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PROCESS FOR THE PREPARATION OF BIS (2,4,6-TRICHLOROPHENYL) UREA

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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 us of any royalty thereon.

This invention relates to a process of manufacturing an impregnite and more particularly has reference to the manufacture of an impregnite adapted for the destruction of vesicant compounds such as mustard gas and the treatment of material for rendering it protective against vesicant gases, vapors, and liquids, such as mustard gas.

It is well known that mustard gas and similar vesicants penetrate ordinary clothing and produce serious, if not fatal irritation of the skin. Many attempts have been made and several developments have been carried out to protect persons exposed to mustard gases and similar substances, by providing clothing which would prevent the vesicant gases contacting with the person's skin.

Impermeable suits have been made which prevent the vesicants from reaching the wearer's skin, but clothing so prepared is uncomfortable to the wearer to such an extent that it is impracticable except for limited uses.

Developments have further produced chemicals which can be impregnated into ordinary clothing, which permits the normal passage of air and moisture through the clothing, the chemicals reacting with mustard or other vesicant liquids and vapors to render them harmless to the skin. This method of protection from vesicant liquids, gases and vapors has desirable advantages, but the chemicals heretofore produced for impregnated clothing have been so unstable in the presence of air or moisture that protection is secured for a few days or weeks only. It will be appreciated that while clothing impregnated with these materials will have utility for a limited time, protection for longer periods of time is very desirable.

A major object of this invention therefore is to provide a method of manufacturing an impregnite suitable for clothing for reacting with mustard gas or other vesicant vapors to render such vapors harmless to the skin, the impregnite remaining fully effective for relatively long periods of time.

Another object of this invention is to provide a method of manufacturing an impregnite for clothing or other material which will react rapidly with mustard gas or other vesicant vapors without the formation of vesicant or otherwise harmful by-products.

Another object of this invention is to provide a method of manufacturing an impregnite for clothing or other material which is reasonably stable in air and moisture and which can be depended upon for protection against vesicant vapors for a reasonable length of time.

A further object of this invention is to provide a method of manufacturing an impregnite which can be readily impregnated into clothing in sufficient quantities to effectively protect the wearer against vesicant gases, and which, when so impregnated into clothing, is not irritant to the skin nor uncomfortable to the wearer.

A further object of this invention is to provide a practicable process for treating an amine to form a diamide, this process proceeding expeditiously and with a minimum

of materials. More specifically, this invention provides a process for phosgenating 2,4,6 trichloraniline to form sym. bis (2,4,6 trichlorphenyl) urea by dissolving the 2,4,6 trichloraniline in nitro benzene and carrying out the phosgenating thereof.

A further object of this invention is to provide a process of making a substantially pure diamide by dissolving an amine in nitro benzene and phosgenating the same.

A further object of this invention is to provide a practicable process for the chlorination of a diamide, using only the theoretically necessary amount of the chlorinating agent, or less than the theoretically necessary amount.

A further object of this invention is to provide a process for introducing active chlorine into a diamide which process is satisfactory for quantity production, using relatively inexpensive apparatus, yielding a product of a high degree of purity, and with a yield efficiency approximating 100%.

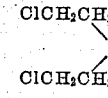
A further object of this invention is to provide a process of chlorinating sym. bis (2,4,6 trichlorphenyl) urea by treatment with sodium hypochlorite under pressure.

A further object of this invention is to provide a process of chlorinating a diamide with sodium hypochloride under a positive pressure of chlorine gas, thus hastening the chlorination and using less than the theoretically necessary correct amount of sodium hypochlorite.

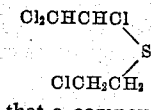
With these and other objects in view which will be apparent from the following description and claims, the invention consists in the ingredients and steps hereinafter set forth and claimed, with the understanding that the several necessary substances and compounds employed in carrying out the invention, and the steps involved in the procedure may be widely varied without departing from the spirit of the invention or the scope of the appended claims.

The present invention comprises the provision of a practicable method of producing a compound which when impregnated into clothing or similar material serves to protect a person wearing the clothing against the vesicant action of mustard gas.

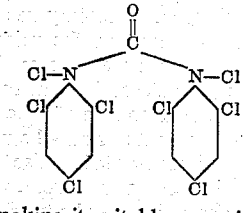
This invention is based on the fact that chlorine will react with mustard gas or similar substances to chlorinate the same and thereby produce compounds which are not vesicant or otherwise harmful. For instance, if mustard gas which is represented by the following formula



is properly chlorinated, a compound is formed which is non-vesicant and may be indicated by the following formula



It has been found that a compound having the following structure

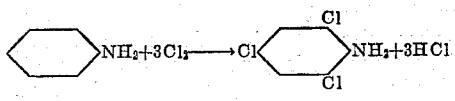


has properties making it suitable as an impregnite against vesicant vapors, liquids and gases.

This compound is a dichlor-diamide and may be named sym. dichlor-bis (2,4,6 trichlorophenyl) urea. In this compound the two chlorine atoms attached to the

nitrogen are active, and consequently the compound may be used to chlorinate mustard gas.

The preferred method of producing sym. dichlor-bis (2,4,6 trichlorophenyl) urea is as follows. Aniline is first chlorinated to form 2,4,6 trichloraniline by any known process. This reaction may be represented by the following

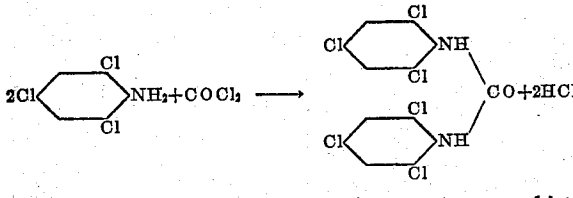


The amine 2,4,6 trichloraniline, is next phosgenated to form sym. bis (2,4,6 trichlorphenyl) urea. It has been found that when 2,4,6 trichloraniline is dissolved in the usual mediums that phosgenation thereof proceeds at a very slow rate. However, if nitro benzene is used as a solvent and the temperature maintained within the range of 100° to 120° C., phosgenation proceeds rapidly with a gradual separation of the desired product. Sym. bis (2,4,6 trichlorphenyl) urea is only slightly soluble in nitro benzene, whereas 2,4,6 trichloraniline is appreciably soluble therein. Therefore, phosgenation of 2,4,6 trichloraniline when dissolved in nitro benzene may be continued until no more precipitation occurs.

Another advantage of this process is that when reasonably pure 2,4,6 trichloraniline is used, the diamide, sym. bis (2,4,6 trichlorphenyl) urea, requires no purification. Furthermore the nitro benzene solvent may be used repeatedly.

One preferred embodiment of the above step of our process may be given as follows: A 10% solution of 2,4,6 trichloraniline in nitro benzene is maintained at a temperature within the range of 100°–120° C., and a current of phosgene is passed thereinto, the solution being continuously mechanically agitated. The sym. bis (2,4,6 trichlorphenyl) urea gradually precipitates in a light fluffy mass, and phosgenation is continued as long as precipitation takes place.

This reaction is as follows:



The diamide, sym. bis (2,4,6 trichlorphenyl) urea, which precipitates is filtered out and the reaction medium is reserved for future runs or further rephosgenated to complete the reaction.

The filtered solid is washed with carbon tetrachloride or other solvent to remove the nitro benzene and is then dried. If reasonably pure trichloraniline has been used, the resulting sym. bis (2,4,6 trichlorphenyl) urea will not need further purification. If purification is desired, however, the material may be re-crystallized from hot nitro benzene.

It will be noted that hydrogen chloride (HCl) is evolved as a reaction product in this process. By maintaining the temperature substantially within the range of 100°–120° C., the hydrogen chloride is rapidly removed, which is another important advantage of the raised temperature.

It will be understood that the process above described, and the materials used in carrying out the same may be varied without departing from the spirit of this invention. For example, other temperatures may be used and various other amines may be phosgenated. Also the invention is not limited to nitro benzene as a solvent, since other compounds of the benzene series may be used, such as o-nitro toluene; also chloro derivatives such as monochlorobenzene; also compounds of the benzene series with pyridine, such as toluene and pyridine.

By the above process, the phosgenation of amines is hastened, and the amount of phosgene necessary is materially reduced. Furthermore, a saving is effected by the repeated use of the benzene solvent and the yield of sym. bis (2,4,6 trichlorphenyl) urea is increased about 10%.

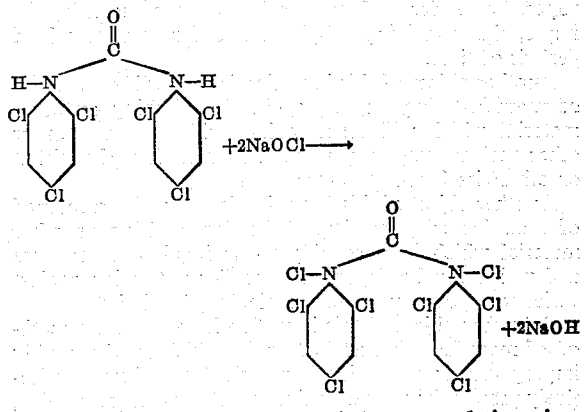
The sym. bis (2,4,6 trichlorphenyl) urea prepared in accordance with the above process or any other process is next chlorinated to introduce active chlorine therein. Prior known methods of introducing active chlorine into sym. bis (2,4,6 trichlorphenyl) urea are unsatisfactory for quantity production on a large scale. Such prior methods require apparatus of excessive capacity, the reaction proceeds slowly, the isolation of the desired product is expensive, the resulting product requires further purification, and the yield efficiency of the reaction is exceedingly low.

In accordance with this invention, the chlorination of of the sym. bis (2,4,6 trichlorphenyl) urea is carried out under pressure, preferably using a hypochlorite as the chlorinating agent, to form a dichlor diamide compound. The preferred chlorinating agent is sodium hypochlorite but varying degrees of chlorination may be accomplished by other agents such as bleaching powder ($CaOCl_2$), calcium hypochlorite ($Ca(OCl)_2$), or other agents of a similar nature. However when chlorinating agents other than sodium hypochlorite are used the yield efficiency is low and the resulting product is impure. If this chlorination is carried out using sodium hypochlorite under a positive or gauge pressure, the formation of the desired sym. dichlor-bis (2,4,6 trichlorphenyl) urea takes place rapidly and may be carried out in relatively inexpensive apparatus, yielding a product of such a high degree of purity that further purification is unnecessary. Furthermore, the yield efficiency of the reaction approximates 100%.

One specific example of this process may be given as follows: Into a reaction apparatus capable of being converted into an autoclave, equipped with a pressure gauge, 100 grams of sym. bis (2,4,6 trichlorphenyl) urea, 600 grams of glacial acetic acid, and 33.8 grams (200% of theoretical amount) of chlorine as 20–25% sodium hypochlorite are introduced. The autoclave is closed and the reaction mixture is heated to a temperature of from 60° to 65° C., for four hours. Under these conditions a positive pressure of 15 pounds is developed in the autoclave. The reaction materials are mechanically agitated during the heating period.

The sym. dichlor-bis (2,4,6 trichlorphenyl) urea is isolated by releasing the pressure in the autoclave, diluting the reaction solution with water, and filtering off the precipitated sym. dichlor-bis (2,4,6 trichlorphenyl) urea. This precipitate is finally washed with water to remove all acid.

The equation representing this chlorination may be written as follows:



This reaction should be carried to completion since otherwise the active chlorine compound may not be so easily isolated by dilution with water as the base compound is also insoluble in water.

This reaction may be carried out with less than the

theoretical amount of sodium hypochlorite, in which case a buffer salt such as sodium acetate ($NaC_2H_3O_2$) is added to neutralize the hydrochloric acid formed.

In the above described process it will be noted that chlorination is carried out under pressure developed by the materials when heated in a closed vessel. This pressure is substantially within the range of 10–20 pounds, and generally about 15 pounds with the quantities given in the above example. However, the chlorination may be carried out equally well and with much less sodium hypochlorite if the reaction is carried out under a positive pressure of chlorine gas.

A preferred embodiment of this portion of the invention therefore, is given in the following specific example. The sym. bis (2,4,6 trichlorphenyl) urea is placed in an autoclave with six times its weight of glacial acetic acid, a 10% excess of the theoretically correct amount of sodium hypochlorite is added and the autoclave is quickly closed.

The reaction mixture is brought to a temperature of about 70° C. and chlorine gas is admitted to the autoclave under substantial pressure, preferably about 45 pounds, from a cylinder connected to the autoclave. Complete chlorination will require about four hours under these conditions.

Chlorination may also be had under a positive pressure of chlorine gas using less than the theoretical amount of sodium hypochlorite. Furthermore, if sodium acetate ($NaC_2H_3O_2$) is added, chlorination may be carried out under positive chlorine gas pressure with as low as 5% of the theoretically necessary sodium hypochlorite. For such a reaction, a weight of sodium acetate equal to one-third the weight of the urea is added.

It will be understood that successful chlorination is not limited to the proportions of reactants given in the above specific examples. The condtiions of chlorination may be varied as regards quantities of materials used, temperature of the reaction, degree of agitation, type of apparatus, positive pressure developed, and pressure of the applied chlorine gas.

The sym. dichlor-bis (2,4,6 trichlorphenyl) urea obtained in accordance with this invention is a stable compound having active chlorine, thus forming an excellent compound for the destruction of and an impregnite for use against mustard gas.

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

While we have described the preferred embodiments of our invention, we wish it to be clearly understood that we do not confine ourselves to the precise steps or ingredients set forth herein 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.

We claim:

1. In a process of making sym. bis (2,4,6 trichlorphenyl) urea, the steps comprising dissolving 2,4,6 trichlor aniline in a solvent of the group consisting of nitro benzene, o-nitrotoluene, monochlorobenzene, and mixtures of toluene and pyridine, and passing a current of phosgene gas through the solution thus formed while maintaining said solution at a temperature of from about 110° C. to about 120° C.

2. The process of claim 1 wherein the solvent used is nitrobenzene.

3. The process of claim 1 wherein the solvent is o-nitrotoluene.

4. The process of claim 1 wherein the solvent is monochlorobenzene.

5. The process of claim 1 wherein the solvent is a mixture of toluene and pyridine.

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