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**MILDEWCIDE AND FLAMEPROOFING COMPOSITION AND PRODUCTS PRODUCED THEREFROM**

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This invention relates to a mildewcide containing composition, a flame retardant containing composition utilizing the mildewcide of the former composition and to products incorporating said mildewcide. More particularly, the invention relates to the employment of copper antimonate as a mildewcide, to its use in flameproofing compositions and to mildewproofed and flameproofed compositions incorporating said copper antimonate.

The term "mildewcide" as used herein has reference to a composition or material which prevents or retards the formation of mildew.

It has been found that copper antimonate either in the anhydrous or hydrated form is an effective mildewcide and that it may be employed in combination with halogenated organic compounds as a flame retardant. Copending application of Anthony Giordano bearing Serial No. 550,760, filed December 2, 1955, contains disclosure relating to the preparation of copper antimonate particularly suitable for the purpose of the herein described invention.

It is apparent that huge quantities of fibrous cellulosic materials such as textile fabrics and wood products become exposed to destruction by fire and rotting annually. A great variety of compounds have been tried and used as agents for protecting the cellulosic materials. Yet, in spite of many advances made along these lines during the past few years, nothing that can be regarded as an ideal universal solution to the problem has been developed.

For imparting fire resistance to materials the various treatments are generally classified as either temporary or durable. For the temporary treatments inorganic salts have usually been incorporated in the fabric as, for example, by impregnation and/or by coating techniques well known in the art. These treatments prove disadvantageous in that usually the salts are water soluble and afford only a temporary remedy. For durable treatments relative insolubility and good adhesive properties of the coating compositions are of importance, and to obtain these latter characteristics, combinations of organic and inorganic materials are normally used. One of the objects of the invention is to provide flame retardant compositions which impart relatively permanent flame retardant properties to fibrous cellulosic materials.

It will be appreciated that the term "fire resistant" is a broad one suggesting the total inhibition of burning or combustion. Actually the act of burning embraces two separate phases: namely, flaming which represents the combustion of gaseous products, and glowing which represents the incandescent flameless combustion of solid matter. Accordingly, in rendering a material fire resistant separate chemical agents are required to inhibit each phase of combustion. Those agents which inhibit the formation and propagation of flame are known as "flame retardants." The agents that inhibit flameless combustion are known as "glow retardants." A fire resistant material, therefore, includes both a flame and a glow retardant or a compound which reacts simultaneously in both respects. The subject compound of the invention is

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a flame retardant when employed in combination with halogenated organic compounds and it is contemplated that the compositions of the herein described invention may or may not have glow retardant compounds incorporated therewith.

Since most fibrous cellulosic materials are not only combustible but also subject to the action of micro-organisms which cause mildew and the ultimate destruction by rotting of the material, it is frequently customary and desirable to incorporate a mildewcide in the cellulosic material as well as to incorporate fire resistant compounds therein. We are unaware of any application wherein a fire retardant or necessary ingredient thereof also has mildewcidal properties, and accordingly one of the principal advantages of the invention described herein is based upon the fact that copper antimonate may not only be employed in fire retardant compositions as an essential ingredient thereof but that simultaneously it acts as a mildewcide in the material treated thereby.

Probably the most universally employed composition for imparting fire resistance to cellulosic materials is a composition employing in combination a metal oxide, a glow retardant and a halogenated organic compound. The halogenated compound as, for example, chlorinated paraffin functions under temperatures at or near the combustion temperature of the cellulosic material to supply chlorine, gaseous hydrogen chloride or other gaseous products which act to smother any flame developed by exclusion of oxygen. On the other hand, the metallic oxides function to stabilize the chlorinated paraffin and retard decomposition by the action of normal heat and light, and furthermore to catalyze the release of the chlorine and/or hydrogen chloride or other gaseous products under combustion conditions. The chlorinated paraffin has an additional beneficial function in that it tends to render the cellulosic material water resistant. It functions to hold the metallic oxide in suspension and in some respects acts as a binder for the metallic oxides.

Although the metallic oxide and chlorinated paraffin combinations have met with wide success, they nevertheless do not render the cellulosic material, for example, a cotton textile, mildewproof. To accomplish this object it is necessary to include an added impregnant as, for example, copper naphthenate, a compound which is a widely employed mildewcide in the textile industry. The copper naphthenate is an excellent mildewcide but it has certain limitations in that it imparts an undesirable odor to the fabric to which it has been applied. Furthermore, the use of copper naphthenate as a mildewcide is limited generally as, for example, in the textile industry to textiles which have dark colors since the copper naphthenate has a strong green color which is imparted to the textile finish. Still another disadvantage in utilizing copper naphthenate is that per se it is a combustible material. Consequently, to flameproof a material containing copper naphthenate the amount of flameproofing agent incorporated in the textile must be increased to compensate for the combustible nature of the copper naphthenate.

Among the various fibrous cellulosic materials which are contemplated for treatment with the compositions of the invention described herein are wood products, papers and textiles, as well as other inflammable cellulosic materials. Thus the copper antimonate containing compositions may be employed to mildewproof and/or flameproof ordinary lumber employed for construction purposes, shingles, fence posts, piling and other products containing wood, such as veneers, etc. Similarly, the compositions of the invention may be employed for rendering papers and textiles such as cotton fabrics, tarpaulins, tentage and other cellulosic materials mildewproof and/or flame resistant. It will be apparent that the materials set forth are given by way of example and

are not to be construed as limiting except insofar as claimed.

The halogenated organic compounds that are employed in combination with copper antimonate for imparting flame retardant properties to cellulosic materials are those halogenated organic compounds known in the art for their flame retardant properties when employed in combination with metallic oxides. Usually the halogen is chlorine although fluorine and bromine have performed beneficially in some cases. Specific examples of the halogenated organic compounds and those which are generally preferred according to the invention, are the chlorinated paraffins, chlorinated vinyl resins and chlorinated rubbers. Preferably the halogenated organic compounds contain from about 40% to about 80% chlorine or higher, although halogenated compounds having a lesser amount of chlorine may be used with less effective results. For example, a chlorinated organic compound having a 30% chlorine content may be employed. Still other halogenated organic materials which may be employed to impart flameproofing properties to cellulosic materials in combination with copper antimonate are the chlorinated vegetable and mineral oils, such as the chlorinated petroleum oils or highly chlorinated tung oil, castor oil, soyabean oil, or in some instances chlorinated fish oil. Still others include halogenated cottonseed oil, coconut oil, bean oil, peanut oil, linseed oil, asphalt and asphalt oils, as well as the chlorinated naphthalenes and chlorinated diphenyls. The essential feature of the chlorinated material is that it release chlorine, hydrogen chloride or other gaseous products at temperatures conducive to combustion.

As in those applications wherein a flame retardant is applied to a cellulosic material, the flame retardant combination of copper antimonate and halogenated organic compound may be applied by impregnating or coating means and by such conventional means as brushing, spraying or dipping, employing a suitable vehicle therefor.

When copper antimonate is being employed merely for its mildewcidal properties, it is preferably dispersed in a suitable vehicle which exhibits adhesive properties towards the cellulosic fibrous material being coated or impregnated therewith. Chlorinated paraffin or other halogenated organic compounds may be used as suitable vehicles for the mildewcide although other vehicles obviously may be employed to an advantage where the simultaneous impartment of flame retardant properties to the impregnated or coated material is unnecessary or undesirable. For example, other vehicles in which copper antimonate may be dispersed are vegetable oils, such as linseed oil, synthetic resin solutions such as the alkyl resins, synthetic gum solutions such as carboxy methyl cellulose, and most other vehicles employed in the paint industry. In general, for the coating or impregnating compound, the vehicle is employed with a suitable solvent whereby the vehicle is maintained in a dissolved state and the contained copper antimonate is maintained in a dispersed state. Suitable solvents for chlorinated paraffins may be aromatic, aliphatic and terpene hydrocarbons, chlorinated aliphatic and aromatic hydrocarbons, ketones, esters, and vegetable and mineral oils.

Because of its mildewcidal properties it will be apparent that any amount of copper antimonate contained by the fibrous cellulosic material in the form of a coating thereon or an impregnant therein will function to minimize in some respects the microbial decomposition of the material. In general, however, it has been found advisable in most applications to have in excess of about 1% contained copper antimonate (equivalent to about .16% elemental copper) based on the weight of the cellulosic material to impart commercially acceptable mildewcidal properties thereto. Since cellulosic fabrics are weakened or degraded by the action of sunlight and copper compounds, especially the salts thereof which enhance photochemical activity through catalytic actions, it is usually desirable to maintain the copper antimonate

add-on less than about 13%. It will be apparent, however, that greater quantities of copper antimonate may be incorporated with the cellulosic materials where such photochemical activity is not detrimental. Preferably, as for example, when the copper antimonate is employed to mildewproof cotton fabrics the amount of contained copper antimonate should be in excess of about 8% by weight of the cellulosic fabric, however. The percentages of copper antimonate heretofore given are based on copper antimonate as employed in the anhydrous form having the empirical formula  $\text{Cu}(\text{Sb}_2\text{O}_3)_2$ . Obviously, correspondingly greater amounts are employed when the hydrated forms are utilized.

The following examples are set forth to illustrate the mildewcidal properties of copper antimonate, while at the same time comparing such properties with those of copper naphthenate. To evaluate the mildew resistant properties of copper antimonate an improvised soil burial test, considered to be the most severe test of microbiological activity, was used. For this test, specimens of treated fabric were buried in fertile soil for various periods of time to induce rotting thereof through the formation of mildew. To verify the microbiological activity of the soil bed and to provide a basic reference standard, control specimens of untreated cotton duck were buried alongside the treated samples. Still other control specimens were impregnated with copper naphthenate in order to provide a comparison of the effectiveness of copper antimonate therewith. The test fabrics for these examples consisted of No. 8 cotton duck strips two inches wide by twelve and one-half inches long. Untreated samples were almost completely decomposed in the fertile soil within ten days after burial therein.

For these specific examples the copper content of the impregnated specimen is set forth as the elemental copper equivalent of the particular copper containing mildewcide being considered. This reporting method enables ready comparison of copper naphthenate and copper antimonate for their mildewcidal properties.

#### Example 1

A test strip was impregnated with copper naphthenate previously dissolved in mineral spirits. The copper equivalent of the copper naphthenate impregnated specimen amounted to 1% copper on the basis of the weight of the untreated fabric. Another strip was impregnated with copper naphthenate previously dissolved in mineral spirits and the copper equivalent of the copper naphthenate impregnated specimen was 1.5% copper. For the strip having a 1% copper add-on, it was found that no mildew formations were present at the end of thirty days. A slight amount of mildew formation was evident on the strip at the end of forty days however. For the strip having a 1.5% copper add-on there was no mildew formation at the end of forty days.

To test the effect of copper antimonate as a mildew retardant, three strips of cotton duck were impregnated with copper antimonate utilizing chlorinated paraffin as a vehicle and utilizing an urea formaldehyde resin to prevent crocking. The relative proportions of the contained ingredients in the fabrics after impregnation were as follows:

|                                                                                                | Parts |
|------------------------------------------------------------------------------------------------|-------|
| Hydrated copper antimonate $\text{Cu}(\text{Sb}_2\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$ ---- | 10.5  |
| 40% chlorinated paraffin (Chlorowax 40) -----                                                  | 10.4  |
| 70% chlorinated paraffin (Chlorowax 70) -----                                                  | 20.8  |
| Urea formaldehyde resin (as solid) -----                                                       | 8.3   |

The above constituents in their indicated proportions were dispersed in varying amounts of a solvent so as to obtain varying amounts of add-on. The solvent comprised a mixture of one part of carbon tetrachloride to two parts of xylene.

The three test strips were then impregnated with the copper antimonate containing compositions so that one strip contained 1% copper, the second strip contained

1.55% copper, and the third strip contained 2% copper, all based on the weight of untreated fabric. The burial tests were such that the specimen having a 1% copper content had no mildew formations after being buried for twenty days, only a slight amount of mildew formation after thirty days burial, and a considerable amount of mildew formation after forty days. With regard to the second specimen having a 1.55% copper content, no mildew formations were noticed after thirty days burial, although there were appreciable amounts thereof after forty days burial. Concerning the third specimen having a 2% copper content, it was found that there were no mildew formations after forty days burial.

#### Example II

To appraise more closely the individual copper antimonate by eliminating possible contributing effects from chlorinated paraffin, 23.75 parts of hydrated copper antimonate ( $\text{Cu}(\text{SbO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) were dispersed in 76.25 parts of a 20% urea formaldehyde solution in xylene. Then, cotton strips were dipped therein so as to obtain dry add-on equivalent to 2% as copper based on the untreated fabric. It was found that no mildew developed on these specimens after forty days burial.

#### Example III

To further evaluate the mildewcidal properties of copper antimonate by eliminating both chlorinated paraffin and the binding resin, hydrated copper antimonate was dispersed in 1% water solutions of carboxymethyl-cellulose containing .8% of sulfonated castor oil as a wetting agent. Two cotton duck test specimens were impregnated to obtain copper antimonate contents respectively of 1.4 and 1.5% equivalent copper based on the weight of the fabric. It was found that none of the specimens showed mildew formations over a forty day burial period.

Copper antimonate per se does not exhibit flame retarding properties other than that retardancy normally attributed to sheer dilution of cellulosic materials with non-combustible materials. Accordingly, it is essential that the copper antimonate be combined with a halogenated organic compound of the types heretofore set forth in order to function as a flame retardant. Thus, the copper antimonate functions in the same manner as the metallic oxides heretofore used in combinations with chlorinated paraffins, chlorinated vinyl resins and chlorinated rubbers. Additionally, of course, it functions as a mildewcide.

A composition for impregnating or coating cellulosic materials for flameproofing purposes utilizing a combination of copper antimonate and a halogenated organic compound will in the broadest sense of the invention merely comprise a halogenated organic compound and copper antimonate wherein the halogenated organic compound is dissolved in a suitable solvent and wherein the copper antimonate is suitably dispersed therein. Suitable solvents which will perform this function may be such solvents as mineral spirits, coal tar naphthas, carbon tetrachloride, xylene, ethyl acetate, the aromatic sulfonates, as well as other well known solvents. Other suitable solvents will be apparent to those skilled in the art. It will also be apparent that although the composition for impregnating or coating fibrous cellulosic materials in its broadest sense merely comprises the halogenated organic compound, copper antimonate and a suitable solvent and/or dispersant, that the invention contemplates the use of suitable pigments, plasticizers and other modifying agents when appropriate. Thus, the composition may contain a suitable glow retardant, such as zinc borate, and an acid acceptor, such as calcium carbonate. Similarly, where it is desirable to employ pigments, etc., compositions containing the basic ingredients of the novel composition may readily be formulated therewith. Similarly, although the invention is primarily directed to mildewproofing and/or flameproofing cellulosic materials, it will be apparent that the novel impregnating or coating

compositions may also be employed in other applications as, for example, for retarding or minimizing the growth of fungi, etc. Another use of the novel coating composition is in decorative paints as well as in paints or compositions used on the bottom of ships for the protection thereof from marine crustaceans.

Concerning the novel coating or impregnating compositions for flameproofing applications, it is generally found that the most advantageous flame retardant properties are brought out when the ratio of the contained halogen content of the halogenated organic compounds to the contained copper antimonate content is from about .4 to about 1.8. Although flame retardancy can be effected by employing an amount of chlorinated organic compound and an amount of copper antimonate which would give a ratio of contained chlorine to contained copper antimonate lower or higher than the preferred ratios, it has generally been found that it is undesirable to do so. For example, as the ratio of chlorinated paraffin is increased as compared to the copper antimonate, the total add-on to the fabric to obtain a particular degree of fire retardancy similarly increases. For example, it has been found for an equivalent degree of flame retardancy for No. 8 cotton duck that the total add-on of all solid materials increases about 50% when the ratio of chlorine to copper antimonate varies from .5 to 1.5.

In its broadest aspect and with respect to materials of the fibrous cellulosic type containing the flame retardant herein described, it is apparent that any impregnation or coating of the materials with the halogenated organic compounds and copper antimonate will cause some flame retardancy. However, it has generally been ascertained that it is desirable to impregnate or coat the fibrous cellulosic materials with the halogenated organic compound in an amount equivalent to from about 2% to about 35% equivalent chlorine by weight of the untreated material and to impregnate or coat the material with copper antimonate in an amount of from about 2.5 to about 31% of copper antimonate by weight of the untreated cellulosic material. Again best results in bringing out the flame retardant properties of the combination are obtained when the halogen content of the chlorinated paraffin to the contained copper antimonate content is from about .4 to about 1.8. Preferably when treating a cotton fabric the amount of chlorine add-on accomplished should be from about 4% to 16% by weight of the untreated material and the copper antimonate add-on should be from about 4% to about 11% by weight of the material.

The following are examples showing the flame retardant properties of the novel compositions of the herein described invention. In the examples the method of evaluating the flame retardancy is the method set forth in the Federal Standard Stock Catalog of January 15, 1949, and specifically in Federal Specifications CCC-D-746 (Duck, Cotton; Fire, Water and Weather Resistant). This test calls for the so-called vertical flame test in which a flame of specified size is applied to a specimen of treated cotton duck fabric for a period of twelve seconds. After removal of the test flame, the treated fabric should not continue flaming for more than two seconds to meet the specifications. A blank, or untreated specimen will continue flaming until completely destroyed. The test fabrics consisted of No. 8 cotton duck with dimension of two inches by twelve and one-half inches.

#### Example IV

The following basic ingredients were dissolved and/or dispersed in a 1 to 2 solvent mixture of carbon tetrachloride and xylene:

|                                              |                                 |
|----------------------------------------------|---------------------------------|
| Copper antimonate (hydrated).....            | 46.5 parts                      |
| 40% chlorinated paraffin (Chlorowax 40)..... | 31.0 parts=12.4 parts chlorine  |
| 70% chlorinated paraffin (Chlorowax 70)..... | 15.5 parts=10.85 parts chlorine |
|                                              | 23.25 parts total chlorine      |
| Urea formaldehyde resin (as solid).....      | 7.0 parts                       |

The purpose of the resin was to insure good binding of the copper antimonate to the fabric fibres. In the composition of solids shown above it can be seen that 2 parts of 40% Chlorowax were used to 1 part of 70% Chlorowax. The 40% Chlorowax is an oily liquid, while the 70% Chlorowax is a fairly hard, resinous solid. By using the 70% Chlorowax alone, it would be possible to attain greater flame retarding efficiency with less total add-on due to the greater supply of available chlorine. Such practice, however, is undesirable because the resulting finish would be very stiff and difficult to handle. The liquid 40% Chlorowax has excellent plasticizing properties so that its addition to the solid Chlorowax greatly improves the handling qualities of the fabric.

Specimens of the fabric were impregnated with the composition in varying amounts by varying the quantity of solvent employed therewith. Thus the fabric specimens were dipped in the composition until completely soaked with treating compositions. Thereafter they were wrung out between rollers, dried and subjected to the flame tests set forth in the Federal Specifications. The following shows the results of three specimens:

| Specimen | Percent Total Add-On | Percent Add-on as Anhydrous Copper Antimonate | Percent Chlorine Add-On | Duration of After-flame in seconds |
|----------|----------------------|-----------------------------------------------|-------------------------|------------------------------------|
| 1-----   | 19.8                 | 7.9                                           | 4.6                     | 3                                  |
| 2-----   | 21.4                 | 8.6                                           | 5.0                     | 1                                  |
| 3-----   | 22.0                 | 8.8                                           | 5.1                     | 0                                  |

NOTE.—Add-ons are based on weight of untreated specimen of fabric.

The above information discloses that for the particular formulation employed, the minimum effective add-on based on the anhydrous copper antimonate add-on to meet the Federal Specifications lies between about 7.9% and 8.8% based on the weight of the untreated fabric. Of course, all add-on in excess of this amount will eliminate all after-flaming.

#### Example V

As another example, the following basic ingredients were dissolved and/or dispersed in a 1 to 2 solvent mixture of carbon tetrachloride and xylene:

|                                              | Parts |
|----------------------------------------------|-------|
| Copper antimonate (hydrated)-----            | 22.3  |
| 40% chlorinated paraffin (Chlorowax 40)----- | 44.6  |
| 70% chlorinated paraffin (Chlorowax 70)----- | 22.4  |
| Urea formaldehyde resin (as solid)-----      | 10.7  |

It will be noted that the above formulation contains a ratio of Chlorowax mixture to hydrated copper antimonate 3 to 1 as compared to Example IV wherein the ratio was 1 to 1. It was found that in this specific example a total add-on of 31% based on the weight of the untreated fabric was required to effect a duration of after-flame in seconds equivalent to zero. The percentage chlorine add-on in this particular example was 10.38 and the percentage anhydrous copper antimonate was 6.1.

It will be apparent from the foregoing that copper antimonate has excellent mildewcidal properties and that furthermore the copper antimonate may be employed effectively in combination with halogenated organic compounds to impart flame retardant properties to fabrics and other cellulosic materials.

What is claimed is:

1. A fibrous cellulosic material impregnated with a composition having flame retardant and mildewcidal properties, said composition essentially consisting of a mixture of copper antimonate and a halogenated organic compound, said organic compound being selected from

the class consisting of halogenated paraffins, halogenated vinyl resins, halogenated rubber, halogenated vegetable oils, halogenated animal oils, and halogenated mineral oils, said copper antimonate being present as a dispersion in said composition in the range from about 2.5% to about 31% by weight of the fibrous cellulosic material, and said halogenated organic compound being present in an amount sufficient to give a range from about 2.0% to about 35% of halogen by weight of the fibrous cellulosic material.

2. A fibrous cellulosic material impregnated with a flame retardant and mildewcide according to claim 1 wherein said halogenated organic compound is a chlorinated compound, the amount of said chlorinated organic compound being such that the chlorine content in the material is from about 4% to about 16% chlorine by weight based on the fibrous cellulosic material, the amount of copper antimonate in the material being within the range from about 4% to about 11% by weight of the fibrous cellulosic material, and the weight ratio of the chlorine to the copper antimonate being within the range from about .4 to one to about 1.8 to one.

3. A fibrous cellulosic fabric impregnated with a composition having flame retardant and mildewcidal properties wherein said composition essentially consists of a mixture of copper antimonate and a chlorinated organic compound having from about 30% to about 80% chlorine by weight of the organic compound, said chlorinated organic compound being chlorinated paraffin, the amount of chlorinated organic compound being such as to give a chlorine content in the fabric from about 2% to about 35% by weight of the fibrous cellulosic fabric, the amount of copper antimonate in the fabric being from about 2.5% to about 31% copper antimonate by weight of the fibrous cellulosic material.

4. A fibrous cellulosic fabric impregnated with a composition having flame retardant and mildewcidal properties wherein said composition essentially consists of a mixture of copper antimonate and a chlorinated organic compound having from about 30% to about 80% chlorine by weight of the organic compound, said chlorinated organic compound being chlorinated vinyl resin, the amount of chlorinated organic compound being such as to give a chlorine content in the fabric from about 2% to about 35% by weight of the fibrous cellulosic fabric, the amount of copper antimonate in the fabric being from about 2.5% to about 31% copper antimonate by weight of the fibrous cellulosic material.

5. A fibrous cellulosic fabric impregnated with a composition having flame retardant and mildewcidal properties wherein said composition essentially consists of a mixture of copper antimonate and a chlorinated organic compound having from about 30% to about 80% chlorine by weight of the organic compound, said chlorinated organic compound being chlorinated rubber, the amount of chlorinated organic compound being such as to give a chlorine content in the fabric from about 2% to about 35% by weight of the fibrous cellulosic fabric, the amount of copper antimonate in the fabric being from about 2.5% to about 31% copper antimonate by weight of the fibrous cellulosic material.

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