

1

2,926,097

FIRE RESISTANT COMPOSITION FOR FABRICS

Martin Leatherman, United States Army, assignor to the United States of America as represented by the Secretary of War

No Drawing. Application November 3, 1944
Serial No. 561,801

12 Claims. (Cl. 106—17)

(Granted under Title 35, U.S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government for governmental purposes, without the payment to me of any royalty thereon.

This invention relates to compositions for rendering fabrics resistant to fire and to penetration by the vesicant vapors commonly used as chemical warfare agents, such as beta, beta dichloro diethyl sulfide. These vapors are of such nature that they are chemically changed and rendered harmless by oxidizing agents, particularly active or nascent chlorine, or by compounds which contain loosely held chlorine. The nature of these compounds will be more fully set forth in the description of my invention. This invention is applicable to all forms of fibrous materials which may be used for clothing, tensing materials, truck covers and the like and of any nature whatsoever. The fibrous materials may be of cotton, rayon, burlap, wool, nylon, silk, etc., since the compositions to be described not only render combustible fibrous materials fire resistant but also increase the fire resistance of difficultly combustible fibrous materials such as wool.

A satisfactory flameproofing treatment for use on garments should alter the normal characteristics of the original textile material as little as possible. The treated fabric should be essentially unchanged with respect to porosity, flexibility and wearing qualities and should be free from dusting, cracking and toxic effects. While it may not be feasible to avoid completely all changes in physical properties of the fabric, the invention about to be described reduces such changes to a minimum.

The principle of my invention resides in the fact that evolution of certain gases from the environment of the fabric at certain elevated temperatures below the combustion point of such fabrics results in complete prevention of flame formation. Among gases which are capable of preventing flame are hydrogen chloride and compounds of nitrogen wherein nitrogen is in reduced form. The formation of such gases at effective elevated temperatures is an essential feature of the compositions comprising my invention and the manner by which such formation is effectively accelerated constitutes the basis of my invention.

As thus far developed, the customary method of imparting vesicant vapor resistance to protective clothing is to impregnate such clothing with certain chloroamides, referred to as impregnites, in conjunction with certain binders. Various binders may be used such as chlorinated paraffin, chlorinated rubber, polyvinyl chloride, mineral oil, etc. For the present invention the preferred binder is chlorinated paraffin. The binder serves to fix the impregnite upon the fibers of the fabric either by a process of adhesion or by dissolving the impregnite or both. In as much as both the impregnite and the chlorinated paraffin tend to develop acidity which is injurious to the impregnated fabrics, it is a known practice in the prior art to add so-called stabilizers or antacid ingredients as integral parts of the impregnating composition. Both

2

calcium carbonate and zinc oxide have been used for this purpose but since the effect desired was solely the neutralization of acidity, the amount used was always small, for example, not to exceed ten percent of the weight of impregnite in the formula.

I have now discovered that if zinc oxide is used in the impregnating formula to the extent of eight to twenty fold that which has been previously used as a stabilizer, new and useful properties result. The reason for this phenomenon is that when an increase of sufficient magnitude in surface area of contact between zinc oxide, impregnite and chlorinated paraffin is produced by increasing the zinc oxide constituent, then the zinc oxide assumes catalytic properties. The effect of this catalytic activity appears to be that at elevated temperatures the evolution of hydrogen chloride from the impregnite and chlorinated paraffin is greatly increased. At the same time, thermal decomposition of the impregnite results in evolution of compounds containing reduced nitrogen. This mixture of evolved gases completely prevents flaming of the impregnated fabric.

In practicing my invention it is necessary that the constituents of my composition be distributed throughout the fabric. If the distribution is too largely superficial, flame resistance decreases. Satisfactory distribution can be secured by a variety of methods. In case the stability of the particular impregnite being used permits, a preferred method consists of dissolving the impregnite and chlorinated paraffin and suspending the zinc oxide in a compatible solvent, the solution-suspension then being applied to fabric by tumbling (dipping combined with agitation), spraying, etc. In some cases it may be necessary to use elevated temperatures in order to effect solution of the impregnite.

In other cases where the impregnite is too insoluble at ordinary temperatures and too unstable at elevated temperatures, my invention envisages a further step which may be used to advantage regardless of solubility of the impregnite. I have found that if a certain amount of an esterified derivative of sorbitol is introduced into my compositions a phenomenal improvement in distribution of the compositions results when these compositions are introduced into textiles. The effect is so pronounced in some cases as to mean the difference between a flameproof and a combustible treated fabric. A sorbitol derivative preferred for my purpose is sorbitan monolaurate wherein elimination of one molecule of water from sorbitol has resulted in an ether linkage between the first and fourth carbon atoms and in which the hydroxyl group on the sixth carbon atom has been esterified with lauric acid. However, sorbitan menopalmitate, sorbitan monostearate and other analogous sorbitan derivatives may also be used.

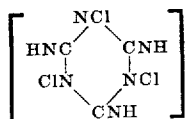
In addition to facilitating distribution of my compositions, the sorbitan derivatives render the treated garments or fabrics much more easily permeable to liquid water. Where flameproof clothing is worn in hot environments as within a tank, such permeability adds to the comfort of the wearer.

When the sorbitan ester is employed, both the impregnite and zinc oxide components may be in suspension and only the chlorinated paraffin and sorbitan ester in solution. This makes possible the use of low cost solvents such as mineral spirits which could not otherwise be used.

In carrying out my invention a preferred impregnite is N,N',2,2',4,4',6,6' octachloro-sym.-diphenyl urea. However, there are a large number of impregnites which possess qualities suitable for my purpose. For example, N,N',3,3',5,5' hexachloro-N,N' diacetylbenzidine; 1,3,4,6-

3

tetrachloro-7,8-diphenylglycoluril; 1,3,4,6-tetrachloro-7,8-dimethylglycoluril and trichloromelamine



are among the compounds that may be used for my purpose. These are all chloramides containing various amounts of active chlorine.

Example I

In practicing my invention a preferred procedure is as follows:

In a suitable vat supplied with a stirrer are mixed:

900 pounds acetylene tetrachloride
22.5 pounds sorbitan monolaurate
90 pounds chlorinated paraffin
90 pounds finely divided N,N',2,2',4,4',6,6' octachloro-sym.-diphenyl urea
907 pounds finely divided zinc oxide

The composition is stirred until a homogeneous solution-suspension is obtained, and this is then poured over the garments or fabrics to be treated, the said garments or fabrics being tumbled or agitated meanwhile. It is preferable that these be freed of moisture by pre-drying in an oven. After the solution-suspension has been thoroughly worked into the garments or fabrics preferably by tumbling, these are then freed of excess treating composition by centrifuging or any other suitable means to wet pick-up of about 140 percent. The volatile solvent is then driven off in a dryer. The weight increase after drying should be preferably between 35 and 40 percent of the untreated weight of the garments or fabrics.

As previously set forth, I may substitutively use other impregnates than N,N',2,2',4,4',6,6' octachloro-sym.-diphenyl urea in the above example and I may vary the proportions of ingredients employed. The presence of sorbitan monolaurate or equivalent is not vital to the workability of my invention since it merely facilitates the desired distribution of treating composition without which flame resistance will not result. For example, if the above described procedure is carried out at 60° C., at which temperature the particular impregnate cited will be in solution, then the sorbitan monolaurate or equivalent may be omitted.

It is usually desired to deposit in treated garments for protective purposes approximately ten percent of impregnate based on untreated weight. Within this limitation the proportion of zinc oxide may be varied from one part impregnate to eight-tenths of one part zinc oxide as a minimum to one part impregnate to two parts zinc oxide by weight as a maximum. The proportion of chlorinated paraffin is not critical within certain limits. In addition to acting to assist in flameproofing, the chlorinated paraffin serves as a binder to hold the solid components on the fibers. If too much is present, the fabric is rendered harsh or clammy whereas if too little is used, flameproofing properties and vesicant vapor resistance of the compositions will be adversely affected. In general, I will not ordinarily desire to use less chlorinated paraffin than fifteen percent nor more than sixty percent of the combined weight of impregnate and zinc oxide present in the compositions.

In practicing my invention, certain instances have been encountered wherein it is desirable to replace the sorbitan monolaurate with other distributing agents. For example, there may be periods, as at present, when gas warfare is not practiced. During such periods, my invention is pri-

4

marily required from only the flameproofing standpoint, while the vesicant resistant features are only required from the emergency standpoint.

However, when sorbitan monolaurate is used as the distributing agent, it causes the stripping of the impregnate composition from the fabric during laundering, thereby making it necessary to reimpregnate the fabric or garment at frequent intervals. Such stripping would be desirable in the event of active gas warfare when the neutralization of vesicants is required. However, when gas warfare is not being practiced, it is desirable to have the clothing, impregnated according to my invention, as resistant to stripping in laundering as possible.

It has been found that in cases where it is desirable to have impregnated fabric and garments highly resistant to stripping, that the sorbitan monolaurate should be replaced with other emulsifying agents, particularly aluminum stearate.

Excellent results and products were obtained when aluminum stearate was substituted for a sorbitan monolaurate in the same proportion, in the specific formulation described above in Example I. A fabric treated with the composition disclosed in Example I, modified by the substitution of aluminum stearate, was found to have no decrease in flame resistance after having gone through three commercial launderings, using Quartermaster Formula G (three 5-minute washings with low titer wool soap followed by three 5-minute rinses with clear water, all at 90° F.). There was no serious loss or stripping of the impregnate content caused by such laundering.

Another material which can be substituted for sorbitan monolaurate for accomplishing the same purpose as aluminum stearate, is sorbitan tetrastearate. This latter material has much less emulsifying properties than sorbitan monolaurate and yields greater launder resistance. In effect, it is probably inferior to aluminum stearate but has the advantage of greater density. This is a desirable feature for shipping purposes. The useful proportions of sorbitan tetrastearate are similar to those of sorbitan monolaurate and aluminum stearate.

The extreme toxicity of the acetylene tetrachloride (tetrachloroethane) makes it very desirable in certain instances to substitute a non-toxic vehicle for applying the flameproofing-vesicant resistant composition. Accordingly, mineral spirits or Stoddard solvent may be substituted for acetylene tetrachloride with necessary adjustments in amount used in order to secure the desired pick-up of 35 to 40% of untreated weight of fabric. The flame resistance of the fabric treated with a composition employing mineral spirits, was satisfactory, but there was appreciable filtering out of solids on the visible surface of the fabric. This caused a greater whitening of the fabric. However, this whitening can be easily neutralized by incorporation of pigments into the compositions. This invention, therefore, contemplates incorporation of pigments for producing or maintaining camouflage effects. Among pigments which are suitable are mixtures of carbon black and yellow iron oxide, and also organic pigments which have been found compatible with the impregnates.

Both the proportions of ingredients present in the compositions and the procedures described are illustrative only and applicant does not wish to be limited except as to the results obtained. If satisfactory distribution of the compositions in the fabric can be secured by use of emulsions such procedure would come within the scope of the invention. In the case of emulsions all of the ingredients would be suspended in water in finely divided form by means of some compatible suspending agent.

I claim:

1. A textile treating composition consisting essentially of from about 65% to about 85% of a chloramide, from about 6% to 10% of a chlorinated paraffin, from about 6% to 10% of a dechlorinating agent, and from about 0.5% to 5% of a distributing agent, said chloramide being

5

selected from the group of compounds consisting of N,N',2,2',4,4',6,6' octachloro-sym.-diphenyl urea, N,N',3,3',5,5' hexachloro-N,N' diacetylbenzidine; 1,3,4,6-tetrachloro-7,8-diphenylglycoluril; 1,3,4,6-tetrachloro-7,8 dimethylglycoluril and trichloromelamine,

said dechlorinating agent being selected from the group of compounds consisting of zinc oxide and calcium carbonate and said distributing agent being selected from the group of compounds consisting of sorbitan monolaurate, aluminum stearate and sorbitan tetralaurate.

2. A composition consisting essentially of one part by weight of N,N',2,2',4,4',6,6' octachloro-sym.-diphenyl urea, from about 0.8 to 2.0 parts by weight of zinc oxide, and 0.6 to 1.5 parts chlorinated paraffin to bind the composition to fabric material.

3. A composition consisting essentially of 936 parts by weight acetylene tetrachloride, 21 parts by weight of a distributing agent selected from the group consisting of sorbitan monolaurate, 62 parts by weight chlorinated paraffin, 83 parts by weight finely divided N,N',2,2',4,4',6,6' octachloro-sym.-diphenyl urea and 127 parts by weight finely divided zinc oxide.

4. A composition consisting of compounds forming an adhesive, fire-resistant, anti-vesicant coating material, said compounds comprising 936 parts by weight of acetylene tetrachloride, 21 parts by weight of sorbitan tetralaurate, 62 parts by weight of chlorinated paraffin, 83 parts by weight of finely divided N,N',2,2',4,4',6,6' octachloro-sym.-diphenyl urea and 127 parts by weight of finely divided zinc oxide.

5. A composition consisting essentially of 936 parts by weight of acetylene tetrachloride, 21 parts by weight of aluminum stearate, 62 parts by weight of chlorinated paraffin 83 parts by weight of finely divided N,N',2,2',4,4',6,6' octachloro-sym.-diphenyl urea, and 127 parts by weight of finely divided zinc oxide.

6. A composition consisting essentially of a chloramide selected from the group of chloramides consisting of N,N',2,2',4,4',6,6' octachloro-sym.-diphenyl urea, N,N',3,3',5,5' hexachloro-N,N' diacetylbenzidine; 1,3,4,6-tetrachloro-7,8-diphenylglycoluril; 1,3,4,6-tetrachloro-7,8-dimethylglycoluril; and trichloromelamine,

zinc oxide in a catalytically active proportion of between 80% and 200% of the weight of the chloramide, and chlorinated paraffin in a proportion of not less than 15% nor more than 60% of the combined weight of said chloramide and said zinc oxide.

7. A composition consisting essentially of a chloramide selected from the group of chloramides consisting of

N,N',2,2',4,4',6,6' octachloro-sym.-diphenyl urea, N,N',3,3',5,5' hexachloro-N,N' diacetylbenzidine; 1,3,4,6-tetrachloro-7,8-diphenylglycoluril; 1,3,4,6-tetrachloro-7,8-dimethylglycoluril; and trichloromelamine,

a calcium carbonate dechlorinating agent in a proportion of between 80% and 200% by weight of the chloramide, and a binder consisting of chlorinated paraffin in a proportion of not less than 15% nor more than 60% of the combined weights of the said chloramide and the said calcium carbonate.

8. A composition consisting essentially of a chloramide selected from the group of chloramides consisting of

N,N',2,2',4,4',6,6' octachloro-sym.-diphenyl urea, N,N',3,3',5,5' hexachloro-N,N' diacetylbenzidine; 1,3,4,6-tetrachloro-7,8-diphenylglycoluril; 1,3,4,6-tetrachloro-7,8-dimethylglycoluril; and trichloromelamine,

6

a dechlorinating agent consisting of zinc oxide in a catalytically active proportion of between 80% and 200% by weight of the chloramide, a binder consisting of chlorinated paraffin, and a solvent in a proportion by weight of not less than 0.5% nor more than 5% of the composition and selected from the group of solvents consisting of aluminum stearate and sorbitan tetralaurate, said paraffin being not less than 15% nor more than 60% of the combined weight of said chloramide and said zinc oxide.

9. A composition consisting essentially of N,N',2,2',4,4',6,6' octachloro-sym.-diphenyl urea, zinc oxide in a proportion of between 80% and 200% by weight of said octachloro-sym.-diphenyl urea, chlorinated paraffin in an amount consisting of not less than 15% or more than 60% of the combined octachloro-sym.-diphenyl urea and zinc oxide, and sorbitan monolaurate in a proportion by weight of not less than 0.5% nor more than 5% of the composition, said octachloro-sym.-diphenyl urea and said paraffin being dissolved in the sorbitan monolaurate and forming with said other compounds an adhesive, fire-resistant, anti-vesicant coating material.

10. A composition consisting essentially of N,N',3,3',5,5' hexachloro-N,N' diacetylbenzidine, zinc oxide in a catalytically active proportion of between 80% and 200% by weight of said hexachloro-diacetylbenzidine, chlorinated paraffin in a proportion of not less than 15% or more than 60% of the combined hexachlorodiacetylbenzidine and zinc oxide, and sorbitan monolaurate in a proportion by weight of not less than 0.5% nor more than 5% of the composition, said hexachloro-diacetylbenzidine and said paraffin being dissolved in the sorbitan monolaurate and forming an adhesive, fire-resistant, anti-vesicant coating material.

11. A composition consisting essentially of 1,3,4,6-tetrachloro-7,8-diphenylglycoluril, zinc oxide in a catalytically active proportion of between 80% and 200% by weight of said tetrachloro-diphenylglycoluril, chlorinated paraffin in a proportion of not less than 15% or more than 60% of the combined tetrachlorodiphenylglycoluril and zinc oxide, and sorbitan monolaurate in a proportion by weight of not less than 0.5% nor more than 5% of the composition.

12. A composition comprising compounds consisting of octachloro-sym.-diphenyl urea and a dechlorinating agent consisting of calcium carbonate in a proportion of not less than 80% nor more than 200% of said urea, said composition also having a binder consisting of chlorinated paraffin in a proportion of not less than 15% nor more than 60% of the combined urea and dechlorinating agent.

References Cited in the file of this patent

UNITED STATES PATENTS

2,286,744	Leatherman	June 16, 1942
2,326,233	Leatherman	Aug. 10, 1943

FOREIGN PATENTS

557,081	Germany	Aug. 18, 1932
588,131	Germany	Nov. 13, 1933
590,796	Germany	Jan. 9, 1934

OTHER REFERENCES

65	Berichte, vol. 34, 1901, pages 1073-1082.
	Berichte, vol. 43, 1910, pages 1992-1996.
	Veddar: "Medical Aspects of Chemical Warfare," 1925, page 126.
	Spans and Tweens, publ. by Atlas Powder Co., 1942, pages 6-7.
70	American Dyestuff Reporter, 1943, vol. 32, pages 375-378 (article on fire-resistant duck by Redmond).

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,926,097

February 23, 1960

Martin Leatherman

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 28, for "tensing" read -- tenting --; line 29, for "materials, t ruck" read -- materials, truck --; same column 1, line 31, strike out "rayon, burlap, wool, nylon, silk, etc., since the compos"; column 3, line 26, for "907 pounds" read -- 90 pounds --.

Signed and sealed this 3rd day of January 1961.

(SEAL)

Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents