

## CHAPTER VII

### LACHRYMATORS

Without question the eyes are the most sensitive part of the body so far as chemical warfare is concerned. Lachrymators are substances which affect the eyes, causing involuntary weeping. These substances can produce an intolerable atmosphere in concentrations one thousand times as dilute as that required for the most effective lethal agent. The great military value of these gases has already been mentioned and will be discussed more fully later.

There are a number of compounds which have some value as lachrymators, though a few are very much better than all the others. Practically all of them have no lethal properties in the concentrations in which they are efficient lachrymators, though we must not lose sight of the fact that many of them have a high lethal value if the concentration is of the order of the usual poison gas. The lachrymators are used alone when it is desired to neutralize a given territory or simply to harrass the enemy. At other times they are used with lethal gases to force the immediate or to prolong the wearing of the mask.

A large number of the lachrymators contain bromine. In order to maintain the gas warfare requirements, it was early decided that the bromine supply would have to be considerably increased. The most favorable source of bromine is the subterranean basin found in the vicinity of Midland, Michigan. Because of the extensive experience of the Dow Chemical Co. in all matters pertaining to the production of bromine, they were given charge of the sinking of seventeen government wells, capable of producing 650,000 pounds of bromine per year. While the plant was not operated during the War, it was later operated to complete a contract for 500,000 pounds

of bromine salts. They will be held as a future war asset of the United States.

The principal lachrymators used during the War were:

Bromoacetone,  
Bromomethylethylketone,  
Benzyl bromide,  
Ethyl iodoacetate,  
Bromobenzyl cyanide,  
Phenyl carbylamine chloride.

Chloropicrin is something of a lachrymator, but it has greater value as a toxic gas.

#### HALOGENATED KETONES

One of the earliest lachrymators used was bromoacetone. Because of the difficulty of obtaining pure material, the commercial product, containing considerable dibromoacetone and probably higher halogenated bodies, was used. The presence of these higher bromine derivatives considerably decreased its efficiency as a lachrymator. The preparation of bromoacetone involved the loss of considerable bromine in the form of hydrobromic acid. This led the French to study various methods of preparation, and they finally obtained a product containing 80 per cent bromoacetone and 20 per cent chloroacetone, which they called "martonite." As the war progressed, acetone became scarce, and the Germans substituted methylethylketone, for which there was little use in other war activities. This led to the French "homomartonite."

Various other halogen derivatives of ketones have been studied in the laboratory, but none have proven of as great value as bromoacetone, either from the standpoint of toxicity or lachrymatory power.

*Bromoacetone* may be prepared by the action of bromine (liquid or vapor) upon acetone (with or without a solvent). Aqueous solutions of acetone, or potassium bromide solutions of bromine, have also been used.

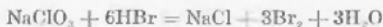
Pure bromoacetone is a water clear liquid. There are great differences in the properties ascribed to this body by different

investigators. This probably is due to the fact that the mono-bromo derivative is mixed with those containing two or more atoms of bromine. A sample boiling at 126-127° and melting at -54°, had a specific gravity of 1.631 at 0°. It has a vapor pressure of 9 mm. of mercury at 20°.

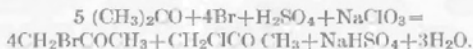
While bromoacetone is a good lachrymator, it possesses the disadvantage that it is not very stable. Special shell linings are necessary, and even then the material may be decomposed before the shell is fired. The Germans used a lead lined shell, while considerable work has been carried out in this country with enamel lined shell. Glass lined shell may also be used. It is interesting to note that, while bromoacetone decomposes upon standing in the shell, it is stable upon detonation. No decomposition products are found after the explosion, and even unchanged liquid is found in the shell. It may be considered as having a low persistency, since the odor entirely disappears from the surface of the ground in twenty-four hours.

Bromoacetone was also used by the Germans in glass hand grenades (Hand-a-Stink Kugel) and later in metal grenades. The metal grenades weighed about two pounds and contained about a pound and a half of the liquid.

*Martonite* was prepared by the French in an attempt more completely to utilize the bromine in the preparation of bromoacetone. They regenerated the bromine by the use of sodium chlorate:



In practice sulfuric acid is used with the sodium chlorate, so that the final products are sodium acid sulfate and a mixture of 20 per cent chloroacetone and 80 per cent bromoacetone, according to the reaction:



This product is equally as effective as bromoacetone alone and is very much cheaper to manufacture. In general its properties resemble very closely those of bromoacetone.

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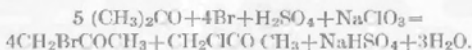
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## GERMAN MANUFACTURE OF BROMOACETONE AND BROMOMETHYLETHYL KETONE\*

These two products were prepared by identical methods. About two-thirds of the product produced by the factory was prepared from methylethyl ketone which was obtained from the product resulting from the distillation of wood. The method employed was to treat an aqueous solution of potassium or sodium chlorate with acetone or methylethyl ketone, and then add slowly the required amount of bromine. The equation for the reaction in the case of acetone is as follows:



Ten kg.-mols of acetone or methylethyl ketone were used in a single operation. About 10 per cent excess of chlorate over that required to oxidize the hydrobromic acid formed in the reaction was used. The relation between the water and the ketone was in the proportion of 2 parts by weight of the former to 1 part by weight of the latter. For 1 kg. mol.-wt. of the ketone, 10 per cent excess over 1 kg. atomic-weight of bromine was used.

The reaction was carried out either in earthenware vessels or in iron kettles lined with earthenware. The kettles were furnished with a stirrer made of wood, and varied in capacity from 4,000 to 5,000 liters. They were set in wooden tanks and cooled by circulating water. The chlorate was first dissolved in the water and then the ketone added. Into this mixture the bromine was allowed to run slowly while the solution was stirred and kept at a temperature of from 30° to 40° c. The time required for the addition of the bromine was about 48 hrs. When the reaction was complete, the oil was drawn off into an iron vessel and stirred with magnesium oxide in the presence of a small amount of water in order to neutralize the free acid. It was then separated and dried with calcium chloride. At this point a sample of the material was taken and tested. The product was distilled to tell how much of it boiled over below 130° when methylethyl ketone had been used. If less than 10 per cent distilled over, the bromination was considered to be satisfactory. If, however, a larger percentage of low-boiling material was obtained, the product was submitted to further bromination. The material obtained in this way was found on analysis to contain slightly less than the theoretical amount of monobromo-ketone.

It was finally transferred by suction or by pressure into tank-wagons. At first lead-lined tanks were used, but later it was found

\* Norris, *J. Ind. Eng. Chem.*, 11, 828 (1919).

that tanks made of iron could be substituted. In order to take care of the small amount of hydrobromic acid, which is slowly formed, a small amount of magnesium oxide was added to the material. The amount of the oxide used was approximately in the proportion of 1 part to 1000 parts of ketone. When the magnesium oxide was used, it was found that the bromoketone kept without appreciable decomposition for about 2 months. The yield of the product from 580 kg. of acetone (10 kg.-mol. wts.) was 1,100 kg. The yield from 720 kg. of methylethyl ketone (10 kg.-mol. wts.) was 1,250 kg.

#### HALOGENATED ESTERS

The use of ethyl iodoacetate was advocated at a time when the price of bromine seemed prohibitive. Because of the relative price of bromine and iodine under ordinary conditions, it is not likely that it would be commonly used. However, it is an efficient lachrymator and is more stable than the halogenated ketones, so that on a smaller scale it might be advisable to use it.

It is prepared by the reaction of sodium iodide upon an alcoholic solution of ethyl chloroacetate. It is a colorless oil, boiling at 178-180° C. (69° C. at 12 mm.) and having a density of about 1.8. It is very much less volatile than bromoacetone, having a vapor pressure of 0.54 mm. of mercury at 20° C. Ethyl iodoacetate is about one-third as toxic as bromoacetone, but has about the same lachrymatory value.

#### AROMATIC HALIDES

"Benzyl bromide" was also used during the early part of the war, usually mixed with bromoacetone. The material was not pure benzyl bromide, but the reaction product of bromine upon xylene, and should perhaps be referred to as "xylyl bromide."

Pure benzyl bromide is a colorless liquid, boiling at 198-199° C., and having an odor reminiscent of water cress and then of mustard oil. The war-gas is probably a mixture of mono- and dibromo derivatives, boiling at 210-220° C., and having a density at 20° C. of 1.3. The mixture of benzyl and xylyl bromides used by the Germans was known as "T-Stoff," while

the mixture of 88 per cent xylyl bromide and 12 per cent bromoacetone was called "Green T-Stoff."

As in the case of the halogenated acetones, it is necessary to use lead lined shell for these compounds. Enamel and glass lined shell may be used and give good results. While they are difficult of manufacture, satisfactory methods were being developed at the close of the war.

"T-Stoff" may be detected by the nose in concentrations of one part in one hundred million of air, and will cause profuse lachrymation with one part in a million. It is a highly persistent material and may last, under favorable circumstances, for several days. While it is relatively non-toxic, French troops were rendered unconscious by it during certain bombardments in the Argonne in the summer of 1915.

A number of derivatives of the benzyl halides have been tested and some have proven to be very good lachrymators. The difficulty of their preparation on a commercial scale has made it inadvisable to use them, and especially inasmuch as bromobenzyl cyanide has proven to be such a valuable compound.

#### BROMOBENZYL CYANIDE

Bromobenzyl cyanide is, chemically,  $\alpha$ -bromo- $\alpha$ -tolunitrile, or phenyl-bromo-acetonitrile,  $C_6H_5CHBrCN$ . It is prepared by the action of bromine upon benzyl cyanide.

Benzyl cyanide is prepared by the action of sodium cyanide upon a mixture of equal parts of 95 per cent alcohol and benzyl chloride. The benzyl chloride in turn is obtained by the chlorination of toluene at 100°. The material must be fairly pure in order that the benzyl cyanide reaction may proceed smoothly. The cyanide is subjected to a fractional distillation and that part boiling within 3 degrees (the pure product boils at 231.7° C.) is treated with bromine vapor mixed with air. It has been found necessary to catalyze the reaction by sunlight, artificial light or the addition of a small amount of bromobenzyl cyanide.

The product obtained from this reaction, if the hydrobromic acid which is formed is carefully removed by a stream



of air, is sufficiently pure for use as a lachrymator. It melts from 16 to 22° C., while the pure product melts at 29° C. It cannot be distilled, even in a high vacuum. It has a low vapor pressure and thus is a highly persistent lachrymator.

Bromobenzyl cyanide is about as toxic as chlorine, but is many times as effective a lachrymator as any of the halogenated ketones or aromatic halides studied. It has a pleasant odor and produces a burning sensation on the mucous membrane.

Like the other halogen containing compounds, lead or enamel lined shell are necessary for preserving the material any length of time. In all of this work the United States was at a very marked disadvantage. While the Allies and the Germans could prepare substances of this nature and use them in shell within a month, the United States was sure that shell filled at Edgewood Arsenal probably would not be fired within three months. This means that much greater precautions were necessary, both as to the nature of the shell lining and as to the purity of the "war gas."

The question of protection against lachrymatory gases was never a serious one. During the first part of the war this was amply supplied by goggles. Later, when the Standard Respirator was introduced, it was found that ample protection was afforded against all the lachrymators. Their principal value is against unprotected troops and in causing men to wear their masks for long periods of time.

The comparative value of the various lachrymators mentioned above is shown in the following table:

Bromobenzyl cyanide .....	0.0003
Maronite .....	0.0012
Ethyl iodacetate .....	0.0014
Bromoacetone .....	0.0015
Xylyl bromide .....	0.0018
Benzyl bromide .....	0.0040
Bromo ketone .....	0.011
Chloroacetone .....	0.018
Chloropicrin .....	0.019

The figures give the concentration (milligram per liter of air) necessary to produce lachrymation. The method used in obtaining these figures is given in Chapter XXI.

## CHAPTER VIII

### CHLOROPICRIN

During the spring of 1917, strange reports came from the Italian front that the Germans were using a new war gas. This gas, while it did not seem to be very poisonous, had the combined property of being a lachrymator and also of causing vomiting. Large number of casualties resulted through the men being forced to remove their masks in an atmosphere filled with lethal gases. The gas had the additional and serious disadvantage of being a very difficult one to remove completely in the gas mask. The first American masks were very good when chlorine or phosgene was considered but were of no value when chloropicrin was used.

One of the interesting facts of chemical warfare is that few if any new substances were discovered and utilized during the three years of this form of fighting. Chlorine and phosgene were well known compounds. And likewise, chloropicrin was an old friend of the organic chemist. So much so, indeed, that several organic laboratories prepared the compound in their elementary courses.

Chloropicrin was first prepared by the English chemist, Steunhouse, in 1848, by the action of bleaching powder upon a solution of picric acid. This was followed by a careful study of its physical and chemical properties, few of which have any connection with its use as a poison gas. The use of picric acid as an explosive made it very desirable that other raw materials should be used. Chloroform, which is the ideal source theoretically (since chloropicrin is nitro-chloroform,  $\text{Cl}_3\text{CNO}_2$ ), gave very poor yields. While it may be prepared from acetone, in fair yields, acetone was about as valuable during the war as was picric acid. Practically all the chloropicrin used was prepared from this acid as the raw material.

## MANUFACTURE

In the manufacture of chloropicrin the laboratory method was adopted. This consisted simply in passing live steam through a mixture of picric acid and bleaching powder. The resulting chloropicrin passes out of the still with the steam. There was a question at first whether a steam jacketed reaction vessel should be used, and whether stirrers should be introduced. Both types



FIG. 27.—Interior of Chloropicrin Plant.

were tested, of which the simpler form, without steam jacket or stirrer, proved the more efficient.

The early work was undertaken at the plant of the American Synthetic Color Company at Stamford, Connecticut. Later a large plant was constructed at Edgewood Arsenal. At the latter place ten stills, 8 by 18 feet, were erected, together with the necessary accessory equipment. The following method of operation was used:

The bleach is mixed with water and stirred until a cream is formed. This cream is then pumped into the still along with a solution of calcium picrate (picric acid neutralized with

lime). When the current of live steam is admitted at the bottom of the still, the temperature gradually rises, until at 85° C. the reaction begins. The chloropicrin passes over with the steam and is condensed. Upon standing, the chloropicrin settles out, and may be drawn off and is then ready for filling into the shell. The yield was about 1.6 times the weight of picric acid used.

#### PROPERTIES

Chloropicrin is a colorless oil, which is insoluble in water, and which can be removed from the reaction by distillation with steam. It boils at 112° C. and will solidify at -69° C. At room temperature it has a density of 1.69 and is thus higher than chloroform (1.5) or carbon tetrachloride (1.59). At room temperature it has a vapor pressure of 24 mm. of mercury. It thus lies, in persistency, between such gases as phosgene on the one hand, and mustard gas on the other, but so much closer to phosgene that it is placed in the phosgene group.

Chloropicrin is a very stable compound and is not decomposed by water, acids or dilute alkalis. The reaction with potassium or sodium sulfite, in which all the chlorine is found as potassium or sodium chloride, has been used as an analytical method for its quantitative determination. The qualitative test usually used consists in passing the gas-air mixture through a heated quartz tube, which liberates free chlorine. The chlorine may be detected by passing through a potassium iodide solution containing starch, or by the use of a heated copper wire gauze, when the characteristic green color is obtained.

An interesting physiological test has also been developed. The eye has been found to be very sensitive to chloropicrin. The gas affects the eye in such a way that its closing is practically involuntary. A measurable time elapses between the instant of exposure and the time when the eye closes. Below 1 or 2 parts per million, the average eye withstands the gas without being closed, though considerable blinking may be caused. Above 25 parts, the reaction is so rapid as to render proper timing out of the question. But with concentrations between 2 and 25 parts, the subject will have an overpowering

impulse to close his eye within 3 to 30 seconds. The time may be recorded by a stop watch and from the values thus determined a calibration curve may be plotted, using the concentration in parts per million and the time to zero eye reaction. Typical figures are given below. It will be noted that different individuals will vary in their sensitivity, though the order is the same.

Conc. p.p.m.	A Seconds	B Seconds
20.0	4.0	5.0
15.0	5.4	5.4
10.0	7.5	7.5
7.5	9.0	10.0
5.0	13.0	15.0
2.5	18.0	30.0

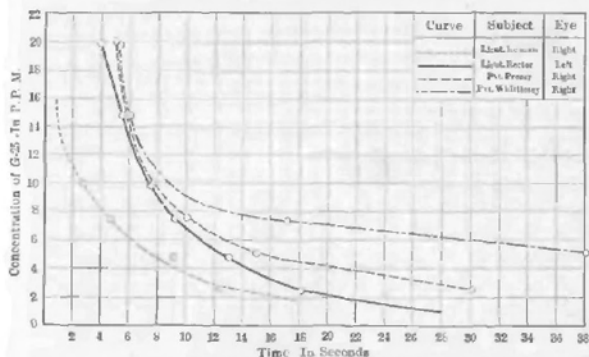


FIG. 28.—Calibration Curve of Eyes for Chloropicrin

### PROTECTION

Because of the stability of chloropicrin, the question of protection resolves itself into finding an absorbent which is very efficient in removing the gas from air mixtures. For-

tunately such an agent was found in the activated charcoal used in the American gas mask. The removal of the gas appears to take place in two stages. In the first, the gas is adsorbed in such a way that the long continued passage of air does not remove it. In the second, the gas is absorbed, and this, really excess gas, is removed by pure air passing over the charcoal. The relation of these two factors has an important bearing on the quality of charcoal to be used in gas masks. It appears that up to a certain point an increase of the quality is desirable: beyond this, it is of doubtful value.

Unlike phosgene, chloropierin is absorbed equally well at all temperatures. Moisture on the other hand has a very decided effect. It appears that charcoal absorbs roughly equivalent weights of chloropierin and of water; the presence of water in the charcoal thus displaces an approximately equal amount of chloropierin.

In the study of canisters it has been found that the efficiency time is approximately inversely proportional to the concentration. Formulas have been calculated to express the relation existing between concentration and life of the canister, and also between the rate of flow of the gas and the life.

While water seems to have a decidedly marked effect upon the life of a canister, this is not true of other gases, and the efficiency of the canister for each gas is not decreased when used in a binary mixture.

#### TACTICAL USES

Because of the high boiling point of chloropierin it can only be used in shell. The German shell usually contained a mixture of superpalite (trichloromethyl chloroformate) and chloropierin, the relative proportions being about 75 to 25. These were called Green Cross Shell, from the peculiar marking on the outside of the shell. Mixtures of phosgene and chloropierin (50-50) have also been used.

The Allies have used a mixture of 80 per cent chloropierin 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 suffi-

ciently 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. It has been claimed that the chloride decreases the amount of decomposition of the chloropicrin upon the bursting of the shell, but careful experiments appear to show that this decomposition is negligible and that the stannic chloride plays no part in it. This mixture was being abandoned at the close of the war.

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 vapor pressure of the chloropicrin, and the consequent absence of pressures even on warm days. As a matter of fact, it was the only filling used for this purpose, though later the stannic chloride was changed, owing to the shortage of tin, to a mixture of silicon and titanium chlorides.

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.