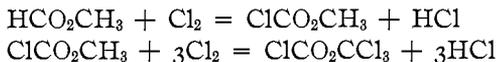


## SUPERPALITE<sup>1</sup>

BY H. P. HOOD AND H. R. MURDOCK

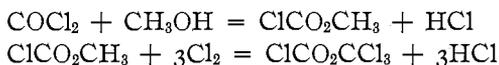
Trichlormethylchlorformate,  $\text{ClCO}_2\text{CCl}$ , is called di-phosgene by the British, surpalite by the French, and superpalite by the Americans. It is a colorless, mobile liquid, with a fairly pleasant sweet odor, boiling at  $127.5^\circ\text{--}128^\circ$  (corr.). It has a vapor pressure of 2–4 mm at  $0^\circ$  and of about 10.3 mm at  $20^\circ$ . Hentschel gives the specific gravity of the pure liquid at 1.6525 at  $14^\circ$ ; but our samples rarely went above 1.64. The refractive index at  $26^\circ$  was found by us to be 1.456 for the D line. Owing to the low volatility, superpalite is used only in shell and not in cylinder attacks. It has been used by the Germans only, who mark these shell with a green cross. The shell usually contain varying mixtures of superpalite and phosgene, though some duds have been found containing superpalite and chlorpicrin; diphenylchlorarsine has also been found in some of the Green Cross shell. The lethal concentration for dogs is 0.25 mg per liter (40 p. p. m.) for exposures of 30 minutes; but the concentration necessary to kill is very much less if the exposure is prolonged. Superpalite owes its importance to its high vapor density, its persistency because of its high boiling point, and to the increased toxicity on long exposure.

Superpalite is probably made as a war gas in Germany by chlorinating methyl formate to chlormethylformate and then chlorinating this to superpalite,

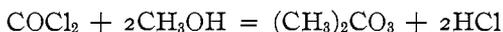


While superpalite has not been used by the Allies as a war gas, it has been prepared in this country for testing purposes by the action of phosgene on methyl alcohol, giving methyl chlorformate, which is then chlorinated to superpalite,

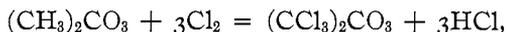
<sup>1</sup> Published by permission of the Director of the Chemical Warfare Service.



In the first stage, a possible side-reaction is



after which the dimethyl carbonate is chlorinated to perchlormethyl carbonate, or triphosgene as the English call it,



which has no toxic value and which has been thrown away in the past although it can be decomposed by prolonged heating into superpalite and phosgene



The chlorination of methyl chlorformate to superpalite takes place when the heated liquid is exposed to intense light while the chlorine is passed in.

Trichlormethylchlorformate was prepared by Hentschel,<sup>1</sup> who proved that it was the final product in the chlorination of methyl formate. The process of chlorination takes place in steps, methyl chlorformate being formed first and then, successively, the monochlor-, dichlor-, and trichlormethyl chloroformates. Methyl formate reacts readily with chlorine in the dark, giving methyl chlorformate. Further chlorination in the dark without the aid of an accelerating agent gives some chlormethyl chlorformate, but the reaction velocity is low and the yield poor. Complete chlorination can only be obtained with light as catalytic agent and near the boiling point of the liquid.

When the United States went into the war, Professor Neher of Princeton for a while made all the superpalite that was needed for testing purposes. He prepared the methyl chloroformate by the action of phosgene on methyl alcohol and chlorinated this compound in light raising the temperature as the chlorination proceeded. He used a "White Flame" cored arc as the source of light. Professor Neher will doubtless publish the details of his work. When the demand for

<sup>1</sup> Jour. prakt. Chem., [2] 36, 99, 209, 305, 468 (1887).

superpalite for testing purposes increased, the production was taken over by Captain Uhlinger, of the Small Scale Manufacturing Section of the Research Division, who substituted nitrogen-filled lamps for the "White Flame" cored arc. Although it did not seem probable that the United States would use superpalite as a war gas, the Catalytic Section was asked to study the problem as a precautionary measure. It was hoped that perhaps some much better method of manufacture might be worked out.

The properties and preparation of superpalite were therefore studied with some care. Superpalite was supplied to us by the Small Scale Manufacturing Section, labelled B. Pt. 125°-130°, sp. g. 1.64. On redistillation it was found that approximately nine percent of this product was perchloromethyl carbonate. Even after a third distillation of the 125°-130° fraction, a three percent residue of crystals was left, showing that this impurity is not easy to remove. The fraction between 125°-130° in the third distillation was used by us as superpalite. The methyl chloroformate was also obtained from the Small Scale Manufacturing Section. Besides a large amount of hydrochloric acid and phosgene, it contained a fair amount of dimethyl carbonate. A typical fractionation of this product made in a long Hempel column is as follows:

58°-62°	8 cc
62°-69°	50 cc
69°-75°	305 cc
75°-85°	40 cc
85°-92°	8 cc

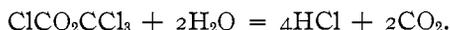
The last fraction consisted mainly of dimethyl carbonate. For our experiments in chlorination, the fraction coming over 71°-75° was taken as the starting point.

When heated to 300°-350° superpalite decomposes into phosgene in the ratio of one mole to two; but this may be the result of a catalytic action. Hentschel<sup>1</sup> states that when

<sup>1</sup> Jour. prakt. Chem., [2] 36, 102 (1887).

perchlormethyl chlorformate is boiled with a reflux condenser, it breaks down to some extent into phosgene which can be detected in alcohol owing to the formation of methylchloroformate. We have found practically no loss of weight when superpalite itself is refluxed at the boiling point for fifteen hours. Since superpalite itself reacts with alcohol, it is possible that Hentschel's results were due to uncondensed superpalite vapor passing through the condenser.

Superalite is hydrolyzed slowly by water at ordinary temperature and fairly rapidly at 100°, the products being hydrochloric acid and carbon dioxide, presumably according to the equation:



Boiling with an aqueous solution of sodium hydroxide for half an hour decomposes it completely. It reacts with methyl alcohol in the cold to give trichlormethyl methoxyformate,



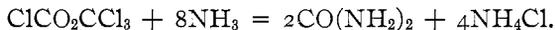
This reaction evolves heat and at higher temperature we get the further reaction,



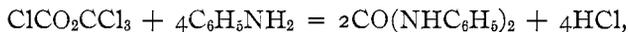
If there is an excess of methyl alcohol, the methyl chlorformate is formed,



Ammonia reacts rapidly with superpalite vapor, forming ammonium chloride and urea,



Aniline reacts to form carbanilid, which is insoluble in water,



and the carbanilid may react with more superpalite according to the equation,



This compound breaks down into carbanil,  $\text{C}_6\text{H}_5\text{NCO}$ .

Superalite does not react directly with benzene but

forms triphenyl carbinol chloride in presence of aluminum chloride,



When silver or sodium nitrite is treated with superpalite, phosgene,  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{CO}_2$  and the chlorides of the metal are obtained.

The catalytic decompositions of superpalite are extremely interesting (Hentschel, Neher). Alumina decomposes it to carbon dioxide and carbon tetrachloride while iron oxide splits it into phosgene. The corresponding chlorides have the same effect but to a lesser degree. Iron oxide appears to decompose the superpalite more rapidly than does alumina. We have found that purified charcoal behaves like iron but is even more active. Vanadium oxide causes a slow decomposition, while uranium oxide causes a more rapid decomposition than does ferric oxide. The decomposition products have not been determined in the case of the vanadium and uranium oxides.

Due to the action of superpalite on most of the common materials used in the laboratory, it has been found difficult to construct apparatus which will withstand its action and that of the intermediate products. Rubber is strongly attacked and the filler used in manufacturing the common rubber articles is believed to decompose the superpalite. Cork will not stand up against chlorine and the intermediates; it becomes swollen and weak but has no decomposing action on the product, so far as we know.

Marshall and Satler recommended analyzing a mixture of air and superpalite vapor by absorbing the superpalite in a three percent alcoholic potash solution. It is reported from France that alcoholic sodium hydroxide may cause some loss of chlorine as carbon tetrachloride. Apmann and Wilson have absorbed the superpalite-air mixture in a  $\text{N}/10$   $\text{AgNO}_3$  solution diluted to twice its volume with alcohol. Winkelmann decomposes superpalite with sodium peroxide. When working with the liquid and not with an air mixture,

heating with aqueous caustic soda on a steam bath for thirty minutes is satisfactory.

In the canister superpalite is decomposed to phosgene by the charcoal and the phosgene is then converted into hydrochloric acid and carbon dioxide. The soda-lime also decomposes superpalite.

It was hoped that it might be possible to reverse the decompositions and to synthesize superpalite either from phosgene or from carbon dioxide and carbon tetrachloride by means of alumina or iron oxide; but we were not successful in this. Although it is possible to oxidize carbon tetrachloride to phosgene by means of carbon dioxide, there is no experimental evidence that superpalite is an intermediate stage in this reaction. Curiously enough, it is quite a simple matter to convert thiophosgene into the corresponding thiosuperpalite and we do not know why a similar reaction does not take place with phosgene. The only two obvious differences are that thiosuperpalite is a yellow liquid at ordinary temperature and phosgene is a practically colorless gas. By using ultra-violet light instead of sunlight, it was hoped to work with rays which are absorbed by phosgene, and by cooling to zero, to cause the ultra-violet rays to act on the liquid. It seems certain that this reaction must take place under some conditions; but we had not found them at the time of the armistice.

Certain preliminary results were obtained with iron oxide which are very interesting scientifically if they are confirmed. There is no evidence that iron oxide causes any measurable conversion of phosgene into superpalite. On the other hand, when liquid superpalite and iron oxide were placed in a sealed tube, the decomposition of the superpalite apparently did not run to a finish at constant temperature. There was a marked decomposition at first, which soon came to an apparent stop. This did not represent a true equilibrium for the decomposition went further if the temperature were raised a few degrees and did not go back again when the temperature was lowered. This experiment extended

over quite a period of time and has not been checked. If it can be repeated, the only possible explanation that one can see is that the decomposition product, phosgene, is adsorbed strongly by the iron oxide and poisons the latter. Raising the temperature displaces some of the phosgene and lets some of the superpalite come in contact with the catalyzer.

This experiment is interesting because of its possible bearing on the Green Cross shell. The ratio of phosgene to superpalite in these shells varies rather remarkably. While, it is possible that the Germans were trying all sorts of fillings this does not seem very probable. It is quite conceivable that they added no phosgene at all or that they added some definite percentage, and that the variations are due to catalytic decomposition of the superpalite by the steel shell under temperature conditions. If this guess should prove to be true, there comes up the other interesting question whether chlorpicrin and diphenylchlorarsine poison the catalytic action of iron oxide on superpalite.

Since charcoal accelerates the chlorination of carbon monoxide to phosgene, it was thought that it might be a good chlorine carrier with methyl chlorformate. While chlorination takes place, no appreciable amount of superpalite can be obtained because this substance is decomposed into phosgene by charcoal. When redistilled superpalite is added to Dorsey charcoal which had been purified by treatment with phosgene, there was a marked evolution of phosgene, and superpalite was lost. To make certain that this was not due to phosgene adsorbed in the pores of the carbon carrying off superpalite when the latter displaced the former, a sample of treated charcoal was heated to redness, allowed to cool in the absence of phosgene, and finally added to a flask containing superpalite. Decomposition took place immediately and phosgene was evolved until the flask was dry. A very rapid decomposition takes place also when superpalite is in contact with ordinary Dorsey charcoal which has not had the phosgene treatment.

In order to determine whether the decomposition of the

superpalite was due to the charcoal or to some impurity in the charcoal, two samples of pure sugar charcoal were prepared by different methods. One sample was made by direct heating and charring, precautions being taken to prevent the introduction of foreign substances. This charcoal was found to decompose superpalite, though much more slowly than the Dorsey charcoal. The second sample of charcoal was made by treating white granulated sugar with a small amount of water and then adding concentrated sulphuric acid. The resulting mass was broken up and washed twelve times by decantation with distilled water. The water was then filtered off and the charcoal dried at  $110^{\circ}$  for a day. This charcoal also decomposed superpalite slowly. It is believed that the decomposition is due to the charcoal and that the power to adsorb phosgene plays an important part in determining the rate at which the liquid is decomposed. Sugar charcoal does not adsorb phosgene well and decomposes superpalite slowly, while Dorsey charcoal is a good adsorbent of phosgene and causes a very rapid decomposition of superpalite.

When methyl chlorformate was chlorinated in presence of powdered charcoal, the volume of the liquid decreased very much. It is believed that superpalite was formed but was decomposed to phosgene by the charcoal and passed off with the hydrochloric acid. The following data were obtained, using redistilled methyl chlorformate and completely dried and fresh Dorsey charcoal. The temperature was kept at  $65^{\circ}$  for 18 hours and then held at  $100^{\circ}$  for 6 hours more.

Initial volume, 650 cc  
Final volume, 315 cc

B. Pt. of fraction	Vol.	Refractive index	Density
$72^{\circ}$ - $105^{\circ}$	85 cc	1.4030	1.324
$105^{\circ}$ - $112^{\circ}$	45 cc	1.4172	1.393
$112^{\circ}$ - $122^{\circ}$	40 cc	1.4185	1.392
$122^{\circ}$ - $135^{\circ}$	55 cc	1.4178	1.378
$135^{\circ}$ - $175^{\circ}$	70 cc	1.4272	1.404
$175^{\circ}$ - $180^{\circ}$	20 cc	1.4400	1.468
	(Superpalite)	1.4533	1.6525)

When carbon tetrachloride is added to superpalite, the rate of decomposition by charcoal is decreased very much. A quantitative set of experiments was made to determine the relative rates of decomposition with different concentrations of carbon tetrachloride and superpalite. Up to 15 percent superpalite there is practically no decomposition; but from this point the rate of decomposition increases practically linearly with the percentage concentration, reaching a value of three grams per minute for the first ten minutes when 50 cc of pure superpalite was added to 9.5 grams of purified Dorsey charcoal. This experiment should be repeated in a sealed tube to see whether the charcoal is poisoned in case phosgene is not allowed to escape.

Experiments were also made to see whether ultra-violet light decomposes superpalite. A quartz flask containing about 200 grams of superpalite was placed as close to the ultra-violet light of a R. U. V. lamp as was practicable. At the end of three days, there was a loss in the weight of 2.7 grams, which might very easily be accounted for by evaporation due to the heating action. The liquid, however, became somewhat yellow, probably due to a small amount of phosgene being formed which was then decomposed by the ultra-violet light into carbon monoxide and chlorine, this latter causing the yellow color. It is evident that ultra-violet light produces but a slight decomposition of superpalite, if any.

Sulphur chloride, phosphorus pentachloride, and selenium tetrachloride were tried as catalytic agents for the chlorination of methyl chlorformate, but without success. A special form of porous silica has been made by Prof. Patrick, of Johns Hopkins University; but it contains traces of iron and alumina, and consequently could not be used.

It is necessary to use a chlorinating agent which will not decompose the superpalite when formed or which will not decompose it rapidly. So far, light is the only catalyst available. Several chlorinations of the methyl chlorformate were made, using ultra-violet light. The chlorine was absorbed as fast as it could be added, the reaction evolving

enough heat to keep the liquid at about  $70^{\circ}$ . It was found that if one added chlorine at a good fast rate until the liquid—fourteen inches from the lamp—absorbed no more chlorine, a yield of about 60 percent monochloromethyl chlorformate was obtained. To increase the chlorine content required a higher temperature and was a much slower process. It was proposed to make a quantitative run in order to find out the rates at which chlorine was taken up as the process was continued to superpalite. A preliminary run was made to determine the length of time required to produce superpalite. A quartz flask of about 200 cc capacity containing 100 cc of methyl chloroformate was clamped as close to the ultra-violet lamp as possible. Chlorine was bubbled through the formate at a rate of a liter a minute and the liquid was chlorinated completely in about three hours, a much shorter time than had been expected. This showed that variations in condition affected the rate of chlorination very much. It therefore seemed useless to make careful quantitative runs to determine the rates of chlorination because the results would hold good only for the particular conditions of each run and would tell nothing of general value. It was thought that the time could be used to better advantage by developing the best possible conditions.

An attempt was made to utilize all the available light from the lamp. Three concentric pyrex glass coils were made which surrounded the quartz ultra-violet lamp. A mixture of chlorine gas and methyl chloroformate vapor was passed through the outer coil, into the middle one, and lastly into the innermost coil and out through a condenser. The first part of the chlorination is very easy and requires but little light. The outer coil being in the shade of the other two, receives only a small amount of light. As the chlorination proceeds, the gases are carried in nearer the lamp, the intensity of light and the temperature both rising. The gases and vapors coming from the coils were cooled in a special condensing apparatus. Under usual running conditions the lamp gave off entirely too much heat, causing a rapid de-

composition of superpalite. It was found that the temperature could be controlled very well by blowing air over the coil; but this decreased the efficiency of the lamp very much. The degree of chlorination could be controlled by varying the rate at which the gases were passed through the coil. From several runs a product was obtained containing approximately 90 percent of the dichlormethyl chlorformate. By decreasing the rate of flow, superpalite was readily obtained. It was planned to determine the best conditions of rate of flow, temperature, and concentrations; but the work was brought to a close before this could be carried out. It was found that the chlorination was more rapid in the liquid than in the vapor phase and an apparatus was therefore designed, based on the principle of the Vanier absorption bottle. The device was a success so far as the physics of it was concerned and there was every indication that it would make a rapid chlorination; but work was stopped before this could be tried out thoroughly.

Before discussing the stages in the chlorination it will be desirable to consider the behavior of the side-product, dimethyl carbonate. The carbonate was prepared by refluxing methylchlorformate and methyl alcohol for two days. When chlorine was bubbled through a mixture of dimethyl carbonate and charcoal at 60°, a product was formed boiling at 138°. There is reason to believe that this is monochlorodimethyl carbonate. On chlorinating the carbonate in the presence of phosphorus pentachloride and charcoal, a product was formed, 60 percent of which boiled at 173°–178°. This is believed to be dichlorodimethyl carbonate. When steel turnings were used in an attempt to chlorinate the dichlorodimethyl carbonate, a decomposition took place into phosgene and formaldehyde. It is believed that the anhydrous ferric chloride is the catalytic agent, because steel does not cause this decomposition nor does crystalline ferric chloride. This particular decomposition is not exceptional, because the product called palite, boiling 105°–112°, which is chiefly monochlormethyl chlorformate decomposes on long stand-

ing into phosgene and formaldehyde. Under the influence of light dimethyl carbonate can be chlorinated to perchlordimethyl carbonate. If this hexachlordimethyl carbonate is distilled in an apparatus using a long distilling column, there is a marked decomposition into superpalite and phosgene, according to the equation,



If perchlordimethyl carbonate is refluxed, the same decomposition to superpalite and phosgene takes place; but the rate of decomposition decreases rapidly as the concentration of superpalite increases. No experiments were carried out to determine whether it would be possible to free superpalite completely from the hexachlordimethyl carbonate by sufficiently prolonged boiling. A mixture of powdered charcoal and powdered perchlordimethyl carbonate showed no signs of decomposition at ordinary temperatures. When heated to the melting point of the carbonate, decomposition to phosgene took place rapidly; but it is hard to say whether the charcoal was decomposing the carbonate or whether under these conditions the carbonate was breaking down into phosgene and superpalite, which latter was decomposing in contact with the charcoal.

The available evidence is that methyl chlorformate is first chlorinated to the monochlormethyl chlorformate or so-called palite, boiling at  $107^\circ$ . The next substitution gives dichlormethyl chlorformate, sometimes called dipalite. This product boils at  $114^\circ$ . The last step gives the trichlor compound or superpalite, boiling at  $128^\circ$ . Since the crude methylchlorformate always contains dimethyl carbonate, we get small amounts of what is believed to be monochlordimethyl carbonate boiling at  $138^\circ$ , and appreciable amounts both of the dichlordimethyl carbonate, boiling at  $180^\circ$ , and of the perchlordimethyl carbonate, a volatile solid melting at  $78^\circ$ .

A series of vapor densities were made with some of these products so as to determine the approximate molecular weights. Runs were first made with a couple of known compounds. The following results were obtained:

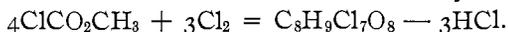
Substance	Temp. of jacket	Molecular weight	
		Found	Calculated
Toluene	142°	94.0	92.0
Methylchlorformate	142	93.9	94.5
Superpalite	142	198.3	198.0
H -107	142	135.0	129.0
H -114	142	166.0	163.5
H -180 (boiling at 175°)	210	177.0	159.0
H -180 (boiling at 178°)	210	173-183	159.0
R -178	210	170-176	159.0

H-107 is the so-called palite and is believed to be monochloromethyl chlorformate. Efforts were made to get a sample boiling accurately at 107°; but it is apparently very difficult to eliminate completely the product boiling at 114°. H-114 is apparently the dichloromethyl chlorformate. H-180 is a product boiling at about 178° and which Hentschel believed to have the formula  $C_8H_9O_8Cl_7$ . It is our belief that this is dichlorodimethyl carbonate. It is never made in large quantities, but seems to be more plentiful when one chlorinates a less pure methyl chlorformate. When dimethyl carbonate is chlorinated in presence of  $PCl_5$  and charcoal a product is obtained which has identical properties, the densities and refractive indices checking as well as the vapor densities. This product is entered in the table as R-178 and was first made by Private Rosenblatt. The value for the molecular weight is too high and a chlorine analysis showed 46.8 percent chlorine instead of the theoretical 44.6 percent. It seems probable therefore that the product is dichlorodimethyl carbonate containing about 9 percent of the hexachlorcarbonate as impurity. No molecular weight determinations were made on the product boiling about 138°; but it is a chlorinated compound obtained from dimethyl carbonate and must apparently be the monochlor substitution product.

Hentschel<sup>1</sup> considers that the chlorination product of

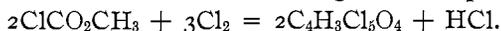
<sup>1</sup> Jour. prakt. Chem., [2] 36, 99, 209, 305, 468 (1887).

methyl chlorformate is a liquid boiling at  $180^{\circ}$ , having the composition  $C_8H_9Cl_7O_8$ , which is formed by the reaction



Our work has shown that this is the dichlordimethyl carbonate and that it is not a substitution product of methyl chlorformate at all. He found a molecular weight of 183.5 for his compound, which corresponds fairly well with the highest figure observed by us and does not correspond at all with Hentschel's formula; but Hentschel assumes decomposition in the vapor.

According to Hentschel the second stage in the chlorination is a liquid boiling at  $108^{\circ}$ – $109^{\circ}$ , having the composition  $C_4H_3Cl_5O_4$ , and formed according to the equation,



This is really the first stage in the chlorination and is impure monochlormethyl chlorformate,  $ClCO_2CH_2Cl$ , boiling at about  $107^{\circ}$ . Hentschel obtained a molecular weight of 137 instead of the 302.5 required by his formula and the 129 required for pure monochlormethyl chlorformate.

The general conclusions of this paper are:

1. Superpalite is decomposed by charcoal and by iron oxide into phosgene. When working in a sealed tube at constant temperature, the reaction apparently comes to a standstill at almost any desired point in presence of iron oxide.
2. Superpalite is decomposed by alumina into carbon tetrachloride and carbon dioxide.
3. Perchlordimethyl carbonate breaks up, when heated, into superpalite and phosgene.
4. When methyl chlorformate is chlorinated in light at suitable temperatures, the products are monochlormethyl chlorformate, boiling at  $107^{\circ}$ ; dichlormethyl chlorformate, boiling at  $114^{\circ}$ ; and trichlormethyl chlorformate, boiling at  $128^{\circ}$ .
5. When dimethyl carbonate is chlorinated, the successive products appear to be monochlordimethyl carbonate, boiling at  $138^{\circ}$ ; dichlordimethyl carbonate, boiling at  $178^{\circ}$ ; and hexachlordimethyl carbonate, melting at  $78^{\circ}$ .

6. It has not been possible to synthesize superpalite directly from phosgene or from carbon dioxide and carbon tetrachloride.

7. An ultra-violet lamp was used in the experiments described in this paper. Professor Neher obtained good results at Princeton with a "White Flame" cored arc, and Captain Uhlinger used a nitrogen-filled incandescent lamp with success. There are no data as to the relative efficiencies of the three forms of light. Since chlorine has an absorption band in the blue and also bands in the ultra-violet, chlorination may be accelerated both by blue light and by ultra-violet light.

This work was begun when the Catalytic Laboratory was under the Bureau of Mines and was continued after the transfer to the War Department. It has been carried on under the general supervision of W. D. Bancroft, W. L. Argo and H. B. Weiser.