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CELLULOSIC TEXTILES PROTECTED AGAINST MILDEW

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This invention relates to cellulosic textile materials, the surface and fibers of which exhibit increased resistance to mildew and rot, and to a treatment whereby such increased resistance may be imparted to cellulosic textiles. It relates in particular to the treatment of cotton textiles and to the treated product.

The problems arising from the mildewing and rotting of cellulosic textiles, especially those which are exposed to the weather in warm humid climates, have long been known. Many materials have been proposed and used to protect cotton cloth and similar textiles from mildew, with varying degrees of success. It has been observed that some of the treating agents are too fugitive to give the desired prolonged protection. Others have a limited application because of their toxic or irritant character which requires them to be handled with caution. Of equal importance is the discovery that even the more permanent and least irritating agents used to increase the resistance of cotton textiles to fungus growth have been defective in the protection afforded to the cloth against various weakening or "tendering" influences. Thus, samples of the treated cloth have been capable to prolonged exposure in humid tropical climates without supporting mold growth, but have become progressively weaker until the cloth has little residual strength. It is now recognized that a satisfactory protectant for such cellulosic textiles should permit them to retain their strength as well as preventing the growth of fungi.

It is accordingly an object of the present invention to provide a cellulosic textile product, the surfaces and fibers of which carry an agent to increase the resistance of such textile to mildew and to minimize loss of strength of the textile during prolonged weathering. A related object is to provide a method of treating cellulosic textiles, such as cotton, linen, ramie, hemp, sisal, jute and the like, to give them increased resistance to mildew and increased retention of strength on ageing. Other and related objects may appear hereinafter.

I have found that the desired results are obtained to a remarkable extent when cellulosic textiles are treated to contain, on their surfaces and in their fibers, an effective fungistatic quantity which is commonly from about 1 to about 5 per cent by weight (more or less) of 2,4'-dihydroxybenzophenone or certain substitution products

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thereof, and that the treated product is unique in the degree of its retention of strength under normally weakening conditions of exposure. The substitution products of 2,4'-dihydroxybenzophenone which have been found to be operative, and which may be used in the present invention are the monochloro- and dichloro-2,4'-dihydroxybenzophenones, and the 4-methyl- and 5-methyl-2,4'-dihydroxybenzophenones. Mixtures of the named substitution products with one another or with 2,4'-dihydroxybenzophenone are also effective materials for use in the invention, as are mixtures of at least 50 per cent of 2,4'-dihydroxybenzophenone with the isomeric but individually ineffective or less effective hydroxybenzophenones wherein the hydroxyl groups are in the 2-, 4-, 2,2'-, 3,3'-, 3,4'-, or 4,4'-positions.

The positions occupied by chlorine atoms in the mono- and dichloro-2,4'-dihydrobybenzophenones contemplated for use in the invention are not known, but the compounds found useful are those which are obtained by direct chlorination of the designated dihydroxy compound until the chlorine content reaches a value from about 14 to about 25 per cent. An underchlorinated product, containing less than 14 per cent chlorine, consists essentially of 2,4'-dihydroxybenzophenone and its mono-chloro derivative, and may be used effectively. Similarly, a slightly overchlorinated product, having a chlorine content, for example, of about 30 per cent, consist of a mixture of some unchlorinated, some mono-chloro- and some trichloro-2,4'-dihydroxybenzophenone together with a preponderant amount of the desired dichloro-compound, and is also effective as an agent to protect cellulosic textiles against attack by mildew and rot without itself causing deterioration of the cloth.

The above-described protective agents may be applied to the textile material by any of several procedures. The most convenient method comprises dissolving the 2,4'-dihydroxybenzophenone or substitution product thereof to form a standard solution in a volatile organic solvent, dipping the cloth in the solution, expressing any excess of solution over that which contains the desired amount of anti-fungus agent, and evaporating residual solvent. This leaves a deposit of the agent in and on the fibers. In commercial practice, the speed at which the cloth passes through the bath is adjusted so that a constant weight of solution is absorbed, and the amount of protec-

tive agent carried out of the bath is directly proportional to its concentration in the bath.

In another procedure, the dihydroxybenzophenone compound, of the group defined, may be dissolved, as described above, using a solvent which is immiscible with water, and the resulting solution may be emulsified as the disperse phase in an aqueous medium and applied to the cloth as an emulsion. Subsequent drying deposits the agent in the cloth. Similarly, the protective agent may be dispersed in, and deposited on the cloth from a liquid sizing material such as a starch dispersion.

Since a large proportion of the cloth which is given commercial anti-fungus treatment is of the water-repellent type, intended for tents, awnings, tarpaulins, sails, and the like, it is convenient to apply the dihydroxybenzophenone compound to the cloth from the bath used to impart water repellency. If the water-repellent is a lacquer type of solution of a film-forming material, the present agents may be dissolved therein. If the water-repellent is or comprises a wax emulsion, the present agent may be dissolved in a suitable solvent, emulsified with water, and mixed in the desired proportions with the wax emulsion before application to the cloth. A particular wax-containing, film-forming solution for imparting water repellency, and which is referred to in some of the following examples as the "binder," is composed of 15 parts by weight of a low viscosity type of ethyl cellulose (48.5 per cent ethoxyl content), 10 parts of castor oil, 25 parts of hydrogenated rosin, and 50 parts of microcrystalline wax, dissolved in a mixture of 85 per cent by volume of a "hydroformed," i. e. cracked and hydrogenated, petroleum naphtha high in cyclic hydrocarbons, and 15 per cent by volume of butanol. To this solution is added the benzophenone derivative, prior to the cloth treating operation. The deposited solids thus contain both the water repellent binder and the anti-fungus agent.

It is a necessary condition that a chemical, to be capable of successful use as an anti-fungus agent in textiles, must show effective control of the commoner mildew and cellulose rotting organisms in laboratory tests using "pure cultures"; it must have low volatility and a degree of thermostability to favor permanence of the material in treated textiles; and, it must show positive control of air-and soil-borne organisms in outdoor exposure tests of treated textiles under conditions to which such textiles may be subjected in use. In preliminary tests, each of the above-named compounds (2,4'-dihydroxybenzophenone and its named substitution products) was found to be effective as a fungistat in pure culture laboratory tests on inorganic salts agar in petri dishes at 30° C. using various known air-and soil-borne fungi. When samples of cotton cloth were treated to contain from 1 to 5 per cent by weight of the same 2,4'-dihydroxybenzophenone compounds, and were inoculated with the same cultures and subjected to a humid atmosphere at 30° C., equally good fungistatic action was noted. The compounds were each found to be as stable and to have at least as low volatility as any of the phenolic types of fungistatic agents commercially sold for the present purpose. The permanence of these compounds in cotton textiles was noted by their continued effectiveness after the treated textiles were subjected to ultra-violet radiations in a "Fadeometer" for 552 hours (23 days). The test organisms, which were controlled both before and after Fadeometer exposture, were *Aspergillus niger* and *Chaetomium globosum*, the latter being a cellulose rotting organism. The favorable results in these preliminary tests justified further tests under more practical conditions, including the soil burial and field exposure tests reported in subsequent examples.

Example 1

Cotton duck (No. 10) was treated with solutions of the compounds listed in the following table, under conditions to deposit in the dried cloth the indicated weights of the respective agents. Samples of the cloth were buried in moist soil for the indicated periods of time, and were then tested to determine the per cent retention of breaking strength. This gives an index of the effectiveness of the treating agents against soil-borne cellulose rotting organisms. For comparison, similar tests were run using certain isomeric, but apparently ineffective, dihydroxybenzophenones, and other tests were carried out using the commercial fungistat, dichlorodihydroxydiphenylmethane.

	Compound	Per Cent by Weight on Cloth	Per Cent Retention of Breaking Strength after Soil Burial for—		
			21 days	42 days	56 days
A	None	----------	0	0	0
B	2,4'-dihydroxy-benzophenone	1	100	---------	97
	Do	2	100	95	100
	Do	3	100	---------	100
C	Monochloro-2,4'-dihydroxybenzophenone	1	97	---------	100
	Do	2	100	97	100
	Do	3	100	100	100
D	Dichloro-2,4'-dihydroxybenzophenone	1	100	100	100
	Do	2	100	93	100
E	2,4'-dihydroxy-4-methylbenzophenone	2	[1] 88	---------	---------
F	2,4'-dihydroxy-5-methylbenzophenone	2	[1] 100	---------	---------
G	60 parts B, 30 parts E, 10 parts F	1	[1] 100	90	---------
	For comparison				
H	2,4'-dihydroxy-5'-methylbenzophenone	2	[1] 13	---------	---------
I	3,4'-dihydroxy-benzophenone	1	<13	0	0
	Do	2	17	0	0
	Do	3	15	0	<13
J	3,3'-dihydroxy-benzophenone	1	25	0	0
	Do	2	57	<14	<14
	Do	3	50	<14	0
K	Dichlorodihydroxy-diphenylmethane	1	100	92	89
	Do	2	100	100	92
	Do	3	99	---------	99

[1] 14 days.

Other samples of the same treated cloths were inoculated with pure cultures of *C. globosum* and *A. niger*, and yet another series was first exposed in a Fadeometer for 23 days and then inoculated with these organisms. Time was allowed for growth of the organism, after inoculation. The following observations were made as to the extent of growth of the test organisms. The samples are identified by the letters appearing at the left in the preceding table.

In the tables to follow, the various degrees of fungistatic effectiveness are indicated by the following conventional symbols:

0=no growth
+=slight growth
++=moderate growth
+++=heavy growth
++++=very heavy growth

Compound	Per Cent	Mildew Readings			
		Not Irradiated		Irradiated 23 Days	
		C. globosum	*A. niger*	*C. globosum*	*A. niger*
A	0	+++	+++	+++	+++
B	1	0	0	0	+++
	2	0	0	0	0
	3	0	0	0	0
C	1	0	0	0	+
	2	0	0	0	0
	3	0	0	0	0
D	1	0	0	0	+
	2	0	0	0	0
E	2	0	0	0	0
F	2	0	0	0	0
For comparison					
H	3	+++	+++	+++	+++
I	3	+++	+++	+++	+++
J	1	+++	+++	+++	+++
	3	++	++	0	+++
K	1	0	0	+++	+++
	3	0	0	++	++

Example 2

Several of the compounds reported in Example 1 were dissolved in the previously defined water-repellent "binder" and were applied to cotton duck so that the cloth contained 2 per cent each of the anti-fungus agent, the film-forming constituents of the binder, and microcrystalline wax. The treated cloths were buried in moist soil, as before, and a measurement was made to determine the per cent retention of breaking strength

after the various lengths of exposure listed in the following table.

Compound	Per Cent Retention of Breaking Strength after Burial for—			
	14 days	28 days	42 days	56 days
Binder only	0	0	0	0
B	100	83	99	96
C	100	86	100	25
D	100	88	100	65
I	34	26	21	<14
J	65	37	29	0
K	92	99	100	99

It may be concluded that the water-repellent binder exerts no significant influence upon the fungistatic effectiveness of the compounds tested.

Example 3

Practical weathering tests on treated cotton fabrics were carried out for periods of three, six, nine and twelve months, beginning each year in March, in the sub-tropical climate of the coastal plain within a few miles of the Gulf of Mexico in southern Louisiana. The cloth samples were mounted on racks facing south and tilted at an angle of 60° with the ground in an open field. After exposure for the stated periods, an observation was made to determine the extent of any mildew growth, and a measurement was made to determine the per cent loss in breaking strength, an index of the combined extent of rotting and of "tendering" of the cloth due either to weathering action or to the chemical, or both.

Compound	Per Cent Fungistat in Cloth	Binder, Per Cent	Visual Observations for Mold Growth				Per Cent Retention of Breaking Strength after Exposure for—	
			3 Months		6 Months			
			Front	Back	Front	Back	3 Months	6 Months
Control—cloth alone	0	0	++++	++++	+++	++++	76	62
Control—cloth and binder	0	4	0	+	++	+++		66
2,4'-dihydroxybenzophenone	1	4	+	0	++	++	78	51
Do	2	4	0	0	+	0	78	56
Do	3	4	0	0	+	0	75	59
Do	1	0	0	+	++	++	75	50
Do	2	0	0	0	+	0	80	60
Do	3	0	0	0	0	0	84	66
Monochloro-2,4'-dihydroxybenzophenone	1	4	0	0	++	++	73	53
Do	2	4	0	0	+	+	77	48
Do	3	4	0	0	+	0	76	56
Do	1	0	0	0	++	++	76	54
Do	2	0	0	0	+	+	81	63
Do	3	0	0	0	0	0	83	61
Dichloro-2,4'-dihydroxybenzophenone	1	4	0	0	++	+	71	51
Do	2	4	0	0	++	0	71	49
Do	3	4	0	0	+	0	73	57
Do	1	0	0	+	++	+++	78	60
Do	2	0	0	+	++	+++	84	67
Do	3	0	0	0	+	++	83	71
50–50 mixture of 2,4'- and 4,4'-dihydroxybenzophenone	2	4	+	0	++	+	64	45
Do	3	4	+	0	+	+	64	47
Do	4	4	+	0	+	0	64	44
Do	2	0	+	+	++	+++	73	51
Do	3	0	0	0	++	++	71	53
Do	4	0	0	0	++	++	71	51
For comparison								
2,2'-dihydroxybenzophenone	3	4	0	0	+	+	67	44
Do	3	0	+	0	++	++	84	51
3-3'-dihydroxybenzophenone	2	4			++	++		66
3-4'-dihydroxybenzophenone	2	4			+++	+++		63
4-4'-dihydroxyzenzophenone	2	4	+	0	+	+	52	35
Do	3	4	+	+	+	+	52	38
Do	4	4	+	0	+	++	52	31
Do	2	0	+	+	++	+++	76	53
Do	3	0	+	++	++	+++	74	46
Do	4	0	+	++	++	+++	71	49
2-hydroxy-5-chlorobenzophenone	3	4	0	0	++	++	66	49
Do	3	0	0	0	++	+++	89	56
Dihydroxydichlorodiphenylmethane	1	4	+	0	+++	++	76	51
Do	2	4	0	0	+++	+	71	48
Do	3	4	0	0	++	0	55	33
Do	1	0	+	0	+++	++++	67	51
Do	2	0	0	0	++	++	58	38
Do	3	0	0	0	++	+	46	25
Copper naphthenate (1% Cu)	1	4	0	0	0	0	49	23
Do	1	0	0	0	0	0	58	28
Phenyl mercuric chloride	0.2	4	+	+	+++	++	51	37
Do	0.2	0	+	+	++	++	61	32

The same relative order of effectiveness was noted at the end of twelve months.

It is observed from the foregoing data that 2,4'-dihydroxybenzophenone, its 4-methyl and 5-methyl analogs, and its mono- and dichloro-substitution products are at least as effective in controlling mildew formation on cotton cloth as are many of the commercial fungistats recommended for this purpose. It is also observed that the treated cloth of the present invention retains its strength to a much greater extent than does cloth treated with any of the usual fungistats. In many cases the time rate of decline of the tensile strength of the present treated fabric is less than half of that normally encountered with other fungistats. This is indicative of a prolongation of the useful life of the cloth, when treated in accordance with the present invention. It is noted that, with many common fungistats, an increase in the amount of fungistat in the cloth is accompanied by a decrease in the strength of the cloth, but that, in contrast thereto, an increase in the amount of the present protective agents induces no decrease and often is accompanied by a greater retention of tensile strength of the treated fabrics.

The invention has been illustrated with reference to the protection of cotton duck, but is not so limited. The indicated advantages accrue to any cellulosic textile containing the present protective agents, and it is immaterial whether the "textile" is a woven cloth, a thread, a yarn, a rope, or a net, of cotton, linen, jute, hemp, sisal, or other cellulosic fiber.

The agents here employed for the preservation of cellulosic textiles may be used as well to protect other susceptible materials, including paper,

wood veneers, adhesives and sizes from attack by mildew.

I claim:

1. A fibrous cellulosic textile product, the surfaces and fibers of which carry from about 1 to about 5 per cent of a material from the group consisting of 2,4'-dihydroxybenzophenone, the mono- and dichloro-derivatives thereof, the 4-methyl and 5-methyl analogs thereof, and mixtures of said compounds.

2. Cotton cloth, the surfaces and fibers of which carry from about 1 to about 5 per cent of a compound from the group consisting of 2,4'-dihydroxybenzophenone, the mono- and dichloro-derivatives thereof, the 4-methyl and 5-methyl analogs thereof, and mixtures of said compounds.

3. Cotton cloth, the surfaces and fibers of which carry from about 1 to 5 per cent of 2,4'-dihydroxybenzophenone.

4. Cotton cloth, the surfaces and fibers of which carry from about 1 to about 5 per cent of a chlorinated 2,4'-dihydroxybenzophenone consisting principally of the mono- and dichloro-derivatives.

5. Cotton cloth, the surfaces and fibers of which carry from about 1 to about 5 per cent of a mixture of 2,4'-dihydroxybenzophenone and its 4-methyl and 5-methyl analogs.

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REFERENCES CITED

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

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