LABORATORY EXPERIMENTS WITH CHEMICAL WARFARE AGENTS[1]

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(Translated from the German)

Editor's Note: This article and those which follow in the series are a translation of a large portion of a German textbook by Walter Kinttof which appeared in 1935 under the title of "Schulversuche zur Chemie der Kampfstoffe." This material is reproduced principally for its value in suggesting practical laboratory experiments of an extraordinarily interesting character, and also to indicate how the interest in chemical warfare was kept alive in Germany between the two World Wars.

INCENDIARIES

FIRE has a twofold duty in warfare. On the one hand it should cause a considerable damage to material, and on the other hand it should demoralize the population—that is, break down its power of resistance. Both aims have been pursued since ancient times and history records numerous cases of it.

As incendiaries, the most difficultly combustible and the most easily inflammable materials have been used, depending on the state of the contemporary chemical knowledge. The effects of these were more or less doubtful. Modern chemistry has put the incendiary technique on a new pedestal. By means of the invention of aluminum-thermo-chemistry by Goldschmidt, incendiary bombs and grenades have been given a new importance which rates them as among the most dangerous weapons since they are very effective in the bombardment of cities due to the fact that flying machines can carry a great quantity of them. Besides this, only phosphorus is essential either by itself or in solution.

PHOSPHORUS AS AN INCENDIARY

Note: For the following experiments yellow roll phosphorus approximately 3 to 4 mm. thick is used. (Use protective goggles! The hands must be protected by means of a towel or something adequate because burning phosphorus produces dangerous and slowly healing wounds on the skin. Stand back while the experiment is being performed.) Some of the experiments must be carried out under a bell jar or outdoors.

EXPERIMENT 1. By means of tweezers a piece of phosphorus approximately one-half an inch long is taken out from the jar containing the phosphorus covered with water and is quickly dried on a blotting paper and placed in an evaporating dish. Another piece of the same size is heated in a second dish by submerging it in hot water at 65°C. (water bath).

Result: Dry phosphorus begins to smoke in the air and ignites automatically and especially quickly when heated to 60°C. (ignition temperature). With considerable heat phosphorus pentoxide forms, volatizing into a dense white smoke.

EXPERIMENT 2. In a solution of 5 cc. of carbon disulfide (CS_2) which is in a test tube (keep away from flame!), place a piece of phosphorus approximately 1 cm. long, and dissolve by shaking. Be careful not to get any of this solution over the hands. By means of an eye dropper, place about 1 cc. of the solution on a blotting paper which is set on a tripod and observe the result. Carbon disulfide evaporates quickly, and the remaining phosphorus spontaneously ignites, but without burning the blotter.

Use: In solution with carbon disulfide, yellow phosphorus is used to fill incendiary bombs, grenades, and mines, being frequently mixed with tar, oil, celluloid, and similar substances (so-called fire producers). As the result of the explosion of the projectile, this solution is sprinkled all around, the carbon disulfide evaporates, and the remaining phosphorus spontaneously ignites and sets the vapors of the carbon disulfide aflame. The effect of this is relatively small, for only easily inflammable material (rubbish) will burn, and solid, compact woodwork (floors, beams) will not be affected by it.

EXPERIMENT 3. A few drops of phosphorus dissolved in the carbon disulfide are placed (*a*) on wood shavings and (*b*) on a piece of wood. After the carbon disulfide has evaporated, the flaming phosphorus ignites the wood shavings, but not the piece of heavier wood.

EXPERIMENT 4. Drop on a piece of burning roll phosphorus (1 cm. long) placed in a porcelain evaporating dish, a few drops of water (be careful, protect your

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hands!), and then pour a larger quantity of water over the phosphorus. Repeat this experiment with a piece of heavier wood.

Result: The few drops of water on the burning phosphorus in the the first case had the effect of spraying the water all around. Only a larger quantity of water could extinguish the fire. Only after the water had been soaked into the wood and the phosphorus dried did the wood ignite again.

EXPERIMENT 5. In some of the manuals for air defense we find that a strong solution of copper sulfate is indicated as making harmless and destroying the effect of phosphorus. Its action and importance can be seen from the following:

To 5 cc. of a five per cent copper sulfate solution contained in a test tube, a 3-cm. long piece of roll phosphorus is added and carefully heated over a Bunsen burner until the phosphorus is melted. The solution is shaken until it becomes decolorized, then cooled and filtered. The product on the filter paper is laid on a metal gauze for the purpose of drying.

In the meanwhile we may observe the following: the melted phosphorus, as a result of shaking in the copper sulfate solution, is divided into drops which become covered by a metallic shiny surface of copper phosphide. The filtered product is not fuming like the original phosphorus, but ignites spontaneously a short period of time after the filter paper dries.

What is the explanation of this phenomenon?

Applications: Since neither water nor copper sulfate solution can eliminate the danger of fire from yellow phosphorus, an attic can be protected against the effects of phosphorus incendiary bombs only by clearing the attic of rubbish and by impregnating or by fireproof-painting the floor and woodwork. If an attic is prepared in such a manner, then we can leave the phosphorus bomb until it burns out, or extinguish the phosphorus with water and take it outdoors. Phosphorus cannot cause fire in a downward direction because oxygen is lacking.

THERMITE AND ELECTRON-THERMITE INCENDIARIES

Note: Unlike previous phosphorus incendiaries, thermite is independent of the oxygen contained in the air. For this reason an initial ignition by some igniting mixture is necessary. This is shown in the following experiments.

EXPERIMENT 6. Five grams of pulverized iron and 5 g. of pulverized potassium permanganate are mixed by means of a spatula in a porcelain evaporating dish. From this mixture a quantity is taken up on the tip of a knife and placed on a small plate of asbestos, then touched by a Bunsen flame or ignited match.

Result: The mixture ignited in the above-mentioned way will be burned off quickly. Here the potassium permanganate acts as oxygen producer. The development of heat is considerable. The mixture is called "Ignit" and will be used in our further experiments as initial ignitor.

EXPERIMENT 7. Mix in seven different porcelain evaporating dishes the following substances in the order indicated:

- 11 g. pulverized iron (melting point 1535°C., boiling point 3235°C.) with 24 g. copper oxide
- 12 g. pulverized zinc (melting point 419.4°C., boiling point 906°C.) with 16 g. copper oxide
- 19.6 g. pulverized zinc with 16 g. iron oxide (Fe_2O_3) grits
- 5.4 g. aluminum grits (melting point 659°C., evaporating point 1800°C.) with 16 g. iron oxide
- 2.7 g. aluminum grits with 12 g. copper oxide (be careful!)
- 2.7 g. aluminum grits with 12 g. zinc oxide
- 3.6 g. magnesium grits (melting point 650°C., evaporating point approximately 1100°C.) with 8 g. iron oxide (be careful!)

Place each of these mixtures on small asbestos plates, making a hole in the center of each pile with a glass rod; fill this hole with "Ignit." When igniting them, be careful to wear goggles and gloves, and stand back while the action is going on. Observe the vigor with which each reaction takes place. Examine the products for color and for magnetic activity.

Result: (*a*) The elements Mg, Al, Zn, Fe, and Cu are arranged in such an order that any one will displace a metal succeeding it when mixed with its oxygen compound. Without an ignition mixture it would be impossible to ignite these mixtures (*i. e.*, by means of a Bunsen burner or matches).

(*b*) When these reactions take place partially, heat quantities are freed sufficient to melt the iron and to boil the copper. The following are exact determinations of the heat of formation referred to one atom of oxygen:

MgO	145.8 cals.
$^1/_3$AlO	131.1 cals.
ZnO	83.0 cals.
$^1/_3$FeO	65.5 cals.
CuO	33.0 cals.

From using the above data it has been observed that "when various elements and oxides are given a chance to react, oxide is formed which at the given temperature develops the greatest heat" (thermodynamic law).

Note: Among the mixtures, that of iron oxide with aluminum is especially suitable for an incendiary. It was discovered in 1894 by Goldschmidt and is called "Thermite." During the World War an attempt was made to increase both its ignitability and effect by the addition of compounds rich in oxygen (lead oxide, barium nitrate, pyrolusite). However, it was noted that such addition is not necessary because its incendiary effect would be rather decreased due to the development of gases. The effect of thermite incendiaries can be increased when we press the thermite mixture very tightly into metal cans by means of a wood or glass rod.

EXPERIMENT 8. (Illustration of the principle of thermite incendiaries.) In a porcelain evaporating dish, the following substances are mixed by means of a spatula:

(*a*) 7.5 g. iron oxide (Fe_2O_3)
2.0 g. pulverized aluminum
or
(*b*) 10 g. iron oxide (Fe_2O_3)
6 g. pulverized aluminum
6 g. pulverized iron
20 g. barium nitrate powder
4 g. potassium nitrate

Note: A similar mixture was used by the Russians during the World War for filling incendiary bombs.

The mixture is pressed tightly into a 10-g. smoke candle box by means of a flat glass rod. Make a hole in the pile and fill it with "Ignit." A sand box should be used as base for the smoke candle box.

EXPERIMENT 9. Get one of these incendiary mixtures (Experiment 8) at its highest combustion point, and by means of crucible tongs (hand and eye protection!), throw it into a conserve box half filled with water which has been placed in a sand box.

Result: The burning thermite mixture is not extinguished by water; rather it "eats" itself through the metal bottom of the container. Explanation?

Note: In similar way as in Experiment 11, aluminum and magnesium can be shown to react with steam with greater intensity.

EXPERIMENT 10. Spray such a mixture when it is at the height of combustion by means of a water stream (sand box and protection of eyes and hands!). Students should stand back a distance of 5–6 meters.

Result: The combustion of thermite upon the addition of water becomes stronger, and the glowing liquid metal scatters around.

EXPERIMENT 11. On the bottom of a quartz test tube pour 0.5 cc. of water and a thimbleful of iron powder. The test tube is placed at a slight angle in a support and is filled along its length with a 10-cm. long layer of metal powder up to half the height of its diameter. Then it is closed by a one-hole rubber stopper connected with a gas delivery tube which leads to a pneumatic trough. The long metal layer is then heated to glowing. The water on the bottom of the tube is boiled and evaporated. The developed gas is collected over water in a 150-cc. cylinder and tested with the Bunsen flame (caution).

Result: Steam reacts with the glowing iron by producing hydrogen according to the equation: $3H_2O + 2Fe = Fe_2O_3 + 3H_2$.

EXPERIMENT 12. Ignite one of the thermite incendiary preparations made according to Experiment 8 or a "Mox" brick on a wood plate placed in a sand-filled box.

Result: The burning thermite composition ignites the hard wood! The liquid metal (iron) "eats" itself downward through the wood. This is the difference between the phosphorus composition and the thermite compound.

EXPERIMENT 13. Paint small pieces of dry pine wood ($20 \times 10 \times 1$ cm.) with a mixture of aluminum oxide, waterglass (sodium silicate), and calcium or zinc chloride. Then let them dry and repeat the preceding experiment.

Note: When a water stream is pointed on a melting thermite mixture, the combustion first increases due to the formation of hydrogen, and only by the further addition of much water will it be possible to slow down the reaction. In reality the simplest thing would be, provided the attic had been fireproofed, to let the thermite bomb burn out and then extinguish the ignited structure with water or some suitable chemical substance. At the same time the red-hot ironcake, which remained after the burning out of the bomb, could be cooled off by the water which had been applied.

Electron-thermite incendiaries are thermite incendiaries which are enclosed in a container made of electron metal (an alloy of 97 per cent magnesium and 3 per cent aluminum). Due to the deflagration of thermite, the electron metal is heated above its melting point, and when it burns, it develops great heat and light. The following two experiments will demonstrate this action.

EXPERIMENT 14. A piece of commercial electron metal or magnesium sheet (10 cm. long and 0.5 cm. wide) is held by means of a crucible tongs in a Bunsen flame and ignited. Perform this experiment on an asbestos sheet or in a sand-filled box. Place the burning metal on a small piece of wood. Cautiously drop water on it from an eye dropper (have the eyes and hands protected!). Sprinkle water on the burning metal by using a watering pot. Finally dip the burning metal in a dish containing a quantity of cold water (caution!).

Result: Burning magnesium or electron metal ignites the dry wood immediately. By sprinkling or dropping a little water, the combustion becomes more vigorous and explosive. A large quantity of water extinguishes the fire by cooling off the metal below its ignition temperature.

Application: The burning up of an electron-thermite bomb can be accelerated by sprinkling it cautiously with water. In this way no scattering of the metal itself occurs. This is caused apparently by the vaporization of the water which exerts pressure on the liquid mass of metal.

EXPERIMENT 15. From a 2-cm. wide and 10-cm. long piece of magnesium sheet, a ring approximately 3 cm. in diameter is formed by cautious bending. This is placed in a cover of a used 10-g. smoke candle box which is set in a box filled with sand. The cover is then filled with thermite composition prepared according to Experiment 8, and it is pressed in by means of a glass rod. Ignition is performed as described in the experiment with the "Ignit" or stormproof match.

Result: An ignited thermite mixture causes the magnesium metal to burn (imitation of the electron-thermite incendiaries).

CHEMICAL FIRE EXTINGUISHERS

In Experiments 1–15 we have treated the incendiaries. Now we want to tell something about the extinguishing of fires caused by them.

It is known that burning material can be extinguished by using quantities of water. This method works in two ways. Primarily, it cools off the burning material below its ignition temperature; secondly, both in the liquid and vapor state, it deprives the fire of the supporter of combustion, *i. e.*, oxygen. The principle of cutting off the oxygen explains the practice of the covering of burning material with dry or wet blankets. The same principle is involved when the chemical extinguisher is brought into use. Chemical fire extinguishers have the following advantages:

1. They can be handled very easily.
2. Small quantities of materials exert an extinguishing effect which is independent of the water contact.
3. They do not cause "water damages" which are always destructive when fire is extinguished by water.

We differentiate between dry, liquid, and foam extinguishers. Of the extinguishers, those filled with noncombustible, therefore flame-extinguishing, carbon tetrachloride cannot be given consideration for the civilian air defense work because in this case, the most essential requirement is to extinguish the fires in a more or less small, confined space. The use of carbon tetrachloride in restricted areas is not advisable due to the formation of phosgene. Therefore, we must not use these kinds of fire extinguishing apparatus nor carbon tetrachloride.

DRY EXTINGUISHERS

Experiment 16. In a test tube which is provided with a one-hole stopper and delivery tube, 4 g. of sodium bicarbonate is heated in the dry state, and the gas formed is passed by means of a long tube into the bottom of a standing cylinder. A burning candle set in the bottom of the cylinder is extinguished at once. If we pour lime water in the cylinder and shake it after closing the mouth by means of a glass plate, a white precipitate of calcium carbonate is formed.

Result: Sodium bicarbonate, as a result of heating, releases carbon dioxide (and water) which puts out the fire.

Experiment 17. A piece of board, 20 × 10 × 1 cm. in size, is placed on a tripod and ignited by means of a Bunsen flame. Then the board is sprinkled using an old sieve with previously sifted sodium bicarbonate; or a fire extinguisher may be made using a mixture of sifted sodium bicarbonate with 2 per cent finely powdered kieselguhr. The fire is extinguished at once due to the evolution of carbon dioxide from the bicarbonate.

Result: Burning wood may be extinguished by dry sodium bicarbonate.

Application: In dry extinguishers, the sodium bicarbonate is sprinkled by gas pressure.

Experiment 18. Experiment 17 is repeated by substituting for the sodium bicarbonate carbon dioxide snow, which can be produced by allowing the carbon dioxide to escape rapidly from a steel cylinder under high compression into a cloth bag (adiabatic cooling). The solid carbon dioxide (sublimation point 78.5°C.) is scattered on the burning wood by means of a wooden spoon.

Result: Solid carbon dioxide (carbon dioxide snow) also can be used as a dry extinguisher.

Application: In the so-called "Polartotal" apparatus.

Note: Solid carbon dioxide is especially suited for extinguishing fires from easily inflammable liquids such as gasoline, benzol, alcohol, various oils, etc.

LIQUID EXTINGUISHERS

Experiment 19. This apparatus is an imitation of the Minimax extinguisher and consists of the lower part of a 300-cc. wash bottle which is closed by a cork with three holes. Through one of the holes goes a tube to the bottom of the bottle. The tube is about 6 mm. in diameter, and the projecting end, which is slightly drawn out, serves as a sprayer. In the second hole is placed a glass tube which acts as a safety valve and a pressure regulator. Finally, through the third hole is placed a glass rod coated with glycerin. The lower end of this rod is connected by means of a perforated cork to a 10-cm. long. thick-walled test tube of conventional diameter. In the lower end of this tube is blown a thin-walled bubble about 5 mm. in diameter.

The bottle is filled with 250 cc. of five per cent sodium bicarbonate solution, and the test tube with a 25 per cent hydrochloric acid solution. When filling the latter, one must take care that a 2–3 cm. high atmosphere column is left over the acid. Then the apparatus is put together and the cork fastened. When the glass rod is carefully pressed down, the glass bubble of the test tube is crushed on the bottom of the wash bottle. By the high pressure of the test tube, some hydrochloric acid at once flows into the bicarbonate solution and the formation of carbon dioxide begins slowly.

Through the sprayer tube the solution is ejected into the air with a range of approximately five to six meters. In the meantime, more hydrochloric acid goes into the bicarbonate solution both as a result of diffusion and by the displacement by carbon dioxide which partly rises in the test tube. In this way a steady carbon dioxide pressure is formed which remains until the bottle is completely emptied so that the safety valve has to be used only occasionally. If the liquid driven out is mixed with carbon dioxide and is directed on burning woodshavings, the fire will be extinguished at once.

Result: Sodium bicarbonate solution may be used advantageously according to the above-mentioned principle as a fire extinguisher. Both the sodium bicarbonate and the bicarbonate acid mixture evolve carbon dioxide. The Minimax fire extinguisher apparatus employs this principle.

A FIRE EXTINGUISHER PRODUCING FOAM

EXPERIMENT 20. In a 300-cc. cylinder standing in a glass dish and filled with 250 cc. of water, 3 g. saponin and 25 g. sodium bicarbonate are dissolved. A thin-bottom test tube filled with hydrochloric acid and provided with a one-hole cork stopper attached to a glass rod is placed in the above solution and is crushed therein. As a result of the evolution of carbon dioxide, a white foam composed of carbon dioxide and saponin is produced, which pours out of the cylinder like a cream. If the production of foam is made in an apparatus in which the sprayer tube is about 8 mm. in diameter, then we can extinguish the fire of a wooden board. (See Fig.1.)

Result: Saponin solution in combination with carbon dioxide develops a strong foam which can be used for extinguishing fires.

Use: In foam extinguishers, the saponin-foam is produced either according to Experiment 20 or from a dry mixture of saponin, sodium bicarbonate, and olaxic acid or aluminum sulfate. To this mixture, water is conducted by a rubber hose. (Explain this reaction.) Perkeo hand fire extinguishers, Minimax foam extinguishers, and foam generators use this principle.

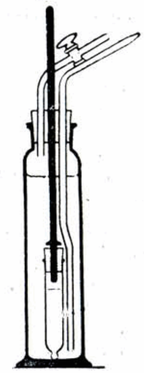

Figure 1