United States Patent Office 2,977,250
Patented Mar. 28, 1961

2,977,250

METALLIC SELENIDE FUNGICIDES FOR OUTDOOR CELLULOSIC TEXTILES

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No Drawing. Filed May 5, 1960, Ser. No. 27,230

1 Claim. (Cl. 117—138.5)

(Granted under Title 35, U.S. Code (1952), sec. 266)

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 the treatment of textile materials. More particularly, the invention relates to the treatment of textile fabrics, composed mainly of cellulose. The cellulosic textiles produced by this treatment have outstanding resistance to microorganisms and outdoor weather.

In general this invention relates to the treatment of textile materials composed mainly of cellulose with selenides so that the cellulosic textile material exposed to direct or indirect sunlight is rendered resistant to attack and staining by microorganisms.

It has been found that essentially insoluble selenides when applied to cellulosic textiles render these textiles resistant to attack by microorganisms when exposed to direct or indirect sunlight.

It has been found that the objects of the present invention can be achieved by treatment of the cellulosic fabric with selenide salts either by precipitation "in situ" alone or precipitation "in situ" followed by treatment with a suitable binding resin or by impregnation of the cellulosic fabric with an emulsion or solution of the selenide salts dispersed in a suitable binder. Suitable binders include alkyd resins, urea resins, melamine resins, vinyl resins, styrene resins, coumarone-indene resins, petroleum resins, silicone resins, maleic resins, phenolic resins, polyethylene dispersions, and butadiene-styrene copolymers.

In general, the process of the invention for rendering a cellulosic textile fabric resistant to the attack of microorganism involves impregnating the fabric with an aqueous-solvent emulsion system containing an alkyd resin binder and a water insoluble metal selenide and drying the impregnated fabric. In this aqueous-solvent emulsion system the selenide is present in an amount sufficient to insure the deposition of at least 0.01% by weight of selenium on the dried fabric.

Selenide salts suitable for use in this invention are insoluble materials that contain a non-alkali metal selenide, when the metal is Bi, Cd, Co, Cu, Pb, Mn, Hg, Ni, Ag, Sn, and Zn. These compounds are effective singly, in combination, in combination with selenium, or in combination with selenium and each other. They may be in combination with other materials such as heavy non-alkali metal sulfides to produce various colored microorganism resistant treated cellulosic textiles. They may be used in combination with other conventional textile treating materials such as wetting agents, softeners, stiffness, and others.

Preparation of these materials can be carried out by any suitable means.

The following examples are illustrative of the invention:

EXAMPLE 1

A dispersion of a finely divided cadmium selenide material containing 3% selenium in an emulsifiable alkyd resin binder was applied to scoured 10.10 oz. cotton duck and allowed to air dry. The ratio of the cadmium selenide containing material to the solid resin was approximately 1 to 2. Approximately 2½% cadmium selenide material and 5% alkyd resin were added to the cotton fabric. Therefore, the fabric actually contained only about .075% selenium. This treated duck was placed on open backed wooden weather exposure racks in an unshaded essentially suburban area in New Orleans, Louisiana. These racks faced south at an angle of 45° and were so constructed that all samples were at a minimum of 30 inches above the ground. After two years of continuous exposure the sample treated with the cadmium selenide containing material was free from any detectable mildew or other microorganism staining or attack. A sample of scoured duck and a sample of scoured duck treated with 5% of the alkyd resin (without the cadmium selenide containing material) was badly stained after only six months of exposure.

EXAMPLE 2

A dispersion of a finely divided cadmium selenide material containing 23% selenium in an emulsifiable alkyd resin binder was applied to 10.10 oz. cotton duck in the same manner and proportions and exposed as described in Example 1. This cadmium selenide treated cotton duck contained about 0.69% selenium and showed no visible evidence of mildew or algae staining or attack after 18 months of outdoor exposure and retained 60% of the original fabric strength as compared to an untreated control sample which was badly discolored by mildew and algae and which retained only 26% of its original strength when exposed for the same period of time.

EXAMPLE 3

Five pigments containing known amounts of cadmium selenide and cadmium sulfide have been used to treat cotton duck to prevent mildew and algae growth. One sample of pure cadmium selenide and one sample of cadmium sulfide were also used to treat samples of the duck. Each of the seven cadmium containing materials were applied to the duck at five levels of add-on ranging from 1% down to .06%. Since one of the pigments contained 3% by weight of selenide ion, the fabric treated with this pigment at .06% add-on of pigment actually contained only 0.0018% selenium. All of the compounds were applied to the fabric samples by first dispersing them in an alkyd resin binder then padding the fabric through the emulsion and drying. In each case the dry add-on of the alkyd binder was about 3.3%. The alkyd resin used here was the same as that used in Examples 1 and 2. One sample of fabric was treated with the alkyd binder alone as a control fabric.

A description of the compounds and the amount applied to the thirty-five samples of cotton fabric is given in Table I.

Table I

CONCENTRATION OF INHIBITORS APPLIED TO FABRIC

Cadmium Containing Material	Selenium in Material, Percent	Amount of pigment or Compound Applied to Fabric, Percent by Wt.				
Pigment 1	3	1	.5	.25	.13	.06
Pigment 2	9	1	.5	.25	.13	.06
Pigment 3	12	1	.5	.25	.13	.06
Pigment 4	23	1	.5	.25	.13	.06
Pigment 5	28	1	.5	.25	.13	.06
Pure CdSe	41	1	.5	.25	.13	.06
Pure CdS	None	1	.5	.25	.13	.06

The samples were exposed outdoors for eight months in the manner described in Example 1. Results of mildew and algae growth on the fabrics after exposure are shown in Table II.

Table II

EXTENT OF MILDEW AND ALGAE INHIBITION IMPARTED TO THE CANVAS FABRIC BY THE COMPOUNDS DESCRIBED IN TABLE I

Cd+Se Containing Material Applied to Fabric	Percent Se in Material Applied	Percent Cd+Se Containing Material on Fabric				
		1	.5	.25	.12	.06
Pigment 1	3	[1] 0	[1] T	[1] X	X	X
Pigment 2	9	0	T	T	X	X
Pigment 3	12	0	0	T	X	X
Pigment 4	23	0	0	0	T	T
Pigment 5	28	0	0	0	T	T
Pure CdSe	41	0	0	0	0	T
Pure CdS	0	X	X	X	X	X

[1] 0=completely free of mildew and algae; T=trace of mildew or algae; X=visible mildew or algae present.

The sample treated with the resin alone showed visible evidence of mildew and algae growth after two months and the amount continued to increase for the entire eight month period.

EXAMPLE 4

The selenide containing material can be dispersed with other materials to produce desired colors and shades on the treated fabric and still produce the desired resistance to microorganisms: A bath composed of the following ingredients was used to produce a khaki colored cotton duck:

2.9 gms. of pigment containing CdSe (28% Se)
4.2 gms. chrome yellow pigment
1.5 gms. raw umber pigment
.6 gm. lampblack

30.4 gms. emulsifiable alkyd resin solution (50% resin solids).

The above was dispersed by means of a sample size paint mill and emulsified in the following mixture:

208 gms. water
104 gms. toluene
104 gms. mineral spirits

This mixture was applied by padding to 10.10 ounce cotton duck so as to deposit approximately .35% of the cadmium selenide containing material on the cotton fabric. A sample so treated was exposed as described in Example 1 for eight months. The exposed sample was free from all visible signs of mildew and algae attack or staining. An untreated sample simultaneously exposed showed considerable evidence of attack by microorganisms.

We claim:

A process for rendering a cellulosic textile fabric resistant to the attack of microorganisms which comprises impregnating the cellulosic textile fabric with an aqueous-solvent emulsion system containing an alkyd resin binder and a water insoluble metal selenide, and drying the impregnated fabric, said selenide being present in said aqueous-solvent emulsion system in an amount sufficient to insure the deposition of at least 0.01% by weight of selenium on the dried fabric.

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