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FIRE EXTINGUISHING PAINT OR COATING COMPOSITION AND PROCESS OF MAKING THE SAME

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My invention relates to a fire extinguishing paint or coating composition and to the process of making the same. More particularly, my invention relates to providing a paint or a coating which when applied to inflammable materials such as cellulose and hydrocarbon compositions, such as wood, fabric, rubber, paper products, which if later, in point of time, are subjected to a temperature of combustion, operates under burning temperatures to extinguish the fire.

This application is a continuation in part of my application, Serial No. 71,204, filed November 24, 1925, for a Fire extinguisher.

My invention is characterized by such intense fire extinguishing properties that if a residence is constructed of wood and the wood products entering into its construction are treated with my invention, that it would be practically impossible to burn that residence; only external localized fire might burn holes through the walls, but such fire will not be supported by the treated wood and so would be extinguished.

It is well recognized that fire is the cause of a great loss of property and life and extensive precautions are taken to limit that destructive force. My purpose is to provide a fire proofing paint which if applied precisely as any ordinary paint, will, in addition to its value as a paint, provide a continuing inactive protection against burning, but that quality only becomes operative when subjected to the heat necessary for the combustion, or burning of the materials which it is intended to protect, and under which fire condition liberates a deoxidizing agent which forthwith operates against further combustion. In short, my purpose in the present invention is to provide protection for inflammable material which is called into effect by the heat of combustion and is comparable, by way of illustrating the idea, to water sprinkler systems which are set off by the fire which is to be extinguished.

By the term paint or coating, I mean to include all types of paints, lacquers, stains, creosote, varnishes, sizings, waxes, and plastic compositions. Thus, it is to be noted, that by coating I do not mean to have my invention strictly restricted to a surface adhering film, but I mean to include coatings such as stains that penetrate into the material to be treated such as cedar shingles and roofing papers which absorb within their cellular structure fibers or pores more or less of the coating applied thereto. Thus, in applying my invention to shingles at the time of manufacture of the same, it is important that the coating be one that is as light in weight as possible to avoid prohibitive freight charges, but, however, the coating as a stain must penetrate substantially beneath the surface in order to remain against the severe weather conditions of rain and sun, and at the same time to carry the finely divided fire extinguishing agent of my invention into the pores of the wood for permanency. Likewise, this penetration applies in the manufacture of artificial roofings of paper and other materials, and to airplane cloths and fabrics and to the insulation fabric for electric conductors. In many of these products there is both a film and a penetration or saturation.

In connection with the treatment of shingles and other products which represent a class of which those enumerated are only typical examples, the coating constituting my invention may be applied either at the time of manufacture or after the product is in position. For example, in connection with shingles, my coating obviously may be applied to the shingles after they have been nailed to the roof. Preferably, however, it is applied at the source of manufacture. The manner in which this coating may be applied may be by brushing, as in ordinary painting, or by spraying, dipping, or the coating embodying the fire extinguishing compound may be impressed directly upon or into the materials being treated. Thus, book paper or book covers and paper for valuable documents may be given a fire protecting coating without detracting from the use for that purpose.

Paints in general may be divided into two classes as respects their method of drying. On the one hand, the first class are those which dry by oxidation of the vehicle, for example—any linseed oil paint. The other class are paints which dry by vaporization of the solvent of the vehicle, for example—many varnishes, paints having a bituminous or resinous vehicle, and paints having a vehicle of the nature of pitches, lacquers or waxes. There are also certain stains used, such as creosote, that do not dry but remain in place upon porous substances.

In providing a paint composition which will have the property of fire proofing the material to which the paint is applied, great caution is necessary to avoid destroying any of its essential paint properties; for example, certain compounds may be added to the linseed oil paints but when so added to impart fire proofing qualities, the drying property of the linseed oil is destroyed and the paint would not become dry. Furthermore, there is the problem of protecting against the use of fire proofing substances that are soluble in water and, consequently, that will be removed by rain or water after application.

The use of any material to provide fire proofing which would become soluble or chemically effected under exposure to the elements inherent in outside use, must obviously be avoided, for instance, Paris green, which is a copper arsenite, is a notoriously poor chemical for use in paints. Furthermore, one essential quality of a paint is its durability, and in providing a fire proofing

composition, no substance or chemical compound must be used which will appreciably lessen its durability, that is, there must be no deleterious reaction between the materials constituting the paint proper and the fire extinguishing agent. The chemicals employed must be such as to not be of a volatile character at normal temperatures in order that they will not be injurious to health or life either during or after application.

In general, and briefly stated, my invention is the discovery of agents which operate by way of deoxidation, or as anticatalysts as respects the burning of inflammable materials and may be incorporated in said coatings, and there be available as a fire extinguishing agent under the action of burning temperatures. In providing such deoxidizing agents, I have found that I may employ certain compounds of arsenic. Also, I have found that certain antimony compounds are also characterized by having such deoxidizing properties. Of these two agents, I find that the arsenic deoxidizing agent, pound for pound, has greater dedoxidizing effect than has the antimony deoxidizing agent. I have found that where arsenites are effective, the corresponding arsenate is effective, and where the antimonite is effective the corresponding antimonate is effective but in practically every instance I have found the arsenite to be more effective than the same weight of the arsenate, and the antimonite to be more effective than the same weight of the corresponding antimonate.

I believe the explanation of the relative advantage of the "ites" for fire extinguishing effects may be due to the fact that the "ates" liberate free oxygen together with the deoxidizing agent. I have also found, to somewhat prove this, that when a non-inflammable oxidizable substance is present with the "ates" their fire extinguishing property is increased. Thus when the calculated amount of finely divided metallic zinc is present with the "ate" required for the calculated amount of oxygen liberated by heat, smaller quantities of the "ate" are required for the same degree of effectiveness when the zinc is omitted. However, there are certain conditions as will be hereinafter set forth, under which a compound of antimony is to be preferred. After extensive investigation of the prior art and literature related to the subject of fire extinguishing, I do not find that any one has taught the deoxidizing effect or the anticatalytic effect of the above mentioned compounds or any other substances to operate against the chemical combination of the oxygen of the air with the distilled inflammable gases of combustible materials. I have noted that during the operation or functioning of the deoxidizing agent in extinguishing a fire that the black smoke normally present during the burning of a hydrocarbon compound is absent. Manifestly, in extinguishing a fire, the greater the volume of the deoxidizing fluid present at a given moment of time, determines in large measure the effectiveness of that agent toward extinguishing the fire, and in this, is comparable in part and by way of illustration to the application of water,—the greater the volume of water applied at any one moment, the greater the fire that it is capable to extinguish.

My experiments teach that the numerous oxy compounds of arsenic and of antimony are characterized by having this deoxidizing effect, i. e., anticatalytic action relative burning. White arsenic, the common form in which arsenic oxide may be obtained on the market, and which has the chemical formula of As_4O_6, has this deoxidizing effect to a considerable extent when converted to a fluid form, which conversion takes place at a very low temperature to form, apparently, a fluid As_4O_6. This temperature is considerably below the burning temperature of most material. For this reason, the effectiveness of the solid As_4O_6 as a deoxidizing agent, is lessened by reason of the fact that portions of the materials which are subjected to the heat of burning but are not yet being burned, have the fire extinguishing agent partially eliminated in advance of its burning, so that when the flame reaches that point to be extinguished the full effect of the fire extinguishing compound is not there. I have discovered that many oxy-arsenic compounds liberate the deoxidizing agent at temperature considerably higher than that at which white arsenic liberates its deoxidizing agent and thus they are not driven off in advance of the approaching flames to the same extent as when white arsenic is used. When I say the deoxidizing agent is fluid As_2O_3, it will be understood that, due to the fact that the reactions are complex, this is only my theory and explanation of the phenomena and it may be that the deoxidizing agent is a lower oxide than the As_2O_3, and possibly it may be the metallic arsenic itself. In thus referring to arsenic trioxide, I mean also to include antimony trioxide relative to which the same statement is in general true. It may be that there is also an oxidizing action as well as said deoxidizing action. This may in part explain the reference above made relative to the fact that in burning a hydrocarbon material, as soon as the so-called deoxidizing agent begins to function, that thereafter the black smoke disappears. It will be remembered that wherever a reduction action is taking place, that there is a corresponding and simultaneous oxidizing action taking place upon the compound causing the reduction.

As respects the suggestion that it may be the fluid metallic arsenic itself that operates as the deoxidizing agent, the reaction may be as follows:

$$5As_2O_3 \xrightarrow{Heat} 3As_2O_5 + 4As$$

That is, it may be that some of the arsenic trioxide molecules inter-react and form the pentoxide and free metallic arsenic. The actual cause or reason for this mysterious prevention of burning is not definitely known or how it acts. Thus in the contact process for making sulphuric acid, a small quantity of arsenic in contact with the platinum catalyst hinders and prevents oxidization of SO_2 to SO_3. It is simply called a "poison" to the catalyzer but is obviously a negative catalyst.

It will be noted also, that in forming As_2O_3 from As_4O_6, for example, which commences at about 800° C. that two volumes of As_2O_3 are formed for each volume of As_4O_6, which increased volume in itself greatly increases the fire extinguishing effect. As the volume of As_2O_3 is increased, by so much does it exclude the air (that is the oxygen of the air) and by so much, i. e. by its excluding effect, increases its effectiveness in addition to its deoxidizing effect, i. e. anticatalytic action, which latter, however, is the primary effect herein sought.

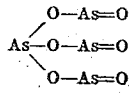
My experiments have shown that the degree of fineness of the deoxidizing producing agent has a bearing upon the rate of liberation of the fluid

deoxidizing agent. The finer the particles, the more rapidly is liberated the same volume of the fluid deoxidizing agent than from coarser particles of the same compound. Since highly dispersed suspensions of the deoxidizing producing substances contain the agent in smaller particles than in a mechanical mixture, some means of obtaining dispersion is thus frequently employed by me to increase the fire proofing effectiveness without increasing the quantity of the deoxidizing producing substance. Thus in the production of shingle stains or in fireproofing creosote, it is of a decided advantage to have the particles of the fireproofing agent dispersed to a high degree. Such fineness permits of deeper penetration into porous substance than does that where there has been no dispersion. For example, in fireproofing creosote, arsenious metarsenite in a pulverulent condition is agitated with the creosote which causes its dispersion throughout the creosote. In some cases I find it is an advantage to add a dispersing agent. For example, benzol sulphonic acid in water causes arsenious metarsenite to disperse in linseed oil.

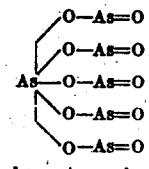
Certain of the oxy-arsenic compounds when broken down by heat, theoretically, at least, liberate fluid As_2O_3 as such and these products are especially effective as fire extinguishers. As it is known that, normally, fluid As_2O_3 does not exist except at temperatures of about 800° C. so that the As_2O_3 which is liberated by chemical breakdown at temperatures below 800° C. is in the case of some of said compounds probably extremely chemically re-active and effective which may account for the exceptional effectiveness of those compounds as a fire extinguisher.

The oxy-arsenic groups besides the oxides are divided into arenites and arsenates. The corresponding antimony compositions into antimonites and antimonates. Each of these groups is divided into three divisions, the ortho, pyro and meta. My experiments indicate that the "meta" division in all of those groups is the one that, pound for pound, provides the greatest fire extinguishing effect, and also that the "meta" is the most inert and durable under climatic conditions than either the "ortho" or "pyro" corresponding compounds. Thus, I find that while the "meta" compounds are broken down more readily by the heat of burning to liberate the deoxidizing agent, at the same time, fortunately, they have apparently a greater stability against chemical change in the absence of such heat of burning.

My experiments have developed the fact, which seems further to substantiate the above conclusions that an arsenious-metarsenite or an arsenic metarsenite is more effective pound per pound than any other arsenic compounds. This arsenious-metarsenite has the following chemical formula $As(AsO_2)_3$, of which the empirical formula is As_4O_6, and which is also the empirical formula for common white arsenic. White arsenic gives an acid reaction as tested with phenolphthalein indicator; my arsenious metarsenite provided by my invention gives an alkaline reaction with that indicator The structure showing the arrangement of atoms of the above arsenious metarsenite of my invention is as follows:

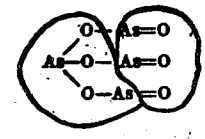


That of arsenic metarsenite is



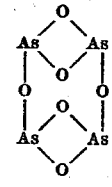
A molecule of arsenic metarsenic can break down into three molecules of As_2O_3.

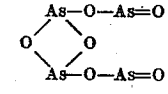
The action of heat on arsenious metarsenite may be illustrated as follows:



The two circles show the splitting up by heat and show how the different parts of the compound are free to combine as $2As_2O_3$.

To be distinguished from the structure of arsenious metarsenite white arsenic (As_4O_6) as commonly obtained on the market ordinarily has one or the other of the following structural formulas according to the authorities:





It will be noted that in the arsenious metarsenite formula, $As(AsO_2)_3$, we have arsenic both on the positive side and on the negative side of the molecule, that is, part of the arsenic is acting as a base and part as an acid, whereas, in the white arsenic, (As_4O_6), the arsenic is altogether on the positive side. The structural diagram shows the three negative radicles containing arsenic to be attached to the same positive atom but are unattached to each other. The structural diagram of the white arsenic does not show this condition. Another practical differentiation, the alkaline reaction of arsenious metarsenite having already been noted, between the two is that while white arsenic prevents the drying of linseed oil, arsenious metarsenite does not have that effect. Thus in the case of arsenious metarsenite we have a compound of such a structural make up that it breaks down apparently into two fluid molecules of arsenic trioxide of the formula As_2O_3, while in the case of the white arsenic, the arsenic trioxide volatilizes as and into fluid As_4O_6.

Thus, the theoretical explanation of why arsenic trioxide in the form commonly known as white arsenic is less effective, may be explained as follows: The solid white arsenic, (As_4O_6) is converted by a relatively low heat, namely 219° C., that is, a heat below that of ordinary burning temperature, into fluid As_4O_6. To convert each volume of this As_4O_6 into two volumes of As_2O_3 requires an extremely high temperature, namely 800° C. or above. Manifestly, as hereinabove indicated, the solid white arsenic (As_4O_6) when in the presence of burning temperature, may be converted in advance of the flame, to fluid As_4O_6 and thereby be dissipated before the flame reaches it and so is not present to the same extent to extinguish said flame.

In contrast with this white arsenic, each molecule of the solid arsenious metarsenite

$(As(AsO_2)_3)$, is converted at a temperature above that required to vaporize the white arsenic, thus minimizing advance dissipation, and at or below the burning temperature of the inflammable materials, directly into two molecules of As_2O_3. Thus it is clear that although white arsenic and arsenious metarsenite have the same empirical formula As_4O_6, nevertheless they have widely different effects for the purposes of my invention, and this, it is suggested, is explained by the above structural formulas.

In applying these arsenic compounds to the making of paints, the following situations as respects the character of the arsenic compound as supplied to the paint composition, are to be noted:

1. White arsenic as such may be employed in the paint composition. However, there are certain limitations in using such compound in paints, in that such arsenic compound has deleterious effect upon the drying of a vehicular oil that dries by oxidation, such as oil of the linseed type. White arsenic is much more soluble in water than arsenious metarsenite and for this reason offers a greater poison danger to life. Where cisterns are employed for catching the water from roofs, such danger may become an important factor.

2. There may be present in the paint composition, white arsenic and with this, another compound such as basic lead carbonate, which may react to form an arsenic compound by heat, which in turn, under the influence of the burning temperature, may be decomposed into the fluid arsenic trioxide As_2O_3 as a deoxidizing agent.

3. An arsenic compound, such as calcium mono-hydrogen ortho-arsenite, that is, where there is only one atom of arsenic per molecule, may be supplied to the paint composition. Since the fire extinguishing function is directly dependent upon the ease and rapidity of liberating the arsenic trioxide in the fluid form, it is manifest that where we have but one atom of arsenic per molecule present, that there is a relatively slow formation of said fluid deoxidizing agent, if at all. This particular form, including the whole of the alkaline earth group, however, is found very stable as respects break down by heat. However, to overcome this, I add a compound, such as basic lead carbonate, that, by double decomposition due to the heat, temporarily at least, forms a compound containing at least two atoms of arsenic, thus producing a molecule of arsenic trioxide, and thus making available, at comparatively low temperatures, in a paint composition, calcium mono-hydrogen ortho-arsenite and similar ortho arsenites of the alkali earth group. The use of insoluble arsenites or arsenates also minimizes the poison danger relative to the use of the more soluble white arsenic.

4. There may be supplied to the paint composition, an arsenic compound in which there is at least (and may be more) two atoms of arsenic per molecule. This appears to be the best possible arrangement because we have two atoms of arsenic, as in zinc metarsenite, immediately available to form one molecule of arsenic trioxide in fluid form. However, this is not true of all compounds having two atoms of arsenic per molecule, such as magnesium pyro-arsenate, here as in some cases it is necessary to supply a compound like basic white lead carbonate, whereby, by the aid of said compound through double decomposition, the two arsenic atoms are made available at or below the temperature of burning. It is also found that many other pyro-arsenates when used alone break down slowly, if at all, by the heat of burning.

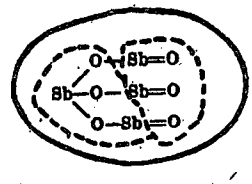
5. There may be supplied to the paint composition, an arsenic compound, the arsenic content of which may be characterized by being very stable toward heat. This occurs in the instance of ammonium magnesium arsenate and ammonium manganese arsenate. Under the influence of heat, the ammonium is readily vaporized, but the arsenic compound resists the action of the heat. With such arsenic compounds, there should be present in the paint composition, another compound such as lead carbonate, whereby under the influence of heat, double decomposition develops which results in liberating fluid arsenic trioxide at or below the gas distillation temperature of the material being protected.

6. There may be supplied to the original paint composition, an antimony compound characterized by being slow in liberating under the influence of heat, the deoxidizing agent. Then it is necessary to have present, a catalytic agent such as cobalt, nickel, manganese, iron, platinum, etc. to accelerate the liberation of said deoxidizing agent. This occurs in the instance of a mixture of antimony trioxide and sodium metantimonate where a catalytic agent such as an oxide of manganese should be present to accelerate the liberation of the deoxidizing agent.

7. There may be present in the original paint composition, an antimonious arsenite, antimonious arsenate, antimonic arsenite and antimonic arsenate. This is well adapted for my purpose, because there is present on the positive side of the molecule, antimony atoms, and arsenic on the negative side, both being effective as deoxidizing or anti-catalytic producing agents.

8. There may be present in the original paint composition, antimony trioxide, where the antimony appears on the positive side, and sodium or potassium met-antimonate in which the antimony appears on the negative side, and basic lead carbonate. This provides a fair fire proof paint where arsenic is not present to act as a deoxidizing agent.

9. There may be present in the original paint composition, antimonious antimonite, antimonic antimonite, antimonious antimonate or antimonic antimonate, or combination of these, in which there is present on both the positive and negative sides of the molecule, antimony available to form the deoxidizing or anticatalytic agent. The following formula illustrates how the structural formation of a molecule of antimonious metantimonite is adapted to break down under the influence of heat at the temperature of burning, to form two molecules of fluid antimony trioxide.



The solid line shows the original molecule, while the dotted lines show the two molecules after the action of heat of burning.

My experiments show this structure to be especially well adapted for producing, under the temperature of burning, the antimony deoxidizing agent.

10. There may be supplied to the original paint

composition, arsenious antimonite, arsenic antimonite, arsenious antimonate, arsenic antimonate or a combination of these. Herein we have arsenic on the positive side and antimony on the negative side of the molecule, both being deoxidizing providing substances under the influence of burning temperature.

11. There may be supplied to the original paint composition an arsenious arsenite, or arsenious arsenate, arsenic arsenite, or arsenic arsenate, the structure of which, as a metarsenite, has already been illustrated hereinabove. These have proven to be among the most effective deoxidizing producing agents.

12. There may be present a compound each molecule of which contains but one atom of arsenic. These molecules being mutually interactive by heat so that two or more atoms of arsenic unite at temperatures at or below the burning temperature to liberate the fluid deoxidizing agent. An example of this is the monoarsenic compound of copper arsenite. Here, then, we have a contrast to situation number three, that is, in place of an alkali earth group member such as calcium mono-hydrogen ortho-arsenite, we may have an easily reducible metallic mono-hydrogen ortho-arsenite as described herein, and here we do not need necessarily, the basic white lead carbonate.

13. There may be supplied to the original coating composition of the cold water type and kalsomine type, the deoxidizing agent producing compound mixed with plaster of Paris or cement or any other material which will set or harden when dried and applied to the walls or ceilings of combustible structures to render them non-combustible, as in the coating of laths, shingles, roofing paper, handle portion of matches, or other materials. Also there may be included borax in the composition for the purpose of forming a glaze under heat of combustion. All of these agents or one or more of them may be added to the composition.

Paint formula No. I.—As illustrating the first situation above, we may have the following formula:

White arsenic	3¼	pounds
Iron oxide pigment for red color	.60	pounds
Asbestine	2	pounds
Gloss oil (a solution of rosin in mineral thinner)	.0585	gal.
Reducing oil (a solution of candle tar pitch in mineral thinner approximately equal parts of each)	.447	gal.
White dryer	.028	gal.
Cobalt dryer	.0106	gal.
Aluminum stearate solution (aluminum stearate dissolved in turpentine)	.092	gal.
Mineral thinner	.154	gal.

The essentials in this formula are the white arsenic, and the vehicle that dries primarily through evaporation of the solvent. The other ingredients are added solely to give desirable paint qualities and may be omitted in part or altogether as the particular requirements demand. It will be noted that I have avoided the difficulty of the effect of the white arsenic upon the drying property of the paint composition, in combining the white arsenic with a vehicle which does not dry by oxidization but which rather dries primarily by evaporation of the solvent of the vehicle.

Paint formula No. II.—As illustrating the second situation above, we may have the following formula:

White arsenic	2½ pounds
Basic lead carbonate	2½ pounds

The balance of the formula may be precisely as that given in the Formula I. In this formula, the essentials are the white arsenic and the basic lead carbonate, and the vehicle of the character given in paint Formula No. I. It will be noted that the amount of the white arsenic is reduced and this is due to the fact that the presence of the lead makes the white arsenic much more effective. This, it seems to me, may be explained by the fact that the white arsenic and lead react under the influence of heat, to produce directly, lead arsenite, which again is immediately decomposed at or below the burning temperature of the material being protected into the deoxidizing agent in the form of fluid arsenic trioxide, (As_2O_3). The greater effectiveness thus provided may also be due to the fact that we have the arsenic trioxide (As_2O_3) in a nascent or highly chemical reactive condition, due to its formation by a chemical reaction at the point of burning.

Paint formula No. III.—As illustrating the third situation above, we may have the following formula:

$CaHAsO_3$	3 pounds
White lead carbonate	4 pounds
Vehicle as in No. I above	1 gal.

The essentials in this formula are the calcium mono-hydrogen ortho-arsenite compound and the lead carbonate. Arsenic in a combined form other than white arsenic is essential in connection with linseed oil or a vehicle which dries or sets primarily by oxidation. However, the vehicle which dries or sets primarily by evaporation of its solvent may be substituted, care only being necessary as respects the arsenic compound when used with a vehicle which sets primarily by oxidation.

In the above formula, it will be noted that I employ a vehicle such as linseed oil, which dries or sets primarily by oxidation. Here, I have found white arsenic cannot be employed because it prevents the vehicle from drying or setting. I avoid this difficulty by providing an arsenic compound which does not have this deleterious effect upon the drying or setting.

I believe one of the reactions to explain why the fluid anticatalytic agent is liberated by the heat of burning, in the above formula is, first the white lead carbonate is readily converted by heat to form lead oxide (litharge); secondly, the calcium monohydrogen ortho arsenite and the lead oxide undergo double decomposition according to the chemical equation:

$$2CaHAsO_3+PbO \rightarrow Pb(AsO_2)_2+2CaO+H_2O$$

Thus forming lead metarsenite, calcium oxide and water vapor. The lead metarsenite then breaks down by the heat of burning to liberate fluid arsenious oxide, thus:

$$Pb(AsO_2)_2 \xrightarrow{Heat} As_2O_3+PbO$$

It is interesting to note in the use of calcium mono-hydrogen ortho-arsenite or similar ortho arsenite, such as the alkali earth group arsenites, that where used alone with linseed oil as the

vehicle, I have discovered that they are not relatively effective as an extinguisher of fire, but when used with candle tar pitch or like bituminous vehicle, that definite fire extinguishing effectiveness is evident, and that other reactive agent need not be added, except for still greater effectiveness, if so desired. This greater effectiveness might be accounted for on the ground that there being present free carbon in the bitumen that the carbon operates as a reducing agent to break down the original molecule of the arsenite to form nascent fluid arsenic trioxide (As_2O_3). In this connection my experience has shown that the effectiveness of various deoxidizing agent supplying materials is regulated in part by the vehicles used, for example, neutral oil, creosote, paraffin wax can be rendered fire extinguishing by employing white arsenic, antimonic metarsenite, arsenious metarsenite. As stated above, white arsenic vaporizes into fluid As_4O_6 at a relatively very low temperature, which is a temperature below the burning temperature of paraffin wax, the burning temperature of which is relatively low. In the use of some arsenic compounds as the source of the deoxidizing agent whose vapor producing point is higher than that of white arsenic, I have found that if a vehicle such as linseed oil is employed with such arsenic compound, that it may not provide a fire extinguishing deoxidizing agent, but when there is substituted for linseed oil, a vehicle such as candle tar pitch, that the deoxidizing agent is liberated under the influence of the burning temperature and the fire extinguishing property is provided. This action may be due to the low burning temperature of linseed oil which has been replaced by the higher burning temperature of candle tar pitch or it may be due to the greater reducing action of the candle tar pitch over the linseed oil. Such an arsenic composition is calcium mono-hydrogen ortho-arsenite.

Paint formula No. IV.—As illustrating the fourth situation above, we may have the following formula.

Zinc metarsenite ..... 3 pounds
Balance of ingredients as in No. I.

The essential of this formula is the arsenic compound which has two atoms of arsenic that readily breaks down under the influence of heat of burning to form arsenic trioxide.

A modified formula of this paint formula may be termed Paint formula No. IV—A, and would be as follows:

Magnesium pyro-arsenate ..... 3 pounds
Basic lead carbonate ..... 3 pounds
Vehicle as in No. I above ..... 1 gal.

The essentials of this formula are the arsenic compound and the lead carbonate. This formula constitutes a fire retardent paint according to the standards hereinafter defined.

Paint formula No. V.—As illustrating the fifth situation above, we may have the following formula:

Ammonium magnesium arsenate ..... 3 pounds
Basic lead carbonate ..... 3 pounds
Vehicle as in No. I above ..... 1 gal.

Here the essentials are the said arsenic compound and the lead carbonate. The said arsenic compound by itself is not suitable as a provider of a deoxidizing agent for the reason that it resists breaking down under heat to form the fluid deoxidizing agent, but when used with other material such as lead carbonate will react to form, for example, a lead arsenate, which in turn under the influence of heat readily breaks up to liberate at burning temperatures, the deoxidizing agent. This formula provides a fire retardent coating according to the requirement of our standards.

Paint formula No. VI.—As illustrating the sixth situation above, I may have the following formula:

Antimony trioxide ..... 2 pounds
Sodium metantimonate ..... 3 pounds
Manganese dioxide ..... 1 pound
Vehicle the same as in No. 1 above.

The essentials of this formula are the antimony compounds and a manganese oxide acting as a catalytic agent and the vehicle.

Paint formula VII.—As illustrating the seventh situation above, I may have the following formula:

Antimonious metarsenite ..... 3 pounds
Vehicle as in No. I above ..... 1 gal.

The essential of this formula is the said antimony arsenic compound. The vehicle may be either of the type that dries or sets primarily upon oxidation or it may be the type that dries or sets primarily by evaporation of the solvent.

A modified formula of this paint formula may be termed Paint formula No. VII—A, and would be as follows:

Antimonic metarsenite ..... 2½ pounds
Vehicle as in No. I above ..... 1 gal.

Paint formula VIII.—As illustrating the eighth situation above, I may have the following formula:

Antimony trioxide ..... 3 pounds
Sodium antimonate ..... 3 pounds
Basic lead carbonate ..... 3 pounds
Vehicle as in No. I above ..... 1 gal.

The essentials of the above formula are the antimony trioxide and the sodium antimonate and the basic lead carbonate. This is good for either type of vehicle, but is more effective when used in connection with candle tar pitch type. For greater effectiveness there may be provided here, a modified formula as VIII—A which consists in adding to formula VIII a catalytic agent such as a manganese oxide. In the place of a manganese oxide, a cobalt, iron or nickel or mercury oxide or metallic platinum may be used.

Paint formula IX.—As illustrating the ninth situation above, I may have the following formula:

Antimonious metantimonite ..... 3 pounds
Vehicle as in No. I above ..... 1 gal.

The essential of this formula is the said antimonite compound.

Paint formula No. X.—As illustrating the tenth situation above, I may have the following formula:

Arsenious metantimonite ..... 3 pounds
Vehicle as in No. I above ..... 1 gal.

The essential of this formula is the said antimonite compound.

Paint formula No. XI.—As illustrating the eleventh situation above, I may have the following formula:

Arsenious metarsenite ..... 3 pounds
Vehicle as in No. I above ..... 1 gal.

The essential of this formula is the said arsenite compound.

Paint formula No. XII.—As illustrating the twelfth situation above, I may have the following formula:

Copper monohydrogen ortho arsenite... 3 pounds
Vehicle as in No. I above..... 1 gal.

The essential of this formula is the said arsenite.

Hereinbefore in those cases where I have specified lead carbonate, the same is done for the reason that basic lead carbonate is a common paint pigment but has the added function set forth above in my formulas, of assisting in liberating the deoxidizing agent quickly at lower temperatures than would otherwise obtain and in some formulas may be substituted by other compounds which would provide a similar reaction, for example, zinc oxide, an oxide of lead, iron oxide, chromium oxide, manganese oxide and lead chromate, etc. Most of the above also serve as pigments for the paint, but for the particular function in question, they need not be true pigments. While the above may be substituted, the lead carbonate generally is more effective in liberating the deoxidizing agent.

In providing stains for shingles, it is important to render fire extinguishing the common vehicles employed in such stains; these vehicles often are paraffin oils and creosote oils. These oils are non-drying liquids used on inflammable materials and may be rendered fire extinguishing by intermixing with them, white arsenic, arsenious metarsenite, antimonic metarsenite, on account of the low temperature at which the fluid deoxidizing agent is liberated.

I have found that my invention has a particularly valuable application in rendering fire extinguishing the insulating fabric or material which is ordinarily used to envelop electric conductors, as wire. In one type of this insulation material, paraffin wax is an important element and is highly inflammable. This ingredient is necessary to render the insulation material water proof and at the same time dielectric. Other insulation materials are bituminous substance, rubber, etc. These can all be fireproofed by incorporating them with the fireproofing agent.

The following coating Formula XIV is one which I have found renders such insulation material fire extinguishing:

Paint formula No. XIV

Paraffin wax..... 2 pounds
White arsenic..... 2 pounds

Paint formula XV

Paraffin wax..... 2 pounds
Antimonic metarsenite..... 2 pounds

In both formulas, each of the ingredients are essential. Fire department authorities have declared that electric wires, as starting and spreading conflagrations, constitute particularly dangerous fire hazards. This is probably largely due to the effects of short circuits or overheating in other ways. When the insulation material is treated with the formula embodying my invention as set forth in Formula XIV or XV such hazard is practically eliminated. The electric conductors are additional hazards in spreading the fire due to the fact that such conductors are ordinarily copper metal and these conduct the heat arising at one point to other points, and the fire thus spreads.

Paint formula XVI

White arsenic..... 6 pounds
Nitrocellulose lacquer..... 1 gal.

These are intimately intermixed. This provides a formula for rendering lacquer fire extinguishing.

Paint formula XVII

White arsenic..... 5 pounds
Candle tar pitch and asphalt..... 1 gal.

This formula is particularly adapted to manufacturing of fire extinguishing artificial roofings or building papers. This composition is intimately mixed and applied while hot.

Paint formula XVIII

Arsenious metarsenite..... 3 pounds
Creosote oil..... 1 gal.

This formula provides a stain particularly adapted for rendering shingles fire extinguishing; likewise wharf piling and lumber. As hereinabove stated, the coating for shingles must be particularly light in weight, otherwise the increase of the freight charges to point of use is prohibitive and the shipping distance in connection with shingles is generally great. The treating of the shingles may most economically be done at or near the place of their manufacture, but where a roof already built is desired to be made fire extinguishing, either the stain or a paint may be applied. Since the stain must be light in weight when applied, it is obvious that the deoxidizing providing compound must be particularly effective to meet the conditions of use of shingles.

It was necessary for me to discover a method to produce many of those deoxidizing agent producing compounds. Also, as an example of my experience with some of the other compounds, I used both zinc arsenite and lead arsenite which I bought on the market, but when employed in my invention in a paint composition, I found that each one failed to work with the necessary effectiveness to extinguish the fire. Even when I employed these compounds in double the amounts prescribed in the above formulas, they failed to give the desired effectiveness, said effectiveness having already been determined by these compounds as produced in my laboratory. The structural atomic arrangement of these undesirable materials were such as to be very resistant to breaking down under temperatures of burning, which required me to develop processes of manufacturing these various substances, nor could I obtain anything in the prior art or literature which explained how to produce these compounds.

In the course of the development of fire extinguishing products, I have discovered the process of making and have made new chemical compounds which are characterized by having the property of liberating readily and freely at or below burning temperature the deoxidizing agent, and at the same time these compounds are characterized by having the property of functioning as pigments for the coating, said pigments combining the desirable qualities of hiding, covering workability with paint vehicles, durability. Also, such new compounds are particularly inactive and indifferent chemically to the ingredients of the paint and to the elements of the atmosphere, i. e. there seems to be no appreciable interaction between said ingredients and elements on the one hand and said new chemical compounds. For example, antimonious metantimonite possesses those qualities; and likewise antimonic metantimonite, antimonious metantimonate and antimonic metantimonate; lead metarsenite, zinc metarsenite, titanium metarsenite.

I have found that the following elements unite to form arsenites, arsenates, antimonites and antimonates, aluminum antimony, arsenic, barium, bismuth, cadmium, calcium, chromium, cobalt, copper, hydrogen, iron, lead, lithium, magnesium, manganese, mercury, molybdenum, nickel, potassium, silver, sodium, strontium, tin, zinc and titanium.

To produce zinc metarsenite, I prepared a water solution of sodium metarsenite by making a mixture composed of 35 gm. arsenic trioxide (white arsenic) 10 gm. C. P. sodium hydroxide and substantially 350 cc. of water to dissolve the product so formed. It was necessary, in order to get complete reaction, to heat to the boiling point of water. After this was so prepared, it was allowed to cool to approximately 45° C. In a separate container, 40 gm. of hepta hydrated zinc sulphate (that is, of sufficient quantity to have a slight excess present when the sodium metarsenite solution is added to same after the reaction process) was dissolved in substantially 350 cc. of water, sufficient to completely dissolve all of the zinc sulphate. The zinc sulphate solution was warmed to 45° C. During the addition of the sodium metarsenite solution to the zinc sulphate, the mixture was agitated and the sodium metarsenite solution was added gradually. The resulting precipitate of zinc metarsenite was permitted to settle and the supernatant water solution was removed. This solution had an acid reaction toward litmus. I washed the precipitate with water at or below 45° C. until no further impurities were present in the zinc metarsenite. I filtered the precipitate and dried in the atmosphere without the application of heat. The temperatures above indicated are important within a certain range as was proven by the fact that when I used temperatures of approximately 100° C., I did not obtain a satisfactory product, the same being affected by hydrolysis. I found by using an excess of caustic soda over that required to form the sodium metarsenite, that a precipitate so formed with the zinc sulphate did not act similarly to the zinc metarsenite obtained above and was not nearly so effective as a producer of a deoxidizing agent. To insure avoiding an excess of sodium hydroxide, the proportions given above provide for having a slight excess of arsenic trioxide, over that necessary for the theoretical chemical reaction to form sodium metarsenite. I obtained much more satisfactory results when I added the sodium metarsenite to the solution of zinc sulphate rather than vice versa; also I found when I dried that precipitate by steam rather than drying at atmospheric temperatures, that I likewise did not get satisfactory results. I mention these various features so that the process of manufacture may be the better understood and to indicate the true composition of the products developed. This product, I term zinc metarsenite.

I have found that the amount of water used in each case can be varied over a considerable range, but at least care must be taken to provide enough water to permit necessary solution of the chemicals. In preparing the above, I employed glass containers and also iron containers.

The process of manufacture of lead metarsenite was the same as that given above for zinc metarsenite with the substitution of the lead acetate for the zinc sulphate.

The following process was developed for producing arsenious metarsenite:

Step No. 1. The sodium metarsenite was prepared in the identical manner described above for zinc metarsenite and the same quantities of ingredients used.

Step No. 2. Arsenious trichloride was prepared by placing 11 gm. of white arsenic in a glass container, followed by 38.5 gm. of 32% hydrochloric acid and substantially 38 gm. water. The whole was then heated until complete solution of the As_4O_6 ensued. This was allowed to cool somewhat before adding it to the sodium metarsenite. The amount of water so added was not sufficient to cause hydrolysis of the arsenious trichloride. The whole then passed into a clear solution by heating to the boiling point of water. I found that this could be cooled to a tepid temperature without either becoming a viscous mass or becoming hydrolyzed. The arsenious trichloride solution was then added to the sodium metarsenite solution which had been cooled to about 20° C. The mixed solutions were agitated and arsenious metarsenite crystals formed that settled to the bottom of the glass container. They were washed with cool water from the faucet. A comparatively large amount of water was used for the washing by decantation until tests proved the absence of all but a slight trace of sodium chloride which was formed as a by-product during the reactions involved in the making of the chemical. It was then filtered and dried in the air and sun.

I also found that there could be substituted a chemically equivalent amount of sulphuric acid for the hydrochloric acid and the resulting arsenious metarsenite had the same characteristic properties as when hydrochloric acid was used.

In general, in the processes of making antimonious metarsenite, antimonious metantimonite, and arsenious metantimonite, the same steps are followed as prescribed above with the obvious substitutions of antimony compounds for arsenic compounds. In making the sodium metantimonite, a part of the process requires more continued heating and more concentrated solutions. Furthermore, in causing the reaction between the positive antimony compound and the sodium metantimonite, more time is required in heating, to completely cause the double decomposition.

In producing the antimonic metarsenite, the sodium metarsenite, having been prepared as set forth, was converted to metarsenious acid by the addition of the calculated amount of hydrochloric acid. The excess of liquid content was removed and a small amount of concentrated hydrochloric acid was added to prevent hydrolysis of the antimonic chloride. To this was added in concentrated form antimonic pentchloride and the same was heated to complete the reaction, washed and filtered as above set forth.

Antimonic metantimonite, in general, was prepared similarly to antimonic metarsenite, substituting the corresponding metantimonite compound for the metarsenite compound to produce the antimonic metantimonite by double decomposition.

In the paint formulas hereinabove set forth, it was found that as the proportions of the deoxidizing agent producing compound are decreased, there is a decrease in the fire extinguishing effectiveness.

The terms "fire retardent" and "fireproof" are merely comparative, and are used herein to describe the relative effectiveness of certain quantities of the deoxidizing agent producing materials used in different coatings.

For illustration, I have developed a test to work to, which test is as follows: I take a kiln dried cedar shingle, approximately 2 inches wide and 16 inches long, having a thickness at the thin end of 1/8th inch and increasing to 3/8th inch at the thick end. I paint this shingle, one coat on both sides starting one inch above the thin end and extending to the upper, or thick end. Such painted surface is permitted to dry for such a period as will permit all the thinner, or volatile solvents, to completely evaporate, i. e. ordinarily twenty-four hours in a warm place. Then by igniting the unpainted thin end and observing the fire resistance when the flame reaches the painted portion of the shingle, a determination can be made as to the degree of fire retardent effect of the coating material under test. The shingle is held at an angle of forty-five degrees and in a place where there are no appreciable drafts of air, but where the air has free contact with the shingle. Care is used to have the shingle as free of moisture as is practically possible by kiln drying and preventing later absorption of moisture. If the fire does not continue to burn the surface paint for a distance of two inches, I call it fireproof. If it burns to not exceed a distance of five inches above the lower line of the paint, I term it very retardent. If it burns above the five inch point but extinguishes above that point, it is retardent and if it burns the whole distance, I term it non-retardent.

In coating the test shingle, I plan a coat of such thickness that one gallon of the coating will cover 150 square feet of surface, the same being evenly distributed upon the surface, this being about the normal coverage which would be employed in coating shingle roofs.

To provide a cold water paint, the following formulas may be employed:

Paint formula No. XIX

Plaster of Paris	4 pounds
Borax	1 pound
Casein	½ pound
Dry sodium arsenite	2 pounds

These are intimately mixed and, when ready to apply, sufficient water is added to make a workable coating, that is, approximately one-half gallon.

Paint formula No. XX

Plaster of Paris	4 pounds
Borax	1 pound
Casein	½ pound
Arsenic trioxide	3 pounds

These are intimately mixed and when ready to apply, sufficient water is added to make a workable coating, that is, approximately one-half gallon.

In the above formulas, wherever we have specified the vehicle of Formula I and where white arsenic is not a constituent, a vehicle which dries primarily by oxidation can be substituted but to provide the necessary paint body, the body forming ingredients must be increased to the desired amount.

To provide against unusual severe exposure to heat of a fire, I would supply a coating comprising a combination of the deoxidizing agent producing compounds which would be liberated at different degrees of temperature. For example, one component of such a coating could be white arsenic, a second could be antimonic metarsenite and a third, arsenious metarsenite and a fourth, zinc metarsenite.

Equivalents for paraffin wax would be beeswax, carnauba wax, Japan wax, cerecine wax and Montan wax.

For my purpose herein, there may be included in alkaline earth groups, calcium, barium, strontium and magnesium and the like.

The advantages of arsenic compounds are their effectiveness and cheapness, while the advantages of antimony compositions are, as hereinabove mentioned, their non-poisonous character and better pigment qualities.

Herein where I have used the term "deoxidizing" in the specification and claims, I mean to describe that property whereby oxidizing, i. e. burning, of heated, distilled, inflammable gases by the oxygen of the air is prevented either entirely or in part. This deoxidizing action may be called an anti or negative catalytic action in that instead of accelerating the action, it definitely opposes the burning.

Herein where I use the word "set" is meant to indicate that the physical condition of the coating film has changed from a liquid condition to a relatively non-tacky, tough, firm coat.

It will be understood that in the use of the anti-catalytic agent, the degree of fineness, as hereinbefore explained, is important, and that such an anti-catalytic agent may be mixed with the other ingredients of the paint in a mechanically finely divided condition. It may be dispersed throughout the vehicle, or it may be in solution in the vehicle, or it may be in the form of an emulsion with the vehicle.

Herein where I have mentioned the vehicle as being resinous, or bitumen, or wax, that for our purposes such descriptive terminology is interchangeable. Although the resin is of a vegetable origin, while the bitumen is of a mineral origin, the waxes may be of either origin. Included in this character of vehicles may be synthetic resins, creosote, rubbers, asphalt, coal tars or other tars, as well as nitrocellulose products.

Herein where I use the term oxy-arsenic I mean to include the arsenates and the arsenites; and where I use oxy-antimonic I mean to include both the antimonates and antimonites. Arsenic or arsenic in its various forms are to be considered, for purposes herein, as metallic.

I have discovered that when I form a coating including antimony trioxide that has been intimately intermixed with a very finely divided catalytic agent such as cobalt oxide, or metallic platinum that upon burning, the deoxidizing action seems to proceed gradually to a certain point and then as a certain degree of heat is developed, of a sudden there is a puffing out or sudden extinguishing of the flame. In providing this coating, I intermix the antimony trioxide with a solution of cobalt nitrate or platinum chloride, as the case may be. I heat this mixture to a temperature such that the cobalt nitrate or the platinum chloride will be decomposed to form respectively cobalt oxide or metallic platinum. Then this product is mixed with the paint composition.

As in the case of white arsenic and arsenious metarsenite which have the same empirical formula, nevertheless differing widely in effect for the purposes of my invention, so likewise, antimony trioxide, as commonly obtained on the market, has the same empirical formula as antimonious metantimonite; nevertheless the latter have widely different effects for the purposes of my invention, that is. the antimonious metanti-

monite is much more effective for the purpose of my invention.

I claim:

1. The process of making a paint composition comprising intimately intermixing with a paint vehicle arsenious metarsenite, said metarsenite being formed by adding, gradually and with agitation, arsenic trichloride in solution to sodium metarsenite in solution, both solutions being approximately 45° C., the resulting precipitate being filtered and washed until substantially free of impurities and dried at relatively low temperature, said trichloride solution being formed by adding to eleven grams of white arsenic substantially thirty-eight grams of thirty-two per cent hydrochloric acid and substantially thirty-eight grams of water, the mixture being heated to approximately 100° C., and said sodium metarsenite solution being formed by adding to substantially thirty-five grams of white arsenic and ten grams of ninety-five per cent sodium hydroxide and substantially three hundred grams of water, heating said solution to 100° C. until reaction is complete and then cooling said solution.

2. A fire extinguishing liquid paint composition for inflammable material comprising an oxidation-inhibitor at combustion temperature in the form of arsenious metarsenite.

CLAUDE S. THOMPSON.