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GAS PROTECTIVE FABRIC AND METHOD OF PREPARING THE SAME

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2 Claims. (Cl. 117—62)

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My invention relates generally to protective fabric and clothing which is permeable to air but impermeable to mustard gas, lewisite, and like chemical warfare agents, and it has particular relation to such permeable protective clothing impregnated with chlorinated imidazolines.

Chemical warfare vesicant agents such as mustard gas (bis beta dichlorethylsulfide), lewisite (chlorvinyldichlorarsine), and the like, as is well known, produce casualties by attacking the flesh to form severe blisters which take long periods to heal. Accordingly, it is necessary that troops or exposed civilian personnel be provided with articles of protective clothing if large numbers of casualties are to be avoided when such vesicant agents are encountered.

The provision of protective clothing that will be permeable to the air so that it may be comfortably worn for long periods of time without interference with normal perspiration through the skin, and which will be of a durable nature capable of storage and laundering without too great loss of protective ability, and yet will not permit penetration by mustard gas, lewisite, and like vesicants, presents a very difficult technical problem. A great deal of research effort has been devoted to this problem in order to find suitable compositions for impregnating permeable clothing.

It is known that the most important and widely used chemical warfare vesicants can be destroyed by the halogenation, particularly by the chlorination, of the same. Accordingly, at present, the most promising answer to the problem of providing permeable protective clothing appears to be the provision of suitable impregnating compositions which will furnish an adequate supply of active chlorine when required. The most important characteristics that such impregnating compositions must have are: that they will not be toxic or irritant to the skin, that they will not destroy or materially affect the fibers of the fabric or clothing, that they will not be washed away to a material extent upon laundering of the clothing, that their chlorinating efficiency will not be lost when the permeable clothing is stored or worn for reasonable periods of time, that they will be readily available and procurable on a quantity production basis at reasonable cost, and that the process of impregnating fabric or clothing therewith will be relatively simple so that special techniques, materials, and equipment will not be required.

At the present time, the impregnating composition adopted as standard for providing permeable protective clothing, and which is now considered to be the best available, is particularly objectionable for the reasons that: it is very difficult to manufacture on a large scale basis and hence is unduly expensive, its manufacturing chlorine efficiency is very low, its chlorine efficiency is relatively low, and the technique, materials, and equipment for small scale field impregnation of clothing with it are special, hazardous, and complicated.

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Accordingly, the object of my invention, generally stated, is the provision of improved permeable protective fabric of the type described and improved impregnating compositions and methods of making the same, the impregnating compositions being particularly characterized by having the following desirable features:

1. Capable of manufacture on a quantity production basis at low cost, from readily available materials, in standard, existing, plant equipment.

2. Have high manufacturing chlorine efficiency.

3. May be readily impregnated in clothing in one step, or in two steps so as to maintain maximum chlorine efficiency, in both cases using readily prepared water solutions, readily available equipment, and extremely simple techniques.

4. Do not require binding agents to hold them to the fibers of the clothing or fabric.

5. Will not be easily removed or washed out during laundering.

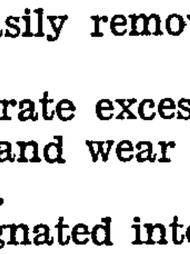
6. Do not deteriorate excessively over normal periods of storage and wear when impregnated in chlorinated form.

7. May be impregnated into fabric and clothing in an unchlorinated state so that the clothing or fabric may be stored practically indefinitely without appreciable deterioration, and may be readily chlorinated under field conditions at any desired time prior to use so as to obtain a maximum chlorine efficiency.

8. Are non-toxic and non-irritant to the skin.

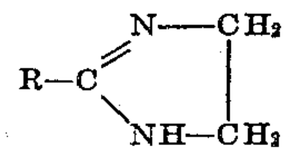
The importance and nature of these and other objects of the invention will be made more apparent, and appreciated more fully, after reference to the following detailed description thereof setting forth by way of illustration certain compositions and methods of applying the same.

It has been found, according to this invention, that the class of organic compounds variously known as the "imidazolines" or the "ethylene-ethenyldiamines," and characterized by the imidazoline ring structure



may be chlorinated so as to have an adequate supply of active chlorine for the requirements of permeable protective clothing. The sub-class of imidazolines formed by substituting at the 2-carbon atom of the imidazoline ring a hydrocarbon or hydroxy hydrocarbon radical of a fatty

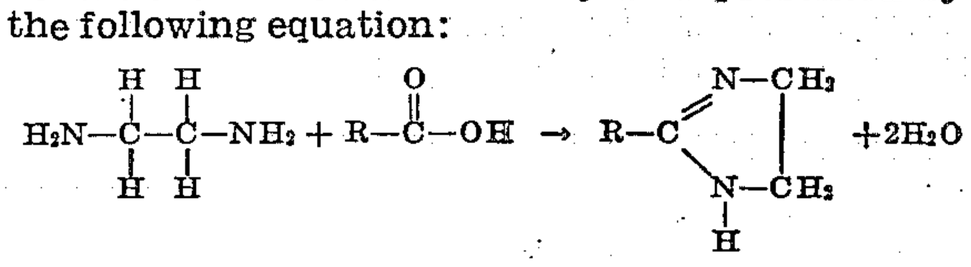
acid, has been found to provide compounds particularly adapted for use in making permeable protective clothing. Such 2-substituted imidazolines may be designated by the general formula



where R stands for the hydrocarbon or hydroxy hydrocarbon radical of a fatty acid. The hydrocarbon and hydroxy hydrocarbon radicals $C_{11}H_{23}$—, $C_{15}H_{31}$—, $C_{17}H_{29}$—, $C_{17}H_{31}$—, $C_{17}H_{33}$—, $C_{17}H_{35}$–, $C_{16}H_{33}CHOH$–, and $C_6H_{13}CHOHC_{10}H_{18}$–, of the commercial fatty acids known as lauric, palmitic, linolenic, linoleic, oleic, stearic, hydroxystearic, and ricinoleic, respectively, have been found suitable for the R group.

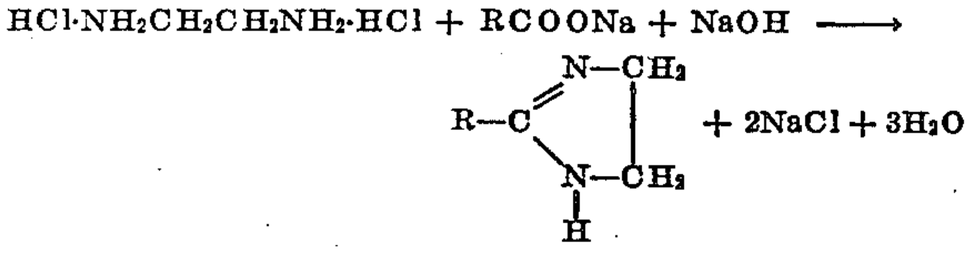
The hydrocarbon and hydroxy hydrocarbon radicals derived from the fatty acids may or may not have various groups and radicals substituted at different carbon atoms in the chains, as long as the adaptability of the compositions for impregnation purposes is not materially changed.

The 2-substituted imidazolines may be readily produced on a quantity production basis according to several methods known to those skilled in the art. One basic procedure is to cause various fatty acids to react with alkylene or polyalkylene polyamines under conditions which produce ring closure. According to one method, commercial fatty acids may be refluxed with a polyamine such as ethylene diamine, while continuously removing the water formed as a result of the condensation. This reaction may be represented by the following equation:



The completion of the reaction depends upon the continuous removal of the two moles of water as the reaction progresses. One efficacious method of removing the water is the use of a material that will form an azeotropic mixture with the water, and which will separate from the water when cooled to a liquid, so that the material can be returned to the reaction mass to remove more water. Toluene and xylene are readily available and serve satisfactorily to remove the water, but many other compounds may be used instead of these.

A somewhat purer product may be obtained by heating ethylene diamine hydrochloride with the sodium salt of the desired fatty acid in a basic solution according to the general equation:



In addition to ethylene diamine, examples of other polyamines which may be used to form 2-substituted imidazolines are: diethylene triamine, triethylene tetramine, tetraethylene pentamine, hydroxy ethyl ethylene diamine, and homologues and derivatives of these amines that will not prevent the formation of at least one imidazoline ring.

Because of the fact that certain of these polyamines are capable of reacting with fatty acids so as to form products having two imidazoline rings, it is possible to make impregnating compounds having a very high percentage of active chlorine. This is possible by reason of the fact that in order for the two-imidazoline-ring compounds to have an affinity for fabric and be adapted for impregnating purposes, it is only necessary to have one high molecular weight fatty acid residue or hydrocarbon radical attached to one of the imidazoline rings of the molecule. Thus, when a two-imidazoline-ring product is made, a mixture of a high molecular weight fatty acid, such as stearic acid, and a low molecular weight fatty acid, such as acetic acid, may be used. In such a case, stearic acid hydrocarbon radicals, $C_{17}H_{35}$—, will be attached to one imidazoline ring of the molecules, while CH_3—, methyl, radicals will be attached to the other imidazoline ring of the molecules. Since the amount of active chlorine which may be carried by the imidazoline compounds depends upon the number of imidazoline rings, it will be seen that it is possible for two-imidazoline-ring compounds having both high and low molecular weight fatty acid hydrocarbon radicals attached to the imidazoline rings to contain a much higher percentage of active chlorine than imidazolines in which a high molecular weight fatty acid hydrocarbon radical is attached to each imidazoline ring.

One example of the use of the higher polyamines in the preparation of two-imidazoline-ring compounds is as follows:

A charge of triethylene tetramine, lauric acid, and toluene is heated to distill and separate the water formed by the reaction from the toluene, returning the toluene to the charge. The heating of the charge is continued until no more water can be removed and the toluene is then distilled off and recovered for use in subsequent runs. When all of the toluene has been removed, the batch is cooled and acetic acid or acetic anhydride is slowly added until the batch becomes slightly acid. The resultant product will be a two-imidazoline-ring compound having the hydrocarbon radicals of lauric acid, $C_{11}H_{23}$—, attached to the imidazoline rings.

In the above procedure, instead of using the required amount of lauric acid, only one half of the required amount may be used at the start of the reaction. When the point is reached where no water can be removed, acetic acid or acetic anhydride can be added in place of the other half of the required amount of lauric acid, provisions being made to prevent the loss of an excessive amount of the acetic acid or anhydride during the addition, and the reaction continued until no more water can be removed.

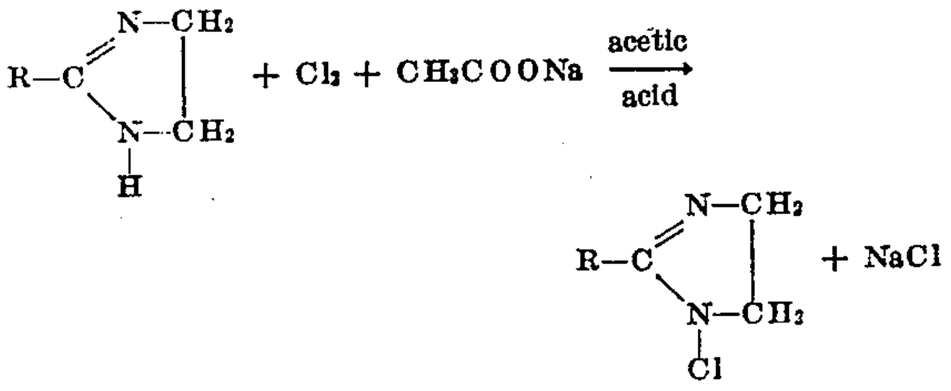
The imidazoline product made with a combination of lauric acid and acetic acid may be chlorinated so as to contain 18.7% of active chlorine, whereas when lauric acid alone is used, the prdouct, because of its higher molecular weight, will contain only about 13.7% of active chlorine.

It will be understood by those skilled in the art that mixtures of various polyamines and mixtures of various fatty acids may be used, since the specific compositions of the imidazone products is not ordinarily of great importance so long as a sufficient amount of active chlorine is carried in the chlorinated product. Thus, mixtures of polyamines such as ethylene diamine and diethylene triamine, and mixtures of commercial fatty acids such as stearic and oleic acids, may be used in making the imidazoline products.

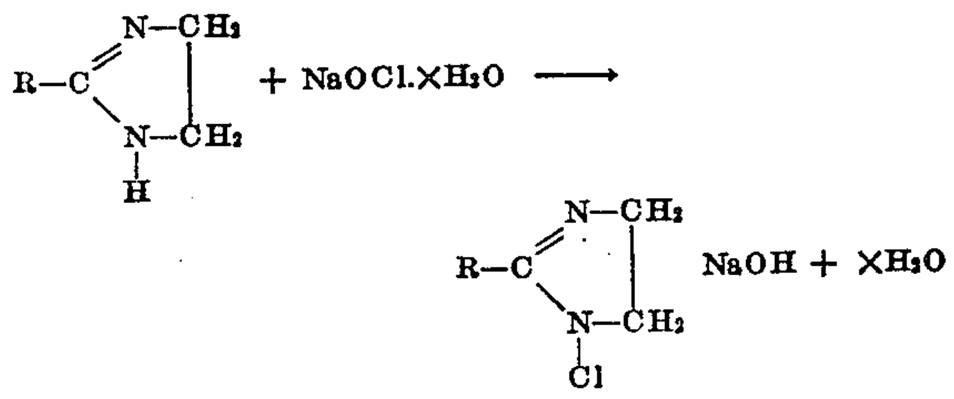
The 2-substituted imidazolines may be chlorinated at the 1-nitrogen position of the imidazoline ring so as to form N-chloro groups hav-

ing active chlorine, according to several different methods of chlorination. By the expression "active chlorine," as it is now used in the art, it is intended to indicate a chlorine atom attached to a trivalent nitrogen atom so that in a water solution the chlorine does not function as anion as is the case when a chlorine atom is attached to a pentavalent nitrogen. The usual test of a compound for "active chlorine" is to determine whether free chlorine is liberated in a neutral potassium iodide solution of the compound. Active chlorine may also in certain instances be detected by the familiar chlorine odor.

According to one method of chlorination, the 2-substituted imidazolines may react with chlorine in a sodium acetate-acetic acid solution according to the general equation:



Another very convenient method of chlorinating the 2-substituted imidazolines is the use of an ordinary sodium hypochlorite solution wherein the chlorination takes place according to the equation:



It will be seen that the only chlorine in the 2-substituted and chlorinated imidazolines of the invention is that in active form and attached to a trivalent nitrogen. Thus, these compounds have a maximum chlorine efficiency for the purposes intended, which is an important factor due to the large war-time demands for this chemical.

Although the structure of the chlorinated imidazoline products having only one imidazoline ring in the molecule is reasonably well established and thought to be that given above, the structure of the chlorinated compounds having two imidazoline rings in the molecule has not been established with certainty. Accordingly, since the question of structure of the chlorinated imidazolines is not completely established, it is not intended that this invention be limited to the specific structures outlined above.

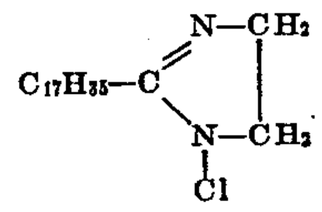
The relative ease with which the imidazolines may be chlorinated makes it desirable to first impregnate fabric or clothing with the required amount of the same and then store the clothing or fabric until a subsequent time, when it is desired to use the protective clothing or fabric for protection against vesicants. There will be practically no deterioration of the 2-substituted imidazolines, even during extended storage of the clothing. At the desired time, the imidazoline in the fabric may be easily chlorinated by simply placing the same in a cool hypochlorite solution for about one-half hour with agitation, or by any other suitable method of chlorination. Thereafter, when mustard gas, Lewisite, or other like vesicants, contact the protective clothing or articles, the active chlorine will quickly react therewith and convert the same into innocuous products before they can penetrate the clothing and attack the skin.

When hypochlorite solutions are used for chlorinating fabric impregnated with imidazoline type impregnites, the pH values and temperatures of such solutions should be controlled in order not to excessively affect the strength of the fabric fibers, as is well understood by those skilled in the art. In this same connection when hypochlorite solutions are used, it will usually be desirable to rinse the treated fabric in a solution of a suitable alkali so that hydrochloric acid present as the hydrochloride of an amine will be removed, thereby preventing this acid from attacking the fabric during storage.

It will be understood that instead of impregnating the clothing and fabric in two steps as outlined above, the fabric or clothing may be impregnated in one step with the initially chlorinated product. Such a procedure should be used where early use of the protective fabric or clothing is contemplated, since, during storage for extended periods, the chlorinated imidazolines will deteriorate to some extent, thus lowering the active chlorine efficiency.

As respects the specific amounts of the impregnite compositions which should be used, the basis used is, the amount of active chlorine present in proportion to the weight of the fabric or clothing. The amount of active chlorine required depends upon the particular purposes and conditions for and under which the protective fabric and clothing is to be used. Under certain conditions, as little as 0.25% active chlorine may be satisfactory, while army specifications adopted for protection against expected field concentrations of vesicants such as mustard gas and Lewisite, require a minimum of 1.5% active chlorine in the fabric.

In each instance enough of the 2-substituted imidazolines should be impregnated into the clothing or fabric so that the required amount of active chlorine from the N-chloro group will be available. For example, if one hundred pounds of dry garments are to be impregnated with 2-heptadecyl N-chloro imidazoline having the formula:



so as to have at least 1.5% or 1.5 pounds of active chlorine, then at least about thirteen pounds of the unchlorinated imidazoline will be required.

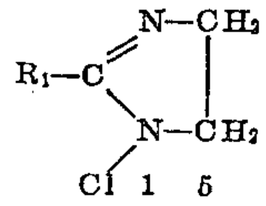
It will be seen that impregnation of protective clothing or fabric with the imidazoline compositions of this invention is particularly adapted to field conditions since only simple water solutions and equipment are required. In fact, when it is desired to chlorinate, in the field, fabric or clothing which has been previously impregnated with the 2-substituted imidazolines, the only required materials and equipment are, a supply of hypochlorite, water, and a container.

Since certain changes and modifications may be made in the foregoing compositions and their methods of preparation, and in the procedures and techniques of applying the same to fabric and clothing, without departing from the scope of the invention, it is intended that all matter

set forth in the foregoing description shall be considered as illustrative and not in a limiting sense and shall be given a construction as broad as is consistent with the state of the prior art.

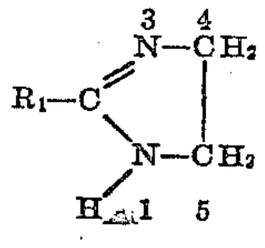
I claim:

1. A gas protective fabric consisting of a normally air permeable textile containing in terms of its dry weight prior to impregnation not less than 0.25% nor more than 1.50% of chlorine attached to the nitrogen atom in the 1 position of an imidazoline impregnated in said fabric of the formula:



R_1 being a fatty acid radical selected from the group of radicals consisting of $C_{11}H_{23}$—, $C_{15}H_{31}$—, $C_{17}H_{29}$—, $C_{17}H_{31}$—, $C_{17}H_{33}$—, $C_{17}H_{35}$—, $C_{16}H_{33}CHOH$—, and $C_6H_{13}CHOHC_{10}H_{18}$.

2. The method of preparing a gas protective fabric which is permeable to air but impermeable to mustard gas, Lewisite, and like chemical warfare vesicant agents, said method comprising first impregnating the fabric with an imidazoline of the general formula:



in which R_1 is a fatty acid selected from the group consisting of $C_{11}H_{23}$—, $C_{15}H_{31}$—, $C_{17}H_{29}$—, $C_{17}H_{31}$—, $C_{17}H_{33}$—, $C_{17}H_{35}$—, $C_{16}H_{33}CHOH$—, and $C_6H_{13}CHOHC_{10}H_{18}$, then chlorinating the trivalent 1-nitrogen atom of the imidazoline by soaking the fabric in a hypochlorite bath, the amount of imidazoline impregnated into the fabric being such that the weight of the active chlorine in the N-chloro group will not be more than 1.50% nor less than 0.25% of the weight of the dry fabric prior to impregnation.

HARRY A. WELDON.

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