

UNITED STATES PATENT OFFICE

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PROCESS OF TREATING CELLULOSE AND
DERIVATIVES THEREOF

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This invention relates to the art of retarding deterioration of organic materials and more particularly to the stabilizing of cellulose, cellulose manufactures, and chemical derivatives of cellulose.

It has been discovered that deterioration of the above materials can be effectively retarded by treating them with small amounts of certain stabilizing chemical agents, namely, esters and N-substituted esters of carbamic, thiocarbamic, thiolcarbamic, and dithiocarbamic acids.

The deterioration of cellulosic substances, such as those with which the present invention is concerned, seems to be induced or accelerated by light, particularly ultraviolet light. In other words the deterioration seems in many instances to be photochemical since its rapidity frequently varies directly with the intensity of the light and with the concentration of ultraviolet light. However, as is well known, cellulosic bodies also deteriorate, though more slowly, in ordinary sunlight (direct or diffused) and in the absence of light, under atmospheric conditions. In the absence of light, this deterioration is often very slow and imperceptible except over long periods of time but takes place nevertheless as evidenced by the discoloration and weakening of paper, books, cotton fabrics, newspaper files, etc., even when stored in dark places at comparatively low temperatures. Thus, while the rate of deterioration may vary with the particular conditions, the present agents will be found effective for retarding it under any given set of conditions. However, neither the nature of the deterioration of cellulosic substances (whether hydrolytic, oxidative, or otherwise), nor the manner in which the present agents function to prevent it, is definitely known, and it is not desired to be confined to any theory thereof.

The general object of this invention is thus to provide methods for retarding the deleterious effects of aging on paper, cellulosic fabrics, and various other cellulosic materials.

A particular object of this invention is to provide methods of decreasing the deterioration, due to or initiated by ultraviolet rays and other causes, of those cellulosic substances included in the group consisting of regenerated cellulose, cellulose ethers, and organic acid esters of cellulose.

These materials may be in the form of fibres,

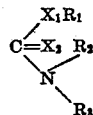
yarns, fabrics, and sheets of different sizes, shapes, and transparency. Examples of cellulose esters with which the present agents may be used effectively are cellulose acetate, cellulose butyrate, cellulose laurate, cellulose isobutyrate, cellulose propionate, cellulose crotonate, etc. Examples of cellulose ethers are methyl cellulose, ethyl cellulose, benzyl cellulose, dodecyl cellulose, crotyl cellulose, cinnamyl cellulose, glycol cellulose, and cellulose glycollic acid. The cellulose esters and ethers may be of the high- or low-substituted type, having, for example, from one substituent group for each eight glucose units up to three substituent groups for each glucose unit.

Another particular object of this invention is to provide methods of retarding the deteriorating effect of aging on various cellulose manufactures included in a group comprising paper, cotton filaments, and woven and knitted fabrics of cotton, linen, ramie, jute, etc.

Other objects and advantages of the invention will be pointed out in the following description or will be apparent from such description.

These objects are accomplished by treating paper, cotton goods, and the other aforementioned cellulosic materials with the mentioned chemical agents, which have the property of stabilizing the cellulosic materials against the injurious effect of aging, whether or not accompanied by exposure to concentrated ultraviolet rays.

The agents employed in this invention may be represented by the general formula



where X_1 and X_2 are oxygen or sulfur, R_1 is a monovalent hydrocarbon radical, and R_2 and R_3 are hydrogen or monovalent organic (especially hydrocarbon) radicals. R_1 , R_2 , and R_3 , for example, may be such general types of hydrocarbon radicals as alkyl, alkenyl, aryl, aralkyl, cycloalkyl, etc., or such particular hydrocarbon radicals as methyl, ethyl, propyl, i-butyl, amyl, decyl, dodecyl, octadecyl, phenyl, tolyl, xylyl, naphthyl, benzyl, cinnamyl, 9,10-octadecenyl, cyclohexyl, naphthenyl, etc.

Instead of esters of carbamic, thiocarbamic, thiolcarbamic and dithiocarbamic acids, salts and N-substituted salts of these acids may be used, e. g., the ammonium, sodium, potassium, calcium, barium, etc., salts. R₁ of the general formula then becomes a metal. Salts are less suitable in this invention, however, because of their instability.

The most effective agents of this invention are the esters and N-substituted esters of carbamic and thiocarbamic acids as exemplified by the following. Most of these compounds are also called urethanes and thiourethanes:

15 *Esters and N-substituted esters of carbamic acid (NH₂COOH)*

Methyl carbamate	N-phenyl ethyl carbamate
Ethyl carbamate	N-tolyl ethyl carbamate
I-amyl carbamate	N-α-naphthyl ethyl carbamate
Dodecyl carbamate	N-phenyl methoxyethyl carbamate
Crotyl carbamate	N-phenyl methyl carbamate
20 9, 10-octadecyl carbamate	N-phenyl crotyl carbamate
Phenyl carbamate	N-phenyl dodecyl carbamate
Tolyl carbamates	N-α-naphthyl dodecyl carbamate
α- and β-naphthyl carbamates	N-phenyl naphthenyl carbamates
Cyclohexyl carbamate	N-acetyl ethyl carbamate
Naphthenyl carbamates	N-methyl ethyl carbamate
Ethoxyethyl carbamate	N-hydroxymethyl ethyl carbamate
25	CH ₂ (NHCOOC ₂ H ₅) ₂
	C ₂ H ₅ OCCOCH(NHCOOC ₂ H ₅) ₂
	N-methyl-N-phenyl ethyl carbamate

Esters and N-substituted esters of thiocarbamic acid (NH₂CSOH)

30 Ethyl thiocarbamate	N-ethyl ethyl thiocarbamate
I-butyl thiocarbamate	N-allyl ethyl thiocarbamate
Phenyl thiocarbamate	N-acetyl methyl thiocarbamate
Tetracetyl glucose thiocarbamate	N-phenyl ethyl thiocarbamate
	N-phenyl cellulose thiocarbamate
	N-α-naphthyl dodecyl thiocarbamate
35	N-phenyl ethoxyethyl thiocarbamate
	N-phenyl naphthenyl thiocarbamate

Other compounds which are useful and included in this invention are the following:

40 *Esters and N-substituted esters of thiolcarbamic acid (NH₂COSH)*

Methyl thiolcarbamate	N-ethyl ethyl thiolcarbamate
Ethyl thiolcarbamate	N-phenyl ethyl thiolcarbamate
Phenyl thiolcarbamate	N-phenyl phenyl thiolcarbamate
45 Dodecyl thiolcarbamate	N-β-naphthyl dodecyl thiolcarbamate
Methoxyethyl thiolcarbamate	N-phenyl naphthenyl thiolcarbamate
Allyl thiolcarbamate	N-phenyl oleyl thiolcarbamate

Esters and N-substituted esters of dithiocarbamic acid (NH₂CSSH)

50 Methyl dithiocarbamate	N-dimethyl methyl dithiocarbamate
Isopropyl dithiocarbamate	N-methyl methyl dithiocarbamate
Allyl dithiocarbamate	N-acetyl ethyl dithiocarbamate
Phenyl dithiocarbamate	N-phenyl ethyl dithiocarbamate
Dodecyl dithiocarbamate	N-α-naphthyl dodecyl dithiocarbamate
55 Naphthenyl dithiocarbamate	N-phenyl naphthenyl dithiocarbamate

The technique of this invention is relatively simple since, in the preferred embodiment of the invention, the substance to be treated is simply wetted thoroughly with a solution of the agent in an appropriate solvent, the latter then being allowed to evaporate under conditions where the agent is retained. The solvent should be readily volatile and should not decompose the agent nor attack the base material.

The following examples, which are not intended to limit the invention, are illustrative of certain of its more specific embodiments:

Example 1

This example illustrates the treatment of viscose rayon with an ester of thiocarbamic acid. Strips of woven viscose rayon fabric one-half inch wide were immersed for one hour in a 5% alcoholic solution of N-phenyl ethyl thiocarbamate (phenyl thiourethane). The excess liquid was squeezed out and the treated strips kept side by side with untreated control strips of exactly the same size and shape for 24 hours at 25° C. and 50% relative humidity. Two of the controls and two of the treated strips were then tested for elongation and breaking strength on a Scott testing machine. The values obtained—approximately the same for both—were taken as 100%. All the remaining strips, together with the remaining controls, were then exposed to ultraviolet rays under a Cooper-Hewitt quartz mercury-vapor lamp in order to accelerate the deterioration of the fabric. All strips were placed at a distance of approximately 24 inches from the lamp where the temperature was approximately 30° C. Exposure was continued for 72 hours, two control strips and two treated strips being removed at the end of 36 and 72 hours, then stored at 25° C. and 50% relative humidity for 24 hours, and finally tested for elongation and breaking strength in the same manner as before exposure. At the end of 36 hours the untreated control had retained 51.6% and the treated fabric 58.5% of the original strength. At the end of 72 hours these values were 28.3% and 48.8% respectively. By this time the untreated control was quite weak, readily torn, and practically useless, but the treated fabric, while definitely weakened, was still usable.

Ethyl thiocarbamate, N-acetyl methyl thiocarbamate N-ethyl ethyl thiocarbamate, etc., may be used in the above example instead of phenylthiourethane and good results obtained in retarding the weakening, discoloration, and general deterioration of the fabric. These agents are also effective with cellulose acetate, cotton, and paper. While they may be used in the raw material, they are more conveniently and effectively applied to some manufacture thereof, as acetate rayon (fibers or fabrics), thin transparent sheets of regenerated cellulose such as those ordinarily used for wrapping purposes, cotton or rayon textiles, rope, threads, etc.

As previously pointed out, these agents are also effective when the treated base material is subjected to light of different types and intensities, and/or when aged in the absence of light, the ultraviolet light merely being used for quick results.

Example 2

This example illustrates the use of an ester of carbamic acid.

Woven viscose rayon fabric is treated with a 5% aqueous solution of ethyl carbamate (urethane) in the same manner as in Example 1. After 36 hours' exposure to ultraviolet light under the same conditions as in Example 1, the fabric retained 66.6% of its original strength while the untreated control retained only 51.6%. The corresponding figures at the end of 72 hours were 47.6% and 28.3%. Urethane is a particularly desirable agent because it may be used in aqueous solutions without sacrifice of effectiveness.

In the above example, the ethyl carbamate may be replaced by methyl carbamate, phenyl carbamate, ethoxyethyl carbamate, etc. and good results obtained. However, appropriate low-boiling solvents which do not attack the base material should be used in applying the agent. Paper, paper pulp, cotton, and cellulose derivatives may also be rendered more resistant to deterioration by treatment with these agents after the general manner of Example 2.

Example 3

This example illustrates the use of an N-substituted ester of carbamic acid.

Woven viscose rayon fabric was soaked in a % alcoholic solution of N-phenyl ethyl carbamate (phenylurethane) and the treated fabric exposed to ultraviolet light together with untreated controls. After 36 hours the treated fabric possessed 63.0% of its original strength, and the control only 51.6%. After 72 hours, these figures were 54.8% and 28.3% respectively.

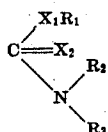
It will be seen from the above examples that impregnated samples of fabric show marked improvement over the untreated samples in their resistance to deterioration as induced or accelerated by ultraviolet light, particularly after the longer period of test.

All the systems in which these agents are used, whether cellulose, a cellulosic manufacture, or a cellulose ether or ester or a manufacture thereof, possess the common feature of a more or less large number of substituted or unsubstituted glucose units or building stones joined together. It is believed that upon aging this structure is affected in some way, and that the agents mentioned herein critically prevent such degradation or deterioration.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

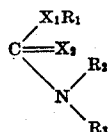
We claim:

1. The process of rendering cellulosic fibres and fibrous manufactures thereof more resistant to the deleterious effects of aging which consists in impregnating them with a small percentage of an agent having the general formula



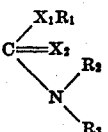
in which X_1 and X_2 are oxygen or sulfur, R_1 is a monovalent hydrocarbon radical, and R_2 and R_3 are hydrogen or monovalent organic radicals.

2. The process of rendering cellulosic fibres and fibrous manufactures thereof more resistant to the deleterious effects of aging which consists in impregnating them with 0.25% to 5.0% of an agent of the formula



wherein X_1 and X_2 are oxygen or sulfur, R_1 is a monovalent hydrocarbon radical, and R_2 and R_3 are hydrogen or monovalent organic radicals.

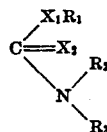
3. The process of rendering paper more resistant to the deleterious effects of aging, by impregnating it with 0.25% to 5.0% of an agent of the formula



wherein X_1 and X_2 are oxygen or sulfur, R_1 is a

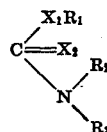
monovalent hydrocarbon radical, and R_2 and R_3 are hydrogen or monovalent organic radicals.

4. The process of rendering cotton and fabricated cotton more resistant to the deleterious effects of aging by impregnating them with 0.25% to 5.0% of an agent of the formula



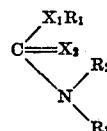
wherein X_1 and X_2 are oxygen or sulfur, R_1 is a monovalent hydrocarbon radical, and R_2 and R_3 are hydrogen or monovalent organic radicals.

5. The process of rendering viscose filaments and fabrics more resistant to the deleterious effects of aging by impregnating them with 0.25% to 5.0% of an agent of the formula



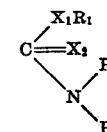
wherein X_1 and X_2 are oxygen or sulfur, R_1 is a monovalent hydrocarbon radical, and R_2 and R_3 are hydrogen or monovalent organic radicals.

6. Cellulosic fibres and fibrous manufactures thereof impregnated with a compound represented by the general formula



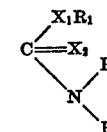
in which X_1 and X_2 are oxygen or sulfur, R_1 is a monovalent hydrocarbon radical, and R_2 and R_3 are hydrogen or a monovalent organic radical.

7. Cellulosic fibres and fibrous manufactures thereof impregnated with 0.25% to 5.0% of a compound of the general formula



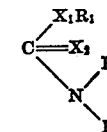
wherein X_1 and X_2 are oxygen or sulfur, R_1 is a monovalent hydrocarbon radical and R_2 and R_3 are hydrogen or monovalent organic radicals.

8. Cellulosic threads, and fabrics impregnated with 0.25% to 5.0% of a compound of the formula



wherein X_1 and X_2 are oxygen or sulfur, R_1 is a monovalent hydrocarbon radical and R_2 and R_3 are hydrogen or monovalent organic radicals.

9. Paper impregnated with 0.25% to 5.0% of a compound of the formula

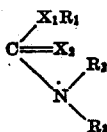


wherein X_1 and X_2 are oxygen or sulfur, R_1 is a

monovalent hydrocarbon radical and R_2 and R_3 are hydrogen or monovalent organic radicals.

10. Cotton and fabricated cotton impregnated with 0.25% to 5.0% of a compound of the formula

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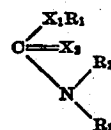


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wherein X_1 and X_2 are oxygen or sulfur, R_1 is a monovalent hydrocarbon radical and R_2 and R_3 are hydrogen or monovalent organic radicals.

11. Regenerated cellulose filaments and fabrics

impregnated with 0.25% to 5.0% of a compound of the formula



wherein X_1 and X_2 are oxygen or sulfur, R_1 is a monovalent hydrocarbon radical and R_2 and R_3 are hydrogen or monovalent organic radicals.

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