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STABILIZATION OF MUSTARD

Rudolph Macy, Baltimore, Md.

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

This invention relates to the stabilization of vesicant chemical warfare agents and more particularly to the stabilization of mustard gas by inclusion of an organic ammonium salt therewith.

The most important chemical warfare vesicant agent is "mustard gas," a dark oily liquid which when pure is bis-(betachloroethyl) sulfide. Although there are several processes for manufacturing mustard, the most important method in this country is the Levinstein process. The product of this process is "Levinstein mustard."

Levinstein mustard is a relatively impure product, and the dichlorethyl sulfide content thereof is in the neighborhood of 70%. The impurities in Levinstein mustard are of a complex nature and have not been completely determined to this date, but are essentially polysulfides of the composition $(ClCH_2CH_2)_2S_x$.

To obtain a chemical agent having excellent vesicant action and improved stability with less odor, through which the presence of the agent can be detected, mustard gas is washed and vacuum-distilled to produce distilled mustard. This distilled product is about 95% pure and it is believed that the impurity is mainly p-dithiane. However, mustard gas thus purified still corrodes steel containers and the corrosion rate is fairly rapid at temperatures in the range of 110° F. to 150° F. The same is true of steam-distilled mustard.

Although Levinstein mustard has very effective vesicant properties, and is substantially equivalent to pure mustard from the vesicant standpoint, it does have the serious objection of being unstable over long periods of storage in steel containers, especially at temperatures of 110° F. to 150° F. The exact reasons for the degradation of Levinstein mustard in storage have not been fully determined in all respects. However, it is known that the instability is due to certain impurities present, since the pure product is much more stable under normal storage conditions in steel containers. A number of theories have been advanced from various sources as to the causes of the instability of Levinstein mustard. Corrosion of steel containers by the mustard molecule is probably due to its "inner salt" nature, and in the case of Levinstein mustard this is enhanced by presence of polysulfides containing labile sulfur. Because of these polysulfides, iron actually dissolves in Levinstein mustard at slightly elevated temperatures. Levinstein mustard is very stable in glass containers, or in steel containers coated with a properly baked-on suitable lacquer.

Regardless of the exact reasons for the instability of Levinstein mustard, the problem is fully recognized and is extremely serious during time of war and national emergency when it becomes necessary to build up a very great strategic reserve of this chemical warfare agent

in contemplation of the fact that chemical warfare may, at any time, be resorted to.

From a practical standpoint, it is necessary to store the bulk of the stock pile of Levinstein mustard in steel drums. Logistical reasons make it necessary to have a sizable proportion of Levinstein mustard supply located in tropical, or near tropical, regions. The high temperatures in such regions greatly hasten the deterioration or degradation of the Levinstein mustard stored in such regions. During the spoilage or deterioration of Levinstein mustard, pressures develop in the steel drums, and eventually, if the product is not used, the deterioration is carried to the point where it is necessary to destroy the portion of the supply which has so deteriorated.

Although the above outlined problem has been known since World War I, when Levinstein mustard was produced and stored on a large scale, there has been heretofore no satisfactory method or means of stabilizing Levinstein mustard with respect to chemical decomposition and development of pressure. A great amount of research effort has been devoted to the problem. However, prior to my invention, the net results of such previous research and investigation of the problem only indicated that ammonia was a partially effective stabilizer for Levinstein mustard, and that partial stabilization could be obtained by the use of small amounts of strong bases. However, none of these methods or means of stabilization was at all satisfactory from a practical standpoint.

While it is possible to stabilize chlorinated hydrocarbons with amines, to stabilize other compositions with ammonium compounds and to inhibit acid baths by the addition of ammonium bases, the problem of stabilizing mustard gas, a chlorinated alkyl sulfide containing polysulfide and iron impurities, has not been approached from this angle since the decomposition causes are essentially non-analogous.

Accordingly, the object of this invention is to provide a stabilized mustard and to prevent deterioration in storage as well as to prevent the attack of ferrous metal containers and munitions by the mustard gas contained therein.

Although the exact mechanism for the corrosion of steel by mustard gas is not known, it is probable that the reaction is due to the ionic nature of the mustard and of the impurities formed. The character of the corrosion of steel is different for Levinstein mustard than it is for steam or vacuum-distilled Levinstein mustard which latter corrode steel at a decelerating rate while the former reacts at an ever increasing (logarithmic) rate. However, whatever the actual mechanism is, I have found that the vesicant agent can be stabilized and the corrosion of steel inhibited, by the addition of organic ammonium salts, particularly tetramethyl ammonium bromide, thereto.

In order to carry out my invention, I have added hexamine and various organic ammonium salts to Levinstein mustard and to distilled mustard. I have found that ammonium salts, particularly quaternary ammonium halides have stabilizing properties. Some of the below-listed compounds, which were tested, were not of the highest purity and gave mediocre results. One compound, however, tetramethyl ammonium bromide, exhibited properties much superior to any stabilizer yet tested, including hexamine, currently adopted as the official stabilizer for Levinstein mustard by the Chemical Warfare Service, which is described in my patent application, Serial No. 591,291, filed May 1, 1945. The ammonium compounds tested included:

Tetramethyl ammonium bromide
Tetraethyl ammonium bromide

Ethyl quinolinium iodide (quinoline ethiodide)
Tris (betachlorethyl) amine hydrochloride
Aniline hydrochloride
N-ethyl di(betachlorethyl)amine hydrochloride
Ethyl ammonium chloride
N-phenyl pyridinium chloride
Tetrakis-(beta chloroethyl)ammonium chloride

Although hexamine at a concentration of 1% is a fairly effective stabilizer for Levinstein mustard, it is rather poor for stabilizing distilled mustard when stored in small steel munitions like the 75-mm. shell. For that reason it has not been adopted as a stabilizer for distilled mustard. A standard sample of distilled mustard when stored in 75-mm. shell at 65° C. for three months decomposes to the extent of 17%, and 1% of hexamine only cuts this down to 12%. In a test with tetramethyl ammonium bromide at 0.5%, the loss of distilled mustard, after 4.5 months at 65° C., was 6%, and in a test with 1%, the loss under the same conditions was only 4.5%.

When tested at concentrations of 0.5% and 1% in Levinstein mustard stored in 75-mm. steel shell at 65° C. for 4.5 months, the freezing points at the end of the test period were respectively 0.6° C. and 3.1° C. This is better than can be obtained with 1% of hexamine.

The pressure stability in shell equipped with gages was much superior with distilled mustard containing tetramethyl ammonium bromide than with distilled mustard containing hexamine. At 1%, the former held pressure development to 50 p. s. i. in 4.5 months at 65° C., whereas hexamine permits pressures of well over 150 p. s. i. In Levinstein mustard, the superiority of tetramethyl ammonium bromide over hexamine with respect to pressure is not so certain, but hexamine is accepted as a fair stabilizer for this type of mustard.

It is apparent from the above that I have invented a stabilized mustard gas which is greatly superior to any previously known. The addition of tetramethyl ammonium bromide to Levinstein mustard or to distilled mustard produces a composition which is much more stable than mustard alone or mustard stabilized with ammonia or hexamine. The attack of ferrous metal storage containers and munitions, particularly small ones, by the vesicant agent is reduced to a minimum, resulting in great savings in material.

Although this invention has been described with relation to the stabilization of mustard gas, quaternary ammonium halides are also useful in stabilizing chlorinated hydrocarbon solvents.

The nature of this invention having been broadly outlined above, and preferred embodiments of the invention having been described, it will be apparent that certain modifications and additional formulations will suggest themselves to those skilled in the art. Accordingly, it is intended that the foregoing descriptive material shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. Stabilized mustard gas containing tetra-lower-alkyl ammonium halide as the stabilizing agent.

2. Stabilized mustard gas containing tetramethyl ammonium bromide as the stabilizing agent.

3. Stabilized Levinstein mustard gas containing tetra-lower-alkyl ammonium halide as the stabilizing agent.

4. Stabilized Levinstein mustard gas containing tetramethyl ammonium bromide as the stabilizing agent.

5. A stabilized distilled mustard gas containing a tetra-lower-alkyl ammonium halide as the stabilizing agent.

6. A stabilized distilled mustard gas containing tetramethyl ammonium bromide as the stabilizing agent.

7. A process for stabilizing mustard gas, comprising adding a tetra-lower-alkyl ammonium halide thereto as the stabilizing agent.

8. A process for stabilizing mustard gas, comprising adding tetramethyl ammonium bromide thereto as the stabilizing agent.

9. A process for stabilizing Levinstein mustard gas, comprising adding a tetra-lower-alkyl ammonium halide thereto as the stabilizing agent.

10. A process for stabilizing Levinstein mustard gas, comprising adding tetramethyl ammonium bromide thereto as the stabilizing agent.

11. A process for stabilizing distilled mustard gas, comprising adding a tetra-lower-alkyl ammonium halide thereto as the stabilizing agent.

12. A process for stabilizing distilled mustard gas, comprising adding tetramethyl ammonium bromide thereto as the stabilizing agent.

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