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PROCESS OF FIREPROOFING

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10 Claims. (Cl. 117-137)

(Granted under the act of March 3, 1883, as amended April 30, 1928; 370 O. G. 757)

This application is made under the act of March 3, 1883, as amended by the act of April 30, 1928, and the invention herein described and claimed, if patented, may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment to me of any royalty thereon.

This application is a division of my pending application for patent, Serial No. 50,763, filed November 20, 1935. This application resulted in the issuance of United States Patent No. 2,167,278.

This invention relates to fireproofing compositions for cellulosic materials and is not to be confused with the fire-resistant coatings abounding in the art which merely burn with difficulty and do not impart fireproof qualities to the materials in or on which they may be incorporated.

The impregnation of cotton fabrics with tin oxide for the purpose of imparting flame-resistance thereto is well known. This process involves first impregnating the fabric with a stannate solution, then drying, followed by precipitating and setting the tin oxide by saturating the fabric with a solution of ammonium sulfate. This is the procedure developed by Perkin (U. S. Patent No. 856,906). By this process the cellulosic material develops a complete inability to propagate flame but it will nevertheless burn without flame, that is by a continuous process of incandescent glowing.

A later discovery improves the Perkin process by impregnating the fabric with a chlorinated resin which prevents the flameless combustion. However, the fabric deteriorates rapidly when exposed to sunlight, whether it contains the tin oxide only or the tin oxide plus the chlorinated resin. Still more recent discoveries involve the use of metallic salt solutions for precipitating and setting the tin oxide in the fabric. By this process the fabric can be given a limited range of color which has been found to lessen the deterioration by sunlight. This process also involves the final addition of a chlorinated resin to the oxide-impregnated fabric.

All of these prior processes require specialized machinery in their application. They also involve a series of steps which increase the cost of the finished product and lessen the field of usefulness.

It appears that the flameproofing property is a function of the surface characteristics of the oxide. Tin oxide is highly colloidal as precipi-

tated by the Perkin process and therefore has an enormous surface area. If the tin oxide is precipitated in mass, washed somewhat and dried, the colloidal particles coalesce and the oxide loses most of its flameproofing power. A considerable number of metallic oxides are capable of flameproofing cellulosic materials provided their physical state is suitable. In the prior art tin oxide was the only metal oxide that could be obtained with the necessary fireproofing properties and that oxide could only be so obtained by precipitating it directly in and on the cellulose material. It was possible to do this without injury to the cellulose fibers because stannate solutions are alkaline. The oxide so precipitated was held so tightly because of its gel-like colloidal nature that it would not dust off of the cellulose fibers. There seemed to be a physico-chemical bond existing between the oxide and the cellulose and this was assumed to have something to do with the flameproofing capacity.

However, I have now made a very remarkable discovery. I have found that, provided the proper physical state is retained, the flameproofing oxides referred to hereinafter do not require to be in immediate contact with the cellulose material in order to impart flameproofness. That is, I can bind the oxides to the cellulosic material in a matrix of chlorinated resin and the cellulose will still be fireproof. The oxide particles are actually suspended in the resin matrix which in turn adheres to the cellulose fibers. This procedure leads to very unexpected results. As long as the oxides are directly in contact with the cellulosic material the tendency to flameless combustion reappears as soon as the superimposed chlorinated resin is destroyed by combustion temperatures, that is, glowing is quite evident in charred areas. However, when the oxide is suspended in the resin matrix the tendency to glow in charred portions is visibly lessened.

When the oxide particles are dispersed in the resin matrix, the pigmenting power of a given fireproofing oxide mixture appears to be lessened and, as a result, deterioration of the fabric upon exposure to sunlight is accelerated. This is largely due to decomposition of the chlorinated resin accompanied by liberation of hydrogen chloride. I have found that by incorporating an additional quantity of an inert pigment into my composition, I can remedy this condition. All pigments are of value but I find those which contain yellow as one color component are especially valuable. I have further found that those pigments in which lead is present tend to acceler-

ate glowing in charred portions but this is not unduly objectionable.

The very great advantage accruing from my discovery is that, for the first time, it becomes possible to prepare a truly weather-resistant fireproofing composition which can be applied to wood, cotton and other cellulose-base materials by the simple process of mixing, dipping, painting or spraying. For example, fabric treated with my composition by simply dipping it into the composition and then drying, is completely and permanently fireproof. It now becomes possible for the first time to prepare a paint-like composition which can be used in the home or elsewhere for finishing or refinishing cotton fabrics. My composition has many ramifications and applications.

In its most valuable aspect my composition is comprised of three components, the oxide component, the resin component and a volatile solvent vehicle.

The final character of the oxides in my composition is all important in determining fireproofing capacity. I may use one or a combination of the oxides of tin, lead, aluminum, titanium, germanium, zirconium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, cadmium and zinc, the term oxide to include hydrated oxides. In the case of some of the oxides mentioned the oxide will have little direct fireproofing capacity and will act chiefly to increase or preserve the fireproofing action of another oxide with which it is mixed. Iron oxide, for example, has very slight fireproofing capacity alone but markedly increases the fireproofing action of tin oxide.

For reasons of expediency or economy I may prefer to use tin or lead oxide combined with one or more of the other oxides mentioned. In that case I may proceed as follows: A solution of a stannate, stannite, plumbate or plumbite is mixed with a solution of a salt of one or more of the metals mentioned above. I may use the solutions in chemically equivalent amounts or I may use an excess of the metallic salts and precipitate the excess with an added base as a final step. By this procedure the alkaline stannate, stannite, plumbate or plumbite reacts with the acidic metal salt with a resultant mutual precipitation of tin or lead oxide with one or more other metal oxides. As a result, the gel-like colloidal tin or lead oxides are intimately intermingled with one or more other oxides with crystalline tendencies, and the precipitated mixture can be filtered, washed and dried and will still be easily reduced to an impalpable powder. A mutual interference is set up in the mixture. On the one hand, the hydrated tin or lead oxide particles do not coalesce and on the other, the particles of the second oxide do not agglomerate to form a crystal structure.

I may utilize any metal which forms compounds analogous to stannates, in the above mutual precipitation procedure. Thus I can so use aluminates, germanates, plumbates, plumbites, silicates, stannates, stannites, vanadates, zincates and all analogous compounds.

I have found that hydrated stannic oxide precipitated from stannates and lead dioxide precipitated from plumbates possess the most readily available flameproofing properties but the flameproofing properties of manganese dioxide and of copper oxides are very pronounced. All oxides may be used as I have indicated to enhance the flameproofing efficiency of stannic and lead

oxides even when the flameproofing effectiveness of the given oxide by itself is negligible.

I am not, however, concerned with the manner of preparing the oxide or mixture of oxides which I may use in my composition since it is possible to use varying procedures. I am not fully cognizant of the factors which determine the fireproofing capacity of metallic oxides and these factors are not necessarily dependent upon the steps by which the oxide is prepared. For example, it might be equally advantageous and effective to precipitate the metallic oxides separately and mix the separate aqueous suspensions; or the aqueous suspensions of the precipitated oxides might be atomized into an evacuated drying chamber. Besides precipitation methods I may use other means of preparing the metallic oxides in effective form, such, for example, as reduction in preparing manganese dioxide from permanganates; alternate reduction and oxidation in the case of copper oxide; in short any method which yields a satisfactory final product. For these reasons I do not restrict myself to any manner of preparation or combination of the oxides in my composition but limit myself only to the fireproofing properties present in the prepared oxide or oxide mixture.

The resin component may be any one or more of a wide range of chlorinated materials, depending upon the use to which the composition is to be put. For use in coating or impregnating textiles a very desirable resin is made by chlorinating a mixture of paraffin wax and petroleum oils. A wide variety of mineral or petroleum oils may be utilized in the mixture. The chemical complexity of such oils is a desirable feature since it leads to greater thermal instability in the finished chlorinated resinous product. Such a chlorinated resinous mixture evolves hydrogen chloride freely when thermally decomposed and hydrogen chloride is an effective combustion preventing gas. By varying the melting point and by using various proportions of paraffin wax in the wax-oil mixture and also by varying the viscosity and type of the oils used, any desired physical state can be obtained in the finished chlorinated product. In general, the chlorine content may approximate 60 percent by weight of the finished product but I do not restrict myself on this point since considerable latitude is possible.

In treating cellulose fibers with my paint composition, the nature of the chlorinated resin is extremely important. I am not aware of all the factors involved but it appears that the property known as wetting power plays a large part. This property is no doubt associated with solution viscosity which in turn is probably related to the size of the resin molecule. At any rate, I have found that compositions prepared with vinyl resins and with chlorinated rubber are of much less value in fireproofing cotton fabrics. There are many materials which can be chlorinated to yield resins which, in organic solution, possess the necessary wetting power. Also, the natural oils, fats and waxes, and long chain alcohols and acids will produce suitable resins upon chlorination.

Another resinous material which is very effective in my composition for purposes other than textile fireproofing is represented by the chlorinated vinyl resins. These resins also evolve hydrogen chloride when heated, and they are usually solid bodies. A composition comprising the fireproofing metallic oxide component and the chlorinated vinyl resin can be used for impregnating textiles but the fireproof qualities im-

parted are much less. However, the viscosities of a volatile solvent solution-suspension of the vinyl resin-oxide composition are higher than the viscosities obtainable with a corresponding concentration of the chlorinated wax-oil resin described above, and thorough impregnation of textiles therefore is more difficult. One use to which the chlorinated vinyl resin-oxide composition may advantageously be put is in binding together shredded corn stalks, sawdust, straw and the like in preparation of structural and acoustical blocks, panels and the like. Such products will be rendered highly fire resistant by my composition. The vinyl resins are capable of imparting considerable structural strength to such products. Another product which can be utilized to advantage in my composition is chlorinated rubber. Chlorinated rubber resins can be made highly water-repellent and when fireproofing oxides are incorporated into these resins an excellent coating composition for wood shingles and the like is obtained. It is to be understood, however, that the uses indicated by me for the compositions comprised of the various materials does not preclude the possibility of using the various compositions interchangeably. Then too I may combine the various resinous materials in any manner I find advantageous.

In addition to the foregoing materials I may utilize chlorinated naphthalene derivatives and the so-called chlorinated diphenyl derivatives in my composition. Also a very satisfactory chlorinated product can be obtained by chlorinating and polymerizing paracymene as a typical representative of the aryl-alkyl compounds. These mixed types of compounds yield very effective fireproofing resins when chlorinated.

This will indicate the wide variety of chlorinated resinous materials which I can employ in my compositions. It is understood, of course, that other halogens may be the equivalent of chlorine in preparing the resin component of my compositions.

As to the relative proportions of oxide component and chlorinated resin component, considerable latitude is allowable. For use in impregnating textiles I have found that proportions of the order of one part of oxide component to two parts of resin component by weight effectively fireproof cellulosic materials when properly incorporated therein. Obviously within the spirit of my invention these proportions may be varied widely, and, again, I restrict myself only by the results obtained. In general, the more effective the flameproofing action of the resin employed the less the proportion of oxide required. In the case where the resin component is low in flameproofing action the proportion of oxide will have to be increased. One measure of the effectiveness of a given chlorinated resin is the volume of hydrogen chloride evolved during thermal decomposition as compared to any other resin.

Before considering the third component of my composition, I wish to define the term "resin" as I have used it. By resin I indicate those liquid, semi-solid or solid bodies, obtained by chlorination, which are indefinite in physical characteristics, such as melting point, in that they change from the liquid to the solid state and vice versa through an appreciable temperature range. To an even greater extent these bodies are characterized by indefiniteness of chemical composition.

The volatile solvent vehicle in my composition plays no part in the fireproofing action and serves

merely to regulate the proportions of fireproofing composition relative to the material being fireproofed. Obviously the more solvent used the less oxide-resin composition will remain in or on the material being treated, but also the lower will be the viscosity of the suspension solution and the more thoroughly the oxide-resin mixture will be impregnated into a fibrous base. For fireproofing textiles the proportion of solvent is such as to deposit, upon evaporation, oxide-resin mixture in amount equal to from 25 to 50 percent of the treated fabric by weight but I do not restrict my proportions rigidly within these limits. I may find it expedient to emulsify the oxide-resin mixture in water and thereby eliminate the solvent component entirely.

In the case of a thermally plastic chlorinated resin where the oxide-resin composition is being used to bind sawdust or fibrous materials into a rigid shape I may dispense with all volatile solvent. As volatile solvent I may employ any solvent which is compatible with the given resin which I may require, and which will be lost by evaporation within the temperature range through which the resin is stable.

In addition to the oxide component, the resin component and the volatile solvent I may include in my composition plasticizing and siccatve agents to modify the physical properties of my compositions. By plasticizing agent I denote any material which softens the chlorinated resin and by a siccatve I indicate any material which lessens tackiness. A wide variety of plasticizers are available. Among those which I may use are tricresyl phosphate, triphenyl phosphate, dibutyl phthalate, tung oil, beeswax and chlorinated diphenyl. I may also include in my composition agents which have mildew-proofing properties, other than such compounds as copper oxide which are mentioned herein. Other compounds of copper may be used such as copper chromate or I may use organic fungicides which are insoluble in water.

Finally I may include any desired mineral or oxide pigment in my composition. Such pigments will usually have no fireproofing properties. An oxide used for pigmenting purposes may have been prepared in such a manner as to have no flameproofing properties, even though such properties might be inherently present. For example, sintered stannic oxide possesses no flameproofing properties, whereas stannic oxide prepared in the manner specified herein does possess excellent flameproofing properties. By proper combinations of pigments and fireproofing oxides in my composition I am able to obtain any color desired.

In preparing my composition in paint form, which will be that used in treating textiles, the resin will be dissolved in a compatible volatile solvent and the oxide component will be ground with the solution by use of the usual paint grinding equipment such as ball mills, burr mills, colloid mills, etc. I may add both the fireproofing oxide and the pigment at the commencement of grinding or I may add the pigment after the grinding is nearly completed. It will be understood that the fireproofing oxides must be as fine as possible to permit the resin solution to carry the oxide particles the more thoroughly throughout the fabric. The pigment, on the other hand, exerts its maximum protective function if it is chiefly on the outer surface of the fabric threads and, therefore, it is not essential that the pigment particles be so highly dispersed. However, this

must not be understood to restrict my procedure in any respect.

I will use essentially the same grinding procedure in the case of any of the oxide-resin combinations cited in these specifications.

Having thus described my invention, I claim:

1. The process of fireproofing a cellulosic-base material comprising coating the material with a suspension of a plurality of metallic oxides selected from the group consisting of oxides of tin, lead, aluminum, titanium, germanium, zirconium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, cadmium, and zinc, in an organic solution of a chlorinated resin, the metallic element of one of said oxides being chosen from the group consisting of tin and lead followed by drying said coating.
2. The process of fireproofing a cellulosic-base material comprising coating the material with a suspension of a plurality of metallic oxides selected from the group consisting of oxides of tin, lead, aluminum, titanium, germanium, zirconium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, cadmium, and zinc, in an organic solution of chlorinated paraffin wax and chlorinated petroleum oil, the metallic element of one of said oxides being chosen from the group consisting of tin and lead followed by drying said coating.
3. The process of fireproofing a cellulosic-base material comprising coating the material with a suspension of a plurality of metallic oxides selected from the group consisting of oxides of tin, lead, aluminum, titanium, germanium, zirconium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, cadmium, and zinc, in an organic solution of a chlorinated resin, the metallic element of one of said oxides being tin.
4. The process of fireproofing a cellulosic-base material comprising coating the material with a suspension of a plurality of metallic oxides selected from the group consisting of oxides of tin, lead, aluminum, titanium, germanium, zirconium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, cadmium, and zinc, in an organic solution of a chlorinated resin, the metallic element of one of said oxides being lead.
5. The process of fireproofing a cellulosic-base

material comprising coating the material with a suspension of oxides of tin and iron in an organic solution of a chlorinated resin followed by drying said coating.

6. The process of fireproofing a cellulosic-base material comprising coating the material with a suspension of oxides of tin and iron in an organic solution of chlorinated resin followed by drying said coating, said suspension being produced by combining in water solution sodium stannate and iron sulfate, separating and recovering the metallic oxides formed, washing and drying the recovered oxides and suspending the dried oxides in an organic solution of a chlorinated resin.
7. The process of fireproofing a cellulosic-base material comprising coating the material with a suspension of oxides of tin and iron in an organic solution of chlorinated resin followed by drying said coating, said suspension being produced by combining in water solution a water-soluble stannate and a water-soluble iron salt of a strong mineral acid, separating and recovering the metallic oxides formed, washing and drying the recovered oxides and suspending them in an organic solution.
8. The process of fireproofing a cellulosic-base material comprising coating the material with a suspension of oxides of tin, iron and chromium in an organic solution of a chlorinated resin followed by drying said coating.
9. The process of fireproofing a cellulosic-base material comprising coating the material with a suspension of oxides of tin, iron and chromium in an organic solution of a chlorinated resin followed by drying said coating, said suspension being produced by combining in water solution a water-soluble stannate, a water-soluble iron of a strong mineral acid and a water-soluble chromium salt of a strong mineral acid, separating and recovering the metallic oxides formed, washing and drying the recovered oxides and suspending them in the organic solution.
10. The process of fireproofing a cellulosic-base material comprising coating the material with a suspension of oxides of tin and cadmium in an organic solution of a chlorinated resin followed by drying said coating.

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