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TREATMENT OF CELLULOSIC BODIES

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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, polycyclic phenols having at least two non-condensed carbocyclic nuclei. Examples of such phenols are p-hydroxy-diphenyl and p-cyclohexyl phenol.

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.

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 therefore 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 these cellulosic substances included in the group consisting of regenerated cellulose, cellulose ethers and organic acid esters of cellulose. The materials may be in the form of fibers, yarns, fabrics, and thin 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, etc. Examples of cellulose ethers are methyl cellulose, ethyl cellulose, benzyl cellulose, dodecyl cellulose, propyl cellulose, cinnamyl cellulose, glycol cellulose, and

cellulose glycollic acid. The cellulose esters and ethers may be of the high or low substituted types, having for example from one substituent group for eight glucose units up to three substituent groups for each glucose unit.

Another 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 such as cotton, linen, ramie, jute, etc. These objects are accomplished by treating paper, cotton goods and the other aforementioned cellulosic materials with a polycyclic phenol having at least two non-condensed carbocyclic nuclei, which compounds have the property of stabilizing the cellulosic materials against the injurious effect of aging or exposure to concentrated ultraviolet rays.

Other objects of this invention and methods for their attainment will be apparent as the description proceeds.

These objects are accomplished by treating paper, cotton goods, and other aforementioned cellulosic materials with a polycyclic phenol having at least two non-condensed carbocyclic nuclei, as illustrated in examples which follow.

Specific examples of some of the suitable stabilizing agents that fall within the scope of this invention are the following phenols which, as will be seen, are of two types, those having non-condensed aromatic nuclei and those having an alicyclic ring.

Non-condensed polycyclic phenols with only aromatic nuclei

o-Hydroxydiphenyl
m-Hydroxydiphenyl
p-Hydroxydiphenyl
p,p'-Dihydroxydiphenyl
o,o'-Dihydroxydiphenyl
m,m'-Dihydroxydiphenyl
Di(4-hydroxyphenyl)-phenylmethane
Di(4-hydroxyphenyl)dimethylmethane
Di(4-hydroxynaphthyl)dimethylmethane
Di(3-methyl-4-hydroxyphenyl)dimethylmethane
ane
Di(4-hydroxyphenyl)methylethylmethane
Di(4-hydroxy-3,5-dimethylphenyl)dimethylmethane
Di(4-hydroxy-3,5-dimethylphenyl)dipropylmethane

The last six phenols of the above table are of particular interest in this invention because in the pure state they have very little if any char-

acteristic odor or tendency to discolor. These phenols may be described generally as polycyclic phenols having at least two non-condensed carbocyclic nuclei and having the para position to their phenolic hydroxyl groups occupied by tertiary aliphatic carbon atoms.

Non-condensed polycyclic phenols having an alicyclic ring

- 10 p-(4-methylcyclohexyl) phenol
- o-Cyclohexyl phenol
- p-Cyclohexyl phenol
- 1,1-di(4-hydroxyphenyl) cyclohexane
- m-Cyclohexyl phenol
- 15 Cycloamyl resorcinol
- 1,1-di(4-hydroxy-3-methylphenyl) cyclohexane
- 1,1-di(4-hydroxyphenyl)-4-methylcyclohexane

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 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 stabilization of cellulose acetate rayon. Strips of the woven fabric $\frac{1}{2}$ " wide were immersed for one hour in a 5% alcoholic solution of p-hydroxydiphenyl. 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 twenty-four 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 of the remaining strips, together with the remaining controls, were then exposed to ultra-violet 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 57 hours. Two control strips and two treated strips were removed at the end of 25 hours and 57 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 25 hours the untreated control retained 7.5% and the treated fabric 60.3% of the original strength. At the end of 57 hours these values were 1.5% and 44.1%, respectively. By this time the untreated control was very weak, readily torn, and wholly useless, but the treated fabric, while definitely weakened, was still usable.

p,p'-Dihydroxydiphenyl, the monomethyl ether of p,p'-dihydroxydiphenyl, di(4-hydroxyphenyl) sulfone, di(4-hydroxyphenyl) ether, di(4-hydroxyphenyl) dimethylmethane, di(4-hydroxyphenyl) dimethylmethane, di(4-hydroxyphenyl) phenyl methane, etc., may be used in the above example instead of p-hydroxydiphenyl and good results obtained in retarding the weakening, discoloration and general disintegration of the fabric. These agents are also effective with regenerated cellulose, cotton, and paper. While they may be used in the raw material, they are more conveniently and effectively applied to some

manufacture thereof as viscose rayon (fibers or fabrics), thin transparent sheets of regenerated cellulose such as those ordinarily used for wrapping purposes, and cotton or rayon textiles, rope, threads, etc.

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

Example 2

Woven viscose rayon fabric was treated with a 5% alcoholic solution of p-hydroxydiphenyl in the same manner as in Example 1. After 36 hours' exposure to ultraviolet light under the same conditions as in Example 1, the treated fabric retained 72.7% of its original strength while the untreated control retained only 51.6%. The corresponding figures at the end of 72 hours were 61.8% and 28.3%.

In the above example the p-hydroxydiphenyl may be replaced by di(4-hydroxyphenyl) ether, m-hydroxydiphenyl, di(4-hydroxyphenyl) dimethylmethane, di(4-hydroxyphenyl) methyl phenylmethane, di(4-hydroxy-3-methylphenyl) dimethylmethane, etc., and good results obtained. That latter three agents are particularly desirable because the treated and aged fabric is quite free from the odor of phenol and also retains its original luster and hue. Phenols not having the characteristic p-tertiary carbon atoms frequently tend to discolor under even normal conditions of exposure and more so in the presence of concentrated ultraviolet light. In substituting these agents for the p-hydroxydiphenyl appropriate low boiling solvents which do not attack the base material should be used in applying these agents. Paper, paper pulp, cotton and cellulose derivatives may also be rendered more resistant to deterioration by treatment with these alternative agents after the general manner of Example 2.

Example 3

Woven viscose rayon fabric was soaked in a 5% alcoholic solution of o-hydroxydiphenyl and the treated fabric exposed to ultraviolet light together with untreated controls. After 72 hours the treated fabric possessed 36.7% of its original strength and the control only 28.3%.

Example 4

Woven viscose rayon fabric was impregnated with a solution of p,p'-dihydroxydiphenyl in a mixture of alcohol and toluene of such concentration (5-7%) to give about 4% by weight of the stabilizing agent upon the fabric. The solvent was then allowed to evaporate and the dry treated fabric exposed to ultraviolet light together with untreated controls. After 36 hours the former possessed 57.7% of its original strength and the control only 51.6%. At the end of 72 hours, these figures were 42.3 and 28.3, respectively.

Example 5

Woven viscose rayon fabric was impregnated with o-cyclohexyl phenol in an amount to give about 4% of the agent based on the weight of the cloth. After 36 hours' exposure to ultraviolet light the treated fabric showed upon test to have 78.5% of its original strength and the untreated control only possessed 51.6%. This example was repeated with p-cyclohexyl phenol and

When better results obtained, the treated fabric, after 36 hours, 86.9% of the original strength. Of all the agents tested, the *o*- and -cyclohexyl phenols gave the best results. This will be evident from a comparison with the examples given above.

Example 6

Strips of paper were immersed for one hour in 10% alcoholic solution of *p*-hydroxydiphenyl. The wet strips of paper were then removed from the impregnating bath and allowed to dry together with untreated controls for 24 hours at 5° C. and 50% relative humidity. The treated and untreated paper strips were then exposed to ultraviolet light in the manner of Example 1 for 6 days. At the end of this time, both were tested for tensile strength. The control strip broke upon application of 2.6 pounds while the treated paper required a tension of 5.0 pounds before breaking. Both strips of paper were cut from the same sheet of paper and were 1/2" wide.

It has been found that an impregnation with about 4% of the stabilizing agent is satisfactory in most instances. The amount required for best results will, however, vary somewhat depending on the particular stabilizer used and the material treated. As a rule, the quantity of the stabilizer should lie within the range 0.25% to 5.0% based on the weight of material treated. Quantities outside this range are, however, still useful and are by no means precluded.

It will be seen from the preceding example that impregnated samples show marked improvement over the untreated samples in their resistance to deterioration as induced or caused by ultraviolet light. It is again desired to point out, however, that the ultraviolet light is only a method for obtaining rapid results. The rate of deterioration is also decreased markedly under other conditions as, for example, in the absence of light and in ordinary sunlight. In other words, the present agents are effective in regarding the deterioration of cellulosic substances when subjected to light of different types and intensities.

It will be noted that all the systems in which the present agents are used are closely related. Regenerated cellulose, cellulose ethers or esters, and manufactures of both, all have a greater or less number of unsubstituted or partially substituted (i. e., etherified or esterified) glucose units joined together in a complex fashion. It seems

reasonable to suppose that the tendency of cellulosic materials to deterioration on aging may be due to disruption of the bonds between glucose units and/or the rearrangement of these units or building stones to a more degraded structure. Thus the systems in which these agents are used not only have a common and distinctive chemical relation irrespective of the processes of the invention, but all these systems are probably affected similarly by all of the agents of this invention.

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 there are no specific limiting embodiments except as defined in the appended claims.

We claim:

1. Paper impregnated with 0.25% to 5.0% of a polycyclic phenol having at least two non-condensed carbocyclic nuclei.

2. The process of rendering paper more resistant to the deleterious effect of aging which consists in impregnating its fibrous mass with 0.25% to 5.0% of a polycyclic phenol having at least two non-condensed carbocyclic nuclei.

3. The process of rendering cotton and fabricated cotton more resistant to the deleterious effect of aging which consists in depositing on the fibrous surfaces 0.25% to 5.0% of a polycyclic phenol having at least two non-condensed carbocyclic nuclei.

4. The process of rendering regenerated cellulose fibres and fibrous manufactures thereof more resistant to the deleterious effects of aging which consists in depositing on the fibrous surfaces 0.25% to 5.0% of a polycyclic phenol having at least two non-condensed carbocyclic nuclei.

5. Fibres and fibrous manufactures thereof of the group consisting of cellulose and regenerated cellulose having deposited on the fibrous surfaces 0.25% to 5.0% of a polycyclic phenol having at least two non-condensed carbocyclic nuclei.

6. Cotton and fabricated cotton having deposited on the fibrous surfaces 0.25% to 5.0% of a polycyclic phenol having at least two non-condensed carbocyclic nuclei.

7. Fibres of regenerated cellulose and manufactures thereof having deposited on the fibrous surfaces 0.25% to 5.0% of a polycyclic phenol having at least two non-condensed carbocyclic nuclei.

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