

1

3,420,700

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

Darrell J. Donaldson and Wilma A. Guice, New Orleans, and George L. Drake, Jr., and Wilson A. Reeves, Metairie, La., assignors to the United States of America as represented by the Secretary of Agriculture
 No Drawing. Filed Apr. 29, 1966, Ser. No. 546,169
 U.S. Cl. 117—138.5 7 Claims
 Int. Cl. D06m 13/50

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 organolead compounds having the formula $R_3Pb-S-R$ 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. 546,182, 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 nonwoven 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 materials 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, de-sized, 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

2

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 rotproofing 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 a solution or emulsion of the organolead compound.

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

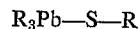
(3) Remove the excess organolead solution by passing the organo fibrous material through a pair of squeeze rolls (padder rolls) adjusted to retain about 60 to 120 weight percent of the solution on the dry weight of the fabric.

(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



where R may be alkyl, aryl, cycloalkyl, or combinations of these. Examples of such compounds are triphenylthiomethyllead, triphenylthioethyllead, triphenylthiopropyllead, triphenylthiobenzyllead, and triphenylthiophenyllead. These organolead compounds may be prepared by conventional chemical means. Excellent results are obtained when the material is impregnated with 0.1 to about 5.0 weight percent of the $R_3Pb-S-R$ solutions and the pickup is about 60 to 120 weight percent.

The organolead compound may be dissolved in an aqueous medium such as ethanol or isopropanol to give concentrations ranging from about 1 to 10 weight percent. However, as the length of the carbon chain in the alkyl group 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 repellents, resins, and colorants. The solu-

tions or emulsions may be applied by other conventional methods known to those skilled in the art such as spraying, dipping, etc.

Impregnating the fibrous material

The organic fibrous material is then impregnated with the $R_3Pb-S-R$ solution, by passing the fibrous material into, and through, the $R_3Pb-S-R$ 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 110% on the weight of the dry fabric. We prefer about 80 to 100 weight percent pickup, or the proper pickup to give 0.1 to about 5.0 weight percent of the $R_3Pb-S-R$ 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 lower temperatures being more suitable for the lower-boiling solvents. If the $R_3Pb-S-R$ 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 tested by burial in soil containing highly active cellulose-destroying organisms and samples are 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 2 days, the untreated fabric showed signs of deterioration (spots) and after 4 days had completely disintegrated.

EXAMPLE 2

Two grams of thiomethyltriphenyllead was dissolved in 198 g. of ethanol. Portions of desized, scoured, and bleached cotton fabric were immersed in this bath and passed through adjustable squeeze rolls set at a high pressure to give a pickup of about 100 weight percent. The fabric was then air dried at an air temperature of about 85° C. After a soil burial test for 42 days, the treated material retained essentially 100% of its original strength.

EXAMPLE 3

Twelve and one half grams of thiopropyltriphenyllead was dissolved in 237.5 g. of chloroform. Portions of cotton fabric were padded with this solution in the same manner as in Example 2. The fabric was still retaining 100% of its strength after 70 days of soil burial.

EXAMPLE 4

Eight grams of thiomethyltriphenyllead was dissolved in 192 g. of chloroform. A portion of the cotton textiles used in Example 1 was treated with this solution in the same manner as in Example 2. The sample was then leached with tap water for 24 hours (see AATCC Method 30–1957–T–C–1). The fabric still retained 100% of its strength after 56 days of soil burial.

EXAMPLE 5

Nine grams of thioethyltriphenyllead was dissolved in 291 g. of chloroform. The fibrous cellulosic material treated with this solution still retained 100% of its strength after 70 days of soil burial.

EXAMPLE 6

A 5% solution of thioethyltriphenyllead in chloroform was prepared. The fabric after treatment with this solution was leached for 24 hours with tap water by AATCC Method 30–1957 T–C–1. The fabric still retained 100% of its strength after 161 days of soil burial.

EXAMPLE 7

A 4.6 percent solution of thiopropyltriphenyllead was prepared in ethanol. This solution was used to impregnate portions of the desized, scoured, and bleached cotton fabric of Example 1 and squeezed to give a wet pickup of 100 weight percent on the dry fabric. After 56 days in the soil burial test bed, the breaking strength was still essentially 100%.

EXAMPLE 8

A solution containing 0.5 g. thioethyltriphenyllead in 99.5 g. ethanol was used to impregnate desized, scoured, and bleached 54 x 48 cotton fabric. The excess was removed by means of a pair of squeeze rolls to give a pickup of 100 percent on the weight of the dry fabric. The wet fabric was dried at an air temperature of about 85° C., and after a soil burial test of 14 days, still retained its original breaking strength.

It should be noted that in all the eight examples above, the treated fabrics did not lose strength during soil burial tests. In fact, one of these samples (Example 6) did not show any loss of strength after 161 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 a thioorganolead compound having the formula $R_3Pb-S-R$ where R is at least one member of the group consisting of alkyl, aryl, and cycloalkyl;

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

(c) removing the excess thioorganolead ($R_3Pb-S-R$) 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 defined by the process of claim 2.

4. The process defined in claim 1 wherein the thioorganolead compound is at least one member of the group consisting of thiomethyltriphenyllead, thioethyltriphenyllead, and thiopropyltriphenyllead.

5. 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 a thioorganolead compound of the formula $R_3Pb-S-R$ where R is at least one member of the group consisting of alkyl, aryl, and cycloalkyl;

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

(c) removing the excess thioorganolead 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.

6. The product defined by the process of claim 5.

7. The process defined in claim 5 wherein the nonaqueous solvent is selected from the group consisting of chloroform, pentane, hexane, and heptane and the thioor-

5

ganolead compound is thiopropyltriphenyllead or thioethyltriphenyllead.

References Cited

UNITED STATES PATENTS

2,763,574 9/1956 Ruperti ----- 117—138.5
 2,938,815 5/1960 Van Bochove et al. -- 117—143 X
 3,119,715 1/1964 Reeves et al. ----- 117—138.5
 3,142,614 7/1964 Ligett ----- 167—22

6

3,183,118 5/1965 Conner ----- 117—138.5
 3,183,149 5/1965 Gonzales et al. ---- 117—143 X
 3,317,345 5/1967 Fluck et al. ----- 117—138.5

5 WILLIAM D. MARTIN, *Primary Examiner*.

THEODORE G. DAVIS, *Assistant Examiner*.

U.S. Cl. X.R.

117—102, 141, 143, 144, 152