

1

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PROCESS FOR PROTECTING WOOL FROM YELLOWING BY APPLYING DIBUTYL BUTANEPHOSPHONATE

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A non-exclusive, irrevocable, royalty-free license in the invention herein described, for all governmental purposes, throughout the world, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to a process for protecting wool from yellowing with age.

It is well known in the art that when wool is originally prepared by scouring and other necessary cleaning methods from raw fleece, it is essentially white in color. However, upon aging the wool does not retain its whiteness but gradually becomes more and more yellow. This color change is of course undesirable and restricts the use of wool mainly to applications wherein it is used in a dyed condition. It is believed that the yellowing of wool and other protein fibers is caused at least in part by the action of light on the fibers—the light in some way causing or accelerating chemical changes which give rise to colored compounds.

It has now been found that if wool is treated with an ester of a phosphorus-containing acid, the tendency of the fiber to turn yellow is greatly diminished or even eliminated completely. As disclosed hereinafter in more detail, the fiber may be subjected to acetylating reagents prior to the treatment with the ester, thus to enhance the protective effect. Another alternative is to remove the major part of the ester after subjecting the ester-treated fiber to a treatment to cause chemical combination of a minor part of the ester with the fiber.

The esters used may be derived from various phosphorus-containing acids, for example, orthophosphoric acid, pyrophosphoric acid, triphosphoric acid, tetraphosphoric acid and organic phosphonic and phosphinic acids such as benzene phosphonic acid, butane phosphonic acid, ethane phosphonic acid, dibenzene phosphinic acid, di-butane phosphinic acid, di-ethane phosphinic acid, and so forth. The alcohol (or phenol) moiety of the compounds may include radicals of the aliphatic, aromatic, alkaryl, aralkyl, or cycloaliphatic types as for example ethyl, propyl, butyl, amyl, hexyl, phenyl, benzyl, methylphenyl, cyclohexyl, and so forth. Included are esters wherein different radicals are attached to the acid moiety and also included are esters wherein the phosphorus-containing acid is only partly esterified. Some particular esters are, for example, triethyl phosphate, tripropyl phosphate, tributyl phosphate, triamyl phosphate, trihexyl phosphate, tricyclohexyl phosphate, triphenyl phosphate, tribenzyl phosphate, tritolyl phosphate, butyl diethyl phosphate, amyl diethyl phosphate, hexyl diethyl phosphate, butyl diphenyl phosphate, amyl diphenyl phosphate, hexyl diphenyl phosphate, dibutyl ethyl phosphate, diamyl ethyl phosphate, dihexyl ethyl phosphate, dibutyl phenyl phosphate, diamyl phenyl phosphate, dihexyl phenyl phosphate, dibutyl hydrogen phosphate, diamyl hydrogen phosphate, dihexyl hydrogen phosphate, tetraethyl pyrophosphate, tetrapropyl pyrophosphate, tetrabutyl pyrophosphate, tetraamyl pyrophos-

2

phate, tetrahexyl pyrophosphate, tetracyclohexyl pyrophosphate, tetraphenyl pyrophosphate, tetrabenzyl pyrophosphate, tetratolyl pyrophosphate, butyl triethyl pyrophosphate, amyl triethyl pyrophosphate, hexyl triethyl pyrophosphate, butyl triphenyl pyrophosphate, amyl triphenyl pyrophosphate, hexyl triphenyl pyrophosphate, dibutyl diethyl pyrophosphate, diamyl diethyl pyrophosphate, dihexyl diethyl pyrophosphate, dibutyl diphenyl pyrophosphate, diamyl diphenyl pyrophosphate, dihexyl diphenyl pyrophosphate, tributyl ethyl pyrophosphate, triamyl ethyl pyrophosphate, trihexyl ethyl pyrophosphate, tributyl phenyl pyrophosphate, triamyl phenyl pyrophosphate, trihexyl phenyl pyrophosphate, diethyl benzene-phosphonate, dipropyl benzene-phosphonate, dibutyl benzene-phosphonate, diamyl benzene-phosphonate, dihexyl benzene-phosphonate, dicyclohexyl benzene-phosphonate, diphenyl benzene-phosphonate, dibenzyl benzene-phosphonate, ditolyl benzene-phosphonate, diethyl butanephosphonate, dipropyl butanephosphonate, dibutyl butanephosphonate, diamyl butanephosphonate, dihexyl butanephosphonate, dicyclohexyl butanephosphonate, diphenyl butanephosphonate, dibenzyl butanephosphonate, ditolyl butanephosphonate, and so forth.

It is to be noted that not all of the esters of phosphorus-containing acids have equal efficacy for reducing the yellowing tendency of protein fibers. It has been observed, for example, that those esters containing butyl groups exhibit greater effectiveness than those compounds containing ethyl or cresyl radicals. Compounds which are preferred as exhibiting greatest effectiveness are tributyl phosphate and dibutyl butanephosphonate, the latter being preferred.

In applying the ester to the fiber, any conventional technique can be used to effectuate a coating or impregnation of the fiber with the ester. The ester may be applied as such or in the form of a solution or dispersion thereof. Thus dipping, spraying, or brushing techniques can be used. The ester may be dissolved in an organic solvent such as ethanol, carbon tetrachloride, chloroform, etc. and this solution applied to the fiber. Generally, more effective results are obtained if the dibutyl butanephosphonate is dissolved in water and this aqueous solution applied to the fiber. Normally a solution containing about 1 to 5% of the ester is used, the wool is soaked therein for about one day, removed, and pressed dry.

One embodiment of this invention involves a procedure wherein the ester-impregnated fiber is subjected to a fixation treatment and then the excess of the ester is removed. This technique is advantageous as it improves the quality of the fiber. Thus when the fiber is impregnated with some esters the fiber tends to develop a somewhat greasy or oily feel which would make the fiber less desirable for some applications. By subjecting the impregnated fiber to the fixative treatment and then removing excess ester, the greasy or oily feel is completely removed and the resulting fiber can be used in any textile application. The fixative treatment involves subjecting the impregnated fiber to light, preferably in the ultraviolet region. This irradiation causes a chemical reaction between the fiber molecules and the ester whereby some of the ester becomes chemically bound to the fiber. This chemical modification of the fiber causes it to resist yellowing by the action of light. After the irradiation is completed, the excess of ester on the fiber is removed by washing with an organic solvent such as ethanol, acetone, chloroform, carbon tetrachloride, ethylene dichloride, etc. The removal of the unreacted ester does not decrease the yellowing resistance of the fiber because the chemically bound ester remains in the fiber.

It has also been found that improved resistance to yellowing is obtained if the fiber is subjected to acetylation prior to impregnating it with the ester. The reason for

3

the desirable effect of acetylation is not known but experimental data indicate that acetylation has a synergistic effect on the prevention of yellowing by treatment with the ester. Acetylation of the fiber can be performed by methods well known in the art, for example by subjecting the wool to reaction at 0 to 100° C. with an acetylating agent such as acetic anhydride or ketene. Usually the wool in its normal, undried condition, containing about 8–12% H₂O, is subjected to the acetylating reagent. The latter for better contact, may be dissolved in an inert solvent such as formamide, glacial acetic acid, carbon tetrachloride, etc.

It is evident that the process of this invention can be applied to the protein fiber in any physical form. Thus the process may be applied to fibers as such or to thread, yarn, woven or knitted fabrics, felts, and so forth.

The following examples demonstrate the invention in greater detail.

Example I

A sample of wool was formed into pads having a weight of 1.5 g. One of the wool pads was placed in 50 cc. of acetic anhydride and allowed to stand therein at 90° for 1 hour to acetylate the wool. The acetylated wool was then washed with water and pressed dry. The acetylated wool was then soaked 1 day in a 1% aqueous solution of dibutyl butanephosphonate then removed from the solution and pressed dry. This product was labeled I-A.

Another wool pad was given the treatment with the dibutyl butanephosphonate solution as above without the prior acetylation. This product was labeled I-B.

The treated samples and a sample of the untreated wool (control), labeled I-C, were then subjected to a mercury vapor lamp as a source of ultraviolet rays thus to measure their resistance to yellowing. After exposure to the ultraviolet light, the samples were then subjected to reflectance measurements with a photometer to measure the percentage of light reflected from the samples. The reflectance values are an index of the whiteness of the wool; the higher the proportion of light reflected, the whiter the wool. The results obtained are tabulated below:

Sample.....	I-A	I-B	I-C
Treatment.....	Acetylation plus dibutyl butanephosphonate	Dibutyl butanephosphonate	None (control)
Reflectance prior to irradiation, percent.....	40.5	40	41.5
Reflectance after irradiation for 24 hrs. percent.....	39.5	30	26
Reflectance after irradiation for 48 hrs. percent.....	39.5	29	22.5
Reflectance after irradiation for 4 days, percent.....	38.5	28.5	19
Reflectance after irradiation for 7 days, percent.....	37	28	17.5

Example II

Pieces of wool flannel cloth were acetylated by soaking

4

in acetic anhydride for 1 hr. at 100° C. The acetylated cloth was then washed and pressed dry (sample A).

One piece of the acetylated cloth was soaked 13 hrs. in a 1% aqueous suspension of tributyl phosphate then pressed dry (sample B).

One piece of the original flannel cloth (not acetylated) was soaked 13 hrs. in a 1% aqueous suspension of tributyl phosphate then pressed dry (sample C).

The above samples plus a piece of the original cloth as a control (sample D) were then subjected to ultraviolet irradiation. The irradiated samples were then subjected to reflectance measurements to determine their relative whiteness as set forth in Example I. The results obtained are tabulated below:

Sample.....	B	C	A	D
Treatment.....	Acetylation plus tributyl phosphate	Tributyl phosphate	Acetylation	None (control)
Reflectance prior to irradiation, percent.....	53	54.5	53	54.5
Reflectance after irradiation for 7 days, percent.....	42	33	28.5	22

Example III

A sample of wool was soaked in a 1% aqueous suspension of tributyl phosphate for 1 day. The wool was then pressed dry and subjected to ultraviolet irradiation for 6 days. The irradiated sample of wool was then washed with ethanol to remove unreacted tributyl phosphate. The wool was then exposed to ultraviolet irradiation for 48 hours. Reflectance measurements were then made on this sample and on a sample of untreated wool which had been irradiated for the same time. It was found that the treated sample had a reflectance of 26% whereas the untreated control had a reflectance of less than 20%.

Having thus described the invention, what is claimed is:

A process for protecting wool from yellowing which comprises soaking wool in an aqueous solution containing about 1 to 5% of dibutyl butanephosphonate for about one day to impregnate the wool with sufficient dibutyl butanephosphonate to make the wool resistant to yellowing, removing the wool from the solution and pressing it dry.

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