Combustion Smokes^{1,2}

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A new development of the late war with the Central Powers was the use of artificial smokes for obscuring purposes. The allied navies made early provision for smoke screens as part of their program for eluding the wily submarine, and in the later days used them in major offensive operations against the submarine bases. The armies also found it economical to lay down smoke barrages before taking the offensive. The first devices were very crude, for little was known concerning the physical properties of such clouds. Consequently, research was necessary along chemical lines to improve the smoke-producing substances themselves and also along mechanical lines to perfect the devices in which the smoke is generated. This paper concerns itself primarily with the chemical developments, which are known as combustion smokes.

In general, we may classify smokes according to the method of generation, as detonation smokes, cold reaction smokes, and combustion smokes. The first class is represented by a bursting shell containing oleum or sulfur trioxide, which creates a cloud by the disintegration of the substance into a screen or mist made up of a myriad of small particles. It takes its name from the detonating charge of TNT or similar explosive used to break it up. The well-known ammonium chloride smoke may be called a cold reaction smoke, because it results from interaction of two gases without appreciable heat change. The combustion smokes, on the other hand, involve exothermic reactions, which disseminate solid material into the air in the form of minute particles. This classification is of course artificial, and some smokes cannot be defined by it. For instance, the smoke produced by the detonation of phosphorus in a 3-in. shell represents both the detonation and the combustion types.

Combustion smokes are used to good advantage in grenades, candles, trench mortar shell, and in navy smoke boxes, designed to be thrown overboard. Other things being equal, the combustion smoke has very decided advantages over the detonation type. Both laboratory and field experiments have proved that a screen secured by combustion persists for a longer time and clings closer to the ground than a cloud realized by detonation. In the case of artillery shell, however, the choice is limited to the detonating type, since a shell fired from a rifled gun travels at enormous velocity and is apt to bury itself from 2 to 6 ft. in the ground. Under these conditions we must have an explosive charge of sufficient power to blow shell fragments and smoke producer from out the ground as desired. An attempt to utilize a combustion smoke in the artillery shell would result in a smothered combustion underground with no real screening effect.

LABORATORY METHODS

Although field experiments are necessary to determine the ultimate value of any substance or device as a smoke producer, a fair determination of relative values may be made in the laboratory. The unit used in the laboratories of the Chemical Warfare Service for comparing relative values of different smoke producers is called the "total obscuring power," or, in abbreviated form, the T.O.P. It is defined as the product of the volume of smoke produced from a unit weight of the original mixture and the density of the smoke. The density is the reciprocal of the depth of smoke layer beyond which it is impossible to distinguish clearly the filament of a 40-watt Mazda lamp. Since the English units are employed for most field work, they are retained for this purpose.

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The chamber used for actual measurements at the American University Experimental Station had a cubical content of 228 ft. In carrying out the determination, the mixture to be tested was placed on the floor of the box and ignited or disintegrated by a detonating charge. The smoke cloud was made of uniform density by means of an electric fan within the box. Readings with a movable pilot lamp were taken over a series of short intervals and the resulting data plotted. Such values as average of maximum T.O.P. could then be read from the curve obtained.

In the interpretation of results, T.O.P. measurements must be supplemented by a careful consideration of the type of device to be used and by actual service tests. The conditions affecting the persistency of a cloud in the open field are often very different from those prevailing in a closed chamber. For instance, it is still an open question whether phosphorus or sulfur trioxide is the more efficient substance to employ in artillery smoke shell, whereas laboratory measurements show the phosphorus to have twice the T.O.P. of sulfur trioxide. The sulfuric anhydride cloud, however, is cooler and has less tendency to rise.

PRELIMINARY WORK

The theoretical basis of American research on combustion smokes was the well-known fact that metals high in the electro-motive series react with organic chlorides to form metallic chlorides, which are sublimed by the heat evolved. A mixture of carbon tetrachloride, zinc powder, zinc oxide, and kieselguhr showed greatest promise and was chosen as a point of departure. On ignition of this mixture, the exothermic reaction disseminates zinc chloride in the air in the form of cloud of fine solid particles, which have obscuring power. The zinc oxide and kieselguhr prevent segregation of components and stiffen the mass. They also serve to prolong the time of burning and to cool the smoke.

Fig. 1

The early mixtures of these four components, however, proved imperfect. The amounts of zinc oxide and kieselguhr that provided for fairly efficient burning only made a thin pasty mass. Although the light gray smoke produced had good obscuring power, the burning was very uneven and considerable residue was left.

THE IDEAL SMOKE MIXTURE

In order to follow a logical line of research, the following desirable features of a combustion smoke mixture were listed:

- 1—The materials must be cheap.
- 2—The materials must be obtainable in large quantities.
- 3—The mixture must be staple.

Fig. 2

Fig. 3

Fig. 4

- 4—The reaction rate must be subject to control, in order to obtain a predetermined fast or slow burning substance.
- 5—The smoke produced must have a high obscuring power.
- 6—The smoke produced must be comparatively cool, in order to slow down dissipation of the cloud.

The preliminary results suggested that five types of material were necessary.

- 1—A metal or metallic oxide capable of producing a readily volatile chloride.
- 2—An oxidizing agent.
- 3—A cooling material.
- 4—An absorbing substance.
- 5—A chlorinating agent.

CHOICE OF METAL

The metals seriously considered were zinc, iron, and aluminium. All substitutes for zinc powder proved inefficient or impracticable. Reduced iron mixtures gave a brown smoke which faded to a white as the cloud drifted from the source. The obscuring power did not compare with that obtained with the zinc combinations. Moreover, reduced iron is not available in large quantities and at reasonable cost. Although not recommended for a screen smoke, a reduced iron mixture was sometimes employed as a signal smoke. Aluminium is more plentiful, but is costly. The smoke produced by aluminium mixtures was white and of fair obscuring power. The laboratory measurements gave no higher T.O.P. values than those obtained with the best zinc mixtures. On the field much less effective covering power was realized on account of the high heat of reaction, which caused the clouds to rise too rapidly. As the standard smoke mixture was improved from time to time, aluminium and iron were tried again but never with success.

SELECTION OF OXIDIZING AGENT

Since white smokes have always proved more effective as screens, one of the criticisms of the first mixtures concerned their color. Although perchlorates and nitrates were tested to neutralize the carbon gray in the original components, sodium chlorate was finally selected for economic as well as chemical reasons. After a series of box and field experiments, a mixture of the following composition was selected:

	Parts
Carbon tetrachloride.....	35.0
Zinc powder.....	40.0
Zinc oxide.....	6.4
Sodium chlorate.....	9.0
Kieselguhr.....	9.6

Results with this mixture suggested the need of changing the cooling and absorbent ingredients. The smoke produced is white and has good obscuring power. In consequence of the high heat of reaction, however, the cloud formed is hot and rises rapidly. Therefore much of the theoretical T.O.P. is lost when burned in the open. Moreover, it is very difficult to control the time of burning due to arching over of the residues left.

CHANGE IN COOLING AGENTS

In order to cool the smoke, zinc oxide was replaced by ammonium chloride, which absorbs considerable heat by its volatilization and partial dissociation. The addition of ten parts of chloride caused a cooler cloud and increased the time of burning. The T.O.P. was correspondingly increased by the volatilized ammonium chloride. The modified mixture is represented by the following formula:

	Parts
Carbon tetrachloride.....	41.4
Zinc.....	35.4
Sodium chlorate.....	9.5
Ammonium chloride.....	10.0
Kieselguhr.....	3.7

One pound of this mixture packed in a can 3 in. in diameter burned in 2 min. The T.O.P. was from 1200 to 1700, while white phosphorus burned under the same conditions gave a value ranging from 4000 to 5000. Unsuccessful attempts were made to increase the amount of ammonium chloride.

REGULATION OF TIME OF BURNING

The substitution of ammonium chloride for zinc oxide did not eliminate the difficulty experienced in control of time of burning. An extensive investigation carried out with large quantities of the mixtures showed that the factors which most influenced the time of burning were mesh of chlorate crystals, percentage of ammonium chloride present, and the type of absorbent used. The finer the chlorate used, the more rapid was the burning. The curve (Fig. 1) showing the time of burning plotted against the mesh of the chlorate flattens somewhat with crystals above 40 mesh. Inasmuch as the change of rate between 40 and 60 mesh is less noticeable, this mesh was usually specified. Mixtures were often calibrated by changing the amount of chloride in the formula.

The use of kieselguhr as an absorbent proved to be the source of many irregularities. During burning it had a tendency to

arch over the combustion surface, causing successive periods of slow and fast burning. Moreover, surveillance tests in the laboratory showed a reaction between carbon tetrachloride and zinc. This deterioration was due to the moisture from the kieselguhr, and ammonium chloride acted as a further catalyzer.

A precipitated magnesium carbonate was fully as efficient as kieselguhr. Its substitution for kieselguhr provided for stability under conditions encountered in transport. Its gradual decomposition by heat made for smoother burning. Magnesium carbonate was employed in practically all the zinc chloride smoke mixtures recommended.

CHLORINATING AGENTS

The advantages of substituting a solid chlorinating agent for carbon tetrachloride were realized from the first. Silicon and titanium tetrachlorides were found to offer no added advantage over carbon tetrachloride. Mixtures containing the silicon compound were peculiarly sensitive, a single drop of water being sufficient to start the reaction.

B. M. SMOKE MIXTURE

The final mixture was called the B. M. smoke mixture, because it was perfected while the American University Experimental Station was still under the Bureau of Mines. The proportions in the following representative formula were varied somewhat, depending on the method and form of device in which the smoke was to be used:

	Parts
Zinc.....	35.4
Carbon tetrachloride.....	41.6
Sodium chlorate.....	9.3
Ammonium chloride.....	5.4
Magnesium carbonate.....	8.3

INFLUENCE OF WEATHER CONDITIONS

T.O.P. measurements in the chamber revealed the fact that weather conditions have a marked influence on the efficiency of the B. M. mixture. Increasing the moisture content of the air raises the T.O.P., while an increase of temperature reduces the T.O.P. When both moisture content and temperature are raised in proportions that may be ordinarily expected in the field, the result is an increased T.O.P. value. Figs. 2, 3, and 4 show the rate of change in T.O.P. under different conditions. In this work the T.O.P. values were taken at 7-min. intervals. The curves give the changes in both the maximum T.O.P. and the average T.O.P. obtained over this period. The average T.O.P. is easily calculated by integration between the fixed limits of the area under the curve.

It is thus evident that the most efficient smoke is produced from the B. M. mixture on a cold, damp day, whereas the poorest cloud results on a warm, dry day. These observations in the T.O.P. chamber were confirmed by field experiments. The increase of obscuring power with humidity is apparently due to absorption of water by the hygroscopic zinc chloride particles. Measurements of the efficiency of phosphorus smokes showed similar effects of humidity and temperature.

METHOD OF IGNITION

The B. M. smoke mixture may be ignited in several ways, but the most simple and fool-proof consists in using a train of preheating agents. The operation and construction of the smoke device in question usually determine the sequence of this train. Generally a delay is convenient between the ignition and the burst of smoke, in order that the operator may get away. The ignition may be caused by the firing of a cap, which starts the time fuse, which in turn ignites a capsule containing a mixture of potassium permanganate and reduced iron. The temperature reached by the oxidation of the reduced iron is sufficient to melt through the capsule and ignite the main B. M. mixture below. A starting mixture of reduced iron and potas-

sium nitrate functions as satisfactorily but possesses two disadvantages: it is not so stable under surveillance tests, and its reaction liberates gaseous products, often with explosive violence and the consequent rupture of the entire container.

CONCLUSION

The B. M. mixture with certain modifications in proportions has been used in grenades, smoke candles, Stokes bombs, Livens projectiles, smoke boxes, and various signal devices. It possesses greater possibilities than phosphorus, and it is possible that it might have displaced phosphorus as the most important smoke producer, if the war had continued. Several suggestions for its use in peace time have been made, but no active development is under way.

Dr. Martin Fischer Tells of European Trip

Dr. Martin Fischer, professor of physiology at the University of Cincinnati, who returned from Europe early in March, gave a highly interesting account of his impressions of conditions in the countries which he visited, at a meeting of the Cincinnati Section of the AMERICAN CHEMICAL SOCIETY, held March 9, in the Chemical Lecture Hall of the University of Cincinnati.

Dr. Fischer had given a series of lectures on colloids at the University of Amsterdam, by invitation, and in addition to his trip to Holland he had also visited parts of England and Germany.

He was impressed with the apparent absence of feeling regarding the late war in both the neutral and warring countries. The people seem anxious to forget all about the war and turn their attention to the problems of reconstruction. There is a marked feeling of friendliness toward the scientific men of foreign countries, and American men of science are particularly popular. They are known abroad by their works.

A change in the general attitude of people toward things of material advantage was observed by Dr. Fischer. People belonging to the educated group, including teachers, physicians, and scientists in general, seem to have been hit hardest by the change of things since pre-war days.

In Holland there are many distinguished scientists who are sometimes classified by Americans as natives of other countries, because of the fact that their articles are published in English, French, or German journals and also because they write their scientific papers in French, English, or German rather than in Dutch.

Dr. Fischer ascribed the splendid development of the Dutch people to the fact that there is keen competition among them at all times. A nation of seven million people confined to a comparatively small area can make as heavy an impress upon the world in general as the Dutch have made, only because of keen competition.

Dr. Fischer concluded his address with a plea for greater work and effort on the part of the American chemist in helping to conserve our natural resources and in developing our man power through the accomplishment of difficult tasks. He called attention to the laws of biology which underlie all human progress, and cited examples of the rise and fall of nations due to the workings of these laws. If we are to develop our brain power we must use our brains, and if we want to keep alive the strong men of our nation we must give them difficult and extensive work to do.

Lectures at the College of the City of New York

Announcement is made of a series of lectures to be held under the auspices of the City College Chemical Society. The lectures, to be given at 4.30 P. M. in the Doremus Lecture Theatre, are as follows:

- MR. ELLWOOD HENDRICK, "Beyond the Laboratory," March 7.
 DR. MARSTON TAYLOR BOBERT, Professor of Chemistry, Columbia University, "The Service of the Synthetic Dye Industry to the State," March 15.
 DR. CHARLES H. MACDOWELL, President, Armour Chemical Co., "The Trial of the Chemist in the Packing Industry," March 23.
 MR. ERNEST M. SYMMES, Hercules Powder Co., "Explosives in War and Peace," April 8.
 DR. DANIEL D. JACKSON, Professor of Chemical Engineering, Columbia University, "Chemical Evolution," April 14.