

UNITED STATES PATENT OFFICE

2,607,729

TEXTILE TREATING COMPOUNDS

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No Drawing. Application June 24, 1950,

Serial No. 170,265

8 Claims. (Cl. 252-8.1)

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This invention relates to novel titanium-anti-
mony compositions useful in treating organic
substances, especially textile materials, in order
to impart valuable properties thereto. More par-
ticularly it relates to the production and use of a
novel composition comprising titanium and anti-
mony, useful for rendering textile materials
flame-resistant.

The various textiles, such as rayon and cotton
goods, present an appreciable fire hazard due to
the ease with which they may be ignited. This
is particularly true in clothing such as light-
weight rayon dress goods or in heavier fabrics
having a pile finish. The finer pile fabrics are
often made by brushing regenerated cellulosic
textiles, e. g., woven or knitted viscose goods, and
these are particularly hazardous due to the ease
with which a flame may spread over the pile ma-
terial. The dangers have been brought to the
attention of the public by the many disasters in
recent years resulting from the increased use of
fabrics having such high susceptibility to flame-
propagation. Action has been taken by the
American Association of Textile Chemists and
Colorists, which has developed a testing method
to determine the flash- or flame-resistance of
textile fabrics. In such a test a rectangle of
treated cloth measuring 2" x 6" must be heated
for fifteen minutes at 105° C. and then cooled in
a desiccator over calcium chloride. The result-
ing dried cloth will have a moisture content of
less than 0.3% under such conditions. The cooled
cloth must then be removed from the desiccator,
supported on a screen held at a 45° angle, and
touched with a 1/2" flame for one second. To pass
the test, pile goods must not show material flash-
ing, even after laundering. Flat or non-pile
goods may be tested similarly, but the flame in
this instance is applied to goods suspended in a
vertical position, and the goods must not con-
tinue to burn after the flame is removed.

Various compounds have been added to, or in-
corporated in fabrics to attempt to render them
fire- or flameproof. The most widely employed
process comprises coating the textile simultane-
ously with a chlorinated resin or chlorinated
paraffin and an inorganic oxidic material. Such
compositions have been used especially to render
tarpaulin tenting material flameproof and for
like military applications. Such a method, how-
ever, substantially changes the character of the
goods because the coating is of substantial thick-
ness and the textile loses its flexibility. Too, al-
though the coating is relatively water-resistant
and thus durable to laundering, it is not resistant

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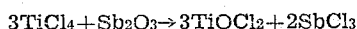
to the solvents used in dry-cleaning but is dis-
solved thereby. Hence, fabrics so treated are not
satisfactory for general clothing purposes and are
not even acceptable for work clothing. In addi-
tion, it has been suggested that fabrics be treated
with an inorganic salt such as a chloride of
titanium, tin or antimony, dissolved either in
water or in non-aqueous solvents like toluene,
ethyl acetate, etc. Fabrics have also been con-
tacted with ammonium sulfamate, alone or in
conjunction with soluble salts, e. g., borates and
the like. However, none of these prior art pro-
cesses has given products which at the same time
meet the above-referred-to AATCC test for flash-
or flame-resistance, are dry-cleaning- and laun-
dering-resistant and give a product having con-
sumer appeal.

More recently it has been proposed to apply a
combined solution of antimony and titanium to
textile materials; such a method is outlined and
claimed in co-pending application Serial No.
724,242, filed January 24, 1947 by F. W. Lane and
myself, which has issued as U. S. Patent No.
2,570,566, dated October 9, 1951. The fabric is
immersed in the antimony-titanium solution;
after a short lag period, the fabric is treated with
an alkaline neutralizing agent, such as ammoni-
um hydroxide or sodium carbonate, and then
rinsed or washed to remove any loosely-held in-
organic oxides and salts. Upon drying, it is
ready for use as a flame-resistant textile. This
method has shown great promise, since it provides
clothing, drapery, curtain, and industrial fabrics
of greater consumer appeal, and having a flame-
resistance which is durable both to laundering
and to dry-cleaning. Most important, of course,
is the fact that it makes economically possible
the obtention of clothing material which passes
the rigid AATCC fire-resistance test and imple-
ments practically the enforcement of fire preven-
tion laws such as that enacted in California.

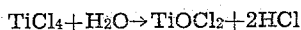
It is among the objects of this invention to sub-
stantially improve upon the operations recited in
the above-mentioned Lane and Dills application
and to provide the textile trade with a flame-
retarding composition comprising titanium and
antimony in more concentrated form. Another
object is to provide a composition which is solu-
ble in an aqueous medium but which may exist
as a solid or powdery material and be transported
in relatively inexpensive containers. A further
object is to provide to the textile-finishing in-
dustry an anhydrous reagent which may be trans-
ported from its point of manufacture to the con-
sumer at decreased shipping charges. Other ob-

jects will become apparent as my invention is further revealed.

The above objects of my invention may be realized in a specific embodiment thereof which comprises reacting antimony oxide with titanium tetrachloride to produce a composition comprising basic titanium chloride, e. g., TiOCl_2 , and a chloride of antimony, e. g., SbCl_3 , as may be illustrated in part by the hypothetical equation:



This reaction takes place with the generation of heat. The product is dry, and will be substantially devoid of visible fumes when there is no excess of anhydrous TiCl_4 therein. In the event that one uses an excess of titanium tetrachloride, a fuming substance results which may be used as such, if suitable packaging and other precautions are taken. However, if it is desired to eliminate the fumes, this may readily be done by the addition of sufficient water to convert the excess TiCl_4 to an oxychloride, e. g.



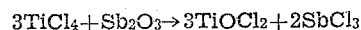
In a preferred embodiment of my invention, I react titanium tetrachloride with antimony oxide, using approximately three mols of TiCl_4 for each mol of Sb_2O_3 in accordance with the first equation given above. This ratio of titanium to antimony has been found quite satisfactory in the flameproofing of fabrics, particularly cellulosic fabrics made of rayon and cotton yarns. The product has been found quite soluble in water or water containing an acid such as hydrochloric, acetic, chloracetic or other similar reagents useful in maintaining titanium and antimony chlorides in solution in a dilute aqueous medium.

When one stirs antimony oxide into titanium tetrachloride, spontaneous reaction may or may not take place, depending on the purity of the reagents and their freedom from moisture as well as the temperature of the suspension. I find it convenient to mix the two reagents under conditions which will give a uniform composition prior to the beginning of the reaction. In other words, I prefer to mix the two in the absence of water and while keeping the temperature low, and then initiate the reaction by adding a trace of water. The latter may be catalytic in its behaviour; or it is also possible that the water-addition generates heat and raises the temperature to the point where the reaction itself starts and spreads.

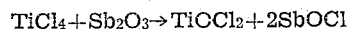
My method of preparing these solid flame-retarding compositions is subject to considerable variation without departing from the spirit of the invention. The product may vary in composition over a considerable range without becoming liquid or even tacky. A free-flowing powder having a variable ratio of titanium to antimony is therefore possible, depending on the amount of each ingredient employed. The use of amounts of titanium tetrachloride in excess of that shown in the hereinbefore-mentioned equation, e. g., four mols of TiCl_4 for each mol of Sb_2O_3 , will result in a reaction product containing residual TiCl_4 . Upon subsidence of the reaction and exposure of the mass to the moist atmosphere, a fuming product is thus obtained. However, if desired, this visible smoke or fume may be avoided by adding to the reaction mass a limited amount of water so as to convert the residual tetrachloride to an oxychloride such as TiOCl_2 . This use of a quantity of water

stoichiometrically equivalent to the excess TiCl_4 present should not be confused with the utilization of a small or trace amount to catalyze or accelerate reaction between the titanium chloride and antimony oxide as above disclosed. The product resulting after the addition of water to react with an excess of one mol of TiCl_4 will contain approximately two atoms of titanium per atom of antimony and will be a dry powder which is free of visible fumes and which may be transported like other powders in simple drums or bags.

The solid flameproofing product of this invention may also be modified by using a larger proportion of antimony oxide, in which event the antimony content will be greater than that provided by the previously mentioned reaction



For instance, equimolar proportions of the reactants may be employed, according to the equation



The antimony will be present either as unconverted oxide, as the normal chloride or as a basic chloride, depending on the conditions of reaction between the titanium tetrachloride and the antimony reagent. Such a product will dissolve in dilute acid, e. g., 20% HCl , to give a clear solution which may be used directly in the treatment of inflammable textile fabrics, or may be further diluted with water or modified in other ways depending on the wishes of the consumer.

To a clearer understanding of my invention, the following specific examples are given, it being understood that they are merely illustrative and are not to be taken as limiting the scope of my invention:

Example I

One hundred parts by weight of antimony oxide were slurried in 190 parts by weight of anhydrous titanium tetrachloride and after a uniform suspension was obtained, water was added in a dropwise manner until reaction set in. Heat was generated and fumes appeared above the reacting mixture. After the initial reaction had subsided, 18 parts by weight of water were slowly added with agitation to the solid reaction product. Fuming ceased and the final product was a dry, powdery material.

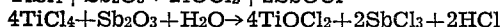
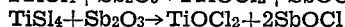
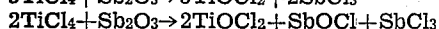
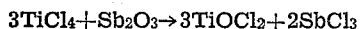
This dry mixture of titanium and antimony chlorides was found to dissolve readily in water acidulated with 20% HCl , and a very concentrated solution could be thus prepared. A portion of this solution containing 400 grams of the combined titanium and antimony (calculated as oxides) was used in the flameproofing of a brushed viscose blanket material having 0.4 inch pile. The blanketing was soaked in this solution for 5 minutes, passed between closely-fitted rolls to remove excess solution, and then, after a 15 minute lag period, immersed in a saturated sodium carbonate solution. The fabric was finally thoroughly scrubbed with soapy water, rinsed, dried, and a portion tested by the AATCC test (dried in a proper desiccator, supported at a 45° angle and touched for 1 second with a 1/2-inch flame). No flashing occurred on the pile surface. Another portion of the treated material was subjected to chemical analysis and found to contain 7.5% TiO_2 and 7.0% Sb_2O_3 .

Example II

One hundred parts by weight of antimony oxide were slurried in 205 parts by weight of TiCl_4 while the latter was being stirred and maintained at a low temperature by water-jacket cooling. No reaction took place during the mixing, but when a uniform suspension was obtained, water was added dropwise to raise the temperature and initiate the reaction. Dense fumes were evolved in the moist air and the reaction was vigorous, continuing for about 15 minutes. Twenty-eight parts by weight of water were then added dropwise with stirring, converting the excess of TiCl_4 to an oxychloride, in which condition it became substantially non-fuming. Stirring was continued until the mixture was free of any lumps, and the solid product was then tested for solubility. It was found to leave some insoluble residue when treated with 10% HCl but to dissolve completely in 20% HCl . The solid analyzed 25.9% TiO_2 , 33.6% Sb_2O_3 , and 42.1% HCl .

The product of this example, like that of Example I, was found to be a valuable flameproofing compound for rendering inflammable textile materials such as rayon and cotton goods fire-resistant.

As disclosed above and illustrated in the examples, I have outlined a method for producing solid compositions useful in the treatment of textiles to reduce fire hazards. These solids are soluble in water or acidulated water or the like, e. g., a 10% or 20% HCl solution, solutions of sulfuric acid, acetic or chloracetic acids, propionic acid, other water-soluble acids, etc. The exact chemistry of the reaction between antimony oxide and titanium tetrachloride is unknown but is believed to follow one or more of the following equations:



One may observe that the process is flexible in that a considerable variation in the ratio between antimony and titanium is possible and the reaction yields a mixture of a chloride and one or more oxychlorides. For reasons of simplicity, I use the term "chloride" to include both the normal chloride and the oxychloride or basic chloride, as for example TiOCl_2 or SbOCl , and it is understood that the extent of the reaction between the two reagents and the chemical composition of the reaction products is not a fundamental of my invention. I regard my invention as a means of preparing a solid material which will readily dissolve in an aqueous system and which is useful as a treating agent for inflammable textile goods to render them fire-resistant. A close examination of the equations given above will show that it is possible to produce solid compositions comprising chlorides of titanium and antimony in which the ratio of antimony to titanium may be as great as two and as low as one-half.

In the examples, I have shown the reaction taking place in the absence of a diluent or solvent. It is naturally essential to avoid contact with a substantial amount of water in order to produce a dry, powdery material; but excess TiCl_4 may be consumed by reaction with an equivalent amount of H_2O . The reaction may be aided and accelerated by the application of a small amount of heat. Additionally, the process

can be carried out in the presence of an organic solvent such as benzene, toluene, or cyclohexane, and it should be understood that such a modification comes within the scope of this invention. The avoidance of such additional reagents is generally recommended, however, for economy as well as for minimizing operational complications.

The solid, soluble concentrates of this invention form aqueous solutions which are particularly effective for treating filaments and films comprising materials which react chemically with them to impart to such filaments and films desired flame-resistance characteristics. Thus, while after-treatment of polyacrylonitrile yarn with these flame-proofing compositions is relatively ineffective, excellent results are obtained by after-treatment of acrylonitrile polymers containing reactive functional groups, such as hydroxyl groups, carboxyl groups, and groups which hydrolyze to these under the after-treatment conditions.

Some of the more successful methods of modifying polyacrylonitrile so that films and filaments can be flame-proofed with the compositions of this invention are: (1) partial hydrolysis to provide amide or carboxylic groups, (2) use of acrylonitrile co-polymer containing such groups as hydroxyl, carboxyl, anhydrides, amides, lactones, esters, and amines; and (3) incorporation of materials containing such groups as these into fibers by impregnation or by inclusion in the spinning compositions. Many of these techniques are applicable to other fibers, and particularly the third treatment could be applied to any synthetic fiber.

I claim as my invention:

1. A solid dry aqueous-media-soluble composition for rendering inflammable textile materials flame-resistant which consists in a reaction mixture of titanium oxychloride with a compound of antimony selected from the group consisting of a basic and normal chloride, the atom ratio of antimony to titanium in said composition being not more than two and not less than one-half.

2. Dry, powdery flame-retarding composition, useful for the treatment of inflammable textile materials and soluble in an aqueous system, which consists in titanium oxychloride and antimony chloride, the atom ratio of antimony to titanium in said composition being not more than two and not less than one-half.

3. A process for the preparation of a soluble, solid flame-retarding composition of matter which comprises mixing in the dry state, antimony oxide with titanium tetrachloride, incorporating a small amount of water therein, and thereby converting the tetrachloride to an oxychloride and the antimony oxide to a chloride, and employing therein such ratio of reactants that the resulting composition contains an atom ratio of antimony to titanium of not more than 2 and not less than one-half.

4. A process for the preparation of solid flame-retarding compositions of matter soluble in aqueous media, which comprises mixing in the dry state antimony oxide with titanium tetrachloride, and adding a small quantity of water thereto, the amount of the reagents being so selected that the product will comprise an oxychloride of titanium and a normal chloride of antimony, with its atom ratio of antimony to titanium being not more than 2 and not less than one-half.

5. A process for the production of a solid, flame-retarding reagent comprising chlorides of tita-

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nium and antimony soluble in aqueous media which comprises mixing together in the dry state antimony oxide and titanium tetrachloride, adding enough water to the mixture to convert any unreacted titanium tetrachloride to titanium oxychloride, and employing said reactants in such proportion that the solid product obtained will contain an atom ratio of antimony to titanium of not more than 2 and not less than one-half.

6. A process for the production of the solid flame-retarding reagent comprising an oxychloride of titanium and antimony chloride soluble in aqueous media which comprises mixing together in the dry state for reaction antimony oxide and titanium tetrachloride, employing an atom ratio of antimony to titanium in the reaction mixture of not more than two nor less than one-half, and then initiating a reaction between the compounds so mixed by adding water dropwise thereto.

7. A process for the production of a solid flame-retarding reagent comprising an oxychloride of titanium and antimony trichloride soluble in aqueous media which comprises reacting together antimony trioxide and titanium tetrachloride by mixing said compounds in the dry state and adding a small amount of water to the mixture, employing an atom ratio of antimony to titanium in the reaction mixture of not more than two and not less than one-half, and adding sufficient water to the reaction product to convert any unreacted titanium tetrachloride to titanium oxychloride.

8. A method for producing a dry solid aqueous-

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media-soluble concentrate useful in solution as a flame-retarding reagent for textiles which comprises intimately mixing titanium tetrachloride and antimony trioxide under anhydrous conditions in a reaction vessel, employing said titanium and antimony compounds in such proportion that the atom ratio of antimony to titanium in the mixture will be not more than 2 and not less than one-half, and then initiating a reaction between said mixed compounds by adding water dropwise thereto until the desired reaction sets in.

WILLIAM L. DILLS.

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

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