PREPARATION AND PROPERTIES OF WAR GASES

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ABSTRACT

The preparation and properties of the most important war gases which were largely used in the field during World War I are briefly reviewed. Technical and tactical aspects of these gases, and methods of their detection and decontamination have been stressed.

The introduction of gas as an effective weapon in the World War I was logical in that the principal combatant nations were highly developed scientifically and industrially. This war had progressed only a few months when it was realized that the mechanical method of conducting war, which had attained its highest degree of perfection, was making no headway. One reason for this was the underground or dug-in method of warfare which was not anticipated. Means were sought to restore open warfare. At the outbreak of the war none of the combatants were prepared to use or defend against gas or chemical attacks.

The requirements which a satisfactory chemical agent for gas warfare must meet are so rigid that only a small group of compounds possess the necessary properties. Among the more important of these requirements are:

1. The chemical should be very toxic in small concentrations and should be difficult to protect against.

2. Volatility should be high enough to allow ready dispersal at temperatures met in both summer and winter warfare, and the material should be readily liquifiable so that it may be loaded into shells and bombs in the liquid state.

3. The chemical should not readily react with or be decomposed by moisture, metals or earth.

4. Stability should be sufficient to withstand storage and the shock of explosion.

5. The chemical should be cheap and easy to manufacture from readily available raw materials in enormous quantities without the use of too highly specialized equipment. It is preferable that the toxic properties develop only in the last stages of manufacture.

Although a number of chemicals have been used sometime or other during the World War I, mainly four or five of them continued to be used throughout the period.

Chlorine (Cl_2)

French: ‘Bertholite’

Chlorine was the first gas used on an effective scale in World War I. It was employed by the Germans against the Allies on April 22, 1915, when 600,0000 lbs of chlorine were released on the front of six Kilometers.

It was the principal gas used for cloud gas attacks. At first, when the Allies had little or no means of protection it was a very effective weapon. Later, when troops were protected with gas masks its effectiveness was greatly reduced. However, in mixture with other gases, such as phosgene and chloropicrin, it continued to be used throughout the war. Further, chlorine has extensive use in the preparation of other war gases.

Chlorine is very readily manufactured by the electrolysis of common salt. Before the World War I several industries were well established from which chlorine was available in large quantities.

At ordinary temperatures and pressures, chlorine is a greenish yellow volatile gas with a characteristic odor. It is readily liquified by moderate pressure (6·57 atmospheres) at ordinary temperatures (20°C). When liquid it has a sp. gr. 1·46 and when a gas, it is 2·5 times heavier than air, so that when released as a cloud it clings well to the ground as it travels down wind. Since liquid chlorine boils at —34·6°C, it readily vapourises at ordinary temperatures, and escapes with vigour from its container, so that it is well adopted for cloud gas operations from cylinders.

In the presence of moisture, chlorine is extraordinarily reactive, attacking almost all metals and organic substances. Although readily soluble in water, it does not hydrolyse easily. 215 volumes of chlorine will dissolve in 100 volumes of water at 25°C. It is very slightly soluble in hot water or in a concentrated salt solution.

Physiologically, chlorine is classified as a lung-injurant agent and is fairly toxic. It has a very irritating effect upon the membranes of nose and throat. Its lethal concentration (2·5 mg. per litre of air for 30 minutes exposure) is very high when compared with some of the gases developed later.

Technical Properties—Chlorine may be used as a gas under pressure or as liquid in steel cylinders. At the temperature of 25°C, 1 litre of liquid chlorine forms 434 litres of gaseous chlorine. In contact with moisture, metals and organic substances, such as plants, it reacts rapidly and is immediately neutralized. This is its principal disadvantage as a chemical agent. However, when strictly anhydrous, it does not attack iron and steel so that it may be kept in such container indefinitely.

Tactical Properties—As a gas at ordinary temperature chlorine can be used for cloud-gas attacks. It was highly effective in the field only as long as no adequate gas masks were available. After that time it was still useful in mixtures with more toxic gases, such as phosgene and chloropicrin.

Detection—Chlorine is easily detected by its characteristic smell, 0·003 mg per litre being perceivable. This concentration is decidedly below irritant and toxic concentration. Potassium iodide paper may be used to detect chlorine, but it is not much more sensitive than the human nose.

Chlorine reacts with 'hypo' (Sodium thiosulphate) with the formation of sodium chloride. Hypo is able to transform a large amount of chlorine, so that it proved a very satisfactory impregnating agent for the early cloth masks.

Phosgene

(Carbcnyl chloride) ($COCl_2$)

French 'Collongite' German: 'D-stoff' British and American: 'CG.'

Phosgene was the second toxic gas to be used in large quantitites during the World War I. It was first employed by the Germans against the British on Dec. 19, 1915, when 88 tons of the gas were released from 4,000 cylinders. Although the protection was adequate phosgene proved a very efficient war gas.

Here again the Germans made use of an industry already established. Phosgene is used commercially in the preparation of certain dyestuffs, especially methyl violet and was manufactured before and during the war by the Baeyer Company and the Badische Aniline Und Soda Fabrik. With its well known toxic properties and its ready availability in large quantities, phosgene was a logical choice of the German chemists for a more powerful substitute for chlorine when the Allies had equipped themselves with masks that afforded adequate protection against chlorine.

Phosgene is manufactured in industry by passing admixture of carbon monoxide and chlorine into catalyser boxes lined with graphite and filled with a porous form of carbon (wood or animal charcoal).

At ordinary temperatures and pressures, phosgene is a colourless gas, which condenses at 8°C to a colourless liquid of specific gravity 1·38. Above 8°C phosgene immediately evaporates although at a slower rate than chlorine and gives off a transparent vapour, 3·5 times heavier than air, with a stiffling but not unpleasant odor resembling new-mown hay.

Phosgene is absorbed by solid materials, such as pumice stone and celite. Pumice stone absorbs more than its own weight of phosgene. Thus 5·7 grams of pumice absorbed 7·4 grams phosgene, which completely evaporated in 60 minutes.

Chemically much more inert than chlorine, phosgene is a very stable compound and it is not dissociated by explosion of even strong bursting charges. It is, however, extremely sensitive to water in contact with which it quickly breaks down into hydrochloric acid and carbondioxide according to the equation

$$CO\,Cl_2 + H_2O = 2HCl + CO_2$$

Physiological action of phosgene is typical of lung injurant agents. Phosgene is more toxic than chlorine. It requires 2·5 mg. per litre of air of chlorine to kill a dog on an exposure of 30 minutes but 0·3 mg. of phosgene will have the same effect. In low concentrations, men may breathe phosgene for some time with apparently no ill effects. Ten or twelve hours later, or perhaps earlier if they attempt any work, the men become casualties.

Technical Properties—Phosgene is stable to explosion and storage, and to iron and steel, if completely dry. Its evaporation is slow, for this reason it must be mixed with equal parts of chlorine for cloud gas attacks. This is due to its low boiling point which also makes the filling a more complicated technical operation. Because of its rapid hydrolysis in the presence of water, phosgene cannot be efficiently employed in very wet weather.

Tactical Properties—Mixed with chlorine, phosgene was first used in cloud gas attacks. These attacks continued for about nine months and were then gradually replaced to a large extent, by gas shell attacks. Throughout the war, this gas was the principal offensive battle gas, being used in enormous quantities in cylinders, artillery shells, trench mortars, bombs and projector drums.

The projectors had a decided advantage over shell in that they held a larger volume of gas and readily lent themselves to surprise attacks. The projector combined the advantages of a gas cloud and gas shell. The density was equal to that of gas cloud and the surprise effect of shell fire was also obtained.

Towards the close of the war, the Germans made use of a mixture of phosgene and pumice stone. While the apparent reason for their use is to prevent the rapid evaporation of the phosgene, it is a question, whether such is the case, for a greater surface is really present in the case of pumice stone than where the phosgene is simply on the ground. Lower initial concentrations were, however, secured due to the smaller volume of phosgene in the shell containing pumice. Pumice does seem to keep the booster from scattering the phosgene high into the air, and at the same time does not prevent the phosgene from being liberated in a gaseous condition. This would indicate that pumice gives a more even and uniform dispersion and a more economical use of the gas.

Owing to its non-persistent nature (the odor disappears in from one and a half to two hours) and to its general properties, phosgene really forms an ideal gas to produce casualties.

Although the boiling point of phosgene (8°C) is considerably below ordinary temperatures, especially during the summer months, the rate of evaporation is so slow that a cloud attack could never be made with it alone. However, when a mixture of (*a*) 25 per cent phosgene and 75 per cent chlorine or, (*b*) 50 per cent phosgene and 50 per cent chlorine is used in warm weather there is no difficulty in carrying out gas attack from cylinders. At the same time the percentage of phosgene in the mixture is sufficiently high to secure the advantages which it possesses.

Detection—Detection of phosgene in air is made by the smell and irritative action of phosgene.

Phosgene is absorbed and decomposed by hexamethylenetetramine (urotropine). This reaction furnished the basis of the first protection used by the British. Later the catalytic decomposition of phosgene into carbon dioxide and hydrochloric acid by the charcoal in the mask furnished protection.

Chloropicrin

(Nitrochloroform) (CCl_3NO_2)

French: "Aquinite"; German: " Klop "; British: " Vomiting gas"; American: "PS".

The next gas to make its appearance in World War I was chloropicrin. This gas was first used by the Russians in August 1916, and was subsequently employed by both Germans and the Allies. It was used alone or mixed with other combat substances in artillery shells, trench-mortars, bombs, and in cylinders for cloud gas attacks. Indeed chloropicrin appears to have been the most widely used combat gas in the war although the total amount used was probably less than that of phosgene and superpalite.

Like chlorine and phosgene, chloropicrin was a well known chemical before the World War I. It was discovered by the English chemist, Stenhouse in 1848 and its chemical and physiological properties had been carefully studied many years during the nineteenth century.

Chloropicrin is rather easily manufactured by the direct chlorination of picric acid. In practice the reaction is carried out by injecting live steam into an aqueous solution of bleaching powder and picric acid. Since large amounts of picric acid are used in industry and for high explosives and since bleaching powder is easily obtainable everywhere, the raw materials necessary in the manufacture undoubtedly account for the widespread use of chloropicrin during the World War I.

Chloropicrin is a colourless oily liquid of sp. gr. 1·66 which boils at 113°C giving off a pungent irritating vapour, 1·6 times heavier than air, and having a sweetish odor resembling that of flypaper. Even at ordinary temperatures chloropicrin evaporates very rapidly and its vapour pressure is quite high e.g. at 20°C it amounts to 18·3 mm. Hg. Its volatility at 20°C is 165·0 mg per litre. Chloropicrin may, therefore, be used in cylinders for cloud-gas attacks if mixed with chlorine. Mixed with 70% chlorine, chloropicrin was used in a large number of British gas attacks.

Chemically chloropicrin is quite a stable compound. It is almost insoluble in and is not decomposed by water; it does not combine readily with either acids or alkalies. Owing to its chemical inertness, chloropicrin does not react with any of the chemicals in the gas mask canister and is removed from the air passing through the canister by the charcoal alone. It is therefore, one of the most difficult of the war gases to protect against, owing to this fact, the protection afforded by gas-mask canisters is usually rated in accordance with the number of hours it will protect against ordinary field concentrations of chloropicrin.

Like chlorine and phosgene, it is a lethal compound which acts primarily as a lung injurant. In toxicity, it is intermediate between chlorine and phosgene as indicated by the following comparative figures.

Lethal Concentrations

Exposure (minutes)	Chlorine (mg. per litre)	Chloropicrin (mg. per litre)	Phosgene (mg. per litre)
10	5·60	2·00	0·50
30	2·53	0·80	0·36

In addition to its lethal (lung injurant) effects, chloropicrin is also a strong lachrimator and has the additional advantage of resistance to ordinary acid gases such as chlorine and phosgene. The injurious effects of chloropicrin also extend to the stomach and intestines, causing nausea, vomiting, colic and diarrohea. These conditions are difficult to combat in the field and often persist for weeks so that even slight cases of chloropicrin gassing frequently involve large casualty losses.

Tactical Properties—The main tactical idea in using chloropicrin, aside from its toxic effect, was to penetrate the mask and produce an intolerable irritation of the eyes, as well as coughing and vomiting from nausea. These effects are sufficient to cause masked troops to remove their masks and thus expose themselves to even more lethal gases, such as phosgene, which would be put over with the chloropicrin.

Because of the high boiling point of chloropicrin (112°C) it can only be used in shell. The German shell usually contained a mixture of superpalite and chloropicrin the relative proportions being about 75 to 25. Mixtures of phosgene and chloropicrin (50-50) have also been used. The Allies have used a mixture of 80 per cent chloropicrin and 20 per cent stannic chloride (so-called N. C.). This mixture combines the advantages of a gas shell with those of a smoke shell, since the percentage of stannic chloride is sufficiently high to form a very good cloud. In addition to this, it is believed that the presence of the chloride increases the rate of evaporation of the chloropicrin.

This N. C. mixture has also been used in Liven's projectors and in hand grenades. The material is particularly fitted for hand grenades, owing to the low vapour pressure of the chloropicrin and the consequent absence of pressures even on warm days.

While chloropicrin is sufficiently volatile to keep the strata of air above it thoroughly poisonous, it is still persistent enough to be dangerous after five or six hours, which would preclude its use on the tactical offensive in ordinary situations.

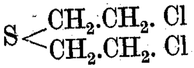
The principal disadvantages of chloropicrin are its relatively low toxicity, as compared to some of the later war gases and the fact that it decomposes upon heating and when subjected to too high an explosive shock. Notwithstanding this latter peculiarity, the results of the World War I showed that chloropicrin could be successfully used in artillery shells if the bursting charges were properly adjusted to this filling.

Detection—Chloropicrin is easily detected (qualitatively) with a test paper which has been previously soaked in a dilute solution of dimethylaniline in benzene. In the presence of chloropicrin there is momentary fading according to the concentration, from bright yellow to dark brown.

The atmosphere may be freed from chloropicrin by the spraying of a solution of 240 grams potassium sulphide in 10 litres of water.

Mustard Gas

Di-β-chloroethyl sulphide,



$$S<\begin{matrix}CH_2.CH_2.\ Cl\\ CH_2.CH_2.\ Cl\end{matrix}$$

French: "Yperite"; German: "Lost"; British and American: "Mustard Gas."

Mustard gas was the most efficacious war gas used during the World War I. The Germans introduced the use of mustard gas on the night of July 12, 1917. Authorities have stated that the introduction of mustard gas changed completely the whole aspect of gas warfare and to a considerable extent the aspect of warfare of every kind.

Mustard gas, chemically, is Di-β-chloroethyl sulphide $(S(CH_2.CH_2Cl)_2$. The name originated with the British Tommy because the crude material first used by the Germans was suggestive of mustard or garlic, although this substance has no relation chemically to the true mustard oils.

Like the other world war gases, "mustard" was not a new or unknown compound. On the contrary, it was discovered sixty years before the outbreak of the war, and its chemical and physiological properties had been studied and were known to science for many years.

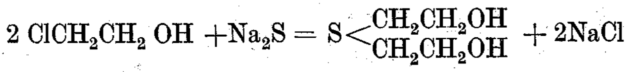
Mustard gas was first obtained (in an impure form) by Richie in 1854. In 1860 it was independently prepared by Guthrie and Niemann by passing ethylene into sulphur chloride. Both these chemists accurately and almost prophetically described its high toxic and vesicant properties. In 1886 the German chemist, Victor Meyer, prepared mustard gas by the action of hydrochloric acid on thiodiglycol and described the terrible effects of the product.

In searching for a more effective combat gas, therefore, the Germans had available many data in the literature concerning mustard gas and had only to make it in quantity and test it in the field.

Di-β-chloroethyl sulphide (mustard gas) was made by two radically different processes during war. The Germans used the more complicated process of Victor Meyer, because they had already available facilities for manufacturing the principal components, and had only to erect facilities for the final step in the process.

(1) *German Process* was briefly as follows:—

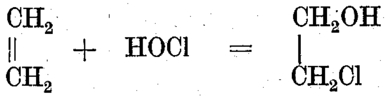
(*a*) Ethylene chlorhydrin was converted into thiodiglycol by Na_2S according to the equation



$$2\,ClCH_2CH_2OH + Na_2S = S<\begin{matrix}CH_2CH_2OH\\CH_2CH_2OH\end{matrix} + 2NaCl$$

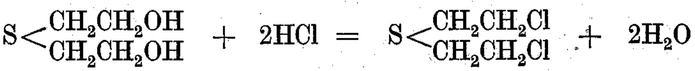
Thiodiglycol

Ethylene chlorhydrin was prepared by passing ethylene into hypochlorous acid.



$$\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + HOCl = \begin{matrix}CH_2OH\\ |\\ CH_2Cl\end{matrix}$$

(*b*) The thiodiglycol was converted to mustard gas by treating with gaseous hydrochloric acid according to the equation



$$S<\begin{matrix}CH_2CH_2OH\\CH_2CH_2OH\end{matrix} + 2HCl = S<\begin{matrix}CH_2CH_2Cl\\CH_2CH_2Cl\end{matrix} + 2H_2O$$

Mustard gas

The German process had two outstanding advantages viz.

(1) The intermediate products possessed no dangerous properties and hence there was no danger to personnel working in the plants on any of the intermediate steps. The only danger involved in the whole process was in the last step of converting the thiodiglycol to form mustard gas. This was a relatively simple reaction that was easy to control, and hence the danger to personnel was far less than in many of the steps of the other process.

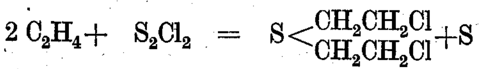
(2) The yield was high and the product pure, since the only other end product was water, which was easily separated by distillation.

On the other hand, the German method had the formidable objection of being a very complicated process, particularly in the method of making the chlorhydrin. To make this intermediate, three steps requiring careful control were necessary; (*i*) alcohol was split into ethylene by passing its vapours over aluminium oxide at 300°C; (*ii*) the ethylene gas was pumped into large reactors containing a paste of bleaching powder which was carefully cooled during the process; (*iii*) the resulting ethylene chlorhydrin was forced out of the paste by steam.

While the foregoing steps in the German process of making mustard gas seem simple, in reality they are very difficult and only a chemical technique excellently organised and backed by a wealth of experience could successfully cope with the technical difficulties encountered.

(2) *Allies' Process*

Allies prepared mustard gas by the older process of Guthrie and Niemann in which it is formed by the direct action of ethylene gas on sulphur monochloride according to the equation:



$$2\,C_2H_4 + S_2Cl_2 = S\begin{array}{l}<CH_2CH_2Cl\\<CH_2CH_2Cl\end{array} + S$$

While this reaction under proper conditions proceeds smoothly, there are actually encountered in quantity production operations several very formidable difficulties. Thus:

(*a*) The reaction occurs spontaneously with the evolution of much heat.

(*b*) Sulphur is set free and the temperature must be carefully controlled in order to keep the sulphur in colloidal suspension and thus prevent its precipitation in solid form in the reaction vessels and connecting pipes.

(*c*) There is also considerable difficulty in separating the mustard gas from the colloidal sulphur, so that the resulting product was not so pure as that from the German process, although, it seemed to be equally as effective in the field.

It is difficult to emphasize sufficiently the extreme danger that is involved in working with mustard gas even under the best of conditions. The workmen must be equipped with masks and the most efficient protective clothing and everything coming in contact with even the vapours of mustard gas must be decontaminated at once with bleaching powder or other neutralizing agents. Notwithstanding all these precautions, casualties will occur owing to carelessness and only the most rigid discipline can keep them within reasonable bounds.

In its pure state Di-β-chlorethyl sulphide is a transparent amber coloured oily liquid of sp. gr. 1·27 which boils with slight decomposition at 217°C yielding a vapour 6·5 times heavier than air. It is almost odorless in ordinary field concentrations and in strong concentration resembles horse radish or mustard. It solidifies at 14° C to form white crystals and for this reason was used by the Germans diluted with a solvent to lower its freezing point and maintain it in a uniform (liquid) state under all ordinary temperatures.

Because of high boiling point mustard gas vaporises very slowly at atmospheric pressure. Its volatility at different temperatures is given below:

Temperature °C	mg. per. m^3
14	345
15	401
18	422
20	425
22	719
35	2,135
39	2,980

The low vapour pressure combined with its relatively high stability allow it to persist in the field undecomposed for relatively long periods.

It is soluble in most organic solvents with the exception of the petroleum hydrocarbons. The mustard gas drops penetrate with great speed and facility any object with which they come in contact. They easily penetrate leather and fabrics of cotton and linen and rubber boots and gloves and all other articles of uniform worn by soldiers. It is because of these remarkable powers of solubility and penetration that mustard gas is so difficult to protect against.

While mustard gas is only slightly soluble in water, it is slowly decomposed thereby. The decomposition proceeds with saponification and the formation of thiodiglycol and hydrochloric acid, according to the reaction

$$S{<}\begin{matrix}CH_2CH_2Cl\\CH_2CH_2Cl\end{matrix} + 2H_2O = S{<}\begin{matrix}CH_2CH_2OH\\CH_2CH_2OH\end{matrix} + 2HCl$$

At ordinary temperatures, water saponifies 25% within 2 hours, 35% within 6 hours and 60% within 24 hours. This hydrolysis takes place on contact with moisture in the air or with water on the ground and thus mustard gas is slowly destroyed whenever these conditions are encountered.

With chlorine, bleaching powder or chloramine mustard gas is transformed by chlorination or oxidation into less toxic compounds that are practically without danger. Bleaching powder and chloramine, therefore, are used for decontamination of men, objects and soil.

Mustard gas is primarily a vesicant, blisters being formed by either liquid or vapour contact. It also attacks the eyes and lungs and is a systemic poison, so that protection of the entire body must be provided. The lethal concentration by inhalation for a 10-minute exposure is 0·15 mg./litre and the lowest concentration that causes irritation in 10 minutes is 0·001 mg/litre.

Tactical uses of Mustard gas

Mustard gas, besides being highly poisonous has so many other important qualities as to have given it the designation during the war of the 'King of battle gases'.

Because of its low volatility mustard gas is very persistent in the field, varying from one day in the open and one week in the woods in summer to several weeks, both in the open and in the woods, in winter. On account of its persistence it has been generally referred to as a defensive gas and for that purpose it is incomparable. The use of sufficient quantities of mustard gas will almost certainly stop the occupation of areas by the enemy and probably even stop his crossing of them. It also enables strong points which it is not desired to attack to be completely neutralised that is, made so unhabitable that the area must be evacuated. It cannot, however, be used on the tactical offensive where friendly troops have to traverse or occupy the infected ground.

Since mustard gas has such a delay action and is effective in such small concentrations, it can be used very effectively in small calibre guns, as the 75 mm or 3 inch. Further more since it lasts for two or three days at the very least, a small number of guns can keep a very large area neutralized with the gas. With phosgene and similar non-persistent gases that volatilize almost completely upon the burst of the shell it is necessary to build up a high concentration immediately. The exact opposite is true of mustard gas. Mustard gas can be fired very slowly with the certain knowledge that all shells fired at one moment will be effective when the next is fired, though twelve hours or more may intervene between the first and last firing. Thus, while with phosgene a large number of guns are needed for a gas attack, with mustard gas the number can be reduced to one-tenth or even less. Mustard gas has been in the past used safely in hand grenades because of its very low vapour tension, whereby the pressure at ordinary temperatures is exceedingly low. This has an important bearing on cylinder and other containers for shipping mustard gas, that is, they need be only strong enough to be safe against handling and not to withstand the high pressure encountered with phosgene or chlorine cylinders.

Technical Properties

Mustard gas is a liquid at ordinary temperatures but solidifies at about 14°C. The ballistic behaviour of the shells is subject to changes when their contents change between solid and liquid with the change of temperature. To avoid this difficulty, mustard gas was used in solutions. As solvents were added, (10 to 25%) carbon tetrachloride, chlorobenzene or nitrobenzene by the German and French armies. The Americans used chloropicrin for the same purpose, considering it an advantage that the latter is also a toxic war gas. However, chloropicrin is also an irritant. Such shells containing chloropicrin act, therefore, less insidiously. The enemy is warned in time of the presence of gas, puts on his mask and is thus protected against the insidious action of the odorless and non-irritant mustard gas.

Not only does the addition of a solvent facilitate the ballistic behaviour of mustard gas shells, but it also increases the volatility of the mustard charge in winter weather and renders it more effective on the terrain. Depending upon the solvent used and the force of explosion of the bursting charge in the shell, the mustard gas solution is scattered in the form of gas clouds or a finely divided spray composed of liquid particles varying in size from an atomized mist to droplets resembling fine rain. The liquid particles are very stable against humidity and cling firmly to the ground and vegetation. The clouds of mustard vapour formed by the explosion of shells are not at all visible in dry weather and only slightly visible in damp weather.

The mustard gas drops penetrate with great speed and facility any objects with which they come in contact. The mustard liquid is thus easily carried about by soldier and spread and evaporated in other previously uninfected places. Frequently in the World War I all the occupants of a dugout were contaminated and made ill by the mustard adhering to the clothing of a single soldier who was not even aware of its presence.

Detection

At first the only method of detecting mustard gas was through the sense of smell. It was then believed that concentration which could not be detected in this way were harmless. Later, this proved not to be the case, and more delicate methods had to be devised.

The chemical warfare service was able to device an enamel and an oil paint which were very sensitive detectors of mustard gas. Both of these were yellow and became dark red in contact with mustard gas. The change was practically instantaneous. The enamel consisted of chrome yellow as pigment mixed with oil scarlet and another dye, and a lacquer vehicle, which is essentially a solution of nitrocellulose in amylacetate. One gallon of this enamel will cover 946,500 sq. cm. or surface equivalent to a band 3 cm. wide on 12,500 seven cm. shells.

The paint was composed of a mixture of 50 per cent raw linseed oil and 50 per cent Japan drier, with the above dye mixture added to the required consistency. In contact with liquid mustard gas, this changes to a deep crimson in 4 seconds. Furthermore, in contact with arsenicals, this paint changes to a color varying from deep purple to dark green, the color change being almost instantaneous and very sensitive, even to the vapours of these compounds. Other substances have no effect upon the paint.

For field work, however, nothing was found equal to the trained nose and it is questionable if any of the *mechanical* means described will be used in the field.

One of the greatest dangers from mustard gas is the lack of any positive means of identifying it in low concentrations in the field. While it has a characteristic odor resembling mustard or horse-radish in strong concentrations, this odor is very faint in concentrations which are still dangerous on exposures of more than 1 hour. Thus, the odor is said to be detectable at 0·0013 mg. per litre but a concentration of 0·001 mg. per litre will cause casualties from conjunct vities on 1 hour's exposure, and such a concentration cannot be detected even by the keenest perception. Moreover, the sense of smell for mustard gas is quickly dulled after initial exposure, so that much stronger concentrations go unnoticed. Also, many odors, such as those produced by the stronger lachrimators mask the odor of mustard gas so that it became a common practice to use such mixtures.

Diphenyl-Chlorarsine

$(C_6H_5)_2$ AsCl.

German: Clark 1; American: D.A,

During the summer of 1917 two new and very important gases were introduced, and as before by the Germans. One of these was diphenylchlorarsine. It is the best of the arsenicals or 'sneezing gas'.

Diphenylchlorarsine was discovered in 1881 by Michaelis and Lacoste. Although this is an old compound, there was no easy method for its preparation on a large scale when first introduced into chemical warfare. During the war it was manufactured by the Germans in accordance with a complicated process of which the following were the principal steps (process A). It was finally discovered that the interaction of triphenylarsine with arsenic trichloride was fairly satisfactory and a plant was erected for its manufacture (process B).

It was stated that the Germans adopted the more complicated method outlined below because they had previously manufactured several of the intermediates in this process and that the equipment of their chemical plants was peculiarly adapted to this process.

Process A.

1. Benzene diazonium chloride was treated with sodium arsenite to form sodium phenylarsenate.

$$C_6H_5—N_2Cl + Na_3AsO_3 = C_6H_5AsO_3Na_2 + NaCl + N_2.$$

2. Sodium phenylarsenate was converted to phenylarsenic acid by treatment with hydrochloric acid.

$$C_6H_5AsO_3Na_2 + 2HCl = C_6H_5AsO_3H_2 + 2NaCl.$$

3. Phenylarsenic acid was reduced to phenylarsenious acid by treatment with sulphurdioxide and water.

$$C_6H_5AsO_3H_2 + SO_2 + H_2O = C_6H_5AsO_2H_2 + H_2SO_4$$

4. Phenylarsenious acid was treated with sodium hydroxide to form sodium phenylarsenite.

$$C_6H_5AsO_2H_2 + 2NaOH = C_6H_5AsO_2Na_2 + 2H_2O$$

5. Sodium phenylarsenite was converted to sodium diphenylarsenite by treatment with benzene diazonium chloride.

$$C_6H_5AsO_2Na_2 + C_6H_5N_2Cl = (C_6H_5)_2AsO_2\ Na + NaCl + N_2$$

6. Sodium diphenylarsenite was treated with hydrochloric acid to form diphenylarsenic acid.

$$(C_6H_5)_2AsO_2Na + HCl \quad (C_6H_5)_2AsO_2H + NaCl.$$

7. This acid was reduced to diphenylarsenious oxide by treatment with sulphurdioxide and water.

$$2(C_6H_5)_2AsO_2 + 2SO_2 + H_2O = [(C_6H_5)_2\ As]_2O + 2H_2SO_4.$$

8. Diphenylarsenious oxide was converted to diphenylchlorarsine by chlorination with hydrochloric acid.

$$[(C_6H_5)_2As]_2O + 2HCl = 2\ (C_6H_5)_2\ AsCl + H_2O$$

Process B.

1. Triphenylarsine is formed by acting on chlorbenzene and arsenic trichloride with sodium.

2. The triphenylarsine is then heated under pressure with more arsenic trichloride and diphenylchlorarsine is thus obtained.

In the pure state, diphenylchlorarsine is a white crystalline solid, of specific gravity 1·4, which melts at 44°C., although the somewhat impure commercial susbstance used during the war melted at 38°C. It boils with decomposition at 383°C. It is insoluble in water, but is readily soluble in organic solvents, including phosgene and chloropicrin. As it is a solid, its vapour pressure (0·0005 mm. Hg. at 20°C) is negligible and its volatility at 20°C is only 0·00068 mg. per litre. Because of this, it was always used in solution in a toxic gas or in a shell which contained a large amount of explosive so that on bursting of the shell the material would be finely divided and scattered over a wide territory, the diameter of the particles thus formed being between 10^{-4} and 10^{-5} cm. It is not decomposed by detonation.

It decomposes rapidly in contact with water, yielding hydrochloric acid and phenylarsenic oxide which is toxic but this action is very slow in a merely humid atmosphere.

Diphenylchlorarsine is effective in extremely low concentrations. Thus, a concentration as low as 1 : 25,000,000 (0,0005 mg per litre) is sufficient to produce marked irritation of the nose and throat, while 0,0012 mg. per litre becomes unbearable after 1 minute. A concentration of 1·50 mg. per litre is lethal after 10 minuetes, and 0·60 mg. per litre after 30 minutes exposure.

Tactical Properties.

Diphenylchlorarsine was introduced simultaneously with mustard gas as an offensive companion thereto, since mustard gas was too persistent to be used on the tactical offensive. The purpose of diphenylchlorarsine was to penetrate the allies' masks, which successfully protected against all the lung injurant agents. This was accomplished by dispersing the chemical substance in the form of a dust which not being a vapour or gas, was not absorbed by the charcoal and soda-lime in the gas mask canister. The dust, thus penetrates the mask and causes violent sneezing. The purpose, of course, is to compel the removal of the mask in an atmosphere of lethal gas.

Technical Properties.

As a solid substance it can be handled easily. The main technical difficulty was to construct a shell which disperses the product. The smoke candles which are more satisfactory in this respect have other tactical disadvantages as dependency upon wind and other weather conditions. When diphenylchlorarsine is pulverized and dispersed by the explosion of a high-explosive (embedded in TNT in the shell) charge and to a far greater extent, when thermally distilled as a toxic smoke, it is broken up into microscopic particles that float in the air and easily penetrate the ordinary gas mask canister.

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