PROCESS FOR PREVENTING YELLOWING OF WOOL

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

This invention relates to processes for protecting wool from the deleterious effects of light. In particular the invention concerns methods for treating wool fibers whereby to produce modified wool fibers having enhanced resistance to the effect of light and which modified wool fibers have a reduced tendency to turn yellow with age as compared with the untreated wool fiber. The invention encompasses in its scope not only the procedures for so treating the wool but also the provision of such modified wool fibers as useful and advantageous articles of commerce. Further objects and advantages of the invention will be obvious from the description herein.

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 is caused at least in part by the action of light, particularly ultra violet rays, on the fibers—the light in some way causing or accelerating chemical changes which give rise to colored compounds. Although the problem of yellowing has been investigated for many years, the fact of the matter is that no successful solution to the problem has been found heretofore.

It has been suggested that certain benzophenone derivatives, particularly those containing hydroxy and methoxy groups, for example, 2-hydroxy-4-methoxy-benzophenone, 2-hydroxy-4,4'-dimethoxy-benzophenone, 2,2'-dihydroxy-4,4'-dimethoxy-benzophenone, can be used to protect various materials especially synthetic resins from the deleterious effects of light. These derivatives are generally applied by mixing them in the monomer prior to polymerization whereby after carrying out the usual polymerization treatment there is produced a resin which exhibits considerable resistance to yellowing when exposed to ultra violet light. However when these derivatives are applied by conventional coating or impregnating techniques to wool, little or no beneficial result is obtained. The reason for the ineffectiveness of the derivatives is not understood but it has been found by laboratory experimentation that such is the case.

It has now been found that if the benzophenone derivatives are sulphonated the resulting benzophenone compounds are effective in protecting wool from the deleterious effects of ultra violet light. It is believed that the sulphonates are effective because they actually combine with the protein molecule of the wool by the formation of salts between the amino radicals in the protein molecule of the wool and the sulphonic acid group in the benzophenone compound. As a result it is believed that the treated wool fiber is actually chemically modified and the benzophenone compound does not merely exist as a physical coating on the fiber as is necessarily the case where the unsulphonated benzophenone derivatives are employed. Regardless of any theoretical considerations, it has been found by actual experimentation that the sulphonated benzophenone derivatives will protect the wool fiber from light whereas the unsulphonated benzophenone derivatives will not.

The protective compounds used in accordance with this invention are derivatives of benzophenone containing hydroxy, alkoxy, and sulphonate groups and are free from chromophore groups other than the carbonyl radical between the two benzene radicals. These compounds may be represented by the following formula:

![Chemical structure](attachment:image)

wherein R is an alkyl radical, such as methyl, ethyl, propyl, isopropyl, and butyl, and the n's are integers from 1 to 2. Specific compounds which may be used in accordance with this invention are given below by way of illustration and not limitation:

2-hydroxy-4-methoxy-benzophenone-5-sodium sulphonate.
2-hydroxy-4-methoxy-benzophenone-3-sodium sulphonate.
2-hydroxy-4-methoxy-benzophenone-5,3'-di(sodium sulphonate).
2-hydroxy-4-ethoxy-benzophenone-5-sodium sulphonate.
2-hydroxy-4-ethoxy-benzophenone-3-sodium sulphonate.
2-hydroxy-4-ethoxy-benzophenone-5,3'-di(sodium sulphonate).
2-hydroxy-4,4'-dimethoxy-benzophenone-5-sodium sulphonate.
2-hydroxy-4,4'-dimethoxy-benzophenone-3-sodium sulphonate.
2-hydroxy-4,4'-diethoxy-benzophenone-5,3'-di(sodium sulphonate).
2-hydroxy-4,4'-diethoxy-benzophenone-3-sodium sulphonate.
2-hydroxy-4,4'-diethoxy-benzophenone-5,3'-di(sodium sulphonate).
2-hydroxy-4-methoxy-4'-ethoxy-benzophenone-5-sodium sulphonate.
2-hydroxy-4-methoxy-4'-ethoxy-benzophenone-3-sodium sulphonate.
2-hydroxy-4-methoxy-4'-ethoxy-benzophenone-5,3'-di(sodium sulphonate).
2-hydroxy-4-methoxy-4'-ethoxy-benzophenone-3-sodium sulphonate.
2,2'-dihydroxy-4-methoxy-benzophenone-5-sodium sulphonate.
2,2'-dihydroxy-4-methoxy-benzophenone-3-sodium sulphonate.
2,2'-dihydroxy-4-methoxy-benzophenone-5,3'-di(sodium sulphonate).
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2,2'-dihydroxy-4-ethoxy-benzophenone-5-sodium sulphonate.
2,2'-dihydroxy-4-ethoxy-benzophenone-3'-sodium sulphonate.
2,2'-dihydroxy-4 - 4' - ethoxy-benzophenone-5,3'-di(sodium sulphonate).
2,2'-dihydroxy-4,4' - dimethoxy-benzophenone-5-sodium sulphonate.
2,2'-dihydroxy-4,4'-dimethoxy-benzophenone-5,5'-di(sodium sulphonate).
2,2'-dihydroxy-4,4' - diethoxy-benzophenone-5-sodium sulphonate.
2,2'-dihydroxy-4,4' - diethoxy-benzophenone-5,5'-di(sodium sulphonate).
2,2'-dihydroxy-4'-methoxy-4'-ethoxy-benzophenone-5-sodium sulphonate.
2,2'-dihydroxy-4 - methoxy-4'-ethoxy-benzophenone-5'-sodium sulphonate.
2,2'-dihydroxy-4'-methoxy-4'-ethoxy-benzophenone-5,5'-di(sodium sulphonate).

The protective benzophenone compounds are applied to the wool fiber by treating the fiber with an acidified, aqueous solution of the agent. Thus the protective benzophenone compound is dissolved in water and the solution is acidified by the addition of about 0.1 to 5% sulfuric acid. Instead of sulfuric acid, other acids such as hydrochloric, phosphoric, hydrobromic, trichloroacetic, formic, acetic, or the like may be used. The concentration of the benzophenone compound in solution can be varied depending on how much of the benzophenone compound is desired to be incorporated into the fiber. For practical purposes solutions containing in the range from about 0.1 to about 10% are used. The fiber is then introduced into the acidified solution, agitation being preferably employed to secure good contact between the solution and fiber. For best results it is preferred to boil the solution while the fiber is maintained therein to obtain complete combination between the benzophenone compound and the protein molecules of the fiber. The amount of benzophenone compound taken up by the fiber will depend on various factors such as the concentration of benzophenone compound in the bath, the temperature of the benzophenone compound, the temperature used, the time of residence in the bath, and so forth. In general it is preferred that the treated fiber contain on the order of 1 to 10% by weight of the benzophenone compound. In some cases a definite improvement in resistance to yellowing will be afforded by an uptake of as little as 0.5%. The uptake can be increased as high as desired above these levels.

The benzophenone protective compounds are usually employed in the form of their sodium salts. However, since the bath is maintained in an acid condition the benzophenone compound exists therein in the sulfonic acid form, and it is in this form that the benzophenone compounds react to the wool by formation of salt linkages between the sulfonic acid radicals of the agents and the nitrogen constituents of the protein. It might be said therefore that the protective benzophenone compounds add to the protein in their acid (sulfonic) form regardless of the fact that they may be originally applied to the bath as salts.

The impregnating bath may contain various ingredients to expedite uptake of the benzophenone compound by the fiber and/or to insure uniform distribution of the benzophenone compound throughout the fiber. Thus salting-out agents such as sodium sulphate, sodium chloride, ammonium acetate, ammonium sulphate, in a concentration of about 0.1 to 10% may be added to the bath. Wetting agents may be added to assist in penetrating the aqueous medium into the fiber. Suitable agents of this type are for example sodium alkyl (C_{12}-C_{18}) benzene sulphonate, sodium tri-isopropyl naphthalene sulphonate, sodium dodecyl sulphate, sodium salt of di-octyl sulpho-succinate, sodium dodecane sulphonate, Turkey red oil, and so forth. The above ingredients are merely named for illustrative purposes; it is obvious that any of the various agents which possess surface active properties and are generally useful in wetting and dispersing applications can be used. In general only a small proportion of the wetting agent on the order of 0.01 to 0.2% is needed.

The impregnation of the fiber with the acidified bath may conveniently be carried out in apparatus conventionally used for dyeing operations. It is also evident that various agents may be added to the bath to accomplish various purposes. For instance one may incorporate in the bath bleaching agents such as hydrogen peroxide, acid dyes, mothproofing agents and the like.

After the fiber is treated with the acidified bath containing the benzophenone compound the fiber is removed from the bath and washed to remove residual acid and other constituents of the bath and then dried. The treatment does not affect the basic qualities of the fiber so that it may be used for any of the usual applications such as making of clothing and so forth. The benzophenone compounds used in accordance with this invention are essentially colorless so that the treated fiber has essentially the same color as the untreated fiber.

The impregnation treatment described above can be applied to the wool in any physical form, for example in the form of fiber, thread, yarn, woven or knitted goods, felts, piece goods and the like. Although the invention is particularly adapted to the treatment of wool it can also be applied to other proteinous fibrous materials such as silk, mohair, furs, animal hair, or synthetic protein fibers produced from casein, peanut protein, soybean protein, keratin, zein, and so forth.

The following examples further demonstrate the invention. These examples are submitted only by way of illustration and not limitation.

**EXAMPLE I**

A 10-gram sample of white wool flannel was immersed in a bath containing 500 cc. water. The bath was brought to 140° F., then 1 g. of Glauber's salt crystals was added. After 5 minutes, 1.25 g. of 2-hydroxy-4-methoxy-benzophenone-5-sodium sulphonate was added to the bath. The liquor was brought to the boil in 0.5 hour and 0.5 g. of sulphuric acid was added. After one hour at the boil, the wool sample was removed, rinsed well in running water and dried. The uptake of 2-hydroxy-4-methoxybenzophenone-5-sodium sulphonate by the wool was 4.5%.

**EXAMPLES II, III, IV**

The procedure as described above was repeated with the sole difference that the proportion of 2-hydroxy-4-methoxybenzophenone-5-sodium sulphonate was varied. The amount of this reagent used and the uptake thereof by the wool are set forth below:

<table>
<thead>
<tr>
<th>Amount of reagent, g</th>
<th>Uptake, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>2.5</td>
</tr>
<tr>
<td>IV</td>
<td>10</td>
</tr>
</tbody>
</table>

To ascertain the degree of protection conferred by the treatment, the four samples of treated wool and a sample of untreated wool (control) were placed 24 hours to the radiation of a low-pressure mercury germicidal lamp having more than 90% of its radiant energy at 2537 Angstroms.
All the wool samples, before and after irradiation, were 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.

**Reflectance measurements of treated and untreated wool**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Uptake of 2-hydroxy-4-methoxy-benzophenone-5-sulphonic acid, percent</th>
<th>Reflectance before irradiation, percent</th>
<th>Reflectance after irradiation, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>51.6</td>
<td>27</td>
</tr>
<tr>
<td>I</td>
<td>4.0</td>
<td>51</td>
<td>44.5</td>
</tr>
<tr>
<td>II</td>
<td>2.6</td>
<td>51</td>
<td>38.5</td>
</tr>
<tr>
<td>III</td>
<td>12.5</td>
<td>51</td>
<td>40.5</td>
</tr>
<tr>
<td>IV</td>
<td>15.7</td>
<td>46.5</td>
<td>40.5</td>
</tr>
</tbody>
</table>

Having thus described the invention, what is claimed is:

1. A method for protecting wool from the deleterious effects of light which comprises impregnating wool with an acidified aqueous solution of a benzophenone compound of the formula:

   \[
   \text{R} - \text{CO} \quad [\text{SO}_3\text{H}]^+ \quad (\text{OH})_n
   \]

   wherein R is a lower alkyl radical, the n's are each integers from 1 to 2, and the said benzophenone compound is free from chromophore groups other than the carbonyl group between the two benzene rings, the impregnation being carried out at about the boiling point of the said solution until the amino radicals of the protein molecule of the wool are chemically combined through salt formation with the sulphonic groups of the said benzophenone compound and until the wool has an enhanced resistance to the effect of light and a reduced tendency to turn yellow with age.

2. The method of claim 1 wherein the benzophenone compound is 2-hydroxy-4-methoxy-benzophenone-5-sulphonic acid.

3. The method of claim 1 wherein the benzophenone compound is 2,2'-dihydroxy-4-methoxy-benzophenone-5-sulphonic acid.

4. The method of claim 1 wherein the benzophenone compound is 2,2'-dihydroxy-4,4'-dimethoxy-5-sulphonic acid.

5. A wool fiber in which amino radicals of the protein molecule of the wool are chemically combined through salt formation with the sulphonic groups of a benzophenone compound of the formula:

   \[
   \text{R} - \text{CO} \quad [\text{SO}_3\text{H}]^+ \quad (\text{OR})_n
   \]

   wherein R is a lower alkyl radical, the n's are each integers from 1 to 2, the said benzophenone compound being free from chromophore groups other than the carbonyl group between the two benzene rings, and the said benzophenone compound being present in a proportion sufficient to give the wool an enhanced resistance to the effect of light and a reduced tendency to turn yellow with age.

6. The wool fiber of claim 5 wherein the benzophenone compound is 2-hydroxy-4-methoxy-benzophenone-5-sulphonic acid.

7. The wool fiber of claim 5 wherein the benzophenone compound is 2,2'-dihydroxy-4-methoxy-benzophenone-5-sulphonic acid.

8. The wool fiber of claim 5 wherein the benzophenone compound is 2,2'-dihydroxy-4,4'-dimethoxy-benzophenone-5-sulphonic acid.

**References Cited in the file of this patent**

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