

UNITED STATES PATENT OFFICE

2,370,405

PROCESS FOR RENDERING MATERIAL
WATER-REPELLENT AND PRODUCTS
THEREFROM

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14 Claims. (Cl. 8—116)

This invention relates to processes for treating textile or other materials to render them water-repellent; and to products therefrom.

This application is a continuation in part of our copending applications Ser. No. 76,738, filed April 28, 1936 (now Patent 2,303,363); and Ser. No. 196,622, filed March 18, 1938 (now Patent 2,340,757).

Processes have been proposed heretofore for making cotton and like material water-repellent by treatment with fatty acid chlorides or fatty acid anhydrides, but these processes have not come into commercial use so far as we are aware.

The principal object of the present invention is to provide a simple process to produce water-repellence in textile and other material, and to produce water-repellent products substantially without impairing the appearance or handle of such material, either colored or otherwise.

The invention comprises the novel products as well as the novel processes and steps of processes according to which such products are manufactured, the specific embodiments of which are described hereinafter by way of example and in accordance with which we now prefer to practice the invention.

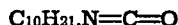
It has been found in accordance with our invention that treatment of textile or other materials, for example cellulose-containing materials, wool, silk, and others may be carried out with isocyanic acid esters of the aliphatic, mixed aliphatic-aromatic or naphthenic series to produce remarkably fine effects including water-repellence. In our above-mentioned copending application Serial No. 76,738, now Patent No. 2,303,363, we disclose and claim treatment of textiles with isocyanates to produce water-repellence and products therefrom. In copending application Serial No. 196,622, now Patent No. 2,340,757, we disclose and claim chemicals which may be employed, for instance but without limitation, in such treatment and processes for making the same. In the present application we disclose and claim treatment of textiles with isocyanates having hetero groups containing N, O, or S, present, for example but without limitation, in groups such as CO.O, O.CO, NH, NH.CO, CONH, SO₂, NH.SO₂, SO₂.NH or as the elements O or S. H may be substituted in these groups by a hydrocarbon radical. In certain of the appended claims, formulae for such isocyanates are used, viz. R.S.CH₂N=C=O and R.O.CH₂N=C=O, in which R represents an aliphatic radical, and R'O phenyl N=C=O, in which R' represents an alkyl

radical, R and R' containing at least 10 carbon atoms.

We have also found in accordance with our invention that corresponding fatty acid azides and carbamic acid halides containing similarly at least ten carbon atoms, upon reaction thereof with textiles and other materials as herein described, are capable of producing water-repellence therein.

Substances which we have successfully employed in accordance with our invention for treatment of materials to produce water-repellence include the following:

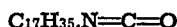
Decyl isocyanate



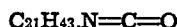
Hexadecyl isocyanate



Heptadecyl isocyanate



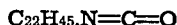
Heneicosyl isocyanate



25 Octadecyl isocyanate



Docosyl isocyanate



30 Hydrated whale oil isocyanate 18-pentatriacontane isocyanate



35 Naphthenic isocyanate



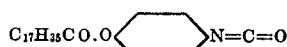
Bicyclic naphthenic isocyanate



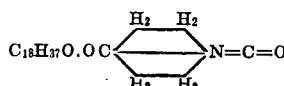
40 Montanyl (hepacosyl) isocyanate



45 1-stearyl-oxy-phenylene-4-isocyanate



4-carboctadecoxy tetrahydrophenyl isocyanate



Cholesterol adipic acid ester isocyanate



Octadecyl oxy acetic acid isocyanate



Dodecyl mercaptan acetic acid isocyanate



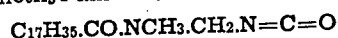
Stearyl glycolic isocyanate



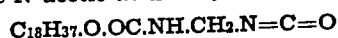
Stearyl amino acetic acid isocyanate



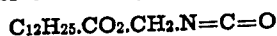
Stearyl methyl amino acetic acid isocyanate



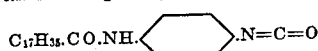
Urethane N-acetic acid isocyanate



Dodecyl ester of carbonyl glycine isocyanate



4-stearyl amino-1-phenyl isocyanate



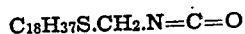
Hexadecyl oxy-phenyl isocyanate



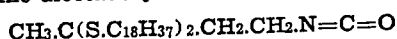
Octadecyl mercapto-propiono isocyanate



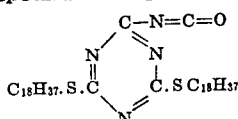
Octadecyl mercapto-acetic acid isocyanate



Levulinic dioctadecyl mercaptol isocyanate



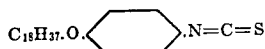
Cyanuric compound having the formula



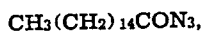
Octadecyl oxy-phenyl isocyanate



Octadecyl oxy-phenyl isothiocyanate



Similarly azides which have been successfully employed are palmitic acid azides



octacosane acid azide (montanyl acid azide) $C_{27}H_{55}CON_3$ and others. Carbamic acid chlorides which may also be employed are for example carbonyl glycine dodecyl ester chloride



and others. With such carbamic acid chlorides it is preferable to use a neutralizing agent such as sodium acetate or pyridine to avoid injury to the fibers.

The substances mentioned are distinguished by the high rapidity of action with textile and other materials, particularly toward cellulose and cellulose derivatives. It is necessary only to bring the material in contact with the treating compound as by passing the material briefly through a solution of the isocyanic acid esters or the like in benzine or a suitable solvent and immediately thereafter subjecting the treated material to drying followed by baking or a com-

bined drying and baking for suitable times and temperatures to produce the desired water-repellence in the material.

It is also possible to add the materials mentioned for producing water-repellence to a spinning solution, for example a spinning solution of acetyl cellulose, in order thus to combine the process of producing water-repellence with the spinning process. Also one may treat fibers of cellulose or cellulose derivatives immediately after the spinning process with the materials herein mentioned to obtain water-repellence. The impregnation of the textile and other materials with the substances for producing water-repellence may be carried out in any desired manner with or without the use of organic solvents such as trichlorethylene, carbon tetrachloride, benzine, etc. In place of an organic solvent an aqueous emulsion of the material may be employed. The material may be soaked, sprayed or otherwise treated for the introduction of the desired substance. The addition of catalytic agents for the purpose of securing the desired effect may be used, but it is not necessary. The water-repellent effects produced by these materials resist domestic washing. After thorough rinsing out of the soap and drying, the textile material again manifests water-repellent properties. It is also resistant to treatment with benzine for the purpose of dry-cleaning.

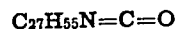
The material treated may be dyed prior to the treatment with the water-repellent agent but instead of soaps or oils employed in such dyeing, a textile auxiliary means should be employed preferably one which is free of "sulpho" or "carboxyl" groups and which on account of the presence of several hydroxyl groups possesses in the molecule water-soluble properties. Such a material is available on the market and is known as "Peregal O" or "Emulphor O" manufactured by I. G. Farbenindustrie of Germany. It is oleypolyglycolicether. A specific example of the use of such material in predyeing fabric is as follows: Mercerized cotton yarn is dyed in the usual manner with Congo red in an aqueous bath containing besides 5 gr. per litre of sodium sulphate and 0.1 gr. per litre of "Peregal O."

After dyeing the material is rinsed well and dried.

The following are examples and embodiments of the invention as we now prefer to carry it out. It is understood that these examples are not to be construed as limiting the invention, except as indicated in the appended claims.

Examples

Example 1.—Montanyl isocyanate



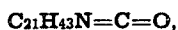
is dissolved in light benzine to give a solution of 0.5–1% approximately. The light benzine is preferably one which is substantially completely distilled at or below 70° C. The specific gravity is approximately 0.66. The benzine should be substantially free from impurities, especially alcoholic admixtures. The solution of montanyl isocyanate in benzine should be clear. The fabric or other material to be treated should be completely clean, that is free of chemicals used for the finishing of textiles, soap residues and the like, and should be dry. It should preferably however contain its natural moisture content. Acetate satin, having acetate silk as warp and viscose crepe as weft, is passed through the solution of montanyl isocyanate in benzine at room

temperature. The solvent is evaporated off at about 80° C. The material is then treated for about 5 hours at a temperature of about 80–85° C. in the drying chamber. If desired, the heating treatment may be considerably shortened. For instance, it may be employed for 1 hour at 110° C. or 5 minutes at 140° C. The durability of the effect produced, however, is better if the treatment is given at a lower temperature for a longer period.

Example 2.—A fabric consisting of pure spun viscose rayon in warp and weft is passed through a 1% solution of hexadecyl oxyphenyl isocyanate in benzene at room temperature. The solvent is evaporated off at about 75° C. and the so-treated material is heated for about 10 minutes, up to about 135–140° C. The time and temperature may be varied but it is generally more favorable to heat for a short time at temperatures over 100° C. The goods should remain about 24 hours thereafter at ordinary temperature as there appears to be an "after action" on the fiber during the 24 hour interval, as a result of which the desired water-repellent effect appears on test.

Example 3.—A printed crepe, having delustered viscose rayon as warp and viscose crepe as weft, is passed through an 0.5% solution of octadecyl isocyanate, $C_{18}H_{37}N=C=O$. The time of passage is about 3 seconds and the solution is at room temperature. Immediately thereafter the so-treated material is subjected for one minute to a temperature of 100° C. (212° F.) and then for two minutes to a temperature of 140° C. (284° F.).

Example 4.—Dyed stockings of Bemberg silk (cuprammonium silk) are immersed in an 0.3% solution of heneicosyl-isocyanate



in benzene at room temperature for approximately 10 seconds, then taken out and, after evaporation of the solvent, treated for 1½ minutes at 150° C.

Example 5.—To 1000 liters of a 20% solution of acetyl cellulose in acetone 4000 grams of n-heptadecyl-isocyanate $C_{17}H_{35}N=C=O$, are added. After well stirring the mixture is allowed to stand for 48 hours. The spinning solution is then forced through fine orifices in a metal cap, called a spinnerette in a downward, vertical direction. The metal cap is enclosed in a tube in which a current of warm air travels upward. The filaments are set by the evaporation of the acetone, which is conducted away and recovered as far as possible.

Example 6.—A cotton tent cloth is passed through a 1% solution of naphthenic isocyanate, $C_{15}H_{33}N=C=O$, in benzene. After the passage which lasts about 4 seconds, the solvent is evaporated off and the material is heated for 2 minutes to a temperature of 150° C.

Example 7.—A fabric, suitable for rucksacks, consisting of linen and cotton is treated with an 0.75% solution of bicyclic naphthenic isocyanate, $C_{20}H_{37}N=C=O$, from Roumanian naphtha in benzene in the same way as described in Example 6.

Example 8.—A viscose spun rayon fabric is passed through an 0.5% solution of 1-stearyl-oxy-phenylene-4-isocyanate,



the further treatment being the same as in Example 3.

Example 9.—Loose undyed, unbrightened spun rayon flock is impregnated in a 2% solution of

octadecyl-oxyphenylisocyanate in benzene for 3 seconds. After impregnation the material is squeezed out or centrifuged from the surplus of the benzene solution. The solvent remaining still on the fibre is then evaporated off and the material is treated for 4 minutes at 140° C. The loose spun rayon flock thus impregnated and heated can be dyed after wetting in the usual manner with direct sulphur or vat colors.

Example 10.—A poplin from mercerized cotton, suitable for rain-proof overcoats is passed through an 0.5% solution of octocosane-acid azide in benzene for 3 seconds at 10° C. The solvent is then removed by heating the fabric to about 100° C. for a short time. Afterwards the material is exposed for two minutes to a temperature of 140° C.

Example 11.—A mixture of amines obtainable by hydrating train oil acids is converted into a mixture of isocyanic esters by means of phosgene and an 0.5% solution in benzene therefrom is prepared. A mixed fabric consisting of mercerized cotton and viscose spun rayon is treated with this solution in the same way as described in Example 10.

Example 12.—A fabric consisting of "Vistra" (spun viscose rayon) is treated with an 0.5% solution of cholesterol-adipic acid ester isocyanate, $C_{27}H_{45}O.CO(CH_2)_4N=C=O$, as described in Example 10.

Example 13.—A wool muslin is treated with an 0.5% solution of cholesterol adipic acid ester azide in benzene, $C_{27}H_{45}O.CO(CH_2)_4CON_3$, as described in Example 10.

Example 14.—A worsted fabric is treated with an 0.5% solution of octocosane acid azide as described in Example 10.

Example 15.—A strong cotton fabric is passed during 3 seconds through an 0.5% solution of montanyl isocyanate, $C_{27}H_{55}N=C=O$, in benzene. The solvent is evaporated off and the material is exposed for 2 minutes to a temperature of 150° C.

Example 16.—A printed crepe consisting of pure natural silk in warp and weft is passed through a 1% solution of heptacosylisocyanate in carbon tetrachloride. The solvent is evaporated off at about 80° C. The material is then treated for about 5 hours at a temperature of about 80–85° C. in the drying chamber.

Example 17.—Fulled cloth consisting of 70% synthetic casein fibre and 30% natural wool is passed through a 1% solution of heptacosylisocyanate in carbon tetrachloride. The solvent is evaporated off at about 80° C. The material is then treated for about 5 hours at a temperature of about 80–85° C. in the drying chamber.

The amount of the ester deposited in all of the above examples on the materials will naturally vary with the weight of the material and its actability. We have found that ordinarily an amount of the ester equal to about 0.5% of the material being treated, is sufficient to give the effect. The increase in weight of the material treated will vary somewhat and is usually less than 1%.

The materials produced in accordance with the above examples show a high degree of water-repellence. They show a lesser absorption of moisture as compared with the known processes for treatment with fatty acid chlorides and fatty acid anhydrides. They show also greatly improved durability toward dry-cleaning, soap washing, etc. as compared with these previous materials. The feel and hang of the materials

having water-repellence as produced above, have not been substantially altered.

The process of the invention, particularly as set forth in the specific embodiments above, may be carried out with simple apparatus at relatively small expense and in a relatively short time.

In the claims where the expression "textile or other material" is employed, it is intended to cover fibers, yarns, fabrics, or other forms of cotton, jute, linen, hemp or rayon, including viscose, cuprammonium or other precipitated cellulose or derivatives of cellulose such as acetyl cellulose and films or tissues therefrom, as well as animal fibers including wool and natural silk. It is also intended to cover leather and wood or other material capable of being rendered water-repellent in accordance with the invention.

The expression "isocyanate," as used in the claims, is intended to include not only isocyanates but also azides which are capable of liberating nitrogen to produce isocyanates and when heated for example at about 100° C. will act upon textile or other material or wool to produce water-repellence in these materials.

While the invention has been described in detail according to the preferred manner of carrying out the process, it will be obvious to those skilled in the art after understanding the invention, that changes and modifications may be made therein without departing from the spirit or scope of the invention, and it is intended in the appended claims to cover all such changes and modifications.

What is claimed as new and desired to be secured by Letters Patent, is:

1. A process for ennobling textile or other material which comprises impregnating the material with an isocyanate containing a radical selected from the group consisting of: an aliphatic and an aliphatic-aromatic radical, each aliphatic radical containing a hetero radical and having an uninterrupted carbon chain of at least 10 carbon atoms, said hetero radical being selected from the group consisting of O, S, O.CO, C.OO, NHCO, CONH, and heating the impregnated material to produce water-repellence therein.

2. A process for ennobling textile or other material which comprises impregnating the material with an aliphatic-aromatic isocyanate, which contains a saturated aliphatic radical having at least 10 carbon atoms in an uninterrupted chain, the isocyanate being joined directly to the aromatic ring and the said chain being separated from the said ring by a radical containing oxygen and heating the impregnated material to produce water-repellence therein.

3. A process for ennobling textile or other material which comprises impregnating the

material with an aliphatic isocyanate in which the aliphatic portion includes a radical containing oxygen and said aliphatic portion contains an uninterrupted carbon chain of at least 10 carbon atoms and heating the impregnated material to produce water-repellence therein.

4. A process for ennobling textile or other material which comprises impregnating the material with an isocyanate having the general formula $R.S.CH_2.N=C=O$, in which R is an aliphatic radical having at least ten carbon atoms, and heating the impregnated material to produce water-repellence therein.

5. A process for ennobling textile or other material which comprises impregnating the material with an isocyanate having the general formula $R.O.CH_2.N=C=O$, in which R is an aliphatic radical having at least ten carbon atoms, and heating the impregnated material to produce water-repellence therein.

6. A textile material having a water-repellent property which is fast to cleansing, made in accordance with the process of claim 2.

7. A textile material having a water-repellent property which is fast to cleansing, made in accordance with the process of claim 1.

8. A process for ennobling textile or other material which comprises impregnating the material with an isocyanate having the general formula $R'.O.phenyl.N=C=O$, in which R' is an alkyl radical having at least ten carbon atoms, and heating the impregnated material to produce water-repellence therein.

9. A textile material having a water-repellent property which is fast to cleansing, made in accordance with the process of claim 1.

10. A textile material having a water-repellent property which is fast to cleansing, made in accordance with the process of claim 5.

11. A textile material having a water-repellent property which is fast to cleansing, made in accordance with the process of claim 8.

12. A process of treating textile material which comprises, impregnating the material with octadecyl-oxy-acetic acid isocyanate, and heating the impregnated material to increase its water-repellence.

13. A process of treating textile material which comprises, impregnating the material with octadecyl mercapto acetic acid isocyanate, and heating the impregnated material to increase its water-repellence.

14. A process of treating textile material which comprises, impregnating the material with octadecyl-oxy-phenyl isocyanate, and heating the impregnated material to increase its water-repellence.

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