

the late war is somewhat uncertain. Thus, Dr. Hanslian  
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says this substance was introduced by the Germans as a filling for artillery shell in August, 1915, under the name of "D-Stoff"; the reports of the Allies' laboratories which analyzed the contents of these early German D shells show that dimethyl sulfate was an ingredient of their chemical contents. On the other hand, Dr. Mueller (21, page 96) emphatically denies the German use of this compound and explains the situation thus:

The oft-repeated statement to the effect that dimethyl sulfate had been used experimentally by the Germans as early as in 1915 is not true. It is to be explained by the fact that methylsulfonyl chloride used at that time temporarily was slightly polluted with a few per cent of dimethyl sulfate, and the impurities still clung to the commercial product after its manufacture. Under no circumstances was dimethyl sulfate purposely added. Those concerned with such matters would never have agreed to its use.

Whether or not the early German use of dimethyl sulfate was deliberate or accidental, it is clear that no one at that time really realized the true combat value of this substance. Thus, it is not only a good lacrimator and very toxic, but is also a fairly powerful vesicant. These properties were later discovered by the French and dimethyl sulfate was adopted by them as a filling for artillery shell and hand grenades in September, 1918, under the name of "Rationite."

Dimethyl sulfate is produced by acting on fuming sulfuric acid with methyl alcohol and distilling in vacuo. Before the war it was used in industry as a methylating agent for amines and phenols and as a reagent for detecting coal-tar oils.

It is a colorless oily liquid, of 1.35 specific gravity, which boils at 188°C. (370.4°F.), yielding a vapor 4.4 times heavier than air with a faint odor of onions.

At ordinary temperatures (68°F.), its volatility is only 3.3 mg. per liter, which is low for a lung injurant but high for a vesicant. Dimethyl sulfate is very readily decomposed by water so that its vapors quickly combine with moisture in the air to form sulfuric acid. This is one of the chief defects of this substance as a chemical agent.

Dimethyl sulfate is a powerful irritant to the mucous membranes, especially the conjunctiva and respiratory system. Its direct toxic action is exerted against the lungs in a manner very similar to that of chlorine, resulting in bronchitis, pneumonia, and lung edema. A concentration of 0.50 mg. per liter is fatal on 10 minutes' exposure. It is, therefore, about as toxic as phosgene. In lower concentrations it exerts a corrosive action on the skin, resulting in a peculiar analgesia of the skin which is said to last for six months after exposure. For this reason, it may also be regarded as a vesicant agent.

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The limited use of this compound during the war did not definitely establish its combat value. However, the high degree to which it is decomposed by water, and even by the moisture in the air, would require that any tactical effects produced be secured by the vapors directly upon the bursting of the shells before these vapors are decomposed by the moisture in the air. This so greatly limits the combat effectiveness of this substance as to raise a serious question regarding its future value as a chemical agent, particularly since other more toxic and more vesicant compounds have been discovered.

#### Perchlormethylmercaptan (SCCl<sub>3</sub>)

##### Carbon Tetrachlorosulfide

During the summer of 1915, while the Germans were experimenting with halogenated esters, the French conceived the idea of utilizing perchlormethylmercaptan as a chemical-warfare gas, and this substance, which was introduced by the French in the battle of the Champagne in September, 1915, constituted the first use of gas shell by the French Army.

Perchlormethylmercaptan may be obtained by the direct chlorination of methylmercaptan (CH<sub>3</sub>SH) or by passing chlorine into carbon disulfide in the presence of a small quantity of iodine as a chlorine carrier. The resulting product is a light yellow liquid, of 1.71 specific gravity, which

boils at 149°C. (300.2°F.), yielding a vapor 6.5 times heavier than air. It lacrimates in concentrations as low as 0.010 mg. per liter and is intolerable at 0.070 mg. per liter. A concentration of 3.00 mg. per liter is lethal on 10 minutes' exposure, which makes it about one-sixth as toxic as phosgene.

Perchlormethylmercaptan has the following disadvantages as a chemical agent:

1. Rather low toxicity.
2. Warning odor which betrays its presence before toxic effects are produced.
3. Decomposes in the presence of iron and steel.
4. Charcoal easily fixes its vapors and furnished complete protection against it.

For these reasons, this compound was soon abandoned in favor of other more effective substances and is not likely to be used again as a chemical agent. Commenting on this gas, Izard (23) says, "Its utilization had no other object than to realize a provisional solution."

#### Phosgene (Carbonyl Chloride) (COCl<sub>2</sub>)

French: "Collongite"; German: "D-Stoff"; British and American: CG

Phosgene was the second toxic gas to be used in large quantities during the war. It was first employed by the Germans, mixed with chlorine, in a cloud-gas attack <sup>155</sup>against the British at Nielette, in Flanders, on Dec. 19, 1915, when 88 tons of gas were released from 4,000 cylinders and produced 1,069 casualties, of which 120 were fatal.

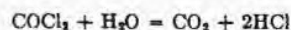
In February, 1916, phosgene was adopted as an artillery-shell filler by the French in retaliation for the German K-Stoff shell. Throughout the remainder of the war, this gas was the principal offensive battle gas of the Allies, being used in enormous quantities in cylinders, artillery shell, trench mortars, bombs, and projector drums. More than 80 per cent of gas fatalities in the World War were caused by phosgene. Concerning the use of phosgene in the World War, see Table XVII, pages 663 ff.

Phosgene was known to chemists for over a hundred years before the World War, being first made by the British chemist John Davy in 1812 by the reaction of carbon monoxide and chlorine in the presence of sunlight. At the beginning of the present century, phosgene was used extensively as an intermediate in the dye industry and had been manufactured on a considerable scale for many years in Germany. 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.

At ordinary temperatures and pressures, phosgene is a colorless gas which condenses at 46.7°F. to a colorless liquid of 1.38 specific gravity. Above 46.7°F., phosgene immediately evaporates, although at a slower rate than chlorine, and gives off a transparent vapor, 3.5 times heavier than air, with a stifling, but not unpleasant, odor resembling new-mown hay.

Aside from its characteristic odor, phosgene may also be detected in the field by its so-called *tobacco reaction*, by which is meant that men who have breathed only very slight amounts of phosgene experience a peculiar flat metallic taste when smoking tobacco. Certain other gases, such as HCN and sulfur dioxide, however, also have this effect and must be distinguished from phosgene by their very different odors.

Chemically much more inert than chlorine, phosgene is a very stable compound and is not dissociated by explosion of even strong bursting charges. When dry, phosgene does not attack iron and may, therefore, be kept indefinitely in iron and steel containers. It is, however, extremely sensitive to water, in contact with which it quickly breaks down into hydrochloric acid and carbon dioxide, according to the equation



Hence, even if slight traces of water are present in loading phosgene into shell, the hydrochloric acid formed will attack the shell walls and generate dangerous pressure in the shell; if sufficient hydrochloric acid is formed, it will eventually destroy the shell. Because of its rapid hydrolysis in the presence of water, phosgene cannot be efficiently employed in