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FUNGUS-PROOFING COMPOSITION

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This invention relates to a process for the treatment of fibrous materials and more specifically to an improved process and composition whereby textiles and other fibrous cellulosic materials may be rendered highly and permanently resistant to attack by fungus and bacteria.

When cellulosic materials such as fabrics are immersed in a bath containing a fungicidal or bactericidal agent such as a solution of 8-hydroxyquinoline, ortho-phenyl-phenol or chlorophenyl-phenol, and subsequently dried, the fabric will attain some degree of resistance to fungicidal and bactericidal action. However, subsequent wetting or laundering of the fabric thus treated tends to remove the fungicidal or bactericidal agent and thereby to reduce drastically the resistance of the fabric to fungi and bacteria. In order to fix the fungicidal agent on the fabric, it has been proposed to form the metallic salt of the agent within the interstices of the fabric. Since the metallic salts of many of the fungicidal agents such as 8-hydroxyquinoline and the chlorophenols are relatively insoluble in most media for treating fabrics, it has been proposed to employ a method whereby after immersion in a solution of a fungicidal agent of this type, the fabric is drained and subsequently passed through a solution of water-soluble metal salt such as calcium, magnesium or other alkaline earth acetates, zinc, aluminum, copper, cadmium, mercury or other heavy metal acetates or nitrates whereby the metal salt of the fungicidal agent is precipitated on the fabric. This method of fixing the fungicidal agent on the fabric has certain disadvantages. For example, a fabric treated by the two-bath method hereinbefore described and subsequently dried contains soluble salts which leach out when the cloth is subsequently laundered or subjected to weathering conditions, impairing the residual protection against fungus and bacteria. Moreover, the two-bath method requires additional equipment and an increased cost for the application of the treatment. In addition, many of the best-known fungicidal agents embodying heavy metal salts of substances such as oxyquinoline are too insoluble in water and in other liquid media suitable for fabric impregnation to provide adequate concentration of the agent in a single bath for proper treatment of the fabric.

One of the objects of the present invention is to provide a process whereby textiles, cordage, paper, wood and other cellulosic or part cellulosic materials may be impregnated with sufficient amount of relatively insoluble fungicidal agents in a single immersion to render the subsequently dried cellulosic material permanently and effectively resistant to the action of fungus and bacteria.

A further object is to provide a novel fungus and bacteria-proofing composition.

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Another object is to provide a novel fungicidal and bactericidal agent.

Other objects will become apparent from the following description and examples.

The improved fungicide-proofing composition of the present invention comprises a water-in-oil emulsion containing in the oil phase thereof a relatively water-insoluble fungicidal agent, such as copper 8-hydroxyquinoline, a modified alkyd resin having a relatively high ratio of fatty acid residue to phthalic anhydride residue, and a mixture of chlorinated diphenyls. As a further embodiment of the invention, a part or all of the modified alkyd resin may be present in the composition in the form of an ammonium soap.

Suitable fungicidal agents for the purpose of the present invention are copper 8-hydroxyquinoline, copper 5,7-dibromo-8-hydroxyquinoline, copper 5,7-dichloro-8-hydroxyquinoline, 5,7-dibrominated hydroxyquinoline, 5,7-dichloro-8-hydroxyquinoline and copper pentachlorophenate. Other metallic salts may be employed in place of the copper salts, for example, zinc, cadmium, aluminum or calcium salts. The copper salts are much to be preferred, however, since they are by far the most effective from the standpoint of insolubility and permanency when incorporated in the cellulosic material.

Modified alkyd resins suitable for the purpose of the present invention are those which are prepared from fatty oils and fatty acids, such as linseed oil and linseed oil fatty acids, phthalic anhydride and glycerol. Other fatty oils or acids or mixtures thereof, such as a mixture of linseed oil, dehydrated castor oil and linseed oil fatty acids, a mixture of linseed oil and dehydrated castor oil, or a mixture of linseed oil, soya bean oil and soya bean fatty acids, may be employed in the preparation of the resin. Likewise, other polyhydroxy alcohols, such as pentaerythritol, may be employed in place of glycerol. Maleic or fumaric acids may be employed in place of part or all of the phthalic anhydride. It is understood that these substitutions give rise in alterations to the properties of the resins. However, as explained hereinbefore, those resins which are soluble in mineral spirits and which emulsify mineral spirits are the resins contemplated as components of the composition of the present invention. Likewise, ammonium soaps formed by the addition of ammonia to the modified alkyd resins which fall in this category are also contemplated as components of the composition of the present invention. Suitable modified alkyd resins for the purpose of the present invention are those which contain, for example, from 20–40% by weight of phthalic anhydride residue and which are soluble in mineral spirits and serve as emulsifying agents for mineral spirits.

The chlorinated diphenyls suitable as compo-

nents of the composition of this invention are the mixtures of chlorinated diphenyls obtained by chlorinating diphenyl and which mixtures contain from 20–68% of chlorine. Also included are those chlorinated diphenyls which contain in addition various proportions of chlorinated terphenyls. Some of these mixtures are liquid at room temperature and others may be melted, for example, on heated metal rolls to become liquids at temperatures ranging from 30–140° C.

The composition of the present invention may also contain a flame-retarding agent such as antimony pentoxide in amounts ranging from 2–10% of the weight of the composition, in which event the quantity of chlorinated diphenyls may be increased to an amount in the range of 10–25% of the weight of the composition.

The emulsion composition of the present invention may contain any desired proportions of water phase to oil phase in the range of 1:4 to 4:1. A desirable proportion is that of 50 parts of water and 50 parts of oil. The quantity of modified alkyd resin employed in the composition may be varied over a wide range, for example, from 2% or less to 10% or more, based on the emulsion composition. The quantity of ammonia employed to form a soap with the residual acidic constituents of the modified alkyd resins depends on the extent to which soap formation is desired and may range from part to total consumption of the acidity available in the resin for this purpose. The quantity of chlorinated diphenyl mixture which may be employed in the composition may be varied over a wide range, for example, from 3% or less to 25% or more. The quantity of fungicidal agent, such as copper 8-hydroxyquinoline, may be varied over a wide range, depending upon the particular fungicidal agent selected, the amount of the agent which is absorbed from the composition in the treatment of a particular type of cellulosic substance to be treated and the amount of the fungicidal agent which is desired on the cellulosic substance after the treatment. Desirable quantities of fungicidal agent in general of the composition of the present invention may range from ½% or less to 5% or more.

In employing the fungus-proofing composition of the present invention, cellulosic materials, such as textiles, cordage, paper or wood, are immersed in the composition to impregnate the cellulosic substance and then are dried. The impregnation may be accomplished in any desired manner, for example, by immersion in a vessel containing the composition, with or without the aid of squeeze rolls, either as a continuous operation or as a batch process. For some types of application, the composition may be brushed on the fabric, paper or wood article. Likewise, the drying operation may be accomplished in any desired manner, for example, by exposing the respective surfaces of the treated article simultaneously or successively to air streams which may be at room temperature or at higher temperatures below the charring point of the cellulosic materials. Textiles, cordage, paper and wood treated with the composition of the present invention are found to be highly resistant to the action of fungus and bacteria. Moreover, the resistance is characterized by a high degree of permanency even when the treated cellulosic material is subjected to severe weathering or, in the application to textiles and cordage, to successive launderings.

The fungicidal and bactericidal composition of the present invention may be formed in any manner desired. A preferred method is that comprising blending the fungicidal agent, the modified alkyd resin and the chlorinated diphenyl on metal rolls, with the application of heat if necessary, until a smooth fluid paste is formed. The paste is then dispersed in mineral spirits. If the ammonium soap of the alkyd resin is to be formed, the necessary quantity of ammonia may be added to the blend on the rolls, or to the mineral spirits dispersion of the blend. Water is then added to the mixture and the mixture is agitated to form the emulsion, for example, by passing the mixture through a colloid mill. While the permanency of many of the fungicidal agents of the type hereinbefore described is substantially enhanced by application to the cellulosic material by means of the composition of the present invention, very outstanding results in this respect are obtained when the fungicidal agent in the composition is 5,7-dibromo-8-hydroxyquinoline, copper 5,7-dibromo-8-hydroxyquinoline, 5,7-dichloro-8-hydroxyquinoline, copper dichloro-8-hydroxyquinoline or copper 8-hydroxyquinoline. These substances in particular are representative of the various fungicidal and bactericidal agents of the type contemplated in the composition of the present invention.

While the alkyd resin in the composition of the present invention aids in the placement and retention of the fungicidal agent within the interstices of the cellulosic material, it also imparts to the treated cellulosic material a certain degree of water repellency. However, it is desirable to treat the cellulosic substance further with a water repellent in order to attain a high degree of water repellency in the fabric treated with the fungicidal composition. It is one of the novel features of the present invention that the composition of the present invention is compatible with a wide variety of water-proofing emulsion compositions and water-proofing components. There water-proofing compositions and components may be acidic, neutral or alkaline in character. Moreover, the application to cellulosic materials of the composition of the present invention containing a water-repellent emulsion has been found to enhance the degree of permanency of resistance of the cellulosic material to the action of molds and particularly when the treated cellulosic materials are subjected to soil burial tests.

Typical water-repellent compositions which may be incorporated in the composition of the present invention are those which comprise aqueous suspensions of waxes and soaps, resinous hydrocarbon-soluble condensation products, such as dimethylol urea resins, dimethylol urea ether resins, tetramethylol melamine resins, tetramethylol melamine ether resins, either alone or in the presence of higher fatty acid soaps, fatty acid amine soaps, fatty acid amides and N-acylated alkylene polyamides. The quantity of water-repellent composition or of water-repellent components to be added to the composition of the present invention is determined on the basis of the amount of water-repellent component of the composition desired on the treated material, the percentage pick-up of such water-repellent components by the material to be treated, and the amount of water-repellent components desired on a particular cellulosic material after the treatment. When the composition of the present invention contains a water repellent, the cellulosic material after treatment is heated in order to set the water-repellent components on the cellulosic material. Temperatures in the range of 120–170° C. have been found suitable for this

purpose. The time of treating may be relatively short, for example, from 5–15 minutes at the desired temperature.

The following examples serve to illustrate the process of the present invention. This invention, however, is not limited to these examples, but contemplated various embodiments and modifications of the invention as described and illustrated herein.

Example I

The following composition was prepared:

	Pounds
Copper 8-hydroxyquinoline	9.5
Modified alkyd resin	11.4
Chlorinated diphenyls	19.0
Ammonia	5.7
Mineral spirits	163.4
Water	171.0

The modified alkyd resin employed in the formulation of the present example was a linseed oil fatty acid - phthalic anhydride - glycerol resin containing approximately 60% of linseed oil fatty acid residue, approximately 25% of phthalic anhydride residue and the balance, glycerine. The chlorinated diphenyls employed were composed of a mixture of chlorinated diphenyls containing approximately 54% of chlorine.

The copper 8-hydroxyquinoline, modified alkyd resin and chlorinated diphenyls were mixed on heated metal rolls at a temperature of approximately 140° C. until the components were thoroughly blended. The ammonia was then incorporated in the mixture and allowed to react with the alkyd resin to form an ammonium soap. The resulting mixture was then dispersed in mineral spirits. The water was added and the entire mixture was passed through a colloid mill to form an emulsion.

A cotton duck fabric was impregnated with the emulsion in a vessel equipped with squeeze rolls and known in the art as a padder. Following the impregnation, the fabric was air dried. A portion of the treated fabric was laundered for 40 minutes at 100° C. with hot soap water, rinsed four times with water and air dried. The laundering procedure thus employed was that known as the standard cotton wash test of the American Association of Textile Chemists and Colorists. Other portions of the treated fabric were leached in running water for periods of 200 hours or more. The treated, unwashed and unleached fabric was found on analysis to contain 1.25% copper 8-hydroxyquinoline; the treated and washed fabric was found to contain 1%, and the fabric treated and leached 200 hours was found to contain 1.05%.

Example II

To 380 pounds of the composition of Example I was added with stirring 80 pounds of a water-repellent emulsion having the following composition:

	Pounds
Oleic acid	10
Ammonia (28%)	8.4
Water	60.6
Paraffin (boiling range 130–133° C.)	10.0
Methylol stearamide	20.0
Butyl ether of tetramethylol melamine	41.0

The water-repellent emulsion was thoroughly mixed with the composition of Example I. A

cotton duck fabric was immersed in the resulting composition, drained, air dried and subsequently heated at 150° C. for 5–10 minutes. The resulting fabric was found on analysis to contain 0.92% of copper 8-hydroxyquinoline. The fabric was also found to possess a high degree of water repellency.

Example III

The following composition was prepared:

	Pounds
Copper 5,7-dibromo-8-hydroxyquinoline	2.5
Modified alkyd resin	3.0
Chlorinated diphenyl mixture (48%)	5.0
Ammonium hydroxide (28%)	1.5
Aluminum di-stearate	2.5
Paraffin wax (130–133° C. boiling range)	3.3
10% solution of ethyl cellulose (20 centipoise viscosity) in toluene	1.0
Urea formaldehyde butyl ether resins	4.1
Mineral spirits	43.0
Water	45.0

The components, with the exception of the mineral spirits and water, were blended on metal rolls. The resulting blend was dispersed in mineral spirits. The water was subsequently added, and the mixture was emulsified by passing it through a colloid mill. Fabrics immersed in the composition, drained, air dried and subsequently heated at 150° C. for 15 minutes were found to have excellent water repellency. Moreover, the fabric was found to contain 1.0% copper 5,7-dibromo-hydroxyquinoline.

Copper 5,7-dibromo-8-hydroxyquinoline may be prepared by adding an aqueous solution of copper acetate to an aqueous solution containing approximately 10% of 5,7-dibromo-8-hydroxyquinoline and approximately 10% of hydrochloric acid. A voluminous yellow precipitate forms. The mixture is desirably neutralized with ammonia and filtered. The precipitate of copper 5,7-dibromo-8-hydroxyquinoline is washed with water and dried. Copper 5,7-dichloro-8-hydroxyquinoline may be prepared in a similar manner, substituting 5,7 - dichloro - 8 - hydroxyquinoline for the 5,7-dibromo-8-hydroxyquinoline in the aforesaid procedure.

In place of copper 5,7-dibromo-8-hydroxyquinoline in the composition of the present invention, 2.5 pounds of 5,7-dibromo-8-hydroxyquinoline, 5,7-dichloro-8-hydroxyquinoline and copper 5,7 - dichloro - 8 - hydroxyquinoline were substituted. Fabrics, cordage, paper and wood treated with the resulting compositions according to the method of the present example were found to possess excellent water repellency. Moreover, the treated specimens were found to contain substantially 1% of the fungicidal agent, and the protection against the attack of molds was found to be substantially permanent.

Example IV

	Pounds
Copper pentachlorophenate	2.5
Modified alkyd resin	3.0
Chlorinated diphenyl mixture (62% chlorine)	5.0
Ammonium hydroxide (28%)	1.5
Mineral spirits	43.0
Water	45.0

The components, with the exception of the mineral spirits and water, were blended together by the method of Example I. The blend was added to the mineral spirits and dispersed

therein. Subsequently the water was added, and the mixture was passed through a colloid mill. Cotton duck fabrics, section of lumber for ammunition boxes, cordage and paper were treated with the composition of this example by immersion in a vessel containing the composition, excess material was drained from the specimen, and the specimen was allowed to air dry. The specimens upon analysis were found to contain sufficient of the fungicidal agent to protect the specimen against the action of molds. Moreover, the degree of permanency of the protection was found to be very satisfactory. In place of copper pentachlorophenate, any other substantially water-insoluble salt of pentachlorophenol may be employed, for example, the calcium, barium, lead, zinc, aluminum, mercury or cadmium salts of pentachlorophenol. These pentachlorophenates are distinguished from the halogenated 8-hydroxyquinoline derivatives and copper salts thereof, and also copper 8-hydroxyquinoline in that the pentachlorophenates appear to produce fungicidal action by the hydrolysis of the salts in the presence of moisture, whereas the halogenated 8-hydroxyquinoline derivatives and the copper salts thereof appear to produce fungicidal action by mere contact of the agent with the mold organisms. It is of interest also that the copper salts of the halogenated and unhalogenated 8-hydroxyquinoline appear from experimental observations to be the only metal salts of these substances which inhibit mold growth completely when applied in the composition of the present invention.

Portions of specimens of cellulosic substances, including wood, paper, textiles and cordage treated with the compositions described in Examples I to IV were exposed to the action of various molds. The treated textile specimens were tested against the organisms *Chaetonium globosum, Aspergillis niger,* Penicillium sp., Metarrhizium sp. by the method described in the Corps of Engineers, U. S. Army, Tentative Specification No. T1452–A, entitled "Processing fabrics, cordage and threads for mildew-proofing." dated January 15, 1943, paragraphs F 3–*a* (3) to 3–*a* (8), inclusive. There was no evidence of fungus growth on the treated specimens. Untreated specimens exposed under similar conditions were heavily attacked by the various species of fungus. Other portions of the textile and cordage specimen were laundered for 40 minutes in soap water at 100° C., rinsed free of soap, dried and exposed to the same molds. There was no evidence of fungus growth on the laundered and exposed specimens. Other portions of the textile and cordage specimens were leached in running water for 200 hours, dried and exposed to the molds. Additional specimens were buried in moist soil rich in acidic humus for a period of several weeks. Upon inspection, the exposed, treated specimens were found to be substantially free of fungus growth.

I claim:

1. The composition described in claim 3 in which the modified alkyd resin is present in part at least as the ammonium soap thereof.

2. The composition described in claim 4 in which the modified alkyd resin is present in part at least as the ammonium soap thereof.

3. A fungus-proofing composition for the treatment of cellulosic substances comprising a water-in-oil emulsion in which the ratio of water phase to oil phase is in the range of 1:4 to 4:1, said emulsion having an oil phase comprising ½–5% of a halogenated 8-hydroxyquinoline derivative selected from the group consisting of 5,7-dibromo-8-hydroxyquinoline, 5,7-dichloro-8-hydroxyquinoline and copper salts thereof, 2–10% of a modified alkyd resin made from a polyhydroxy alcohol, phthalic anhydride and a modifying substance selected from the group consisting of fatty oils and fatty oil acids, said resin containing 20–40% of phthalic radical calculated as phthalic anhydride, said resin being soluble in mineral spirits, 3–25% of a chlorinated diphenyl mixture containing 20–68% of chlorine, and mineral spirits.

4. A fungus-proofing and water-proofing composition for the treatment of cellulosic substances comprising (1) a water-in-oil emulsion in which the ratio of water phase to oil phase is in the range of 1:4 to 4:1, said emulsion having an oil phase comprising ½–5% of a halogenated 8-hydroxyquinoline derivative selected from the group consisting of 5,7-dibromo-8-hydroxyquinoline, 5 7-dichloro-8-hydroxyquinoline and the copper salts thereof, 2–10% of a modified alkyd resin made from a polyhydroxy alcohol and a modifying substance selected from the group consisting of fatty oil and fatty oil acids, said resin containing 20–40% of phthalic radical calculated as phthalic anhydride, said resin being soluble in mineral spirits, 3–25% of a chlorinated diphenyl mixture containing 20–68% of chlorine and mineral spirits and (2) a resinous hydrocarbon-soluble condensation product selected from the group consisting of dimethylol urea resins, dimethylol urea ether resins, tetramethylol melamine resins and tetramethylol melamine ether resins.

5. A fungus-proofing composition for the treatment of cellulosic substances comprising an oil-in-water emulsion, in which the ratio of water phase to oil phase is in the range of 1:4 to 4:1, said emulsion having an oil phase comprising ½–5% of 5,7 dibromo-8-hydroxyquinoline, 2–10% of a modified alkyd resin made from a polyhydroxy alcohol, phthalic anhydride and a modifying substance selected from the group consisting of fatty oils and fatty oil acids, said resin containing 20–40% of phthalic radical calculated as phthalic anhydride, said resin being soluble in mineral spirits, 3–25% of chlorinated diphenyl mixture containing 20–68% of chlorine and mineral spirits.

6. A fungus-proofing composition for the treatment of cellulosic substances comprising an oil-in-water emulsion in which the ratio of water phase to oil phase is in the range of 1:4 to 4:1, said emulsion having an oil phase comprising ½–5% of copper, 5.7-dibromo-8-hydroxyquinoline, 2–10% of a modified alkyd resin made from a polyhyroxy alcohol, phthalic anhydride and a modifying substance selected from the group consisting of fatty oils and fatty oil acids, said resin being soluble in mineral spirits, said resin containing 3–25% of a chlorinated diphenyl mixture containing 20–68% of chlorine, and mineral spirits.

7. A fungus-proofing composition for the treatment of celulosic substances comprising an oil-in-water emulsion in which the ratio of water phase to oil phase is in the range of 1:4 to 4:1, said emulsion having an oil phase comprising ½–5% of copper, 5,7-dichloro-8-hydroxyquinoline, 2–10% of a modified alkyd resin made from a polyhydroxy alcohol, phthalic anhydride and a modifying substance selected from the group consisting of fatty oils and fatty oil acids, said resin containing 20–40% of a phthalic radical calculated as phthalic anhydride, said resin being soluble in mineral spirits, 3–25% of a chlorinated

diphenyl mixture containing 20–68% of chlorine, and mineral spirits.

8. A fungus-proofing and water-proofing composition for the treatment of cellulosic substances comprising (1) a water-in-oil emulsion in which the ratio of water phase to oil phase is in the range of 1:4 to 4:1, said emulsion having an oil phase comprising ½–5% of a halogenated 8-hydroxyquinoline derivative selected from the group consisting of 5,7-dichloro-8-hydroxyquinoline, 2–10% of a modified alkyd resin made from a polyhydroxy alcohol, phthalic anhydride and a modifying substance selected from the group consisting of fatty oils and fatty oil acids, said resin containing 20–40% of a phthalic radical calculated as phthalic anhydride, said resin being soluble in mineral spirits, 3–25% of a chlorinated diphenyl mixture containing 20–68% of chlorine and mineral spirits, and (2) a water-repellent emulsion containing as the active water-repellent component thereof a resinous hydrocarbon-soluble condensation product selected from the group consisting of dimethylol urea resins, dimethylol urea ether resins, tetramethylol melamine resins and tetramethylol melamine ether resins.

9. A fungus-proofing and water-proofing composition for the treatment of cellulosic substances comprising (1) a water-in-oil emulsion in which the ratio of water phase to oil phase is in the range of 1:4 to 4:1, said emulsion having an oil phase comprising ½–5% of a halogenated 8-hydroxyquinoline derivative selected from the group consisting of 5,7-dichloro-8-hydroxyquinoline, 2–10% of a modified alkyd resin made from a polyhydroxy alcohol, phthalic anhydride and a modifying substance selected from the group consisting of fatty oils and fatty oil acids, said resin containing 20–40% of phthalic radical calculated as phthalic anhydride, said resin being soluble in mineral spirits, 3–25% of a chlorinated diphenyl mixture containing 20–68% of chlorine and mineral spirits, and (2) a water-repellent emulsion containing as the active water-repellent component thereof a resinous hydrocarbon-soluble condensation product selected from the group consisting of dimethylol urea resins, dimethylol urea ether resins, tetramethylol melamine resins and tetramethylol melamine ether resins, said water-repellent emulsion containing in addition thereto a water repellent agent selected from the group consisting of waxes and soaps.

10. As an article of manufacture, a textile containing within its interstices a composition comprising a halogenated 8-hydroxyquinoline derivative selected from the group consisting of 5,7-dibromo-8-hydroxyquinoline, 5,7-dichloro-8-hydroxyquinoline and the copper salts thereof, a modified alkyd resin made from a polyhydroxy alcohol, phthalic anhydride and modifying substance selected from the group consisting of fatty oils and fatty oil acids, said resin containing 20–40% of phthalic radical calculated as phthalic anhydride, said resin being soluble in mineral spirits, and a chlorinated diphenyl mixture containing 20–68% of chlorine, said composition having been applied to said textile in the form of a water-in-oil emulsion in which the oil phase contained ½–5% of said halogenated 8-hydroxyquinoline derivative, 2–10% of said modified alkyd resin, 3–25% of said chlorinated diphenyl mixture and mineral spirits, and said mineral spirits and water having been removed subsequent to the application of said emulsion to said textile.

11. As an article of manufacture, a textile containing within its interstices a composition comprising a halogenated 8-hydroxyquinoline derivative selected from the group consisting of 5,7-dibromo-8-hydroxyquinoline, 5,7-dichloro-8-hydroxyquinoline and the copper salts thereof, a modified alkyd resin made from a polyhydroxy alcohol, phthalic anhydride and a modifying substance selected from the group consisting of fatty oils and fatty oil acids, said resin containing 20–40% of phthalic radical calculated as phthalic anhydride, said resin being soluble in mineral spirits, a chlorinated diphenyl mixture containing from 20–68% of chlorine and a water repellent resin hydrocarbon-soluble condensation product selected from the group consisting of dimethylol urea resins, dimethylol urea ether resins, tetramethylol melamine resins, tetramethylol melamine ether resins, said composition having been applied to said textile in the form of a water-in-oil emulsion in which the oil phase contained ½–5% of said halogenated 8-hydroxyquinoline derivative, 2–10% of said modified alkyd resin, 3–25% of said chlorinated diphenyl mixture and mineral spirits and said mineral spirits and water having been removed subsequent to the application of said emulsion to said textile.

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