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PROCESS FOR IMPARTING ROT-RESISTANCE TO AN ORGANIC TEXTILE MATERIAL AND THE RESULTING MATERIAL

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A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, 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 producing rot-resistant organic fibrous materials and to the products so produced. More specifically, it deals with the application of solutions, or emulsions, of certain organo-lead compounds having the formula R_3PbY to hydrophilic, organic fibrous materials. The resultant treated products have improved resistance to microbiological degradation, are not discolored, and retain their chemical properties. Most important, they have exceptional resistance to physical damage.

The process which is the subject of this invention is a separate and distinct embodiment of the process disclosed in our application, Ser. No. 546,169, filed of even date.

The term "fibrous organic material," as used herein, includes any hydrophilic fibrous material, i.e., organic materials which absorb or adsorb water, such as cotton, viscose rayon, cuprammonium rayon, ramie, jute, wool, paper, paperboard, and the like, including their chemical and/or physical modifications, which may be impregnated with a liquid, and dried. They may be in the form of free fibers, sliver, yarn, thread and woven or non-woven fabrics. We prefer the use of "spun" textiles such as threads or woven fabrics.

The term "rot resistant" relates to bactericidal chemicals which when present in the fibrous material are capable of destroying or retarding the action of organisms which normally destroy (rot) hydrophilic organic fibrous materials. Without the aid of such bactericidal chemicals, desized, scoured, and bleached cotton fabrics, or greige goods, are completely destroyed in "soil-burial tests" in about two to four days. This will be discussed more fully in an example below.

It is an advantage of the process of this invention that the fibrous organic materials may be processed by conventional techniques employing conventional equipment.

Heretofore, the protection of fibrous organic (textile) materials from attack by bacterial organisms has posed serious problems for the textile industry, and particularly when dealing with the manufacture of textiles for outdoor use where they may be alternately exposed to rain, cloudy weather and the heat of a hot sun; or for cotton canvas, one side of which is in contact with the ground.

Ideally, the chemical which provides resistance to biological degradation should be one which is easily and simply applied; it should be capable of protecting the fibrous organic material from destructive organisms or be capable of destroying these organisms at low concentrations of the chemical; it must maintain this activity over long periods of time; it must not discolor or physically damage the fibrous material; and it must be compatible with colorants deposited on, and in, the fibrous organic (textile) material for decorative or other purposes, such as waterproofing.

It has been known to treat fibrous materials to render them rot resistant. Toxic chemicals such as mercury compounds have been used but fibrous materials containing toxic chemicals may be dangerous to humans and animals. Deposition of bactericidal chemicals on fibrous materials frequently produces discoloration or tendering of the substrate. Many chemicals are expensive while others require large amounts of the rot-proofing chemical and accordingly also are expensive. Thus, it is seen that there is a real need in the textile industry for an effective method of destroying rot-producing organisms unattended by the above-described disadvantages.

We have now found that by impregnating organic fibrous materials with solutions of certain organolead compounds, it is possible to destroy or retard the highly active, cellulose-destroying organism thereby rendering these materials "rot-resistant" in a remarkably efficient and simple manner.

In general terms, the process of our invention may be described as follows:

(1) Prepare an aqueous solution or emulsion of the organolead compound.

(2) Impregnate the organic fibrous material with the lead solution.

(3) Remove the excess organolead solution by passing the organo fibrous material through a pair of squeeze rolls (padder rolls) adjusted to retain about 60 to 120 weight percent of the solution on the dry weight of the fabric.

(4) Dry the impregnated fibrous material.

The process is simple and easily applied. Low concentrations of the organolead compounds serve to completely and quickly destroy or retard the highly active cellulose-destroying organisms and obviate the problem of undesirable color, toxicity, or loss of strength.

Preparation of organolead solutions

The organolead compounds have the formula R_3PbY where R is alkyl, aryl, cycloalkyl or combinations of these. Y is an anion including acetate, laurate, imidazole, hydroxide, halogen and the like. These organolead compounds may be prepared by conventional chemical means. Excellent results are obtained when the material is impregnated with 0.5 to 5.0 weight percent of the R_3PbY solutions and the pickup is 60 to 120 weight percent.

Examples of the preferred R_3PbY compounds are N-(tributylplumbyl) imidazole, triphenyllead acetate, triphenyllead laurate, and tributyllead acetate.

The organolead compound may be dissolved in an aqueous medium such as ethanol or isopropanol to give concentrations ranging from about 1 to 40 weight percent. However, as the length of the carbon chain in the anion increases, certain nonaqueous solvents such as toluene, mineral spirits, carbon tetrachloride, chloroform and the like are satisfactory solvents. The aqueous or nonaqueous lead solutions may be used as such or the nonaqueous solutions of lead may be emulsified to form emulsions. These emulsions may be oil-in-water, or water-in-oil types. They may comprise surface active agents, water repellants, resins and colorants. The solutions or emulsions may be applied by other conventional methods known to those skilled in the art such as spraying, knife coating, dipping, etc.

It is within the scope of our invention to add a minor portion of an aqueous soluble thickener such as a low viscosity carboxymethyl cellulose having a viscosity of about 5–20 cps. to the aqueous solution of the organolead compound. Amounts of thickener ranging from about 1 to 4 weight percent on the total weight of the solution is a good practice. The thickener may first be wet with an equal weight of an alkyl alcohol such as ethanol or iso-

propanol and stirred into the water with a high-speed stirrer to form a uniform mix, after which a small quantity of a cationic surface-active agent such as (N-acetyl-N-ethylmorpholinium ethosulfate) may be added slowly with rapid stirring. The solution of R_3PbY is then slowly added with rapid stirring, preferably at a temperature ranging from about 50° to 75° C., and rapidly stirred until a uniform mixture is obtained.

Impregnating the fibrous material

The organic fibrous material is then impregnated with the R_3PbY solution, by passing the fibrous material into, and through, the R_3PbY solution. The excess organolead solution is then removed by passing the impregnated material through squeeze or padder rolls to remove excess solution. Amounts remaining in the wet fabric may vary from about 60 to 120 percent on the weight of the dry fabric. We prefer about 80 to 100 weight percent pickup, or the proper pickup to give about 0.5 to 5.0 weight percent of the R_3PbY on the weight of the dry fibrous material.

Drying the impregnated fibrous material

The impregnated material is then dried by conventional textile methods. We prefer hot air at a temperature of about 60–130° C., preferably about 75° to 90° C. The exact temperature range will depend upon the solvent, the presence of thickener, etc., the lower temperature being more suitable for the lower-boiling solvents. If the R_3PbY is present as a resinous emulsion, higher temperatures from about 130° to 160° C. may be required to cure and fix the resin.

The textile materials so treated have retained essentially 100% of their strength during the test periods, are not discolored, and their chemical properties remain unchanged.

The treated organic fibrous materials, especially cotton fabrics which are woven or nonwoven, are then buried in soil containing highly active cellulose-destroying organisms and samples removed at various intervals for testing using the AATCC Standard Method 30–1957 T–B–3. The following tests were made on desized, scoured, and bleached 54 x 48 cotton fabric. The results follow:

EXAMPLE 1

Samples of untreated, desized, scoured and bleached 54 x 48 cotton fabric were placed in a rot bed and inspected daily. After two days, the untreated fabric showed signs of deterioration (spots) and after four days had completely disintegrated.

EXAMPLE 2

A 5% solution of N-(tributylplumbyl) imidazole in ethanol was prepared. Desized, scoured and bleached 54 x 48 printcloth was immersed in the solution and the excess liquid removed by passing the sample through a conventional textile padder with a tight squeeze roll. The fabric was then dried in hot air at 85° C. The treated fabric was then placed in a rot bed. After 56 days of soil burial, the fabric still retained 100% of its original strength.

EXAMPLE 3

A 2% (2 g.) solution of N-(tributylplumbyl) imidazole in ethanol (98 g.) was prepared. Four grams of low viscosity carboxymethyl cellulose (CMC) was wet with about 2 g. ethanol and then dissolved in 95 g. water using a high-speed magnetic-type stirrer. Two g. of a 35% cationic dispersant (N-acetyl-N-ethyl-morpholinium ethosulfate) was then blended with the CMC solution which was gradually warmed to about 70° C. The N-(tributylplumbyl) imidazole was then stirred slowly into the warm CMC solution.

Desized, scoured and bleached 54 x 48 cotton printcloth was then impregnated with this solution, the excess removed by passage through squeeze rolls and the fabric dried in hot air at an air temperature of about 150° C.

The treated fabric retained all its strength (100%) after 70 days of soil burial.

EXAMPLE 4

A 5% ethanol solution of triphenyllead acetate was prepared. Cotton fabric was immersed in this solution and passed through adjustable squeeze rolls to remove excess liquid. Without drying this process was repeated and the fabric was then air dried at 85° C. The fabric retained 100% of its original strength after 42 days of soil burial.

EXAMPLE 5

Cotton samples were padded with a 0.5% ethanolic solution of N-(tributylplumbyl) imidazole in a similar manner as described in Example 2. The fabric retained 100% of its original strength after 28 days of soil burial.

EXAMPLE 6

5 grams of triphenyllead laurate solution were dissolved in 95 grams of chloroform. Cotton fabrics were padded with the above solution as in Example 2. The fabric retained 100% of its original strength after 42 days of soil burial.

EXAMPLE 7

Cotton fabric was treated with 0.5% N-(tributylplumbyl) imidazole as in Example 5. The fabric, after treatment, was leached for 24 hours (see AATCC Method 30–1957 T–C–1) then tested for rot resistance by the soil burial method. The fabric still retained 100% of its original strength after 28 days.

EXAMPLE 8

2 grams of tributyllead acetate was dissolved in 17 g. isopropanol. 2 g. CMC and 2 g. of the cationic dispersant of Example 3 were dissolved in 180 ml. water by the procedure of Example 3, after which the tributyllead acetate was added to the warm (70° C.) CMC solution. Sufficient water was then stirred into the tributyllead acetate-CMC solution to give a total of 200 g.

Cotton fabric was then padded with this solution and dried by the procedure of Example 3. The treated fabric retained essentially 100% of its original strength after 28 days of soil burial.

It should be noted that in all the eight examples above, the treated fabrics did not lose strength during soil burial tests, and one of them (Example 3) after 70 days. These results were unexpected.

We claim:

1. A process for rendering organic fibrous materials rot-resistant comprising the steps:
   (a) preparing an aqueous solution comprising 0.5 to about 5.0 weight percent of an organolead compound having the formula R_3PbY where R is at least one member of the group consisting of alkyl, aryl, and cycloalkyl, and Y is an anion selected from the group consisting of acetate, imidazole, hydroxide and halogen;
   (b) impregnating the organic fibrous material with the organolead solution;
   (c) removing the excess organolead (R_3PbY) solution by passing the impregnated organic fibrous material through a pair of squeeze rolls adjusted to retain from about 60 to 120 weight percent of the solution on the dry weight of the fibrous material; and
   (d) drying the impregnated fibrous organic material.

2. The process defined in claim 1 wherein the organic fibrous material is a cellulosic fibrous material.

3. The product resulting from the process of claim 2.

4. The process defined in claim 1 wherein the organolead compound is at least one member of the group consisting of N-(tributylplumbyl) imidazole, triphenyllead acetate, and tributyllead acetate.

5. The process defined in claim 1 wherein the aqueous

solution comprising the organolead compound also contains a thickener and a surfactant.

6. The product resulting from the process of claim 5.

7. The process defined in claim 5 wherein the aqueous solution comprises from about 8 to 50 percent ethanol, 0.5 to 5.0 percent organolead compound, 45 to 90 percent water, 1.0 to 2.0 percent low viscosity carboxymethyl cellulose, and 1 percent cationic surfactant, all percentages by weight.

8. A process for rendering organic fibrous materials rot-resistant comprising the steps:

(a) preparing a nonaqueous solution comprising 0.5 to about 5.0 weight percent of an organolead compound where R is at least one member of the group consisting of alkyl, aryl and cycloalkyl, and Y is an aliphatic radical having 12 to 20 carbon atoms;

(b) impregnating the organic fibrous material with the organolead solution;

(c) removing the excess organolead solution by passing the impregnated organic fibrous material through a pair of squeeze rolls adjusted to retain from about 60 to 120 weight percent of the solution on the dry weight of the fibrous material; and

(d) drying the impregnated fibrous organic material.

9. The product resulting from the process of claim 8.

10. The process defined in claim 8 wherein the nonaqueous solvent is selected from the group consisting of chloroform, pentane, hexane, and heptane and the organolead compound is triphenyllead laurate.

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