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PRESERVATION OF CELLULOSIC MATERIALS

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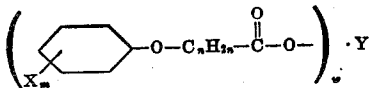
This invention relates to the preservation of cellulosic materials and is particularly concerned with a method for protecting fibers and fibrous manufactures of cellulose against mildew and rot.

Fabrics, thread, yarn, fibers, paper, molded fibers, and the like of cellulosic origin, are commonly attacked by fungi and bacterial organisms. As a direct result, the cellulosic materials become stained, of reduced tensile strength, and otherwise deteriorated. In efforts to impart to fabrics and the like properties of resistance to fungal and bacterial attack, such materials have been subjected to treatment with a wide variety of preservatives.

Among the substances heretofore suggested for the treatment of cellulosic products, have been phenols and phenolates and particularly polyhalogenated phenols and their salts. These compounds have had wide acceptance as wood preservatives and otherwise where the control of mold and bacterial growth on a solid surface has been desired. In the treatment of fibrous products, however, the polychloro-phenolic toxicants are of limited value only. A particular disadvantage of such polyhalo-aromatic derivatives is their relatively high vapor pressure whereby they are soon dissipated away from and out of loose structures such as fabrics and the like, and the latter become vulnerable to attack and decomposition.

It is an object of the present invention to supply an improved method for the preservation of fibrous cellulosic materials. It is a further object to provide a such method employing a polyhalogenated aromatic compound which method will not be subject to the disadvantages characterizing previous operations with compounds of this general type. Other objects will be apparent from the following specification and claims.

In accordance with the present invention, it has been discovered that fibrous manufactures of cellulosic nature are protected against mildew attack and rot by treatment with a compound having the formula



wherein X represents halogen, Y represents hydrogen, ammonium or a metal salt-forming radical, n is an integer from 1 to 3, inclusive, m is an integer not greater than 5 and w is an integer equal to the valency of Y. The compounds as disclosed are relatively non-volatile, adhere tenaciously to fiber surfaces treated therewith, and are substantially odorless.

The preservative compounds may be applied to the fibers and fibrous products in any convenient manner. The preferred embodiment of

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the invention contemplates the treatment of the cellulosic material with a solution of the acid or acid salt in suitable solvent. This may be accomplished simply by immersing the fabric or other fibrous product in a solution of preservative, and thereafter vaporizing off the solvent.

An alternate procedure includes separately contacting the cellulosic material with aqueous solutions of an inorganic salt of a heavy metal and of an alkali metal salt of a halo-phenoxy-aliphatic acid. The water insoluble heavy metal salt of the halo-phenoxy-aliphatic acid is thereby precipitated within the interstices and on the surfaces of the article under treatment, whereby the fungicidal and bactericidal effect of the preservative is exerted over a considerable period of time. The order in which the alkali salt and heavy metal salt solutions are applied to the fibrous product is immaterial. Thus either may be employed as the primary treatment, followed by wetting of the fibrous product with the other.

The amount of the preservative compound employed in accordance with the present invention varies considerably with the product to be preserved, the conditions under which protection is to be accomplished, and the particular compound selected for use. In general, an amount of the preservative equal to from about 0.5 per cent by weight to 10 per cent by weight of the fibers or fibrous manufactures under treatment accomplishes the desired control of mildew and rot producing organisms. Preferred concentrations for toxicant are from 1.0 to 5.0 per cent by weight of the cellulosic article. Solutions containing from about 1 to 10 per cent by weight of toxicant and operation so as to obtain from about 50 per cent to 150 per cent by weight wet pick-up generally give satisfactory results.

While any suitable halo-phenoxy-aliphatic acid or its salts may be employed in accordance with the present invention, best results have been obtained with the free acids and difficulty water-soluble salts thereof. The preferred toxicants are halo-phenoxy-acetic acid and its salts. Particularly effective compounds are the salts of 2,3,4,6-tetrachlorophenoxy-acetic acid.

Any fiber or fibrous manufacture of cellulosic origin may be preserved in accordance with the method of the present invention, and the procedures, as described, are particularly applicable to the protection of textile materials such as threads, yarns, cotton duck, canvas, cable wrappings, braid, burlap, osnaburg, and the like from attack by rot producing organisms.

Among the solvents which may be employed in accordance with the present invention are water, ethanol, methanol, isopropanol, acetone, methyl ethyl ketone, dioxane, benzene, carbon tetrachloride, ethylene chloride, carbitol, Cello-solve, methyl Cellosolve, and the like. The solvent selected for any given operation is largely

dependent upon the solubility characteristics of the particular acid or acid salt to be applied as a preservative material, and the conditions under which drying is to be accomplished.

The following examples illustrate the invention, but are not to be construed as limiting:

Example 1.—2,3,4,6-tetrachlorophenoxy-acetic acid was dissolved in ethanol to form solutions containing 1, 2, 3, and 4 per cent by weight of the acid. Segments of 10 ounce cotton duck were passed through these solutions to obtain a 100 per cent by weight wet pickup. The canvas pieces were then air-dried and subjected to various tests to determine their resistance to mildew and rot.

In one such series of determinations, the organisms *Chaetomium globosum* and *Aspergillus niger* were grown in petri dishes on malt extract agar media. Just prior to the sporulation of the mature mold growth, sections of the treated canvas were placed firmly in contact with and over the pad of mycelia. The canvas pieces were allowed to remain in such position until the mold surfaces had sporulated (generally from 24 to 48 hours), and then removed and placed on an inorganic salts agar, incubated for three weeks, and examined for evidence of attack by mold. In these determinations, all of the treated canvas samples were 100 per cent resistant to *Aspergillus niger*. The samples containing 3 and 4 per cent of 2,3,4,6-tetrachlorophenoxy-acetic acid were unattacked by *Chaetomium globosum*. Those containing 1 and 2 per cent of the preservatives were not adequately protected. Untreated canvas specimens were found to be completely covered with a luxuriant growth of mycelia and spores of both organisms.

Example 2.—In a further testing operation, sections of the canvas treated as described in Example 1 were buried along with untreated specimens in rich, well composted soil heavily abundant in mold and rot organisms. The earth and samples were incubated at a soil temperature of 75° F. and under carefully controlled conditions of moisture. Canvas pieces were removed from the earth after 14 days and 28 days and tested for retention of tensile strength. The original canvas had a tensile strength of 100–110 pounds per inch. The following table sets forth the results obtained with the several samples subjected to soil burial:

Compound	Per Cent by Wt. in sample	Per Cent Retention of Tensile Strength After—	
		14 Days	28 Days
2,3,4,6-tetrachlorophenoxy-acetic acid.....	1	99	68
Do.....	2	91	101
Do.....	3	106	104
Do.....	4	109	0
Untreated control.....	—	0	0

Example 3.—Operations similar to those described in Examples 1 and 2 were carried out with canvas pieces containing 1, 2, 3, and 4 per cent by weight of the copper and zinc salts of 2,3,4,6-tetrachlorophenoxy-acetic acid calculated on the basis of the free acid. These canvas pieces were prepared by a two-bath treatment in which the fabric was first passed through an aqueous solution of the sodium salt of the acid in appropriate concentration. The wet cloth, containing 100 per cent by weight pickup, was then passed through a 5 per cent by weight solu-

tion of copper sulfate or zinc chloride and dried.

The copper and zinc salts at all concentrations gave complete protection against *Chaetomium globosum* and *Aspergillus niger* in the determination as described in Example 1. The results obtained in the soil burial tests (as described in Example 2) were as follows:

Compound	Percent by Wt. in sample	Percent Retention of Tensile Strength After—	
		14 Days	28 Days
2,3,4,6-tetrachlorophenoxy-acetic acid, Copper salt.....	1	45	18
Do.....	2	104	42
Do.....	3	105	71
Do.....	4	109	99
2,3,4,6-tetrachlorophenoxy-acetic acid, Zinc salt.....	1	50	9
Do.....	2	74	118
Do.....	3	96	94
Do.....	4	116	103
Copper sulfate.....	5	30	0
Zinc chloride.....	5	11	0
Untreated control.....	—	0	0

Example 4.—4 per cent by weight of a number of representative aryloxy-aliphatic acids and their salts were deposited on sections of ten ounce cotton duck. Treatment was accomplished by wetting the canvas with a 4 per cent by weight solution of the selected toxicant so as to obtain a 100 per cent by weight wet pickup. Each canvas section was then dried and exposed to the action of *Chaetomium globosum* as described in Example 1. The following table sets forth the results obtained in this operation.

Table

Compound	Solvent Employed	Per Cent Control
phenoxy-acetic acid.....	ethanol.....	0
(6-chloro-2-xenoxy)-acetic acid.....	methyl ethyl ketone.....	60
(4-tertiarybutyl-phenoxy)-acetic acid.....	ethanol.....	50
(2-carboxy-phenoxy)-acetic acid.....	dioxane.....	0
2-chlorophenoxy-acetic acid.....	methyl ethyl ketone.....	100
4-chlorophenoxy-acetic acid.....	do.....	100
2,4-dichlorophenoxy-acetic acid.....	do.....	100
2,3,4,6-tetrachlorophenoxy-acetic acid.....	ethanol.....	100
2,3,4,6-tetrachlorophenoxy-acetic acid, zinc salt.....	dioxane.....	100
2,3,4,6-tetrachlorophenoxy-acetic acid, copper salt.....	do.....	100

It was evident from the foregoing that the halogen substituted phenoxy-aliphatic acids were specific against the rot organism *Chaetomium globosum* and that this property was not shared by aryloxy-aliphatic acids as a class.

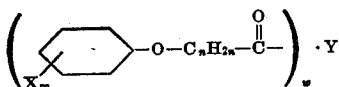
While the foregoing examples have been particularly concerned with certain chlorophenoxy-aliphatic acids and their salts, it is to be understood that other halo-phenoxy-aliphatic acid compounds may be similarly employed. Representative of such compounds are the following: 4-bromophenoxy-acetic acid, 2,4,6-tribromophenoxy-acetic acid, pentabromophenoxy-acetic acid, (2,6-dichloro-4-bromo-phenoxy)-acetic acid, 4-iodophenoxy-acetic acid, 2,4,5-trichlorophenoxy-acetic acid, 2,4,6-trichlorophenoxy-acetic acid, pentachlorophenoxy-acetic acid, 2,3,4,6-tetrachlorophenoxy-propionic acid, 2,4,5-trichlorophenoxy-butyric acid, 4-bromophenoxy-propionic acid, 2,4-diodophenoxy-butyric acid, lead salt of 4-chlorophenoxy-acetic acid, lead salt of 2,3,4,6-tetrachlorophenoxy-propionic acid, lead salt of 2,4-dibromophenoxy-acetic acid, cadmium salt of 4-iodophenoxy-acetic acid, cadmium

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salt of 2,4,6-tribromophenoxy-propionic acid, cadmium salt of pentachlorophenoxy-butyric acid, silver salt of 2-chlorophenoxy-butyric acid, silver salt of 3-bromophenoxy-acetic acid, silver salt of 2,3,4,6-tetrachlorophenoxy-propionic acid, mercury salt of 2,4-dibromophenoxy-acetic acid, mercury salt of pentachlorophenoxy-butyric acid, mercury salt of (2,4-dichloro-6-bromophenoxy)-propionic acid, aluminum salt of 4-chlorophenoxy-acetic acid, aluminum salt of 2,4,6-tribromophenoxy-propionic acid, magnesium salt of 2,3,4,6-tetrachlorophenoxy-acetic acid, magnesium salt of 2-chlorophenoxy-butyric acid, calcium salt of 2,4,5-trichlorophenoxy-propionic acid, calcium salt of 4-iodophenoxy-acetic acid, barium salt of 2,5-dichlorophenoxy-acetic acid, barium salt of 2,4-dibromophenoxy-propionic acid, barium salt of pentachlorophenoxy-butyric acid, ammonium salt of (2-iodo-4-chlorophenoxy)-acetic acid, ammonium salt of 2,4,6-trichlorophenoxy-propionic acid, ammonium salt of (4-chloro-2,6-dibromo-phenoxy)-butyric acid, potassium salt of 2,3,4,6-tetrachlorophenoxy-acetic acid, sodium salt of 2-bromophenoxy-butyric acid, etc. Similarly, mixtures of any two or more of these salts and/or acids may be employed.

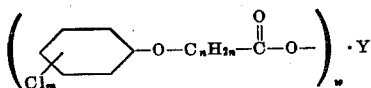
I claim:

1. The process of protecting textile materials of cellulosic origin against attack by mildew and rot which includes the step of depositing on the fibrous surfaces of the textile material from 0.5 to 10.0 per cent by weight of a compound having the formula



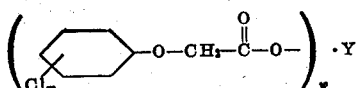
wherein X represents a halogen selected from the group consisting of chlorine, bromine, and iodine, Y represents a member of the group consisting of hydrogen, ammonium and a salt-forming metal, n is an integer from 1 to 3, inclusive, m is an integer not greater than 5, and w represents an integer equal to the valency of Y.

2. The method for rot and mildew-proofing textile materials of cellulosic origin which includes the step of depositing on the fibrous surfaces of the textile material from 0.5 to 10.0 percent by weight of a compound having the formula



wherein Y represents a member of the group consisting of hydrogen, ammonium and a salt-forming metal, n is an integer from 1 to 3, inclusive, m is an integer not greater than 5, and w represents an integer equal to the valency of Y.

3. The method for rot and mildew-proofing textile materials of cellulosic origin which includes the step of depositing on the fibrous surfaces of the textile material from 0.5 to 10.0 percent by weight of a compound having the formula

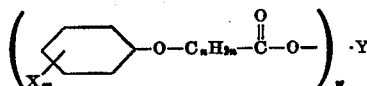


wherein Y represents a member of the group consisting of hydrogen, ammonium and a salt-forming metal, m is an integer not greater than 5, and w represents an integer equal to the valency of Y.

4. The process of protecting textile materials

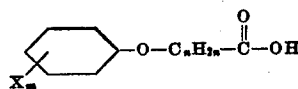
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rot which includes the steps of (1) wetting the fibrous surfaces of the textile material with a solution in volatile organic solvent of a compound having the formula



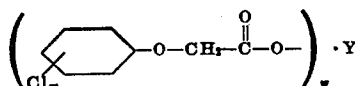
wherein X represents a halogen selected from the group consisting of chlorine, bromine, and iodine, Y represents a member of the group consisting of hydrogen, ammonium, and a salt-forming metal, n is an integer from 1 to 3, inclusive, m is an integer not greater than 5, and w represents an integer equal to the valency of Y, and (2) drying the textile material.

5. The process of protecting textile materials of cellulosic origin against attack by mildew and rot which includes the steps of (1) wetting the material with an aqueous solution of a water-soluble alkali metal salt of a halophenoxy-aliphatic acid having the formula



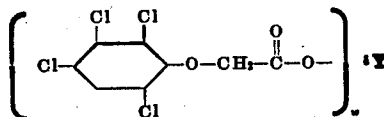
wherein X represents a halogen selected from the group consisting of chlorine, bromine, and iodine, n is an integer from 1 to 3, inclusive, and m is an integer not greater than 5, (2) treating the wet material with an aqueous solution of a heavy metal salt as a precipitating agent, and (3) evaporating the water out of the material.

6. The method for rot and mildew-proofing textile materials of cellulosic origin which includes the step of depositing in and on the fibrous surfaces of the textile material from 1.0 to 5.0 percent by weight of a compound having the formula



wherein Y represents a member of the group consisting of hydrogen, ammonium, and a salt-forming metal, m is an integer not greater than 5, and w represents an integer equal to the valency of Y.

7. The method for rot and mildew-proofing textile materials of cellulosic origin which includes the step of depositing in and on the fibrous surfaces of the textile material from 1.0 to 5.0 percent by weight of a compound having the formula



wherein Y represents a member of the group consisting of hydrogen, ammonium, and a salt-forming metal, and w represents an integer equal to the valency of Y.

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The following references are of record in the file of this patent:

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