

## UNITED STATES PATENT OFFICE

2,540,119

## METHOD OF REMOVING VESICANT PARTICLES

Ernest L. Jackson, Washington, D. C., assignor to  
the United States of America as represented  
by the Secretary of War

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1

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

This invention relates in general to protective clothing and more particularly has reference to a process of treating material for rendering it resistant to vesicant gases and vapors, and to the product resulting from the treatment.

Previous to this time, it has been attempted to fix chlorine on material for protecting against such gases as mustard, but the impregnated cloth has increased in weight and has been characterized by stickiness. Also, the permeability of the same has been lowered to such an extent as to make clothing made of material so treated, uncomfortable to the wearer.

A primary object of this invention is to provide material relatively impermeable to vesicant gases or vapors.

Another object of this invention is to provide material having semi-permeable properties, that is, material which is permeable to air and inert gases, but impermeable to mustard gases and similar substances.

Another object of this invention is to devise a process for producing material having properties rendering the same impermeable to mustard gases and substances having similar properties.

Yet another object of this invention is to provide a process for fixing chlorine on textile material without appreciably affecting the desirable permeable characteristics thereof.

A further object of this invention is to provide a process for chlorinating material to render the same impervious to mustard gas and similar substances without materially increasing the weight of the material.

Still another object of this invention is to devise a process of treating clothing to render the same impervious to vesicant and toxic gases or vapors, such as mustard gas, Lewisite and similar substances.

A still further object of this invention is to devise a process for fixing chlorine in material to render the same impervious to mustard gas and similar substances without appreciably changing the desirable physical characteristics thereof.

With these and other objects in view which may be incident to my improvements, the in-

2

vention consists in the method to be herein set forth and claimed, with the understanding that the several necessary steps comprising the invention may be accomplished in any order found most suitable for carrying the same into practical effect, without departing from the spirit of the invention and the scope of the appended claims.

The present invention comprehends directly fixing chlorine by a chemical combination on material having the characteristics of wool so as to render the same impervious to mustard gas and similar vesicant and toxic gases. One manner of practically effecting the concept of the invention is to subject wool or similar materials, to a chlorinating process involving the use of a mixture of a stable hypochlorite and a suitable alcohol. The invention also comprehends incorporating the chlorinating agents, mentioned above, in an inert solvent. By the process forming the subject matter of the invention, wool having its normal water content under usual atmospheric conditions may be chlorinated or it may first be dried before subjecting it to chlorination. In either instance, the wool is washed with a solution of an inert solvent subsequent to chlorination and may also be dechlorinated and washed again.

Wool is considered to be composed of a protein substance, known as keratin. It has been found that when wool is subjected to the action of chlorine, that a reaction takes place between the chlorine and the wool which, it is thought, produces chloramines. However, it has been found that in some instances no chloramines have been formed. Regardless of the theory of the reaction which takes place between the wool and the chlorinating agent, there is a change effected in the characteristics of the wool which is desirable for certain purposes, among which is that of rendering mustard gas and similar substances non-vesicant.

In permeable protective clothing, it is desired to incorporate therein as high a percentage of active chlorine as can be introduced into wool without damage of the cloth. Wool which contains 4 per cent to 7 per cent of active chlorine is practical for use as protective clothing. The active chlorine, as considered here, is determined by titration of the iodine liberated by a known



3

weight of the chlorinated wool from the acidified solution of potassium iodide and is calculated on the basis of one chlorine atom being the equivalent of two atoms of iodine. Processes employed in the past for the introduction of more than 4 per cent of active chlorine into wool by means of chlorinating agents in aqueous medium, such as hypochlorous acid, cause considerable damage to the wool, rendering it substantially useless.

In practicing the process to be hereinafter described, I am able to introduce either small or large percentages of chlorine into wool to suit the requirements for which the cloth is intended without causing damage thereto and so controlling the process that the same is attended by uniform results.

I have found that a mixture of an organic hypochlorite possessing suitable stability and certain alcohols affords an efficient chlorinating agent for permanently fixing any desired percentage of chlorine on wool without causing damage thereto. Particularly adapted to this purpose are tertiary butyl hypochlorite and absolute methyl alcohol. In order to obtain a better control with the reactive agents, I have found it preferable to incorporate the same in an inert solvent such as carbon tetrachloride.

While I have employed carbon tetrachloride with marked success and although I deem it preferable to employ a mixture of tertiary butyl hypochlorite and absolute methyl alcohol in solution with an inert solvent such as carbon tetrachloride, any other suitable organic hypochlorite having suitable stability such as tertiary amyl hypochlorite may be used and also any primary or secondary alcohol containing from one to five carbon atoms, such as absolute ethyl alcohol, also propyl, primary and secondary butyl and primary and secondary amyl alcohols. The use of ingredients other than those preferred, however, have been found less satisfactory as the pronounced instability of other mixtures and the limited amount of chlorine which can be introduced into the wool by the use of the same lessen the utility of these alcohols.

In practicing my invention, I have treated wool containing the normal water content of the same under usual atmospheric conditions and also dried wool. With the use of wool containing the normal water content under usual atmospheric conditions, the percentages of active chlorine up to four and five tenths per cent by weight of the wool may be introduced into the same without damage. In chlorinating wool which has been dried, however, such as over phosphorus pentoxide or other efficient desiccating agents, or by heating in a stream of dried air at about 85° C., as high as six to seven per cent of active chlorine may be introduced into the wool without affecting the quality thereof.

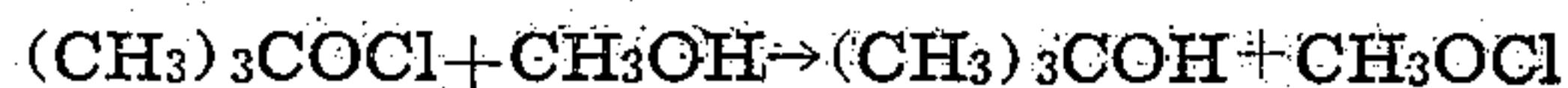
As will hereinafter appear, chlorination of wool by means of a stable hypochlorite and an alcohol incorporated in an inert solvent, may be easily controlled, while obtaining uniform results, and at the same time the chlorination re-

4

quires but a relatively small amount of time for completion. Moreover, it is to be noted that only small amounts of the hypochlorite are required and the most of it is actually utilized in the chlorination reaction. With the use of an inert solvent, such as carbon tetrachloride, a large volume of chlorinating bath may be obtained with a small amount of hypochlorite. During chlorination, the presence of water greatly damages the wool and for this reason it is preferred to use anhydrous hypochlorites and alcohols.

The actual chlorinating agent in the reaction of tertiary butyl hypochlorite and absolute methyl alcohol with wool is of an entirely different character from that which operates in the chlorination of wool with tertiary butyl hypochlorite alone. When anhydrous tertiary butyl hypochlorite is mixed with absolute methyl alcohol, a violent reaction has been found to occur after a short time interval, and the rate of the chlorination reaction involving a mixture of tertiary butyl hypochlorite and absolute methyl alcohol proceeds much more rapidly than with the use of tertiary butyl hypochlorite alone.

While I do not wish to limit myself to any explanation of the reaction which occurs when methyl alcohol is mixed with tertiary butyl hypochlorite, I believe that the actual chlorinating agent is methyl hypochlorite, which is believed to be formed according to the following equation:



In a similar manner, ethyl hypochlorite, in the nascent state is probably the actual chlorinating agent in the reaction of tertiary butyl hypochlorite and absolute ethyl alcohol with wool.

The following examples, as given in the tables, will more fully illustrate the invention, but it is to be distinctly understood that they are not intended to constitute any limitations in the scope thereof.

In the following tables particular attention should be given to the effects produced upon the percentages of chlorine fixed on the wool by the variation of the concentration of the hypochlorites and alcohols disclosed, as well as their volumes and that of the inert solvent. Also to be noted are the variations in temperatures and the time for which the wool is subjected to the chlorinating bath. Moreover, the initial condition of the wool prior to chlorination and its effect upon the final results noted should be considered.

The data tabulated in the first table was obtained from experiments conducted in the chlorination of woolen cloth which had been dried in a vacuum desiccator over phosphorus pentoxide for forty-eight hours. In regard to the tearing strength of the chlorinated cloth, it was found that it was substantially the same as that of the original cloth for each experiment carried out.

Table 1

Tertiary Butyl Hypochlorite		Methyl Alcohol		Carbon-tetrachloride, cc.	Time, Min.	Temp., °C.	Wool Used, g.	Per Cent Active Chlorine in Cloth
cc.	Per Cent	cc.	Per Cent					
25	7.2	20	5.8	300	45	32-34	14	6.8
25	11.8	20	9.4	167	20	32-34	15	5.3
25	15.1	20	12.1	120	20	32-34	15	6.0



5

It has been mentioned that the process of the present invention may be applied to the chlorination of undried woolen cloth. However, the chlorination of undried woolen cloth to fix percentages of active chlorine on the wool higher than 4 per cent to 4.5 per cent causes damage to the cloth. Table 2 illustrates the results obtained in the chlorination of woolen cloth containing its normal water content under the prevailing atmospheric conditions. To be noted is the fact that the wool was undamaged in experiments in which 1.2 per cent, 3.3 per cent and 3.8 per cent of active chloride was introduced into the cloth, while the experiments introducing 5.3 per cent and 6.5 per cent of active chlorine into the wool damaged the cloth.

Table 2

Tertiary Butyl Hypochlorite		Methyl Alcohol		Carbon tetrachloride, cc.	Time, Min.	Temp., °C.	Wool Used, g.	Per cent Active Chlorine in Cloth
cc.	Per cent	cc.	Per cent					
10	3.1	8	2.5	300	20	23-26	3	1.2
20	5.9	20	5.9	300	13	22-30	2	5.3
25	7.2	20	5.8	300	10	20-25	3	3.8
25	7.2	20	5.8	300	18	20-25	3	6.5
25	10.2	20	8.2	200	5	22-29	3	3.3

In the foregoing tables it should be noted that the time of the reaction may be varied to regu-

content under usual atmospheric conditions is chlorinated to fix percentages of active chlorine on the wool of a higher range than from 4 to 4.5 per cent, the wool is slightly damaged as pointed out in the consideration of Table 2.

Wool may also be chlorinated by means of a mixture of tertiary butyl hypochlorite and absolute methyl alcohol without the use of carbon tetrachloride or other diluents. Under these conditions, the reaction proceeds at such a rapid rate that proper control of the reaction is difficult. This may be readily observed from an inspection of Table 3, wherein wool containing its normal water content under prevailing atmospheric conditions is chlorinated by the use of tertiary butyl hypochlorite and methyl alco-

hol without employing a diluent such as carbon tetrachloride.

Table 3

Tertiary Butyl Hypochlorite		Methyl Alcohol, cc.	Time, Sec.	Temp., °C.	Wool Used, g.	Per Cent Active Chlorine in Cloth	Condition of Chlorinated Cloth
cc.	Per Cent						
10	9.0	100	15	23-24	2	1.7	Undamaged.
21	17.3	100	15	22-23	2	1.9	Do.
34	28.8	84	22	21-22	2	5.4	Slightly damaged.
50	45.4	60	15	23-26	2	5.4	Do.
50	45.4	60	60	4-7	3	4.6	Undamaged.
78	71.5	31	15	23-25	2	3.0	Do.

late the amount of chlorine which it is desired to introduce into the wool. The amount of active chlorine introduced into the wool may also be controlled by varying the relative amounts of tertiary butyl hypochlorite, methyl alcohol and carbon tetrachloride and regulating the time the reaction is allowed to proceed. In addition to this, the time of the reaction may be greatly reduced by additionally increasing the concentrations of the reactive constituents, and also by decreasing the quantity of solvent and raising the temperature at which the reaction is carried out. It will be manifest, however, that the reaction must be controlled within certain limits, for if wool containing the normal water

As previously pointed out, the process forming the subject matter of the present invention may also be carried out with a mixture of tertiary butyl hypochlorite and absolute ethyl alcohol. The use of carbon tetrachloride as a solvent for the reactants facilitates control. However, chlorination by means of tertiary butyl hypochlorite and absolute ethyl alcohol is less satisfactory than chlorination with tertiary butyl hypochlorite and absolute methyl alcohol.

In the following Table 4, illustration of the results obtained in the chlorination of woolen cloth, containing its normal water content under prevailing atmospheric conditions, with tertiary butyl hypochlorite and absolute ethyl alcohol in carbon tetrachloride are given.

Table 4

Tertiary Butyl Hypochlorite		Ethyl Alcohol		Carbon-tetrachloride, cc.	Time, Min.	Temp., °C.	Wool Used, g.	Per Cent Active Chlorine in Cloth	Condition of the Chlorinated Cloth
cc.	Per Cent	cc.	Per Cent						
25	25	75	75	None	0.6	25-35	2	1.0	Damaged.
25	7.1	25	7.1	300	25	21-25	3	0.4	Undamaged.
25	7.1	25	7.1	300	60	21-50	3	1.5	Slightly damaged.
25	25	25	25	50	3.5	23-60	2	5.2	Badly damaged.



While I, as previously stated, prefer to carry on my chlorinating process within a mixture of tertiary butyl hypochlorite and absolute methyl alcohol, I may substitute other organic hypochlorites having suitable stability, in place of the tertiary butyl hypochlorite. For example, wool may be chlorinated for use as protective clothing by means of a mixture of tertiary amyl hypochlorite and methyl alcohol.

Having described the process in general, and given tabulated results obtained from carrying out the same, one specific example will be given to more fully illustrate the invention, although it is to be understood that the invention is not to be limited by the proportions of the reactants given therein or of the treatment, as it is obvious that the method may be varied, as previously outlined, without departing from the spirit of the invention or exceeding the scope of the appended claims.

Before chlorination, the woolen cloth is dried for about forty-eight hours in a vacuum desiccator over phosphorus pentoxide at approximately 10 mm. pressure. The dried wool is then chlorinated by means of a solution of 25 cc. of anhydrous tertiary butyl hypochlorite (about 98 per cent available chlorine) and 20 cc. of anhydrous C. P. methyl alcohol in 300 cc. of carbon tetrachloride, which has been dried over calcium chloride. To carry out the chlorination reaction, a 750 cc. Erlenmeyer flask, which is provided with a rubber stopper having two openings therein, is employed. In one of the openings there is inserted a thermometer which is in contact and partially immersed in the reaction solution. The other opening is provided with an outlet tube attached to a calcium chloride drying tower. Throughout the reaction the flask is kept closed. By warming the chlorinating solution in a bath of water, its temperature is raised to 32° C. Within five minutes after mixing the constituents of the solution, about 15 g. of dried wool is quickly transferred from the desiccator to the chlorinating bath. Due to the heat of the reaction, the temperature of the bath soon begins to rise and slight cooling becomes necessary. The solution is frequently shaken or mechanically stirred and its temperature is kept at 32° C. to 34° C. throughout the reaction.

This treatment of the cloth is continued from forty to forty-five minutes after which the solution is quickly decanted, and the wool, while still in the flask is washed with carbon tetrachloride. After the washing, just described, the wool is quickly removed from the flask and again washed in three baths of carbon tetrachloride. It will be found that cloth treated in this manner contains from 6 per cent to 7 per cent of active chlorine based on the weight of the wool.

If desired, the cloth may be washed with water after thoroughly washing with carbon tetrachloride. By varying the time of the chlorination reaction, the active chlorine on the wool can be brought to the amount desired. In a typical experiment, the amount of active chlorine fixed on the wool in forty-five minutes was 6.7 per cent.

It will be apparent from the foregoing descrip-

tion that the presence of small amounts of water in the chlorinating reagents is not detrimental to any appreciable extent. As water has a tendency to damage wool and in any substantial quantity does cause damage with increasing amounts, it is preferred, as previously indicated, to employ anhydrous reagents.

From the foregoing description it will be appreciated that an improved process for the chlorination of wool to render the same impervious to mustard gas and the like, without causing damage to the wool, has been provided by treating the wool with a mixture of suitable alcohols and organic hypochlorites possessing the required stability. By the use of carbon tetrachloride as a solvent for the alcohol and the hypochlorite an easily controllable process of chlorination is afforded. It should also be noted that with the ease of control, by the variation of the concentration of the chlorinating solution, the time of the reaction, and the temperature at which it is carried out, the amount of active chlorine fixed to the woolen cloth may be varied to meet the particular requirements called for.

In the foregoing description and accompanying claims the terms vesicants, or vesicant gases or vapors are intended to include gases, vapors or liquids. The term mustard gas designates the vesicant compound bis (beta-chlorethyl) sulphide which may be in the gaseous, vapor or liquid stage.

Although I have described the preferred embodiment of my invention, I wish it to be understood that I do not confine myself to the precise details herein set forth by way of illustration, as it is apparent that many changes and variations may be made therein by those skilled in the art, without departing from the spirit of the invention or exceeding the scope of the appended claims.

I claim:

1. A method of removing vesicant particles from vesicant contaminated air which comprises passing the air through woolen material which has been treated with a tertiary alkyl hypochlorite and an absolute alcohol from the group consisting of methyl alcohol and ethyl alcohol incorporated in an inert solvent.

2. A method according to claim 1 in which the absolute alcohol is methyl alcohol.

3. A method according to claim 1 in which the absolute alcohol is ethyl alcohol.

4. A method of removing vesicant particles from vesicant contaminated air which comprises passing the air through woolen material which has been treated with tertiary butyl hypochlorite and absolute methyl alcohol incorporated in an inert solvent.

ERNEST L. JACKSON.

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