregnating a cotton fabric with an aqueous dispersion of an organic compound having a plurality of $-N=C=X$ groups, wherein X is a chalcogen of atomic weight not greater than 33, and baking the impregnated material.

8. Process for the improvement of cellulosic material which comprises heating a cellulosic material with an organic compound having two $-N=C=X$ groups, wherein X is a chalcogen of atomic weight not greater than 33.

9. Process which comprises impregnating a cellulosic material with a solution, in an inert solvent, of an organic compound having two $-N=C=X$ groups, wherein X is a chalcogen of atomic weight not greater than 33, and baking the impregnated material.

10. Process which comprises heating a cellulosic material in a solution, in an inert solvent, of an organic compound having two $-N=C=X$ groups, wherein X is a chalcogen of atomic weight not greater than 33.

11. Process for the improvement of cellulosic material which comprises heating a cellulosic material with an organic diisocyanate.

12. Process which comprises heating a crimped viscose rayon yarn impregnated with an organic diisocyanate having a bivalent hydrocarbon radical of six carbon atoms between the two isocyanate groups.

13. A product of the heat treatment of a crimped viscose rayon yarn with an organic compound having a plurality of $-N=C=X$ groups, wherein X is a chalcogen of atomic weight less than 33, said baked product having a substantially greater wet breaking strength than the untreated yarn.

14. A product of the heat treatment of a crimped viscose rayon yarn with hexamethylene diisocyanate.

15. A new cellulose derivative comprising the reaction product of a cellulosic material and an organic compound having a plurality of $-N=C=X$ groups, wherein X is a chalcogen of atomic weight less than 33.

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