THE INACTIVATION OF PHOSPHORUS ON THE SKIN

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White phosphorus as a hazard may appear in a variety of physical forms. Of these the most important are: (1) solid, (2) dissolved in solvents (CS₂, benzene, mineral oil), (3) dissolved in solvents + rubber. The use of copper sulphate solutions for the inactivation of phosphorus on the skin has long been practised, and has been suggested by the Ministry of Home Security (1942) as a method in the case of burns from bombs containing phosphorus. An improved composition in which copper sulphate is dissolved in aqueous glycerol has been claimed by Godding and Notton (1942). The very high glycerol content in this preparation is a serious drawback to its general use in the event of the widespread use of phosphorus bombs. An examination of the question of inactivation of phosphorus in the conditions listed above has drawn attention to the limitations of the methods hitherto proposed. We now describe a preparation of our own which has certain advantages.

According to the form in which the phosphorus is present on the skin, the aim of treatment is:

For solid phosphorus, to coat the element with a non-ignitable layer and to render large particles visible and thus amenable to mechanical removal; in the case of minute particles, to convert the element completely to an inactive form, allowing of removal by washing.

For phosphorus in solution, to inactivate the element by means of an agent which mixes freely with the solution or which brings about efficient emulsification, allowing of intimate contact with the inactivating agent.

For phosphorus in solvents containing rubber, to inactivate the element in the highly viscous mass by means of an agent which permits ready emulsification and which, in addition, allows complete removal of the rubber from the skin.

Copper compounds in a suitable physical form can bring about all of these desired effects.

Mode of Action of Copper Compounds on White Phosphorus

Whilst the blackening which rapidly follows the application of copper salts to white phosphorus is commonly held to be due to the formation of non-igniting copper phosphide, this is not the whole story. Copper phosphide is certainly produced, but this is followed by a reaction leading to the formation of various phosphorus acids—mainly phosphoric—and metallic copper (see Straub, 1903; Bird and Diggs, 1914). The main reaction is the formation of metallic copper, as follows:

Thus, if CuSO₄ is used, a necessary accompaniment of the reactions is the formation of sulphuric acid and phosphoric acid, which adds to the acidity already present if the phosphorus has ignited. The consequent need for thorough alkalization has been stressed by Godding and Notton (1942) and Jones (1942).

In the circumstances in which aqueous copper sulphate would be used in inactivating solid phosphorus in a burnt area nothing like complete inactivation of the element could be obtained. If, further, the phosphorus is in a form with which water does not readily mix, then inactivation can be expected only at the interfaces of the two liquid phases. In the special case of incendiary-bomb compositions, of a highly viscous nature, the application of aqueous copper sulphate cannot be expected to be effective. Godding and Notton's mixture was devised to overcome this difficulty and, as we shall see, is a distinct advance, but it has the disadvantage of demanding considerable glycerol and not acting very effectively on solid phosphorus or phosphorus in solution (CS₂, benzene, oil).

If an incendiary mixture containing rubber dissolved in a solvent be smeared on the skin the rubber adheres to the skin and in a few moments white fume appears but there is no rapid ignition. If now Godding and Notton's mixture be applied and rubbed well in, a greenish mass is formed, slowly turning brown and staining the skin. With continued rubbing the rubber in the composition is in part detached, but the greater portion of it is not readily removable, and may contain active phosphorus. If the incendiary composition is treated with Godding and Notton's mixture on a watch-glass reaction is rapidly initiated, but to obtain complete inactivation it is necessary to continue to mix energetically for a considerable period.

A New Preparation for inactivating Phosphorus

Having regard to the fact that phosphorus is essentially lyophilic in nature and thus not readily wetted by water, it appeared to us that the reaction of inactivation might be hastened by the presence of a fat-solvent, using the copper in an oil-soluble form. If, further, the solvent used were capable of dissolving rubber a marked advance might be expected. Such a mixture has been devised. It consists of copper oleate, trichloroethylene, Turkey-red oil (70% ammonia-finished), and surgical spirit, and is prepared as follows: 25 g. copper oleate, is dissolved in 35 g. trichloroethylene; 25 g. of Turkey-red oil (sulphonated castor oil, 70% ammonia-finished) is incorporated into the mixture, after which 15 g. of surgical spirit is added. The copper content of this solution may reach 2.5%, but varies according to the quality of oleate. The presence of the alcohol cannot be dispensed with in cases of compositions containing rubber; but in other circumstances (e.g., phosphorus as an industrial hazard) it may with advantage be omitted.

This solution is readily prepared (Godding and Notton's mixture is not easily prepared), is perfectly homogeneous, and is deep blue-green in colour; it is a solvent for rubber and is easily emulsified with water. The constituents are available.* Its effects on phosphorus in various forms are summarized in the following table of comparison with other preparations:

Form in which Phosphorus is Present	1% CuSO ₄ Aqueous Solution	CuSO ₄ , Glycerol, and Starch Mixture of Godding and Notton	Oil-soluble Cu Preparation
Solid	Rapid surface inactivation only	Very slow surface inactivation	Very rapid inactivation, with disintegration of the surface layers
Solution in CS ₂	Inactivation at interface only	Inactivation at interface	Rapid and complete inactivation
Solution in benzene	" "	" "	" "
Solution in liquid paraffin	" "	More rapid inactivation due to some emulsification	" "
Solution in benzene and rubber	Poor and incomplete owing to lack of emulsifying properties	Very rapid and complete if well mixed, due to good emulsification	Rapid and complete inactivation. The reaction, once started, proceeds to completion with great speed

Advantages of the New Method

The following are the advantages of the new preparation: (1) It is readily miscible with oil, being dissolved in an oil-solvent which is also a solvent for rubber. This allows intimate contact with white phosphorus as well as with any oily composition in which phosphorus may be dissolved—e.g., in an incendiary bomb or other weapon. (2) It reacts progressively with phosphorus, not merely inactivating the surface of contact but transforming the element into easily removable products. (3) Since the preparation contains its own emulsifying agent (Turkey-red oil), it is completely removed from the skin by

* Copper oleate is a commercially available material, but in case it cannot be obtained, an equally effective material (although of lower copper content) can be prepared in the following way: Copper sulphate (10 g.) is dissolved in hot water (40 c.cm.) and 70% Turkey-red oil, ammonia-finished (25 c.cm.), added, with stirring. An insoluble copper derivative separates, and after cooling is decanted from the water. The oily copper compound is dissolved in trichloroethylene (35 c.cm.) and any remaining water separated off. A further addition of 70% Turkey-red oil (25 c.cm.) is made, and finally surgical spirit (20 c.cm.).

water, carrying with it any oil or rubber that may have been associated with the phosphorus, as well as the detritus from the inactivating reaction. The skin is left almost entirely clean and unstained.

Anaesthetized rats were treated, after dehairing, with a few drops of white phosphorus dissolved in CS_2 , and, after allowing the solvent to evaporate, the layer of phosphorus was inactivated by application of the above copper preparations. There was considerable difficulty in applying the 1% copper sulphate aqueous solution, since the rat's skin and the phosphorus layer are alike difficult to wet with aqueous solutions. The copper-glycerol mixture was better in this respect but reacted slowly compared with the oil-soluble copper preparation. Minute pieces of phosphorus applied to the skin were rendered inactive by the oil-soluble copper solution and disintegrated, while the copper sulphate solution and the copper-glycerol mixture rendered them inactive but left them entire. Here again the 1% copper sulphate reacted more quickly than the copper-glycerol once it had been brought into intimate contact with the phosphorus.

Phosphorus applied to the skin either alone or in solution in CS_2 appears to have no immediately deleterious action. Its danger resides wholly in its liability to ignite and cause burns which do not easily heal. This point was shown not only by animal experiments but by application to the human skin. Phosphorus allowed to ignite on the skin (after evaporation of the CS_2 , in which the phosphorus was dissolved) is immediately extinguished by the oil-soluble copper preparation, and inactivation of the phosphorus begins almost at once.

Proposed Procedure for dealing with Phosphorus on the Skin

1. Extinguish burning areas (immersion in water or wet fire-blankets).
2. Apply oil-soluble copper compound to areas contaminated with phosphorus (swabbing, pouring over areas, in some cases even immersing affected parts: manner of application will suggest itself according to circumstances. In general it will be best to deal with the affected parts piecemeal while keeping the waiting parts wet with water).
3. After well-established and obvious inactivation of the phosphorus (in general, in from a few seconds to one or two minutes), wash the treated area with tepid water and swab off the contaminating material.
4. Treat area with excess sodium bicarbonate, working up into a paste with water.
5. Treatment of the burn itself will naturally depend on circumstances, but if all the phosphorus is inactivated and removed and all acidity is neutralized, accepted methods on the lines of antiseptics and mild tanning should be applicable. The location of the burn, its depth, and the amount of tissue destroyed must all be considered in the treatment. General rules for all cases are misleading.

Summary

The phosphorus-inactivating properties of 1% aqueous copper sulphate, the copper sulphate-glycerol-starch composition of Godding and Notton, and a new composition containing copper in an oil-soluble form made from copper oleate, Turkey-red oil (sulphonated castor-oil), trichloroethylene, and surgical spirit have been compared. The last is shown to be the most effective way of inactivating phosphorus, especially when associated with oil, solvents, or rubber. A procedure is suggested for dealing with cases contaminated with material from self-igniting bombs containing phosphorus, oil, solvents, and rubber.

N.B.—It must be pointed out that the treatment proposed is for phosphorus on the skin. The high content of trichloroethylene precludes use of the composition for such internal injuries as were

recently described by Blaxland (1942), in which elemental phosphorus was diffusely implanted in the tissues.

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MODIFICATION FOR CO_2 ABSORPTION WITH THE FIELD-PATTERN BOYLE'S APPARATUS

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With the object of effecting economy of gases I have devised a modification of the field-pattern Boyle's apparatus by which carbon dioxide absorption may be used. This has proved to be very satisfactory in practice. The essential additions are a flowmeter for "basal" oxygen and a soda-lime canister. A description of these impro-

FIG. 1.—Front view; CO_2 absorber in section. A, Plug. C, Scale. B, Magill's bag-mount. R, Rubber connexions. (Other reference letters explained in text. Scale of drawings, $1/4$ size.)

visions is given in the hope that it may be of use to other anaesthetists.

The Flowmeter

The flowmeter (Figs. 1, 4, and 5) was designed to fit inside the sight-feed bottle, and is of the water-depression type. Its design was restricted by the limited space available. The oxygen cylinder is connected to the middle sight-feed tube, CO_2 not being used. Oxygen thus passes to the top of the bottle by way of the metal sleeve and tube (D), and escapes through a glass capillary (M). T indicates a connexion to the glass depression tube (B). The scale was cut from zinc-alloy sheet, and is wired to the normal oxygen sight-feed tube. Calibration was carried out by timing the displacement of water from a large measuring bottle. Preliminary experiments determined the proper size of capillary tube to obtain the desired range—200 to 650 c.cm. a minute.

Nitrous oxide is run in through the normal sight-feed tube.