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BANCROFT'S

HISTORY OF THE CHEMICAL WARFARE SERVICE

IN THE UNITED STATES. Part I,

BY

10

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The use of poison gases by the Germans at Ypres on April 22, 1915, marked a new era in modern warfare. The popular opinion is that this form of warfare was original with the Germans. Such, however, is not the case. According to an article <sup>(1)</sup> in the Candid Quarterly Review, <sup>(2)</sup> "All they can claim is the inhuman adoption of devices invented in England, and by England rejected as too horrible to be entertained even for use against an enemy". The use of poison gases is even earlier in origin than this article claims.

(1) Called to my attention by Major C.J. West.

(2) Vol. 4, p.561 (1915)

The first recorded effort to overcome an enemy by the generation of poisonous and suffocating gases seems to have been in the wars of the Athenians and Spartans (431-404 B.C.) when the Spartans besieged the cities of Plataea and Belium. They saturated wood with pitch and sulphur and burned it under the walls of these cities in the hope of choking the defenders and rendering the assault less difficult. Similar uses of poisonous gases are recorded during the Middle Ages. In effect they were like our modern stink balls, but were projected by squirts or in bottles after the manner of a hand grenade. The legend is told of Prester John (about the eleventh century), that he stuffed copper figures with explosives and combustible materials which caused great havoc when emitted from the mouths and nostrils of the effigies.

The idea referred to by the writer in the Candid Quarterly is due to the English Admiral Lord Dundonald, and appeared in the publication entitled "The Pamure Papers".

"The great Admiral Lord Dundonald - perhaps the ablest sea captain ever known, not even excluding Lord Nelson - was also a man of wide observation, and no mean chemist. He had been struck in 1811 by the deadly character of the fumes of sulphur in Sicily; and, when the Crimean War was being waged, he communicated to the English Government, then presided over by Lord Palmerston, a plan for the reduction of Sebastopol by sulphur fumes. The plan was imparted to Lord Panmure and Lord Palmerston, and the way in which it was received is so illustrative of the trickery and treachery of the politician that it is worth while to quote Lord Palmerston's private communication upon it to Lord Panmure:-

LORD PALMERSTON TO LORD PANMURE.

"House of Commons, 7th August, 1855.

"I agree with you that if Dundonald will go out himself to superintend and direct the execution of his scheme, we ought to accept his offer and try his plan. If it succeeds, it will, as you say, save a great number of English and French lives; if it fails in his hands, we shall be exempt from blame, and if we come in for a small share of the ridicule, we can bear it, and the greater part will fall on him. You had best, therefore, make arrangements with him without delay, and with as much secrecy as the nature of things will admit of."

"Inasmuch as Lord Dundonald's plans have already been deliberately published by the two persons above-named, there can be no harm in now republishing them. They will be found in the first volume of The Panmure Papers pp.340-342) and are as follows:-

.(ENCLOSURE)

"BRIEF PRELIMINARY OBSERVATION.

"It was observed when viewing the Sulphur Mines, in

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July in 1811, that the fumes which escaped in the rude process of extracting the material, though first elevated by heat, soon fell to the ground, destroying all vegetation, and endangering animal life to a great distance, as it was asserted that an ordinance existed prohibiting persons from sleeping within the distance of three miles during the melting season.

"An application of these facts was immediately made to Military and Naval purposes, and after mature consideration, a Memorial was presented on the subject to His Royal Highness the Prince Regent on the 12th of April, 1812, who was graciously pleased to lay it before a Commission, consisting of Lord Keith, Lord Exmouth, and General and Colonel Congreve (afterwards Sir William), by whom a favourable report having been given, His Royal Highness was pleased to order that secrecy should be maintained by all parties.

(Signed) Dundonald.

7th August, 1855"

"MEMORANDUM"

"Materials required for the expulsion of the Russians from Sebastopol:

Experimental trials have shown that about five parts of coke effectually vaporize one part of sulphur.

Mixtures for land service, where weight is of importance, may, however, probably be suggested by Professor Faraday, as to operations on shore I have paid little attention. Four or five hundred tons of sulphur and two thousand tons of coke would be sufficient.

"Besides these materials, it would be necessary to have, say, as much bituminous coal, and a couple of thousand barrels, of gas or other tar, for the purpose of masking fortifications to be attacked, or others that flank the assailing positions.

"A quantity of dry firewood, chips, shavings, straw, hay, or other such combustible materials, would also be requisite quickly to kindle the fires, which ought to be kept in readiness for the first favourable and steady breeze."

Dundonald.

7th August, 1855.

"Note.- The objects to be accomplished being specially stated the responsibility of their accomplishment ought to rest on those who direct their execution.

"Suppose that the Malakoff and Redan are the objects to be assailed it might be judicious merely to obscure the Redan (by the smoke of coal and tar kindled in 'The Barries'), so that it could not annoy the Malakoff, where the sulphur fire would be placed to expel the garrison from the Malakoff, which ought to have all the cannon that can be turned towards its ramparts employed in overthrowing its undefended ramparts.

"There is no doubt but that the fumes will envelop all the defense from the Malakoff to the Barracks, and even to the line of battleship, the Twelve Apostles, at anchor in the harbour.

"The two outer batteries, on each side of the Port, ought to be smoked, sulphured, and blown down by explosion vessels, and their destruction completed by a few ships of war anchored under cover of the smoke."

"That was Lord Dundonald's plan in 1855, improperly published in 1908, and by the Germans, who thus learnt it, ruthlessly put into practice in 1915.

"Lord Dundonald's memoranda, together with further elucidatory notes, were submitted by the English Government of that day to a committee and subsequently to another committee in which Lord Playfair took leading part. These committees with Lord Dundonald's plans fully and in detail before them, both reported that the plans were perfectly feasible; that the effects expected from them would undoubtedly be produced; but that those effects were so horrible that no honorable combatant could use the means required to produce them. The committees therefore recommended that the theme should not be adopted; that Lord Dundonald's account of it should be destroyed. How the records were obtained and preserved by those who so improperly published them in 1908 we do not know. Presumably they were found among Lord Pamure's papers. Admiral Lord Dundonald himself was certainly no party to their publication.

"Thus it will be seen that the plan which England had rejected as being too horrible for use in warfare has been, through the deplorable conduct of those who somehow obtained and published it, stolen from us by the Germans, and first used against us. That having been done, we cannot choose but retaliate in kind; for when such methods of warfare are used against we must, for our own protection and that of our soldiers, ourselves use means similar and as efficacious. Such means lie ready to our hand in Admiral

Lord Dundonald's plans; and it is to be presumed that they are now worked out and perhaps improved upon by the modern chemists so as to enable us effectually to give back to the Germans as good a gas as they send us."

The writer in the *Candid* quarterly is wrong in saying that the Germans learned of the British suggestion to use poisonous gases in warfare from the publication of "The Panurge Papers" in 1908. While the complete details first became available then, a reference to the matter was published in 1854, at which time a gas mask had been developed to protect the British themselves against poisonous gas. This was invented by Dr. J. Stenhouse and was described by Dr. George Wilson.<sup>(1)</sup>

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(1) *Trans. Roy. Scottish Soc. Arts*, 2, Appendix O, p. 198 (1854).  
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"Dr. Wilson commenced by stating, that having read with much interest the account of Dr. Stenhouse's researches on the deodorizing and disinfecting properties of charcoal, and the application of these to the construction of a new and important kind of respirator, he had requested that accomplished chemist to send one of his instruments for exhibition to the Society, which he had kindly done. Two of the instruments were now on the table, differing however, so slightly in construction, that it would be sufficient to explain the arrangement of one of them. Externally, it had the appearance of a small fencing-mask of wire gauze, covering the face from the chin upwards to the bridge of the nose, but leaving the eyes and forehead free. It consisted essentially, of two plates

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of wire gauze, separated from each other by a space of about  $1/4$  or  $1/8$  of an inch, so as to form a small cage filled with small fragments of charcoal. The frame of the cage was of copper, but the edges were made of soft lead, and were lined with velvet, so as to admit of their being made to fit the cheeks tightly and inclose the mouth and nostrils. By this arrangement, no air could enter the lungs without passing through the wire gauze and traversing the charcoal. An aperture is provided with a screw or sliding valve for the removal and replenishment of the contents of wood charcoal. The apparatus is attached to the face by an elastic band passing over the crown of the head and strings tying behind, as in the case of the ordinary respirator. The important agent in this instrument is the charcoal, which has so remarkable a power of absorbing and destroying irritating and otherwise irrespirable and poisonous gases and vapours that, armed with the respirator, spirits of hartshorn, sulphuretted hydrogen, hydro-sulphuret of ammonia, and chlorine may be breathed through it with impunity, though but slightly diluted with air. This result, first obtained by Dr. Stenhouse, has been verified by those who have repeated the trial, among others by Dr. Wilson, who has tried the vapours named above on himself and four of his pupils, who have breathed them with impunity. The explanation of this remarkable property of charcoal is two-fold. It has long been known to possess the power of condensing into its pores gases and vapours, so that if freshly prepared and exposed to these, it absorbs and retains them. But it has scarcely been suspected until

recently, when Dr. Stenhouse pointed out the fact, that if charcoal be allowed to absorb simultaneously such gases as sulphuretted hydrogen and air, the oxygen of this absorbed and condensed air rapidly oxidizes and destroys the accompanying gas. So marked is this action, that if dead animals be imbedded in a layer of charcoal a few inches deep, instead of being prevented from decaying as it has hitherto been supposed that they would be by the supposed anti-septic powers of charcoal, they are found by Dr. Stenhouse to decay much faster, whilst at the same time, no offensive effluvia are evolved. The deodorizing powers of charcoal are thus established in a way they never have been before; but at the same time it is shown that the addition of charcoal to sewage refuse lessens its agricultural value contemporaneously with the lessening of odor. From these observations, which have been fully verified, it appears that by strewing charcoal coarsely powdered to the extent of a few inches, over church-yards, or by placing it inside the coffins of the dead, the escape of noisome and poisonous exhalations may be totally prevented. The charcoal respirator embodies this important discovery. It is certain that many of the miasmata, malaria, and infectious matters which propagate disease in the human subject, enter the body by the lungs, and impregnating the blood there, are carried with it throughout the entire body, which they thus poison. These miasms are either gases and vapours, or bodies which, like fine light dust, are readily carried through the air; moreover, they are readily destroyed by oxidizing agents, which convert them into harmless, or at least non-poisonous substances, such as water,

carbonic acid and nitrogen. There is every reason, therefore, for believing that charcoal will oxidize and destroy such miasmata as effectually as it does sulphuretted hydrogen or hydrosulphuret of ammonia, and thus prevent their reaching and poisoning the blood. The intention accordingly is that those who are exposed to noxious vapours, or compelled to breathe infected atmospheres, shall wear the charcoal respirator, with a view to arrest and destroy the volatile poisons contained in these. Some of the non-obvious applications of the respirator were then referred to:-

1. Certain of the large chemical manufacturers in London are now supplying their workmen with the charcoal respirators as a protection against the more irritating vapours to which they are exposed.

2. Many deaths have occurred among those employed to explore the large drains and sewers of London from exposure to sulphuretted hydrogen, etc. It may be asserted with confidence that fatal results from exposure to the drainage gases will cease as soon as the respirator is brought into use.

3. In districts such as the Campagna of Rome, where malaria prevails and to travel during night or to sleep in which is certainly followed an attack of dangerous and often fatal ague, the wearing of the respirator even for a few hours may be expected to render the marsh poison harmless.

4. Those, who as clergymen, physicians, or legal advisers, have to attend the sick-beds of sufferers from infectious disorders, may, on occasion, avail themselves of the protection afforded by Dr. Stenhouse's instrument during their intercourse with the sick.

5. The longing for a short and decisive war has led to the invention of a "suffocating bomb-shell," which on bursting, spreads far and wide and irrespirable or poisonous vapour; one of the liquids proposed for the shell is the strongest ammonia, and against this it is believed that the charcoal respirator may defend our soldiers. As likely to serve this end, it is at present before the Board of Ordnance.

"Dr. Wilson stated, in conclusion, that Dr. Stenhouse, had no interest but a scientific one in the success of the respirators. He had declined to patent them, and desired only to apply

his remarkable discoveries to the abatement of disease and death. Charcoal had long been used in filters to render poisonous water wholesome; it was now to be employed to filter poisonous air."

I have not been able to find any reference in the scientific literature as to the action taken by the English Government in regard to Stenhouse's mask; but the quotation from the *Candid* quarterly clears up the matter. Since poisonous gases were not to be used, it was unnecessary to provide a defense against them.

One of the early, if not the earliest, suggestion as to the use of poison gas in shell is found in an article on "Greek Fire" by E. W. Richardson (<sup>(1) 6</sup> ~~Popular Science Review~~, 3, 176 (1864):

~~He says:~~  
*(1) Popular Science Review, 3, 176 (1864).*

*Followed*

"I feel it a duty to state openly and boldly, that if science were to be allowed her full swing, if society would really allow that 'all is fair in war', war might be banished at once from the earth as a game which neither subject nor king dare play at. Globes that could distribute liquid fire could distribute also lethal agents, within the breath of which no man, however puissant, could stand and live. From the summit of Primrose Hill, a few hundred engineers, properly prepared, could render Regent's Park, in an incredibly short space of time, utterly uninhabitable; or could make an army of men, that should even fill that space, fall with their arms in their hands, prostrate and helpless at the host of Sennacherib.

"The question is, shall these things be? I do not see that humanity should revolt; for would it not be better to destroy a host in Regent's Park by making the men fall as in a mystical sleep, than to let down on them another host to break their bones, tear their limbs asunder, and gouge out their entrails with three-cornered pikes;-- leaving a vast majority undead, and writhing for hours in torments of the damned? I conceive, for one, that science would be blessed in spreading her wings on the blast, and breathing into the face of a desperate horde of men prolonged sleep - for it need not necessarily be a death - which they could not grapple with, and which would yield them up with their implements of murder to any enemy that in the immensity of its power could afford to be as merciful as Heaven.

"The question is, shall these things be? I think they must be. By ~~what~~ compact can they be stopped? It were improbable that any congress of nations could agree on any code regulating means of destruction: but if it did, it were useless; for science becomes more powerful as she concentrates her forces in the hands of units, so that a nation could only act, by the absolute and individual assent of each of her representatives. Assume, then, that France shall lay war to England, and by superior force of men should place immense hosts, well armed, on English soil. ~~It is~~ probable that the units would rest in peace and allow sheer brute force to win

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its way to empire? Or put English troops on French soil, and reverse the question?

"To conclude, War has, at this moment, reached, in its details, such an extravagance of horror and of cruelty, that it cannot be made worse by any art, and can only be made more merciful by being rendered more ~~terribly~~ energetic. Who that had to die from a blow would, <sup>not</sup> rather place his head under Nasmyth's hammer, than to submit it to a drummer-boy armed with a ferule?"

The Army and Navy Register of May 29, 1915, reports that "among the recommendations forwarded to the Board of Ordnance and Fortifications there may be found many suggestions in favor of the asphyxiation process, mostly by the employment of gas: contained in bombs to be thrown within the lines of the foe, with varying effects from peaceful slumber to instant death. One ingenious person suggested a bomb laden to its full capacity with snuff, which should be so evenly and thoroughly distributed that the enemy would be convulsed with sneezing, and in this period of paroxysm it would be possible to creep up on him and capture him in the throes of the convulsion."

That the use of poison gases was not new in the minds of military men follows logically from the fact that at the Hague Conference in 1893, the Governments represented - and all the warring powers of the present great conflict were represented - pledged themselves not to use any projectiles whose only object was to give

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out suffocating or poisonous gases. At the Congress of 1907, article 23 of the rules adopted for war on land states:

"It is expressly forbidden (a) to employ poisons or poisonous weapons."

It is interesting to note in this connection that the American and German delegates to the 1899 Congress ---- refused to commit their countries against the use asphyxiating gas in projectiles (Literary Digest, 50, 1064, (1915).

Admiral Mahan's memorandum of his reasons \* \* \* \* for opposing the provisions is, in part, as follows:

"No shell emitting such gases is as yet in practical use or has undergone adequate experiment; consequently, a vote taken now would be taken in ignorance of the facts as to whether the results would be of a decisive character, or whether injury in excess of that necessary to attain the end of warfare, of immediately disabling the enemy, would be inflicted.

"The reproach of cruelty and perfidy addressed against these supposed shells was equally uttered previously against fire-arms and torpedoes, although both are now employed without scruple. \* \* \* \*

"It is illogical and not demonstrably humane to be tender about asphyxiating men with gas, when all were prepared to admit that it was allowable to blow the bottom out of an ironclad at midnight, throwing four or five hundred men into the sea to be choked by the water, with scarcely the remotest chance to escape."

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Before the war suffocating cartridges were shot from <sup>the</sup> ~~the~~ <sup>26 mm</sup> ~~cartridge~~-throwing rifle <sup>by the French.</sup> ~~of 26 mm.~~ These cartridges were charged with ethyl bromacetate, a slightly suffocating and non-toxic lachrymatory. They were intended for attack on the flanking works of permanent fortifications, flanking casements or caponiers, into which they tried to make these cartridges penetrate by the narrow slits of the loopholes. The men who were serving the machine guns or the cannon of the flanking works would have been bothered by the vapor from the ethyl bromacetate, and the assailant would have profited by their disturbance to get past the obstacle presented by the fortification. The employment of these devices, not entailing death, did not contravene the Hague conventions.

The first gas attack of the present war was launched by the Germans at Ypres on April 22, 1915. It is probable that plans for this attack had been under way for months, at least from Christmas, 1914. The introduction of toxic gases in modern warfare is ascribed by <sup>it</sup> Col. Auld <sup>(1)</sup> to Professor Walther Kernst of the University of Berlin, while the actual field operations are said to have been under the

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 (1) Gas and Flame, 15, (1918)  
 -----

general direction of Professor Haber of the Kaiser Wilhelm Physical Chemical Institute of Berlin. Some writers have felt that the question of preparation had been a matter of years, rather than months, and refer to the work on industrial gases as a proof of this statement. The fact that the gas attack was not more successful, that the results to be obtained were not more appreciated, and that better preparation against retaliation had not been made, argues

against this idea of a long period of preparation. That such was the case is most fortunate for the Allied cause, for had the German high command known the real situation at the close of the first gas attack, or had ~~it~~ <sup>the attack</sup> been more severe, the outcome of the war of 1914 would have been very different.

The first suggestion of the gas attack of April 22nd came to the British Army through the story of a German deserter. He told that the German Army was planning to poison their enemy with a cloud of gas, and that the cylinders had already been installed in the trenches. No one believed the story, largely because, in spite of the numerous examples of German barbarity, the English did not believe the German capable of such a violation of the Hague rules of warfare, even though he had not signed their agreement. The story appeared in the summary of information <sup>from</sup> headquarters ("Comic Cuts") and as Tuld says "was passed for information for what it is worth". But the story was true, and on the afternoon of the 22nd of April, all the conditions being ideal, the beginning of "gas warfare" was launched. Details of that first gas attack will always be meager, for the simple reason that the men who could have told about <sup>them</sup> never came back.

In this attack the Germans made use of chlorine discharged from steel cylinders, presumably because chlorine was a volatile, corrosive substance which was available on a large scale. On the other hand chlorine reacts so readily with most substances that it can be stopped very easily, which was very fortunate because it thus became possible for the Allies to provide protection in a very short time. A cloth bandage steeped in the sodium hyposulphite solution of the photographers and wrapped over the nose and mouth gives fairly satisfactory protection against chlorine. These bandages do not protect the eyes and the Germans promptly went over tear gas or lacrymators in shell because the substances used for this purpose, bromoacetone and ethyl bromide, are liquids at ordinary temperatures and do not pass into vapor rapidly enough to be used in cylinders. In every-day life we distinguish sharply between gases, liquids and solids; but this distinction does not hold in gas warfare where the word gas is used loosely to denote any substance, solid, liquid or gas which is dispersed in the air and which irritates the lungs, eyes or skin. Protection against the tear gases was given by hoods with eye-pieces and later by goggles. The hoods could be impregnated with chemicals.

Chlorine was used in the gas attacks by the Germans from April to June, 1915; but in December of that year a mixture of chlorine and phosgene,  $\text{COCl}_2$ , was made use of. The new gas, phosgene, could not be ~~employed~~ <sup>employed</sup> done in cylinders because it boils at  $-10^\circ\text{C}$  and therefore does not vaporize sufficiently rapidly. On the other side it has three to four times its weight of chlorine, the latter is vaporized the phosgene rapidly enough for use in cylinder attacks. Phosgene is seven times as toxic as chlorine, a gas to stop, and was a delayed action which ~~was~~ <sup>is</sup> still more dangerous. To stop phosgene the British hoods had

the first French masks were impregnated with a solution of sodium phenolate and urotropine (hexamethylene tetramine). The British changed before long from the hood, or helmet as it was called, to an ingenious mask with a box respirator or canister attachment. The air which the man breathed passed first through the canister which contained chiefly soda-lime granules and charcoal, both of which stop gases much more effectively than do the solutions in the fabric of the masks.

The next improvement in the offensive was the use of chlorpicrin in shells, the liquid being scattered by the explosion of the booster in the shell. Chlorpicrin,  $\text{CCl}_3\text{NO}_2$ , is a liquid boiling at  $112^\circ\text{C}$ , which is much less toxic than phosgene, but which is distinctly lachrymatory and which causes vomiting, and which makes it difficult for the soldier to keep on his mask. Its great advantage lay in the fact that it was not stopped by the charcoal at use at that time in the mask. The quality of the charcoal was improved at once and the new charcoal was so good that it stopped practically all <sup>toxic</sup> gases under fairly well. With the introduction of the new charcoal, chlorpicrin was not so effective as phosgene and it was still used, especially by the allies.

If the Germans had had the tactical use of poisonous gases worked out long before the war, they never could have waited until the return of 1915 before using phosgene or until 1917 before using chlorpicrin. If they had started in with chlorpicrin, it would have been ~~absolutely~~ impossible for the allies to have devised any protection in any reasonable time and they would have been absolutely helpless. It is quite clear that the Germans were developing the principles of gas warfare as the conditions changed. While they were far enough ahead of

the Allies to be the first to try out each new gas, they were never able to turn their temporary advantage into victory.

This is shown very strikingly in the development of mustard gas, so-called, and of toxic smokes. In July 1917 the Germans began using mustard gas, a liquid boiling at about 217°C which attacks the skin, causing bad burns that may incapacitate a soldier for a number of weeks. While the mask protects the face satisfactorily, the problem of protecting the whole body is a very serious one. Special ointments and special clothing were devised at once; but these were not really satisfactory at the time and the face was slight and the best protection was not to keep troops long in gassed areas. Fortunately the Germans did not discover a good method of making mustard gas and their supply was consequently always limited. If they had had from the start the method which the British developed, things might have gone very differently during 1918.

It had always been known that the chlorine did not stop to these smokes as it had been necessary to put in wet cloths in order to keep atomic chlorine <sup>smoke</sup> from getting through. The Germans took advantage of this <sup>the fact</sup> very finely divided as it passed through the canisters and developed their so-called choking gas. This is a high-boiling liquid, diphenylchlorarsine, which they discovered as a very fine smoke by means of an explosive. In order to protect soldiers, besides the mask, special filtering gas <sup>or</sup> ~~canisters~~ <sup>are</sup> used. To equip the armies of the western front with supplies of this sort on short notice would have been an impossible task. Fortunately the Germans did not devise any really satisfactory chemical gas for this substance and the allies had sufficient warning to have enabled them to have met the danger if it had arisen. 3.

While a great many substances have been studied with reference to their use in gas warfare, relatively few have been used to any great extent. It may therefore be desirable to give a brief outline of some of the properties of the more important war gases.

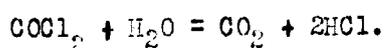
Chlorine, Cl<sub>2</sub>, ~~was first used in April, 1915.~~ It is a greenish-yellow gas with a suffocating and irritating smell. It boils at  $-35.6^{\circ}$ , and the vapor pressure of liquid chlorine is 3.66 atmospheres at  $0^{\circ}$  and 11.5 at  $40^{\circ}$ . The molecular weight is 71, so that the vapor is nearly 2.5 times as dense as air (71/28.8). The density of liquid chlorine is 1.4635 at  $0^{\circ}$  and 1.4108 at  $20^{\circ}$ . It is easily prepared and easily liquidified. It is so volatile that it can be used in a cylinder or cloud attack. To prevent the cooling of the cylinders the discharge tube runs to the bottom as in a soda siphon and evaporation takes place outside the cylinder.

Chlorine is not very toxic, the lethal concentration being 2.5 mg/liter (770 p.p.m.) for dogs on 30 minutes exposure. It is very corrosive but reacts so readily with most things that it is easily stopped. In the canister with the soda-lime it reacts directly with the soda-lime. It is also absorbed by charcoal and reacts with moisture, according to the equation  $2\text{Cl}_2 + 2\text{H}_2\text{O} = 2\text{HCl} + 2\text{HClO} = 4\text{HCl} + \text{O}_2$ , the hydrochloric acid being taken up by the soda-lime. Dry chlorine does not react with iron and can therefore be kept in steel cylinders.

Phosgene, COCl<sub>2</sub>, ~~was first used in December, 1915.~~ It is a colorless gas with a smell like rusty hay. It boils at  $8.2^{\circ}$  and the vapor pressure of liquid phosgene is 1.6 atmospheres at  $20^{\circ}$  and 3.1 at  $40^{\circ}$ . It is over three times as dense as air. The density of

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the liquid is 1.432 at 0°. It is not sufficiently volatile to be used by itself in cloud attacks and is always mixed with chlorine in such cases, the mixture usually containing 20 - 25% phosgene. It is about seven times as toxic as chlorine, the lethal concentration for dogs on 30 minute exposure being 0.35 mg. per liter (80 p.p.m.) Phosgene reacts readily with water according to the equation:



In the canister, phosgene is absorbed by charcoal and reacts with the moisture in the latter to form carbon dioxide and hydrochloric acid, which are taken up by the soda-lime. Soda-lime does not absorb or decompose phosgene sufficiently rapidly to give adequate protection. The charcoal gives the activity and the soda-lime the capacity. Increased moisture in the charcoal increases its efficiency towards phosgene.

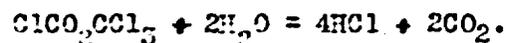
Chlorpicrin,  $\text{CCl}_3\text{NO}_2$ , is a colorless liquid, boiling at 112°, and having a vapor pressure of 8.8 mm/ at 0°, 14.0 mm/ at 15°, and 23.8 mm/ at 25°. The vapor is nearly six times as dense as air. The density of the liquid is 1.69335 at 4° and 1.6539 at 20°, the two determinations not being made by the same man. ~~the~~ melting point is ~~17.2°~~ 17.2°. Chlorpicrin is not sufficiently volatile for use by itself in cloud attacks. While it has been used mixed with 75% chlorine, it is usually fired in shell. It is moderately toxic (0.8 mg/ per liter, 110 p.p.m.); somewhat lachrymatory (0.16 mg/ per liter) and liable to cause vomiting, thus forcing removal of the mask. It was <sup>not</sup> stopped satisfactorily by the charcoal <sup>used</sup> in the masks. The present laboratory charcoal is about one thousand times as effective as the earlier material.

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Trichloromethylchloroformate,  $\text{ClCO}_2\text{CCl}_3$  is called diphosgene by the British, surpalite, by the French, and superpalite by the Americans. It is a colorless, mobile liquid with a fairly pleasant sweet odor. It boils at  $133^\circ$  and has a vapor pressure of 1-4 mm at  $0^\circ$  and of 10.5 mm at  $20^\circ$ . The vapor is over seven times as dense as air and is twice as dense as phosgene. The density of a pure sample of the liquid is 1.687 at  $0^\circ$  and 1.656 at  $20^\circ$ . Owing to the low volatility superpalite is used only in shell. It has been used only by the Germans, who mark these shells with a green cross. The shell usually contain 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 shells.

The lethal concentration for dogs is 0.05 mm per liter for exposure of 30 minutes (940 ppm.) but it is much lower on longer exposures. Superpalite owes its importance to its high vapor density, to its persistency because of its high-boiling-point, and to the increased toxicity on long exposures.

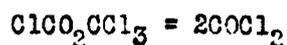
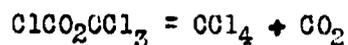
Superpalite is hydrolyzed slowly by water at room temperature and fairly rapidly at  $100^\circ$ , the products being  $\text{HCl}$  and  $\text{CO}_2$ , presumably according to the equation,



Boiling with an aqueous solution of sodium hydroxide for half an hour decomposes it completely.

Alumina causes superpalite to decompose into carbon tetrachloride and carbon dioxide, while iron oxide and charcoal decomposes it to phosgene.

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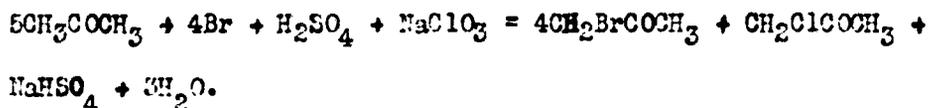
Some preliminary experiments seem to indicate that in a sealed tube at constant temperature, the decomposition of superpalite in presence of iron oxide does not run to an end, even though the reverse reaction does not take place. This raises the question whether the Germans really put a mixture of superpalite and phosgene into their shell or whether the extremely variable concentration of phosgene may be due to the catalytic decomposition by the steel shell. There are no experiments as yet to show what effect chloricrin has on this decomposition. In the canister, superpalite is decomposed by the charcoal to phosgene, which is then decomposed by moisture. Superpalite is also decomposed readily by soda-lime.

Bromacetone,  $\text{CH}_3\text{BrCOCH}_3$  is a water-clear liquid which turns brown or black on standing, owing to charring. It boils with decomposition at about  $126^\circ$ , and the vapor pressure of the crude product is 1.0 mm/ at  $10^\circ$  and 9.0 mm/ at  $20^\circ$ . It is not quite five times as dense as air. The density of the liquid is given as 1.631 at  $0^\circ$  and 1.603 at  $20^\circ$ . It causes lachrymation at 0.0013 mg/ per liter (0.21 p.p.m.) when pure and at 0.001 mg/ per liter when containing 20% chloroacetone (Martonite) although the chloroacetone is a poorer lachrymator than bromoacetone. Being fairly volatile and readily decomposed, it is classed as a non-persistent lachrymator. Troops can advance a few hours after the shelling. Bromoacetone attacks steel and most other metals and must be used in shell lined with lead, glass or enamel.

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Bromacetone is only slightly soluble in water; but readily miscible with alcohol and acetone. Traces of water stabilize the product somewhat and addition of chloracetone seems to have the same effect. There is some reason to believe that the instability is due to the presence of some impurity, but it is not known what impurity has this effect. Both the charcoal and the soda-lime in the canisters stop bromacetone.

The French have manufactured a mixture of about 80% bromacetone and 20% chloracetone, which they call Martonite. In order to prevent the loss of half the bromine as hydrobromic acid, they add a mixture of sodium chlorate and sulphuric acid to oxidize the hydrobromic acid. The reaction is as follows:



Brommethylethylketone, is a mixture of  $\text{CH}_2\text{BrCOC}_2\text{H}_5$  boiling at  $155^\circ$  and of  $\text{CH}_3\text{COCHBrCH}_3$  boiling at  $135^\circ$ . It is made by brominating methylethylketone,  $\text{CH}_3\text{COCH}_2\text{CH}_3$ . It lachrymates at 0.009 mg/ per liter (1.3 p.p.m.) and is substituted <sup>for</sup> ~~from~~ bromacetone solely on account of shortage of acetone. Shell must be lined to prevent corrosion.

Xylyl bromide,  $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Br}$ , is a mixture of the ortho, meta, and para compounds, and boils at about  $212^\circ$ . It lachrymates at 0.002 mg/ per liter (0.25 p.p.m.) and is classed as a persistent lachrymator. Lined shell must be used. Both the charcoal and the soda-lime stop xylyl bromide. The mixture of the three xylenes, which is ordinarily called xylene, is heated, exposed to sunlight, and treated with bromine. Under these conditions the bromine sub-

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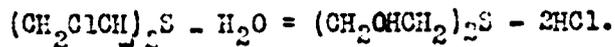
stitutes in the methyl side-chain and not in the benzene ring. Care must be taken not to carry the bromination too far, as the dibromide is of no value. Xylyl bromide is sometimes called tolyl bromide because the bromine substitution compound of toluene is called benzyl bromide.

Mustard Gas, so-called,  $(\text{CH}_2\text{ClCH}_2)_2$  melts at  $14.2^\circ$ , when very pure, to a colorless, oily liquid which boils at  $217^\circ$  at 750 mm. The name was given to it by the British soldiers and is an unfortunate one because the compound has nothing to do with what the chemist calls mustard oil. The vapor is a little less than six times as dense as air. The vapor pressure of a sample melting at  $13.8^\circ$  was about 40 mm/ at  $140^\circ$ , 30 mm/ at  $120^\circ - 125^\circ$ , 20 mm/ at  $111^\circ$ , and 12 mm/ at  $97^\circ$ . Some British data are 44 mm/ at  $128^\circ - 132^\circ$  and 10 mm/ at  $109^\circ$ . The density of the liquid referred to water at  $0^\circ$  is 1.2700 at  $15^\circ$ , 1.2686 at  $25^\circ$ , and 1.2584 at  $35^\circ$ . Owing to the low vapor pressure the substance can be used only in shell and is very persistent. The Germans have marked their mustard gas shell with a yellow cross.

The lethal concentration is 0.05 mg/ per liter (7 p.p.m.). The liquid produces burns which appear 4 - 12 hours after exposure and heal very slowly. The vapor also causes burns but to much less extent. It attacks the eyes, causing conjunctivitis and temporary blindness. The percentage of deaths is rather low with mustard gas, only about 5%, but this is not due to any low toxicity. It is because the number of casualties due to burns is very large. A comparison with phosgene, which does not burn the skin, is therefore quite improper.

Mustard gas is very slightly soluble in water, less than 0.1%. It is freely soluble in alcohol, ether, chloroform, tetrachloroethane, chlorobenzene, and trioxymethylene. It is miscible in all proportions with ligroin above 19° and with kerosene above 25.6°. At a pressure of 760 mm/ 100 volumes of dichlorethyl sulphide dissolve 182 volumes of ethylene at 15° and 100 volumes at 95°. At 6° mustard gas dissolves about 3% of dry hydrochloric acid. At room temperature it dissolves about one percent of sulphur, the solubility becoming about 6% at 100°. Dichlorethylsulphide is hydrolyzed very slowly by cold water and quite rapidly by hot water to thiodiglycol, which is harmless.

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Sulphur dichloride reacts rapidly with mustard gas, forming the tetrachlorosulphide. It is this property which makes sulphur dichloride such a valuable reagent in the laboratory for removing mustard gas. The reaction also takes place in carbon tetrachloride solution and more slowly the more dilute the solution. Sodium sulphide solution reacts, forming the ring compound S:(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>:S. Chloramine - T (p-toluene sodium sulphochloramine) and dichloramine-T (p-toluene sodium sulphochloramine) react vigorously with mustard gas, forming white, crystalline compounds which are not irritating.

Hydrocyanic acid, HCN, is a colorless, mobile liquid boiling at 26.5°. The vapor is slightly less dense than air. The toxic concentration for dogs is about 0.08 mg/liter (90 p.p.m.) but dogs, as has been stated, are exceptionally sensitive to this gas.

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There is no cumulative effect and neither the British nor the Germans have ever used hydrocyanic acid. The French have used ~~in~~ a mixture called Vincenite; but there seems to be no evidence of its value.

Cyanogen Chloride,  $CNCl$ , is a colorless liquid, boiling at ~~plus~~ <sup>+</sup>  $12.6^{\circ}$  and solidifying at about  $-7.3^{\circ}$ . The vapor pressure is 444 mm/ at  $0^{\circ}$  and 682 mm/ at ~~plus~~ <sup>+</sup>  $10^{\circ}$ . The density of the vapor is only a little more than double that of air. The density of the liquid is 1.22 at  $0^{\circ}$ . It is a good lachrymator ( $0.015$  mg/~~per~~ liter) *and* is highly toxic, low concentrations causing cramps in the chest and higher concentrations causing symptoms similar to those of hydrocyanic acid. Like hydrocyanic acid there is no cumulative effect. The toxic concentration for dogs is  $0.20$  mg/~~per~~ liter (72 p.p.m.); but dogs are the most sensitive to cyanogen chloride of any of the animals.

When dry, cyanogen chloride does not attack iron, lead or silver, but does attack copper. If moist, it attacks all these metals. Cyanogen chloride goes through the German mask very rapidly, which is the reason that the Allies hoped to use it on the Western Front. It is stopped by the American charcoal but not for very long.

Bromobenzylcyanide,  $C_6H_5CHBrCN$ , is a colorless solid melting at  $29^{\circ}$ . The crystals soon turn pink owing to a slight decomposition, which does not proceed far however. The commercial product melts at  $16^{\circ} - 22^{\circ}$  and the crystals are varying shades of dark brown, often with a marked greenish tinge. The vapor pressure is given as 0.025 mm/ at  $0^{\circ}$  and 0.250 mm/ at  $40^{\circ}$ . The compound decomposes before the boiling point is reached, even in a high vacuum. The density of the solid is about 1.51 at  $25^{\circ}$ .

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Brombenzyl cyanide is a very effective lachrymator. Most people can detect it at 0.021 parts per million and are lachrymated at 0.04 parts per million (0.00033 mg ~~per~~ liter).

The compound is insoluble in water, moderately soluble in cold alcohol, freely soluble in hot alcohol, and soluble in ether, glacial acetic acid, carbon bisulphide, and benzene. It is hydrolyzed very slowly by boiling water and by cold solutions of sodium hydroxide. A cold alcoholic solution of sodium hydroxide decomposes it rapidly, forming sodium bromide. It is oxidized slowly by potassium permanganate, bleaching powder, chromic acid mixture, etc. Brombenzyl cyanide attacks all metals except lead rapidly and does corrode lead. It would probably have to be loaded in enamel-lined or glass-lined shell. The magnesium and kaolin cements are satisfactory in presence of brombenzyl cyanide. It does not react with mustard gas. The charcoal in the American canister stops it <sup>fairly</sup> well; but the German charcoal appears ~~not~~ <sup>to</sup> be ~~so~~ <sup>so</sup> effective.

Chloroacetone,  $C_6H_5COCH_2Cl$ , is a colorless crystalline solid, melting at  $58^{\circ} - 59^{\circ}$  and boiling at  $245^{\circ} - 247^{\circ}$ . The vapor pressure is about 0.003 mm at  $0^{\circ}$ , 0.019 mm at  $25^{\circ}$ , and 0.056 mm at  $37^{\circ}$ . The density of the solid is 1.354 at  $0^{\circ}$  and 1.263 at  $55^{\circ}$ . The pure compound causes lachrymation in the majority of cases at 0.00031 mg ~~per~~ liter (0.046 p.p.m.), so that this substance is about equivalent to brombenzyl cyanide.

Chloracetophenone is insoluble in water but soluble in alcohol, benzene, ether, and chloroform. It is soluble to the extent of two percent in pure silicon tetrachloride but is insoluble in commercial silicon tetrachloride and titanium tetrachloride. It does not react with ammonium nitrate, trinitrotoluene or amatol when heated at 100° for twenty-four hours. It can be used in steel shell.

Ethyl iodacetate,  $CH_3ICO_2C_2H_5$ , is a colorless oil of extremely penetrating odor which turns brown in the air with liberation of iodine. It decomposes if boiled in the air. The vapor pressure is 250 mm/ at 143° and 0.87 mm/ at 30°. The density of the liquid is 1.8520 at 4°. The toxic concentration for dogs is about 1.6 mg./ per liter; but the substance is primarily a lachrymator. Nine people out of ten tested were lachrymated at 0.17 parts per million. Owing to the scarcity of iodine this is not a very satisfactory substance for war purposes. It was made by the English at a time when the price of bromine was very high. It is made by treating an alcoholic solution of ethyl bromacetate or ethyl chloracetate with powdered potassium iodide.

Acrolein,  $CH_2=CHCHO$ , is a colorless liquid with a pungent smell, boiling at 52.4°. The vapor is only about 1.5 times as dense as air, which is a distinct disadvantage. It is primarily a lachrymator, one part in a hundred thousand being intolerable. It is about as toxic as phosgene, however, and causes nausea and heart trouble, besides affecting the memory. Since it was not stopped till by the early German war gas, great things were expected of this gas. It is not stable under ordinary conditions and polymerizes readily.

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While one can stabilize the compound in the laboratory fairly well, it is a very difficult matter to do this on a commercial scale. The French have used it a little in hand grenades for clearing dug-outs, because it was not necessary to store the material; but it would be a waste of time, with our present knowledge, to send acrolein across the sea.

Arsine,  $AsH_3$ , is a colorless and almost odorless gas, boiling at  $-85^\circ$ . It is less than three times as dense as air. The vapor pressures, as determined by Faraday in 1845, are 8.96 atmospheres at  $0^\circ$  and 13.2 atmospheres at  $15.6^\circ$ . The density of the liquid is given by Richter and Myers as 1.47 at  $-10^\circ$ , 1.44 at  $0^\circ$ , and 1.37 at  $22^\circ$ . The toxic concentration for dogs is 0.30 mg/liter (200 p.p.m.)

Liquid arsine does not redden litmus. The gas decomposes fairly readily in air. In a sealed glass tube, it decomposes into metallic arsenic and hydrogen; but this change does not take place when the tube contains liquid arsine. The decomposition seems therefore to be due to the catalytic action of the walls on arsine vapor. It has not been used in gas warfare; but if the war had lasted, the Allies might have experimented with liquid arsine in cylinders. There have always been rumors that the Germans were going to use it and consequently protection against it had to be supplied. Neither charcoal nor soda-lime stops it satisfactorily; but it is stopped by soda-lime granules impregnated with sodium permanganate. The potassium salt is less soluble and cannot be used.

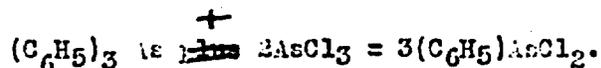
~~DIPHENYLCHLORARSINE~~

Diphenylchlorarsine,  $(C_6H_5)_2AsCl$ , is a solid melting at about  $44^\circ$  and boiling at about  $330^\circ$ . The vapor pressure is 25 mm at  $233^\circ$  and 7 mm at  $180^\circ$ . The density of the vapor is about nine times that of air. The density of the crystals is 1.4233 at  $15^\circ$ . It is used in shell in presence of high explosive which scatters it as a very fine powder or smoke in the air. The Germans marked these shells with a blue cross. The lethal concentration is about 0.1 mg per liter but the substance is used chiefly to cause sneezing and thus to force removal of the mask, and is often called "sneeze gas." It can be detected at one part in a hundred million, produces nasal irritation at one part in fifty million, and is intolerable at one part in a million, attacking the eyes as well as the respiratory tract. It was first used by the Germans in July 1917. It is not soluble in water or ammonia but is readily soluble in alcohol, ether or benzene. It is hydrolyzed by water to  $(C_6H_5)_2AsOH$  and is oxidized by concentrated nitric acid to diphenyl arsenic acid. Chlorine destroys the irritating effect of diphenylchlorarsine, probably due to formation of  $(C_6H_5)_2AsCl_3$  or  $C_6H_5)_2AsOCl$ , though it is possible that the chlorine either causes the agglomeration of the smoke or causes it to be stopped by the canister. Phosgene has no such effect but phosgene containing one percent of chlorine does, and it is stated that a marked increase in the opacity of the cloud is noticed.

The vapor of diphenyl chlorarsine is stopped by charcoal; but the suspended substance passes through either as solid or liquid and must be stopped by special paper filters or otherwise.

~~PHENYL DICHLORARSINE~~

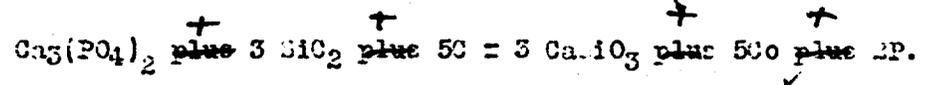
Phenyldichlorarsine,  $C_6H_5AsCl_2$ , is a highly refractive liquid boiling at  $252^\circ - 255^\circ$ . The vapor pressure is 27 mm at  $142^\circ$ . The substance blisters the skin much more rapidly than mustard gas. A burn up to four days old would be judged 3 - 4 times as extensive as a mustard gas burn of the same age and equally as severe. The burns heal more rapidly than those from mustard gas, so that the usefulness of this liquid is not established. A 60% yield can be obtained by heating triphenylarsine and arsenic chloride in suitable proportions in an autoclave at  $250^\circ$  for 14 hours.

~~METHYL DICHLORARSINE~~

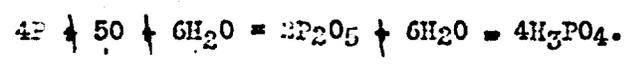
Methyl dichlorarsine,  $CH_3AsCl_2$ , is a colorless liquid with a powerful burning odor. It boils at  $131.5^\circ$  and has a vapor pressure of about 2.2 mm at  $0^\circ$  and 19.3 mm at  $35^\circ$ . The vapor is between five and six times as dense as air. The density of the pure liquid is given by Lichter and Byers as 1.873 at  $0^\circ$  and 1.81 at  $35^\circ$ . The toxic concentration for dogs is 0.30 <sup>mg</sup> mg/liter (78 p.p.m.) The substance begins to irritate the nose at a concentration of about 1.3 parts per million. As a liquid, methyl dichlorarsine is less irritant to the skin than phenyl dichlorarsine, but the vapor is much more irritating owing to the higher concentrations attainable. The advantage which this substance may have over mustard gas is that there may be a large number of casualties due to vapor burns. It also goes through clothing more rapidly than mustard gas.

In addition to the toxic gases, several substances have been used as irritant or concealing smokes.

Phosphorus is prepared by heating phosphate rock with sand and coke in an electric furnace.

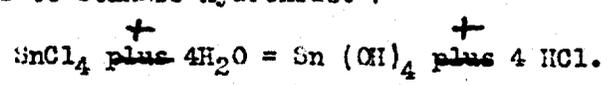


Phosphorus comes on the market either as white (yellow) or red phosphorus. Either form burns to phosphorus pentoxide and is then converted to phosphoric acid.



Since one pound of phosphorus takes up 1.33 pounds of oxygen and 0.9 pounds of water, it is not surprising that phosphorus is the best smoke producer per pound of material. In addition to its use as a smoke producer, it is used in incendiary shell and for coating tracer bullets. For incendiary shell the English use a very fine powder of red phosphorus mixed with twice its weight of white phosphorus. Experiments in this country indicate that a better procedure is to use a conglomerate of lumps of red phosphorus embedded in white phosphorus because this mixture burns less rapidly.

Tin tetrachloride, SnCl<sub>4</sub>, is a liquid made by treating tin with chlorine. It boils at 114°, and fumes in moist air because it hydrolyzes to stannic hydroxide. |

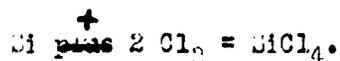


It makes a better and more irritating smoke for shell and hand grenades than either silicon tetrachloride or titanium tetrachloride. It goes through the charcoal and the soda-lime; but is stopped by the layers

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of cotton wool in the canister. Since there is practically no tin produced in this country, silicon tetrachloride and titanium tetrachloride have been developed as substitutes.

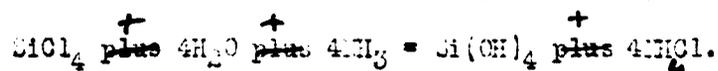
Silicon tetrachloride, SiCl<sub>4</sub>, is made from silicon or from impure silicon carbide by heating with chlorine in an electric furnace



It is a colorless liquid, boiling <sup>at</sup> about 58° and fuming in moist air owing to hydrolysis



It is not much good in shell but is better on moist cool days than on warm dry ones. An ammonia cylinder and a silicon tetrachloride cylinder with liquid carbon dioxide as propellant give a first-class smoke when the jet from the two cylinders impinge



This is used in the Navy smoke funnel to protect vessels from submarine attack and <sup>in</sup> portable cylinders to mask the advance of infantry. By adding a lachrymator to silicon tetrachloride we get a mixture which works well in hand grenades for mopping up trenches.

Titanium tetrachloride, TiCl<sub>4</sub>, is made from rutile, TiO<sub>2</sub>, by mixing with carbon and heating in an electric furnace. A carbide is formed which is said to have the composition Ti<sub>5</sub>C<sub>4</sub>Ti<sub>4</sub>; but the actual composition may vary from this to the carbide TiC. When these products are heated with chlorine, titanium tetrachloride is formed. This is a colorless, strongly refracting liquid which boils at about 136°, is stable in dry air, and fumes in moist air. It is

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said that the addition of water to form  $TiCl_4 \cdot 5H_2O$  gives a good smoke and that the hydrolysis to  $Ti(OH)_4$  gives a poorer smoke. Titanium tetrachloride is poorer than tin tetrachloride and silicon tetrachloride in hand grenades. In the smoke funnel it is better than tin but not so good as silicon. Since it costs more than silicon tetrachloride, it would really be used only in case of a shortage.

GENERAL DEVELOPMENT

In February of 1917, war between the United States and Germany seemed inevitable, so the Director of the Bureau of Mines, Mr. Van. H. Manning, called the attention of the War Department to the already existing technical organization in the Bureau for the study of poisonous gases in mines, and offered the facilities of the Bureau to the War Department for work on poisonous gases in warfare. A meeting was arranged between representatives of the Bureau and the War College, the latter organization being represented by Brigadier General Kuhn and Major L. P. Williamson. At this conference the War Department accepted enthusiastically the offer of the Bureau of Mines and agreed to support the work in every way possible.

Mr. George A. Surrall was detached to Washington in April by Mr. Manning and placed in charge of the work which was carried on with the funds of the Bureau of Mines until July 1, 1917, after which funds were supplied by the War Department and Navy Department.

At the first meeting called by Mr. Manning for the technical solution of some of the problems, there were present:

- Mr. Van. H. Manning, Director, Bureau of Mines
- Mr. Geo. S. Rice, Chief Mining Engineer, Bureau of Mines
- Mr. J.W. Paul, Mining Engineer, Bureau of Mines
- Mr. A.C. Fieldner, Chief Chemist, Pittsburgh Station,  
Bureau of Mines
- Dr. Yandell Henderson, Consulting Physiologist, Bureau of Mines
- Prof. W. E. Gibbs, Mechanical Engineer, Bureau of Mines
- Major L. P. Williamson, War College
- Mr. G. A. Surrall.

In April the following committee on gases used in warfare was formed by the National Research Council for the purpose of cooperating with the Bureau of Mines:

Mr. Van. H. Manning, Chairman, Director, U.S. Bureau of Mines  
 Col. E. I. Libbitt, Officer of Ordnance, U.S.A.  
 Major L. P. Williamson, Medical Department, U.S.A.  
 Lieutenant T. S. Wilkinson, Bureau of Ordnance, U.S.N.  
 Medical Director, J.D. Gatewood, Medical Department, U.S.N.  
 Dr. M. T. Bogert, Professor of Organic Chemistry, Columbia University  
 Dr. Carl L. Alberg, Chief, Bureau of Chemistry, U.S. Department of Agriculture.

A few months later the committee was re-formed, owing to the resignation of certain army and navy officers, as follows:

Mr. Van. H. Manning, Chairman, Director, U.S. Bureau of Mines  
 Dr. Geo. B. Hale, ex-officio, Science and Research Division  
 National Research Council  
 Major R. A. Millikan, ex-officio, Science and Research Division  
 National Research Council  
 Dr. Carl L. Alberg, Chief, Bureau of Chemistry, U.S. Department of Agriculture.  
 Major H. J. Atkinson, Corps of Engineers, U.S.A.  
 Dr. M. T. Bogert, National Research Council  
 Major Bradley Dewey, War Defense Service, Surgeon General's Office  
 Lieutenant Commander A. H. Marks, U.S.N.  
 Lieutenant Joseph K. Phelps, F.A. Surgeon, Bureau of Medicine and Surgery, U.S.N.  
 Captain E. J. W. Kippelie, Bureau of Ordnance, U.S.A.  
 Lieutenant T. S. Wilkinson, Bureau of Ordnance, U.S.N.

After the literature on gas warfare received in this country from France and England had been digested, definite lines of research were mapped out. It was felt that the most important <sup>thing</sup> ~~work~~ <sup>was to develop</sup> ~~to do with the develop-~~ <sup>ment of</sup> gas masks for the army. This meant <sup>studying</sup> ~~working~~ on charcoal, soda-lime, and various mechanical parts of the mask, such as the facemask, elastic, eyepieces, mouthpieces, noseclip, hose, can, valves, etc. Work was started at the Bureau of Mines Laboratory at Pittsburgh. One of the first men added to Mr. Surrell's staff was Bradley Dewey, research chemist for the American Sheet & Tin Plate Company at Pittsburgh. It was soon deemed advisable to

separate the manufacturing from the research end. On \_\_\_\_\_, 1917  
 Mr. Bavey was commissioned a major in the Sanitary Corps and was placed in  
 charge of the Gas Defense Service, his duty being to manufacture masks and  
 all appurtenances, while Mr. Burrell remained in charge of all the research  
 work. The Research Staff grew so rapidly that sufficient labor facilities  
 were not available either in Washington or in any one place. Before long,  
 research work was being carried out at the Bureau of Mines, Pittsburgh, Pa.;  
 the National Carbon Company, Cleveland, Ohio; the Forest Products Laboratory,  
 Madison, Wisconsin; the University of Chicago; the research laboratory of the  
 American Sheet & Tin Plate Company, Pittsburgh, Pa.; the Bureau of Chemistry  
 Laboratory, Washington, D.C.; the Yale Medical School Laboratory, New Haven,  
 Conn.; the Massachusetts Institute of Technology, Cambridge, Mass.; the Mellon  
 Institute, Pittsburgh, Pa.; and elsewhere. In the summer of 1917 <sup>the American</sup>

*University generously offered its buildings and (Methodist) labor grounds rent free.  
 These were made with the American University in Washington (Methodist)  
 A good deal of reconstruction was necessary and these  
 buildings to occupy its buildings and grounds. These laboratories became*

available in the autumn, and later the Catholic University of America placed  
 part of its chemical laboratory at the disposal of the Bureau of Mines for  
 research work.

The procurement of toxic gases and the filling of shell was as-  
 signed to the Trench Warfare Section of the Ordnance Department, Captain  
 (afterwards Lt. Colonel) E.J.W. Ragsdale in charge. In June 1917, General  
 Crozier, then Chief of the Ordnance Department, approved the general pro-  
 position, submitted by Captain Ragsdale, of building a suitable plant for  
 filling shell with toxic gas.

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While the regular artillery handle gas shell, special troops are required for cylinder attacks, Stokes mortars, Livens' drums, etc. General Pershing accordingly advised by cable the organization and training of such troops and recommended that they be placed, as in the English Army, under the jurisdiction of the Engineer Corps. On August 15, 1917, the General Staff authorized one regiment of gas and flame troops, which was designated the 30th Engineers. Major (afterwards Colonel) A. J. Atkinson was placed in charge. At first it was intended that this regiment should consist largely of chemists; but it was pointed out by the British officers in this country that this was not necessary; and consequently many of the chemists were transferred so that their special training might be utilized more effectively.

In September 1917 a Gas Defense Field Training Section had been started in the Sanitary Corps under Captain (afterwards Major) J. H. Walton, Jr. It was soon found that neither the Training Section nor the Divisional Gas Officers should be under the Medical Department and in January 1918, the organization was transferred to the Engineer Corps.

In the spring of 1917 Professor G. A. Hulett of Princeton University was sent abroad by the Bureau of Mines and the National Research Council to study the question of gas warfare. It was ~~soon~~<sup>evident</sup> that definite steps must be taken to develop gas warfare and Professor Hulett returned to this country with a letter, dated August 4, 1917, in which General Pershing said: "Dr. Hulett has been of the greatest assistance to this office in the study of its organization of a Gas Service and it is desired to utilize in our organization his very expert technical knowledge. It is recommended that all Chemical or Gas Service of the United States be united under one head who shall be an officer of the United States Army with

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suitable rank, staff, etc. In all technical questions the chemical service of the United States should be guided by the experience of the Service in France as this Service is being developed here and improvements occur which should be adopted here as they appear. A Laboratory Service for the American Expeditionary Force should be organized and sent to France at once. It is desired that the experience and knowledge of Mr. Sallet be utilized in creating this organization and that he be sent as a member of it with appropriate rank. For your information there is enclosed herewith a copy of the Chemical Organization which has been adopted for the American Expeditionary Force, which Mr. Sallet is in a position to explain in all details, and the reasons for its adoption."

On September 3rd, 1917, an order was issued establishing a Department of the American Expeditionary Forces in France to be known as the Chemical Service under Lieut. Colonel (afterwards Brigadier General) W. W. Yates. This is the organization referred to in General Pershing's letter and the details are shown in the organizational chart, which also calls for some kind of administrative centre in the United States. On September 21, 1917, the War College, therefore, submitted a memorandum for the Chief of Staff in which was urged the militarizing of the research laboratory under the Bureau of Mines at the American University. The belief was also expressed that a distinct gas service should be established

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operating under one head, the Director of Gas Service, who should report directly to the Chief of Staff and who should have as his assistants, an Assistant Director of Gas Service in the Ordnance Department in immediate charge of the production of gas shells, projectiles and other offensive apparatus, and an Assistant Director of Gas Service in charge of the Chemical Service Section. The Bureau of Mines objected to this plan on the ground that greater flexibility for research could be obtained under civilian management than under military control. The recommendation was disapproved by the Secretary of War; but on October 16<sup>th</sup>, 1917, the Secretary of War authorized the establishment of a Gas Service in which an officer of Engineers not above the rank of colonel, and recommended by the Chief of Engineers, should be appointed Director of Gas Service and ordered to report to the Chief of Staff for duty. As assistants he was to have one Ordnance Officer not above the rank of Lieutenant Colonel, recommended by the Chief of Ordnance, one Medical Officer not above the rank of Lieutenant Colonel, recommended by the Surgeon General, and one officer of the Chemical Service Section of the National Army, recommended by the Director of Gas Service. There was authorized the raising and maintaining, by voluntary enlistment or draft of a Chemical Service Section of the National Army with the following personnel

Commissioned:

2 lieutenant colonels  
 4 majors  
 6 captains  
 10 first lieutenants  
 25 second lieutenants  
 47 total commissioned

Enlisted:

10 sergeants, 1st class  
 15 sergeants  
 20 corporals  
 50 privates, 1st class, and privates.  
 5. 95 total enlisted.

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On November 1<sup>st</sup>, 1917, there was created the first administrative unit of the chemical service in the United States, which holds also the distinction of being the first recognition of chemistry as a separate branch of the military service in any country or any war. Colonel Chas. L. Potter of the Engineers was appointed Director of Gas Service and Prof. Wm. H. Walker of the Massachusetts Institute of Technology, who had been for a short time in charge of the Helium Production of the Bureau of Mines was commissioned Lieutenant Colonel and made Assistant Director of Gas Service and Chief of the Chemical Service Section. Major S. J. M. Auld, Chemical Adviser to the British <sup>War Military</sup> Mission, and Captain H. W. Dudley <sup>of the British War Mission</sup> acted as liaison officers for offense and defense problems.

On September 26<sup>th</sup>, 1917, General Pershing had cabled:

"Send at once Chemical Laboratory complete with equipment and personnel, including physiological and pathological sections, for extensive investigations of gases and powders. Arrangements made for physiological chief from medical personnel now in Europe. The laboratory is to be auxiliary to the one in the United States and is for local emergency investigations to meet the constant changes in gases and powders used by the enemy and by ourselves."

Dr. W. F. Bacon of the Mellon Institute of Pittsburgh was commissioned Lieutenant Colonel to organize and take charge of the laboratory in France and Prof. G. N. Lewis of the University of California and Dr. W. A. Hamer of the Mellon Institute were commissioned Majors on his staff. Men were secured, a complete laboratory equipment was purchased, and Lieutenant Colonel Bacon sailed for France about January 1<sup>st</sup>, 1918. *Much of the equipment went astray in France and did not become available until May 1918.* All the men in the French laboratory were in uniform and belonged to the same organization, the Chemical Service Section. At the American University Experiment Station of the Bureau of Mines most of the research

men were civilians and those who were in uniform were distributed among the Ordnance Department, the Sanitary Corps, the Corps of Engineers, the Signal Corps, the Aviation Section, and the Chemical Service Section. It seemed wiser to transfer all the chemists in uniform to the Chemical Service Section and to make provision that the civilian chemists might be taken into the Chemical Service Section if they so desired. Accordingly a request was made for an enlargement of the Chemical Service Section so that the personnel should be as follows:

Commissioned

Lieutenant Colonels	2
Majors	20
Captains	30
First Lieutenants	50
Second Lieutenants	125
	<u>227</u>

Enlisted

Sergeants, 1st class	50
Sergeants	75
Corporals	100
Privates, 1st class	100
Privates	200
Total Enlisted	<u>525</u>

This personnel was authorized on February 15<sup>th</sup>, 1918.

In the meanwhile Colonel Potter had retired from the position of Director of Gas Service and had been replaced by Lieutenant Commander A. H. Marke, who resigned his commission in the Navy and was appointed civilian Director of Gas Service. Owing to ill health Mr. Marke did no active work

and all the duties of the office fell to Lt. Colonel Walker until March 1913 when he was transferred to the Ordnance Department, made a Colonel, and given charge of the shell filling plant at Pigewood, Maryland. To succeed him Prof. H. T. Rogert of the University of Columbia, *who was in Washington as Chairman of the Chemistry Committee of the National Research Council*, was commissioned Lieut. Colonel and appointed assistant Director of Gas Service and Chief of the Chemical Service Section.

The personnel authorization of February 15, 1913, was not adequate for long and in April Lieutenant Colonel Rogert requested an enlargement of the personnel to the following amount, which was authorized on May 6th:

Commissioned

Lieutenant Colonels	2
Majors	20
Captains	35
First Lieutenants	111
Second Lieutenants	235
Total Commissioned	395

Enlisted

Sergeants, 1st class	80
Sergeants	120
Corporals	170
Privates, first class	250
Privates	300
Total enlisted	920

Lieutenant Colonel Rogert also recommended on April 17, 1913, that the Chemical Corps, Chemical Service Section, be made a separate organization or corps like the Ordnance or Medical Department, but this was disapproved. Cobalt blue and golden yellow, the colors of the American Chemical Society, were adopted about this time as the colors for the hat cords of the enlisted men, instead of the colors of the Engineers which had been worn hitherto.

With the increasing demands of gas warfare, the danger of a possible shortage of graduate chemists seemed threatened. Therefore, on May

28<sup>th</sup>, 1918, at the urgent request of the Chemical Service Section, the Adjutant General ordered that all enlisted men who were graduate chemists should be assigned to duty where their special knowledge and training could be fully utilized and that they should not be sent overseas unless they were to be employed on chemical duties. It was also ordered that, whenever chemists were needed by one of the Bureaus or Staff Corps, requests should be made of the Chief of the Chemical Service Section for recommendation of men having the qualifications necessary for the particular class of work in question. If men having chemical qualifications were wanted only for a short period of time they would be attached temporarily to the Bureau or Staff Corps, but when the duty was of a permanent nature instructions would be issued covering their transfer. ✓ Whenever the chemists thus attached or transferred were no longer needed for purely chemical duties a report was to be made to the Chief of the Chemical Service Section in order that they might be assigned to chemical duties at other places.

*and six months before fighting At the beginning of May, over a year after the United States entered the war*

*into the line* practically every branch of the United States Army had some connection with Gas Warfare. The Medical Corps directed the Gas Defense Production. Offense Production was in the hands of the Ordnance Department. Alarm devices, etc. were made by the Signal Corps. The Gas and Flame troops formed the 30th Regiment of Engineers and the Field Training Section of the the Gas Defense Training had been transferred from the Sanitary Corps to the Engineers Corps. Research work was being carried on by the Bureau of Mines, a branch of the civilian Department of the Interior. Besides this a Chemical Service Section had been formed primarily to deal with overseas work. While the Director of Gas Service was expected to coordinate all the activities of the various departments dealing with

chemical warfare, he had no authority to control policy, research, or production.

In order to improve these conditions Major General W. L. Sibert, a distinguished Engineer Officer who had built the Gatun locks of the Panama Canal and who had commanded the First Division in France, was appointed Director of Gas Service on May 11, 1918, and was instructed to formulate a plan for better coordination of the several departments dealing with gas warfare. On May 20, 1918, General Sibert sent to the Chief of Staff a request for the following transfers:

- 1st: The Gas Defense Service of the Medical Department.
- 2nd: The Edgewood Arsenal and all operations there and elsewhere that concern the manufacture of gas warfare material, and the loading of shell with gas material.
- 3rd: All proving ground operations that are connected with gas warfare.
- 4th: The manufacture of all signal and alarm devices for gas warfare.

On July 13, 1918, this transfer was authorized and General Sibert took over from the Ordnance Department the whole staff of Edgewood Arsenal under Col. Walker, and from the Sanitary Corps the Gas Defense Service under Lieut. Col. Dewey. Later the Gas Defense Training Section and the Gas and Flame Troops were transferred from the Corps of Engineers to the Chemical Warfare Service. On July 21, 1918, the Medical Section of the Gas Defense Service was transferred from the Sanitary Corps to the Chemical Warfare Service, remaining in charge of Colonel W. J. Lyster who was given a temporary detail under General Sibert. This division was charged with the necessary research work in the medical field pertaining to protective devices and to war gases and other toxic substances; including prophylactic and curative measures in connection with the experimenting, producing, and handling of them; also with the inspection of the organization for protection of employees against war gases and other toxic substances at plants handling these substances, and the making of appropriate reports and recommendations thereon, with a view to developing and standardizing an effective system."

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On June 25<sup>th</sup> President Wilson ordered that the American University Experiment Station be transferred from the Bureau of Mines to the War Department and placed under the Director of Gas Service. In connection with this transfer Secretary Baker wrote President Wilson as follows:

WAR DEPARTMENT  
Washington

June 25th, 1918.

My Dear Mr. President:

In connection with the proposed transfer of the chemical section at American University from the Bureau of Mines to the newly constituted and consolidated Gas Service of the War Department, which you are considering, I am specially concerned to have you know how much the War Department appreciates the splendid services which have been rendered to the country and to the Army by the Department of the Interior, and especially by the Bureau of Mines under the direction of Dr. Manning. In the early days of preparation and organization, Dr. Manning's contact with scientific men throughout the country was indispensably valuable. He was able to summon from the universities and the technical laboratories of the country men of the highest quality and to inspire them with enthusiastic zeal in attacking new and difficult problems which had to be solved with the utmost speed. I do not see how the work could have been better done than he did it, and the present suggestion that the section now pass under the direction and control of the War Department grows out of the fact that the whole subject of gas warfare has assumed a fresh pressure and intensity, and the director of it must have the widest control so as to be able to use the resources at his command in the most effective way possible. The proposal does not involve the disruption of the fine groups of scientific men Dr. Manning has brought together, but merely their transfer to General Sibert's direction.

Respectfully yours

Newton D. Baker.

The President.

Upon receipt of this letter President Wilson wrote as follows to Director Manning in recognition of his services and that of the bureau under him:

THE WHITE HOUSE

26 June, 1918.

Washington.

My dear Dr. Manning:

I have had before me for some days the question presented by the Secretary of War involving the transfer of the chemical section established by you at the American University from the Bureau of Mines to the newly organized Division of Gas Warfare in which the War Department is now concentrating all the various facilities for offensive and defensive gas operation. I am satisfied that a more efficient organization can be effected by having these various activities under one direction and control, and my hesitation about acting in the matter has grown only out of a reluctance to take away from the Bureau of Mines a piece of work which thus far it has so effectively performed. The Secretary of War has assured me of his own recognition of the splendid work you have been able to do, and I am taking the liberty of enclosing a letter which I have received from him, in order that you may see how fully the War Department recognizes the value of the services.

N.

I am to-day signing the order directing the transfer. I want, however, to express to you my own appreciation of the fine and helpful piece of work which you have done, and to say that this sort of team work by the bureaus outside of the direct war-making agency is one of the cheering and gratifying evidences of the way our official forces are inspired by the presence of a great national task.

Cordially yours,

WOODROW WILSON.

Dr. Van. H. Manning,  
Chief, Bureau of Mines,  
Department of the Interior.

In a memorandum to the Chief of Staff on July 5th, 1918, General Sibert proposed to divide the activities of the Chemical Warfare Service into an office organization consisting of a Director, an Assistant Director, a Technical Advisory Staff, a Liaison Service and an Administrative Bureau with the following divisions: Overseas; Research; Development; Proving; Gas Defense Production; Gas Offense Production; and Gas and Flame Troops. He requested the following personnel:

1 major general  
2 brigadier generals  
14 colonels  
51 lieutenant colonels  
180 majors  
464 captains  
857 1st lieutenants  
792 2nd lieutenants  
2361 Total Commissioned

91 master engineers, senior grade  
152 master engineers, junior grade  
13 regimental sergeants major  
24 regimental supply sergeants  
33 battalion sergeants major  
35 battalion supply sergeants  
206 1st sergeants  
363 sergeants, 1st class  
86 mess sergeants  
186 supply sergeants  
947 sergeants  
1912 corporals



The Relations Section, under Col. Bogert, saw to it that men who were essential to chemical industries vital to the war were kept at their posts because they would be of far greater value to the country there than at the front, and a transfer would have curtailed and delayed the output of munitions. This Section also arranged that a certain number of enlisted chemists were sent back to the universities on indefinite furlough to assist in teaching. This was very important because the chemical staffs of the colleges had been badly crippled by the demand for chemists. If the chemical departments had had to give up important parts of their work, there would have been no continuous supply of chemists and the Government would have been handicapped badly, because the war demands for chemists were increasing rapidly. After the armistice was signed, this Section acted for a while as an employment bureau securing positions for chemists who had been demobilized and discharged.

15a

Colonel Bull, Col. Walker, Col. Bogert, Col. Dewey, Colonel Surrall, Col. Dorsey, Major (afterward Lt. Col.) Bacon, and Messrs. Kohler and Lewis, who were in charge of Offense and Defense Problems, respectively in the Research Division. The appended chart shows the administrative organization in the autumn of 1918.

*Inset  
18a*

To meet the needs of the rapidly expanding military establishment abroad, the Adjutant General directed, on September 24, 1918, that two additional Gas and Flame regiments be organized. Several well-known base-ball players were given commissions in order to recruit them to the popularity of the general public which did not understand that these men were selected for their <sup>superior</sup> ability as leaders and not for actual or future ability as athletes.

On October 30, 1918, a final increase in personnel was authorized as follows:

"(1) Under authority conferred by the Act of Congress 'authorizing the President to increase temporarily the military establishment of the United States,' approved May 18, 1917, and the Act of Congress approved July 9, 1918 (Pub. 193), the President directs that, for the period of the existing emergency, the enlisted strength being raised and maintained by draft, the Chemical Warfare Service, exclusive of such as regiments as have been or may be hereafter authorized, and of such personnel as may be authorized by Tables of Organization for the Headquarters of Divisions, Army Corps and Field Armies, shall consist of: —

- |                                |  |
|--------------------------------|--|
| 1 Major General                | 168 Master Engineers, S.G.               |
| 2 Brigadier Generals           | 323 Master Engineers, J.G.               |
| 12 Colonels                    | 34 Regimental Sergeants Major            |
| 65 Lieut. Colonels             | 35 Regimental Supply Sergeants           |
| 275 Majors                     | 41 Battalion Sergeants Major             |
| 646 Captains                   | <del>42 Battalion Supply Sergeants</del> |
| 941 First Lieutenants          | 156 1st Sergeants                        |
| <u>1109</u> Second Lieutenants | 1242 Sergeants, 1st class                |
| 3051 Total Commissioned        | 126 Mess Sergeants                       |
|                                | 166 Supply Sergeants                     |
|                                | 2 Stable Sergeants                       |
|                                | 2074 Sergeants                           |

4064 Corporals  
 132 Buglers  
 570 Cooks  
 388 Mechanics  
 1450 Wagoners  
 1 Horseshoer  
 1 Sandler  
 6234 Privates, 1st Class  
11841 Privates  
 29090 Total enlisted

"and the President further directs that for each Division that has been or may be authorized, there shall be Chemical Warfare Service personnel for the Division headquarters, as is prescribed by the Tables of Organization. That for each 4 combat divisions or Major fraction thereof there shall be Chemical Warfare personnel, as prescribed by Tables of Organization, for Army Corps Headquarters; and that for each 20 Squad Divisions or Major fraction thereof, there shall be Chemical Warfare Service personnel, as prescribed by Tables of Organization, for an Army Headquarters."

Owing to the signing of the armistice on November 11, 1918, this actual personnel was not received.

DIRECTOR OF  
CHEMICAL WARFARE  
MAN GEN W L STREET

ASST DIRECTOR  
BRIG GEN H C HEWCOMER

BOARD OF  
CONTRACT REVIEW

STAFF  
COL W L YOSTER  
LT COL G B THUMMER  
LT COL DON ABERNETHY

MEDICAL  
DIVISION  
COL W L YOSTER

TRAINING  
DIVISION  
LT COL G H LEWIS

RESEARCH  
DIVISION  
COL G A SHERBELL

GAZ DEFENSE  
RESEARCH DIV  
COL A R WALKER

GAZ DEFENSE  
RESEARCH DIV  
COL H R EVANS

GAZ DEFENSE  
RESEARCH DIV  
COL H R EVANS

GAZ DEFENSE  
RESEARCH DIV  
COL H R EVANS

ADMINISTRATIVE SERVICES

PERSONNEL  
SECTION  
MAJ GEN R F MILL

PERSONNEL  
SECTION  
MAJ GEN R F MILL

TRAINING  
SECTION  
COL G H LEWIS

RESEARCH  
SECTION  
COL G A SHERBELL

RESEARCH  
SECTION  
COL G A SHERBELL

RESEARCH  
SECTION  
COL G A SHERBELL

PERSONNEL  
SECTION  
MAJ GEN R F MILL

PERSONNEL  
SECTION  
MAJ GEN R F MILL

TRAINING  
SECTION  
COL G H LEWIS

RESEARCH  
SECTION  
COL G A SHERBELL

RESEARCH  
SECTION  
COL G A SHERBELL

RESEARCH  
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COL G A SHERBELL

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MAJ GEN R F MILL

PERSONNEL  
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MAJ GEN R F MILL

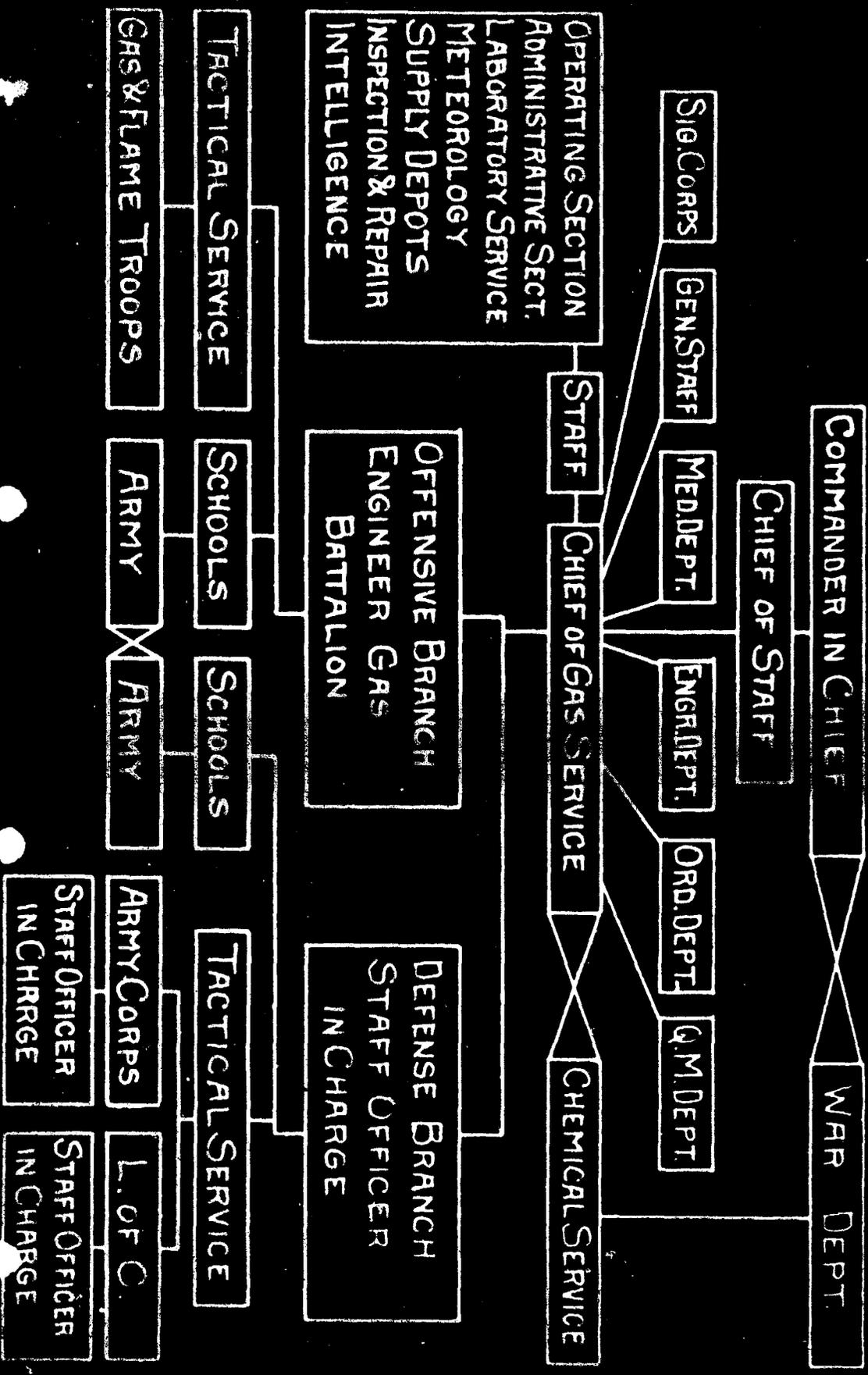
TRAINING  
SECTION  
COL G H LEWIS

RESEARCH  
SECTION  
COL G A SHERBELL

RESEARCH  
SECTION  
COL G A SHERBELL

RESEARCH  
SECTION  
COL G A SHERBELL

AMERICAN EXPEDITIONARY FORCE  
 GAS SERVICE ORGANIZATION  
 SERVICE IN FRANCE SERVICE IN U.S.



(3)

RESEARCH DIVISION

In the preceding chapter it has been shown that the first war work was started in the Bureau of Mines under Mr. Van. H. Manning with Mr. G. A. Burrell in immediate charge, and that various changes took place whereby the organization under Mr. Burrell finally became the Research Division of the Chemical Warfare Service, having been transferred from the Department of the Interior to the War Department, <sup>for</sup> the first five months the research work was done in affiliated laboratories scattered over the country; but in September 1917 the buildings of the American University in Washington became available and what was later the Research Division became known as the American University Experiment Station of the Bureau of Mines. The organization at that time was as follows:

- Van. H. Manning, Director of the Bureau of Mines
- G. A. Burrell, Assistant to the Director, in charge of the Investigations
- L. K. Leslie, in charge of Defense Problems
- Yandell Henderon, in charge of Medical Science Problems
- J. E. Lewis, in charge of Chemical Research
- A. C. Fleisher, in charge of Gas Mask Research
- C. A. Smith, in charge of Hygiene Research
- W. M. McKesson, in charge of Small-scale Manufacturing
- H. H. Clark, in charge of Mechanical Research
- E. K. Marshall, in charge of Instructional Research
- Luson Stone, in charge of Administrative Section.

RESEARCH LABORATORIES

- |  |                                |
|--|--------------------------------|
| Johns Hopkins University,                | L. H. Child and J. L. Frayer   |
| Princeton University,                    | A. H. Haight and T. Lamer      |
| National Carbon Co. Cleveland            | H. C. Anderson and L. C. Shady |
| Helm Park, Cleveland                     | C. H. Correy                   |
| Harvard University,                      | H. F. Keadler and I. Baxter    |
| Yale University                          | H. F. Underhill                |
| Columbia University                      | C. H. Sawyer                   |
| Ohio State University                    | C. E. Beard <i>R. Withrow</i>  |
| Bryn Mawr College                        | H. F. Brunel                   |
| Massachusetts Institute<br>of Technology | S. I. Harrison                 |
| <i>Cornell University</i>                | <i>L. M. Dennis</i>            |

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As time went on there were many changes. Dr. John Johnston was placed in charge of Offense Problems, a position corresponding to that of W. K. Lewis in defense matters. When Johnston resigned to go to the National Research Council, <sup>Dr.</sup> M. P. Kohler was called from Harvard to fill the vacancy. The work on chemical research became more than one man could handle and was divided into two parts, Offense chemical research under J. F. Morris and Defense ~~Chemical~~ <sup>Chemical</sup> Research under A. I. Lane. When Morris left to take charge of the London office, L. W. Jones was called from the University of Cincinnati. Dr. F. F. Underhill was placed in charge of ~~the~~ Therapeutic Research and Major M. S. Minternitz in charge of Pathological Research, both with headquarters at New Haven. The Pharmacological Research was later split into two parts, one under Captain M. K. Marshall and the other under Dr. A. T. Loewenstam. Dr. Loewenstam was appointed advisor on pharmacological problems. When the transfer from the Bureau of Mines to the War Department was made, Messrs. Underhill, Minternitz, and Marshall were transferred to the Medical Division. The Mechanical Research was split into two at one time under H. H. Clark and H. E. Fogler. Later it was consolidated under H. E. Fogler. When Captain (later Major Lt. Col.) McInerney retired, in the fall of 1917, to give his whole time to work for the Ordnance Department, H. E. Rowland took his place. Later this work was consolidated with that of H. W. Taylor under the charge of Mr. Lester. Mr. Lester was commissioned Colonel and placed in charge of the Development Division. Dr. (afterwards Major) Andrew Fox was in charge of the shell-plant manufacturing. Branch Laboratories were also established at the University of Illinois under M. Loewenstam, and Cornell University under H. W.

Briggs, at Yale University under T. B. Johnson, at Clark University under C. A. Kraus, at Worcester Polytechnic Institute under W. B. Jennings, and at Harvard University under Reid Hunt, while the branch laboratory started at the University of Wisconsin had been transferred to the Medical Division.

Dr. Malliken left the Institute of Technology to become a Major in the Chemical Warfare Service with duties at Headquarters.

The Catholic University of America placed a large portion of its new chemical laboratory at the disposal of the Research Division and Columbia University provided facilities for a number of experiments on a semi-large scale. Even after the transfer to the American University, the Pittsburgh laboratories of the Bureau of Mines were used for investigations.

In order to keep in touch with the country at large Secretary Lane appointed an advisory board consisting of W. H. Nichols, Chairman, E. C. Franklin, Wm. Hoskins, C. E. Parsons, Ida Bomsen, T. W. Richards, and F. P. Venable. This board was continued by General Sibert but was never called together by him.

At the time the armistice was signed, the organization of the Research Division was as follows:

- |                          |  |
|--------------------------|--|
| Colonel G. A. Burrell,   | Chief of Research Division                         |
| Dr. W. K. Lewis,         | In charge of Defence Problems                      |
| Dr. E. P. Kohler,        | In charge of Offense Problems                      |
| Dr. Reid Hunt,           | Advisor on Pharmacological Problems                |
| Lt. Col. W. D. Bancroft, | In charge of Editorial Work and Catalytic Research |
| Lt. Col. A. B. Lamb,     | In charge of Defence Chemical Research             |
| Dr. L. W. Jones,         | In charge of Offense Chemical Research             |
| Major A. C. Fieldner,    | In charge of Gas Mask Research                     |
| Major G. A. Richter,     | In charge of Pyrotechnic Research                  |
| Dr. A. S. Loevenhart,    | In charge of Pharmacological Research              |

Major R. C. Tolman, In charge of Dispersoid Research  
Major W. S. Rowland, In charge of Small-Scale Manufacturing  
Major B. B. Fogler, In charge of Mechanical Research & Development  
Captain G. A. Rankin, In charge of Explosives Research  
Major Richmond Levering. In charge of Administrative Section.

*The maximum staff was about 1900, consisting of 1200 technical men and 700 service assistants. The latter included stenographers, clerks, accountants, purchasing agents, machinists, instrument makers, etc.*

The chief functions of the Research Division are:

1. To make and test compounds which may be of value in gas warfare, determining the properties of these substances and the conditions under which they may be effective in warfare.
2. To develop satisfactory methods of making such compounds as seem promising.
3. To develop the best methods of utilizing these compounds.
4. To develop materials which shall absorb or destroy the war gases, studying their properties and determining the conditions under which they may be effective.
5. To develop satisfactory methods of making such absorbents, etc. as may seem promising.
6. To do the research work in connection with masks, canisters, protective clothing, etc.
7. To develop incendiaries, smokes, signals, etc. and the best methods of utilizing them.
8. To co-operate with the manufacturing divisions in regard to difficulties arising during manufacture.
9. To cooperate with other branches of the Government, civil and military, in regard to war problems.
10. To collect and make available to the Director of Chemical Warfare Service all information in regard to the chemistry of gas warfare.

In one sense the research division is the most important of all because without the research work nothing could be done. In another sense it is the least important of all, because it never delivers anything tangible. Its results are turned over to the production divisions which actually make the gases or the masks. A somewhat similar distinction occurs between the production divisions of the Army and the fighting divisions. The soldier can not fight unless he is fed, clothed and armed to some extent; but it is the soldier at the front who <sup>o</sup> sees the actual fighting and drives the enemy back.

As has been stated the term "war gas" is a flexible one and includes solids, liquids, and gases. It is only necessary that the substance should have sufficiently marked characteristics to make it useful in gas warfare. It may be poisonous, like phosgene; it may produce tears, like bromobenzyl cyanide; it may cause nausea, like calocypicrin; it may cause sneezing, like diphenylchlorarsine; it may cause burns, like mustard gas; it may have a foul smell though otherwise harmless, like butyl mercaptan; or it may produce a smoke with high obscuring power, like phosphorus. Of course several of these properties may be combined in a single substance. To be of real value a compound must have some one of these properties to a marked extent. When dogs are exposed for thirty minutes, the concentration which kills is 0.8 mg per liter for calocypicrin, 0.35 mg per liter for phosgene, 0.05 mg per liter for mustard gas. In other words a gas which requires a concentration of 1.0 mg per liter to kill a dog on a thirty minute exposure is scarcely worth considering as a toxic gas unless it has some other striking characteristic such as going through

the mask readily. Most men are lachrymated by bromoacetone at 0.0013 mg per liter, by ~~xylyl~~ xylol bromide at 0.002 mg per liter, and by bromobenzyl cyanide at 0.00033 mg per liter. A substance which requires a concentration of 0.003 mg per liter to cause lachrymation would probably not receive further consideration.

Another determining factor in the use of any gas is the availability of raw materials. It would be useless to consider iodine compounds as toxic gases because it would be impossible to get enough iodine to make a supply of material which would count. The English did use ethyl iodoacetate for a lachrymator at a time when the price of bromine was very high; but lachrymators act at much lower concentrations than toxic gases and are also not used so often. Curare is a deadly poison; but the available annual supply in this country probably does not exceed one gram and the unit for toxic gases is thousands of tons.

A good method of manufacture should be at hand. If the substance is good enough, it will be made by ~~any~~ method, however wasteful, as was shown when the Germans made mustard gas by the chloroacetic method; but this is not true in most cases. The Allies would probably have used trichloroethylchloroformate, superphosite, if a good method of manufacture had been developed; but the waste of chlorine was so great as to overbalance the distinct merits of the compound.

A substance must be stable or fairly stable. If it polymerizes too rapidly, hydrolyzes too rapidly, is too inflammable, or gets its picket on detonation, it cannot be used effectively. Under ordinary circumstances acrolein polymerizes too rapidly to be made in the United States because the shells are likely to be loaded in this country 3 - 6 months before they are

fired. Our limits as to stability against polymerization must therefore be more rigid than those of the British and French who can use their material, if necessary, within a month or two after loading. As a matter of fact the French have used acrolein in hand grenades. While it is possible to stabilize acrolein when made in small quantities, it is doubtful whether this could be done satisfactorily in large-scale manufacture.

Arsenic trichloride hydrolyzes too rapidly to have any value and hydrogen sulphide is so inflammable that it is dangerous to use in cloud attacks, as the English found to their cost. Chloroform decomposes to some extent when fired in shell but not enough to be serious. On the other hand tetrachloro dinitro ethane, an otherwise promising smoke, is destroyed pretty completely when fired in a three inch shell.

It may be worth while to outline the general procedure when a new toxic substance is ~~to be considered~~ <sup>developed</sup> by the Research Division. The substance in question may have been used by the Germans or the Allies; it may have been suggested from outside; or the staff may have thought of it from a search of the literature, from analogy, or from pure inspiration. The Offence Research Section makes the substance. If it is a solid it is sent to the Dispersal Section where methods of dispersing it are worked out. When this has been done, or at once if the compound is a liquid or vapor, it is sent to the Toxicological Section to be tested for toxicity, lachrymatory power, etc. If the report is favorable, the compound is then turned over to a number of different sections.

The Offence Research Section tries to improve the laboratory method of making. When this has been done fairly satisfactorily, the Chemical Production Section starts making it on a large scale, from fifty

pounds to a ton, as the case may be. It then goes outside the Research Division either to the Development Division for further study or to the Gas Offense Production Division for manufacture on a large scale. While the Offense Research Section is working out an improved laboratory method, the compound is sent to the ~~analytical~~ <sup>Gas Mask Research</sup> Section, ~~to~~ <sup>and the Defense Research Section who</sup> develop methods for determining its purity and for analyzing mixtures in air and who make tests to see whether the canisters will stop the substance. chemical

The compound is also sent to the Pyrotechnic Section who study its behavior when fired in shell. If it does not decompose too seriously when detonated, tests are made at Lakenham by the Proving Division in cooperation with the Pyrotechnic Section and the Toxicological Section to learn the effect when shell ~~is~~ loaded with the compound are fired from guns on the range with animals placed suitably in or near the trenches.

While this is going on, the ~~Defense Research~~ <sup>Chemical</sup> Section is studying what change in the ingredients in the canister may be necessary. If the compound is not stopped readily, some new mixture or compound must be developed to meet the emergency. This section together with ~~the analytical~~ <sup>other sections</sup> Section will also work out methods for detecting the gas in the field. The problem of making ointments and special clothing to protect against such things as mustard gas is a problem which is attacked by one or more branches of the defense organization. If a change in the canister is necessary, this is referred to the Mechanical Research Section who may have to develop new filters to protect against smokes. The details in regard to protective clothing are handled in part by this section. The results obtained by the defense organization are transmitted to the Defense Proc-

auction Division which has charge of the commercial production of all defense material.

The Medical Division also studies the ~~wars~~ gases with reference to effect produced, susceptibility of different men, pathological details, and methods of treating gassed cases. With mustard gas it is found that <sup>2-3</sup> ~~about two~~ percent of the men tested are extremely sensitive and <sup>white</sup> ~~about two~~ percent <sup>are to be classed as</sup> ~~extremely~~ insensitive, the supersensitive men being <sup>20-40</sup> ~~perhaps~~ <sup>more than</sup> one hundred times as sensitive as the insensitive men. This is a very important test to make because men who are extremely susceptible are practically certain to become casualties if set to manufacturing mustard gas.

S.A.

9.

The first work of the Research Division consisted in developing the mask and the absorbents, because it was absolutely essential to protect the soldiers against the gases which the Germans were using. On the other hand it is rather more interesting to start with the offense side. In addition to studying the gases already in use by the Germans, it was desired to develop better ones if possible. As a preliminary step this involved a search of the literature to see what was known in regard to toxic gases. Professor Baizeroville sent in an especially long list of compounds that might be of use and others furnished similar information. Professor E. E. Reid organized the chemical laboratories of the country to a considerable extent, getting the various organic chemists to prepare samples of different substances for toxicity tests. After the American University Experiment Station got into full swing, this work was taken over by Dr. (afterwards Lt. Col.) Norris.

It was of course necessary to know the toxicity of these substances and methods were at once developed for doing this. The results were obtained almost exclusively at the American University Experiment Station by the Research Division; but this is purely a consequence of the particular organization and it is therefore wiser to present this work under the Medical Division, which is where it belongs theoretically, though not actually.

In the summer of 1917 the gases which the American Army expected to use on the Western Front were chlorine, phosgene, chlorpicrin, hydrocyanic acid, bromacetone, and xylol bromide, with phosphorus and stannic chloride as the smokes. It was also hoped to use acrolein because it

was not stopped readily by the German mask. A good deal of thought was ~~also~~ <sup>being</sup> given to possible methods of producing high concentration of carbon monoxide because no mask stopped that satisfactorily at that time.

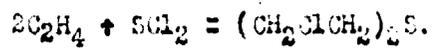
Superpalite was ~~also~~ <sup>another</sup> gas which might be used, though that went into the discard early, because it was harder to make than phosgene and seemed to have no special advantage. It was not till much later that the Allies discovered that the toxic effect of superpalite increased enormously on long exposures, it being, for instance, much less toxic to dogs than hydrocyanic acid on a thirty-minute exposure and more toxic if the exposure lasts two hours.

The use of mustard gas by the Germans in the summer of 1917 and of diphenylchlorarsine in the autumn changed the view-point considerably and the possibility of using cyanogen chloride, cyanogen bromide, or arsine made a great deal of research work necessary, while the development of brombenzyl cyanide by the French and of chloracetophenone in this country destroyed all interest in such lachrymators as bromacetone and xylol bromide.



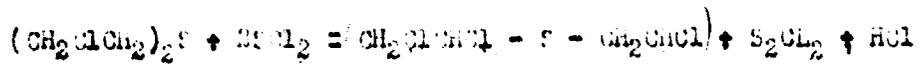
A contract for making mustard gas by this method was made with the Commercial Research Company; but was afterwards cancelled. This is the method by which the Germans made all their mustard gas. The difficult step in it is the manufacture of the chlorhydrine. As this was a commercial product in Germany, it apparently never occurred to the Germans to get a better method and they were handicapped in consequence because they never succeeded in making mustard gas on a really large scale. When they had accumulated enough stock they ~~made~~ <sup>made</sup> a mustard gas attack and then had to wait several months until they could get another supply.

On paper the simplest method <sup>of</sup> making mustard gas is by the interaction of ethylene and sulphur monochloride



This had actually been tried at the Mellon Institute in the autumn of 1917.

The first reaction is the formation of mustard gas; but a side reaction usually takes place rapidly according to the equation



This product is not toxic but boils at almost the same temperature as mustard gas thus giving rise to much confusion until the boiling point was adopted as the criterion of purity.

Early in January 1918 the British learned that Professor Lope had succeeded in making impure mustard gas by this method and a little later Lope made the important discovery that a very pure mustard gas could be prepared by the interaction of ethylene and sulphur monochloride at 60°. The equation may be written

*but it was shown by <sup>Beilstein</sup> (afterwards Major) Conrad that the reaction*  

$$2C_2H_4 + S_2Cl_2 = (CH_2ClCH_2)_2S + S$$
*took place unassistedly in two stages, the first being*



The intermediate product is unstable, splitting off hydrochloric acid readily and going over into thick, black, unobtainable oils. To keep the amount of this product to a minimum it is evidently desirable to have the concentration of ethylene as high as possible. It is practically certain that there is a reversible equilibrium between sulphur monochloride, sulphur dichloride, and sulphur,

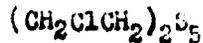


and that the actual reacting substance is sulphur dichloride at low concentration.

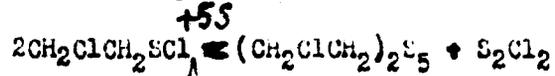
In making mustard by the sulphur chloride process it is not advantageous to go above 50°C because the intermediate product decomposes too readily and an impure product is obtained. At lower temperatures the reaction takes place more slowly; but it was shown by Levinstein in 1914 that this can be counterbalanced by using mustard gas as a solvent and making the sulphur monochloride as a catalyst. In this application it is quite practical to operate *commercially at 30-35°C.* Ethylene is fairly soluble in mustard gas, by keeping this substance always in excess, a relatively high concentration of dissolved ethylene is obtained. This high concentration, increased the speed of reaction sufficiently to compensate for the lower reaction velocity due to the lower temperature. The great advantage of working at the lower temperature is that the free sulphur is kept more easily in colloidal solution, the product being a clear yellow liquid which does not deposit sulphur even on long standing. At higher temperatures it is possible to keep the sulphur in suspension by dissolving 0.2 percent of metallic antimony in the sulphur monochloride. The colloidal sulphur can be precipitated by adding the

mixture to 120° for a few hours and then cooling, or by passing in a little ammonia gas.

The yield of mustard gas is about 85% of the theoretical but only about 50% of the theoretical amount of free sulphur <sup>is found,</sup> the balance probably being present as organic polysulphides, of which one very possibly has the formula



It is thought probable that this product is formed according to the equation

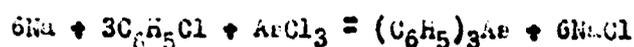


The English made ethylene by the action of concentrated phosphoric acid on alcohol. This was tried out by the Small-Scale Manufacturing Section but was not found so satisfactory as the catalytic decomposition of alcohol by means of kaolin as recommended by the French. Improvements introduced here were the thorough scrubbing of the ethylene and the subsequent drying with sulphuric acid together with the use of filter blocks through which to introduce the ethylene into the reaction kettle. About 700 lbs. of mustard gas were made in consultation by the Research Division before the process was turned over to others for development on a large scale.

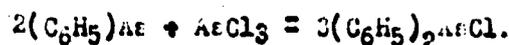
A similar procedure was followed with other gases. The laboratory methods were worked out by the Offensive Chemical Research Section; a considerable amount of the material was made by the Small-Scale Manufacturing Section and then the process was turned over to the Development Division or to the Offensive Production Division as the case might be. ~~In all cases~~ The

Research Division, <sup>always</sup> kept in fairly close touch with the large-scale production, so as to be able to straighten out difficulties that might arise.

In carrying out this programme, the Small-Scale Manufacturing Section made approximately the following amounts of certain gases: mustard gas, 700 lbs.; benzobenzyl cyanide, 600 lbs.; butyl mercaptan, 1100 lbs.; chloracetophenone, 1000 lbs.; diphenylchlorarsine, 4000 lbs.; nitrogen tetroxide, 3000 lbs.; dichloromethyl arsine, 2000 lbs.; diisobutylamine chlorarsine, 4000 lbs.; cyanogen chloride, 4600 lbs.; cyanogen bromide, 600 lbs.; liquid arsine, 2000 lbs.; superpalite, 800 lbs. The manufacture of some of these called for a very extensive preliminary scientific study. For instance diphenyl chlorarsine was being used by the Germans; but nobody among the Allies had any idea how it could be made satisfactorily. It was finally discovered that it could be made in two stages, by the interaction of sodium, chlorobenzene and arsenic trichloride to form triphenyl arsine



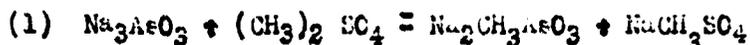
and then heating triphenyl arsine with arsenic trichloride in an autoclave,



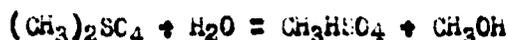
The real problem was not so much the reactions involved as how to handle the sodium properly. The British do it in <sup>in</sup> small lumps; but the American method seems a better one. Twenty-two blocks of sodium weighing <sup>2.5</sup> 2.5 lbs. each were placed on an 8-mesh screen and melted, the oxide and some unreacted sodium remaining on the screen. The melted sodium was driven by carbon dioxide pressure through a special spraying nozzle into cold benzene which was stirred vigorously. This gave a finely divided sodium which reacted readily with chlorobenzene and arsenic trichloride. If the sodium is run in too rapidly, so much benzene is vaporized that a fog is formed. ~~after~~

After the reaction has taken place, the sodium chloride sludge is filtered and vacuum-treated with steam to recover some of the benzene. The yield of triphenyl arsine is about 85% of a product 95% pure.

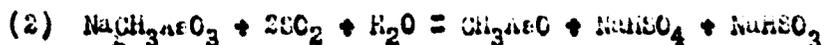
The Germans used ethyldichlorarsine apparently because they had no satisfactory method of making methyl dichlorarsine, which is <sup>a</sup> more satisfactory substance. The Research Division developed methods for making both. The methyl dichlorarsine can be made in three stages, starting with sodium arsenite and making from this disodium methyl arsenite, which is then converted into methyl arsine oxide. The first reaction is carried out at 85°.



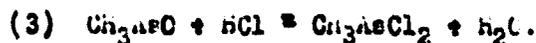
Possible disturbing side reactions are:



Sulphur dioxide is then passed in at 50° - 55°.

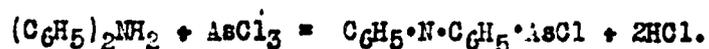


The bisulphite thus formed is decomposed with sulphuric acid because otherwise if sulphur dioxide were set free in presence of methyl dichlorarsine, the escaping gas would carry off a great part of the methyl dichlorarsine with it. The methyl arsine oxide is then converted into methyl dichlorarsine by the action of hydrochloric acid at a temperature above 85°.



16a

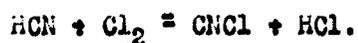
An arsenic compound which formed an excellent smoke was obtained by Dr. (afterwards Major) Adams through the condensation of arsenic trichloride with diphenylamine. The reaction is



The same product was discovered independently but a little later by the British, who assigned to it the structure formula  $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{AsCl} \end{array} \text{C}_6\text{H}_4$ . The substance, which is known as D. M., forms yellow crystals melting at  $193^\circ\text{C}$ . It is strongly irritant to the respiratory tract. A concentration of 0.3 p.p.m. produces a very irritant atmosphere, causing coughing (in some observers), pains in the chest, and to a less extent in the throat and nose, together with the general symptoms of nasal catarrh. Qualitatively the physiological effects of pure D. M. differ considerably from those of diphenylchlorarsine. They develop more slowly and last longer. The method of manufacture is very simple. The arsenic trichloride and diphenylamine are heated together until the temperature of the reacting mass is  $190^\circ\text{C}$ , the temperature is held between  $170^\circ$  and  $180^\circ\text{C}$ , at which point xylene is added to dissolve the D. M. The solution is drawn off, allowed to cool, and the crystals removed by filtration. The yield in the small-scale manufacturing was about 64% of the theoretical.

Cyanogen chloride had been made by the French and their method was adopted here, but a good deal of work had to be done in regard to details. The general method is very simple and consists in the chlorination

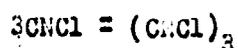
of aqueous hydrocyanic acid at low temperatures.



Two disturbing side-reactions are the hydrolysis of cyanogen chloride in presence of hydrochloric acid



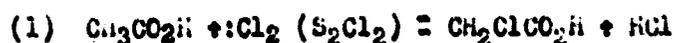
and the polymerization of cyanogen chloride in presence of chlorine.



The actual method was to add chlorine to 8% HCN at temperatures not lower than  $-2^\circ\text{C}$ . or higher than  $+2^\circ\text{C}$ . This extremely narrow temperature range is necessary because the catalytic decomposition by hydrochloric acid becomes serious at higher temperatures, and at low temperatures the rate of chlorination is too slow. After chlorination a little hydrocyanic acid is added to react with any excess chlorine and the product is distilled in a jacketed, discontinuous still with a reflux cooler kept at  $0^\circ-5^\circ$ . The balance of the hydrochloric acid is removed by passing through a tower filled with limestone. The water content can be cut down to 0.1% by means of anhydrous calcium chloride; but this is unnecessary because the product is quite stable when saturated with water (about 1%).

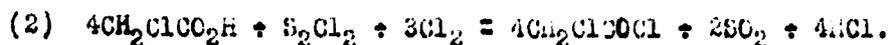
Chloroacetophenone was made by chlorinating acetic acid to monochloroacetic acid, converting this to chloroacetyl chloride, and then causing this product to react with benzene in presence of aluminium chloride.

The chlorination of acetic acid is run at the boiling point in presence of sulphur monochloride.

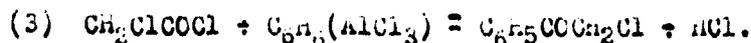


The necessary conditions for a high yield of monochloroacetic acid and a

low one of dichloroacetic acid are effective stirring and rapid evolution of chlorine. It is essential to use pure monochloroacetic acid for the next stage which consists in the chlorination of chloroacetyl chloride at 40° in presence of sulphur chloride.



The third stage consists in the reaction between chloroacetyl chloride and benzene in presence of sulphur chloride.



Chloroacetophenone is an unpleasant substance to handle because it is not only a violent lachrymator but is also extremely painful in its effects on the skin and on the mucous membrane of the nose and throat. Contact with the substance either in the solid or the concentrated vapor form causes an intense burning sensation of the skin which lasts several hours. Washing with water merely aggravates the matter and should be resorted to as little as possible. The best and quickest relief is obtained by washing repeatedly with gasoline or kerosene which dissolve the product and also carry it away by evaporation. On cool dry days the lachrymatory effect is much decreased and it is correspondingly increased in hot, rainy weather. The dry crystals can be handled with comparative comfort due to the limited vaporization at ordinary temperature, while a solution of the product in a readily volatile liquid, such as benzene or alcohol, is much more violent in its effects. Steam is also an excellent carrier.

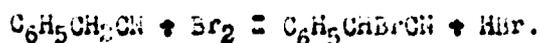
In handling chloroacetophenone, rubber gloves offer a limited protection as the product soon works through the rubber. The fabricant gloves made by the DuPont Company were better in this respect but were

objectionable in being so inelastic and prone to crack. Gas tight goggles had to be worn in the plant practically all the time, and masks were necessary during certain operations.

Brombenzyl cyanide can be made by converting benzyl chloride into benzyl cyanide



and brominating the latter



The method employed in this country was based on the French method but involved a number of modifications.

Dry sodium cyanide will not react with benzyl chloride, and a saturated aqueous solution of sodium cyanide reacts very slowly at the boiling-point of the mixture (about 80°C) even when the stirring is very vigorous. This is due in large part to the immiscibility of the two liquids for the reaction goes practically to completion in three hours if there be added an amount of 95% alcohol equal in weight to the benzyl chloride. It is essential that the benzyl chloride should be fairly pure, ninety-five percent or it boils between 175° and 185° C, the boiling point of pure benzyl chloride being 179° C. Free toluene in the benzyl chloride retards the reaction between sodium cyanide and benzyl chloride. Benzal chloride should be eliminated because it forms benzaldehyde and other more complicated compounds which interfere with the purification of the benzyl cyanide.

After completion of the reaction about 70% of the oil layer in the still is fairly pure benzyl cyanide, while the re-

aining 30% is composed of tarry substances, the formation of which seems unavoidable since no method has been found of preventing their occurrence. After most of the alcohol has been removed by distillation, the ~~crude~~ <sup>cruffy</sup> benzyl cyanide may be subjected to fractional distillation to purify it from unchanged benzyl cyanide and from the tarry matter; but this entails the removal of the residual tar from the fractionating still, which is a very difficult and unpleasent manufacturing operation. The desired result is secured by introducing live steam immediately after the removal of the alcohol and without removing the sodium chloride solution. The oil remains on top of the aqueous solution which facilitates greatly its removal by the steam. The distillation proceeds with no by-product, no increase in the amount of tar, and no decrease in the yield of re-purified benzyl cyanide.

The dried crude benzyl cyanide must be purified by fractional distillation. This involves a high temperature if done at atmospheric pressure and a very careful regulation of the vacuum if done at diminished pressure, because it is necessary to control what the benzyl cyanide should boil at which ~~is~~ <sup>2-3</sup> no rear of 11.7°C, the boiling-point of the pure compound. Some methods were developed successfully; but the fractionation under diminished pressure seems the better of the two. The vacuum obtained at 15.5 inches under which conditions the corrected boiling-point of benzyl cyanide is 150°C. Live steam must not be in contact with the crude benzyl cyanide, because any unchanged benzyl

chloride present will react with the iron with sudden evolution of heat, the reaction taking place with explosive violence. Furthermore, any iron salts which may be carried over interfere with the subsequent bromination. It is therefore necessary to line all iron apparatus. Enamel ware is unreliable at high temperatures and consequently the fractionating still has to be lined with lead. Besides giving a purer product, the distillation under diminished pressure has the advantage of lessening the danger of melting the lead lining of the still.

*Hay* It is possible to get complete conversion of benzyl cyanide to brombenzyl cyanide if conditions are arranged carefully. The pure benzyl cyanide is heated to 70° C and a definite mixture of dry air and bromine vapor is admitted. For a given amount of brombenzyl cyanide, the theoretical amount of bromine vapor is used and the corresponding theoretical amount of hydrobromic acid is evolved. The reaction must be started by sunlight, artificial light, or by admitting some brombenzyl cyanide made in a previous batch. This latter method is by far the easiest for manufacturing purposes and is a sure way of starting the reaction, which then goes to completion without further aid. The hydrobromic acid can be absorbed easily in water or in a caustic soda solution. The bromine must be admitted as vapor. If any liquid bromine comes in contact with the benzyl cyanide, a red oil is formed and this has no chloratory power. The bromine vapor must not be introduced too rapidly as a high concentration leads to the formation of the same dibromide. Sufficient air must be ad-

mitted with the bromine to sweep out the hydrobromic acid or else a hydrobromide may be formed. Too much air must not be admitted because then some of the bromine passes through without reacting. Iron must not be present because it acts as a catalyzer, causing the bromine to substitute in the ring instead of in the side chain. Moisture must be kept out. The bromine vapor may be cut off during a run, if desired; but it is very important not to cut off the air current, unless air alone has been run through long enough to remove all the hydrobromic acid.

When pure, bromobenzyl cyanide melts at  $29^{\circ}\text{C}$ ; but such a product can be obtained only by recrystallizing from alcohol and this is not necessary for war purposes. The melting point of the manufactured product varies between  $15^{\circ}\text{C}$  and  $25^{\circ}\text{C}$ , depending on the purity of the fractionated benzyl cyanide. The product is never a dry solid on crystallization, there always being a slight amount of oil, which is dark brown while the crystals are yellow. The highly purified product is colorless but soon turns yellow owing to incipient decomposition, which apparently stops soon.

Bromobenzyl cyanide is an extremely persistent heavy metal. A number of the 6-inch bombs filled with high explosive and bromobenzyl cyanide were fired in a bomb-pit; and a week later it was impossible to work in the bomb-pit without a mask for more than a few minutes owing to severe irritation. It is the bromobenzyl cyanide which was still present in spite of the fact that the bomb-pit had been washed and covered over with a floor and had been flushed with sodium carbonate solution.

objectionable in being so elastic and prone to crack. ~~As a result~~ ~~it~~ ~~was~~ ~~found~~ ~~that~~ ~~it~~ ~~was~~ ~~not~~ ~~possible~~ ~~to~~ ~~work~~ ~~in~~ ~~the~~ ~~plant~~ ~~practically~~ ~~all~~ ~~the~~ ~~time~~, ~~and~~ ~~repairs~~ ~~were~~ ~~necessary~~ ~~during~~ ~~certain~~ ~~operations~~.

Butyl mercaptan was made by the method outlined by ~~Saunders~~; but all the details had to be worked out here. The laboratory method was developed by Dr. Reid at the Johns Hopkins University. The general method is to pass butyl alcohol vapor and hydrogen sulphide over a specially prepared thoria heated to about 400°.



The catalytic agent is prepared by mixing pure with a saturated solution of thorium nitrate, drying in air, and igniting at 450° in an air current. The final product contains about 24% thoria. There is danger of a side-reaction, the butyl alcohol splitting off water to form butylene instead of reacting with the hydrogen sulphide. ~~A very satisfactory resin, somewhat analogous to diphenylchlorarsine was prepared by Dr. Adams by the interaction of diphenylamine and arsenic trichloride. This product, usually known as D.T., was made independently and very nearly as early by the British.~~

At one time it was thought possible that certain fluorine compounds might be desirable and a method of obtaining fluorine was needed. Heitsch had prepared fluorine by electrolyzing at low temperature hydrofluoric acid to which a little potassium fluoride had been added. Heitsch used a platinum anode; but it was found that the amount of corrosion was too large to make this a possible method on any except the most resistant laboratory acids. A graphite anode went to pieces while merely standing in the acid. It was found however that fluorine could be obtained very satisfactorily by electro-

~~208~~ 24

lyzing a fused bath of acid potassium fluoride at 225° - 250°C in a copper containing vessel using a graphite anode. It is probable that still better results could be obtained with a graphite anode, graphite diaphragm, and graphite containing vessel, this last serving as cathode. No actual use was found for the fluorine and the method was not pushed beyond the laboratory stage.

Boron trifluoride was prepared by heating together boron trioxide, calcium fluoride, and concentrated sulphuric acid. It proved not to be sufficiently toxic for use in chemical warfare and was not a fluorinating agent. No experiments as to the joint action of boron trifluoride and fluorine on organic compounds.

24

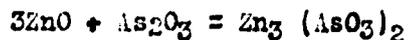
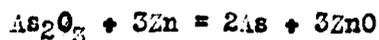
During the war many suggestions were made that arsine should be used. The popular plan was to use magnesium arsenide which would hydrolyze in moist air, setting free arsine. The experiments made by the Research Division showed that the hydrolysis does not take place rapidly enough under ordinary conditions to give an effective concentration of arsine. <sup>At the time of the armistice</sup> Experiments were still under way to determine whether this material could be used effectively in the rain. While the use of magnesium arsenide or of any arsenide was not very promising, there seemed to be a distinct possibility of using liquid arsine. The gas is fairly instable and decomposes into arsenic and hydrogen. On the other hand, the ~~distilled~~ liquid seems to be pretty stable when dry and prevents the decomposition of the vapor. The reason for this is not known definitely. It seems probably that arsine as gas decomposes only in contact with the walls of the containing vessel and that this decomposition is prevented when the walls are wetted with liquid arsine.

The manufacture of arsine takes place in two stages, the formation of zinc arsenide and the decomposition of it. ~~To make~~ <sup>is made in</sup> zinc arsenide, a cast-iron kettle, ~~and~~ <sup>is</sup> painted on the inside with a mixture of graphite and oil to prevent the reaction mixture adhering to the walls. Equal weights of zinc, 10-10 mesh, and metallic arsenic, 10-60 mesh, are well mixed, charged into the cold kettle, covered with a layer of ~~cold~~ charcoal, and heated for 30-40 minutes. When there is a strong evolution of brown fumes, the heating is stopped. The reaction mixture, when cooled, is a brittle coke-like mass which can be removed easily from the kettle. The reaction can be written



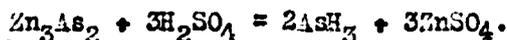
23a

It is important that the zinc should contain less than two percent of oxide and the arsenic less than five percent. The heat of reaction of pure zinc and pure arsenic is relatively low and the reaction is not nearly so violent as with magnesium and arsenic. *When* there are oxides present the reaction becomes more violent, other compounds being formed.



The zinc and arsenic must be mixed in about the proportions indicated. When an excess of zinc is used, the arsenic obtained by decomposing the arsenide contains so much hydrogen as to make the problem of liquefaction a very serious one.

Arsenic is obtained from zinc arsenide by the action of dilute sulphuric acid, 20% by weight, according to the equation



When arsine is ~~evolved~~ <sup>cooled</sup> in presence of moisture, a white crystalline hydrate is formed,  $\text{AsH}_3 \cdot 6\text{H}_2\text{O}$ , which is slightly less dense than liquid arsine, is soluble in it to the extent of 0.3%, and decomposes readily to give metallic arsenic, which may precipitate reddish or in the black metallic form, according to the conditions. It is absolutely essential to remove all moisture from the gas. This can be done by passing the gas over quick-lime. After the arsine has been liquefied under pressure *at a* <sup>temperature of about  $-5^\circ\text{C}$ ,</sup> most of the hydrogen can be separated readily. Owing to the presence of hydrogen it is necessary to run up to 115 lbs. pressure to liquefy the arsine, instead of the 96 lbs. theoretically necessary. The containers for liquid arsine are steel cylinders. The gaseous arsine analyzes about 33.4%  $\text{AsH}_3$ , the remainder consisting of hydrogen and air. The manufacture of liquid arsine was distinctly a creditable performance.

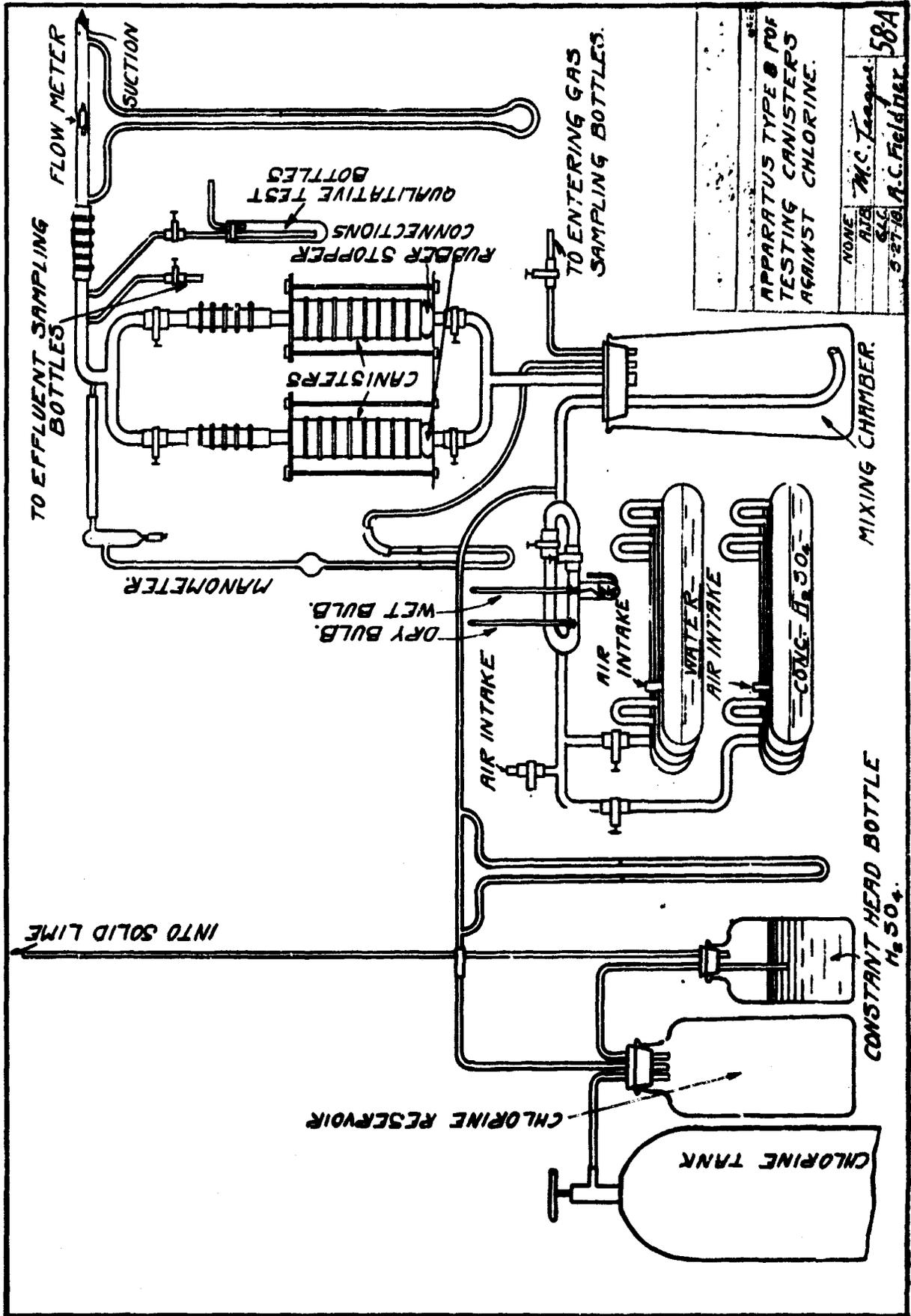
3.

Since the gas is readily inflammable its tactical use presents some difficulties and nobody knows the exact value of the substance as a war gas.

23c

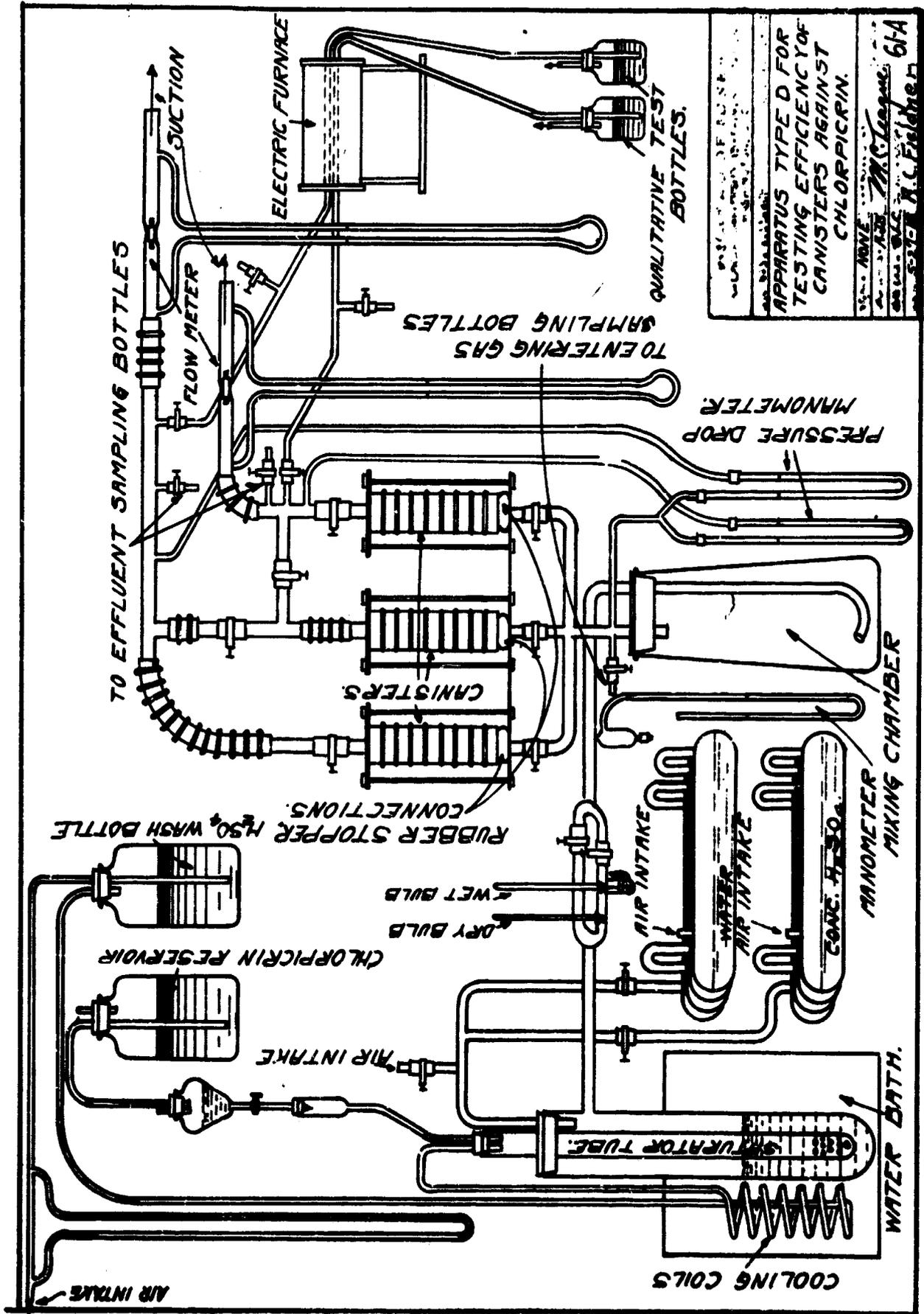
As a preliminary to the study of the properties of toxic gases and of the means of defending against them, it is necessary to be able to detect and determine these gases. An analytical and testing section, *known as the Gas Mask Research Section,* was therefore one of the first to be established and it was kept busy from morning till night in spite of the fact that all the other sections co-operated in developing methods of analysis and testing. The details of analytical methods are not specially thrilling to anybody except a technically trained man, so it will perhaps be sufficient to say that satisfactory methods were worked out for analyzing every toxic gas with which the Research Division had to deal. Three typical cases may be mentioned however, the testing of canisters developed by the Gas Mask Research Section, the field tests for mustard gas developed by the Gas Mask Research Section and the Defense Chemical Research Section, and the special paint for shell developed by the Offense Chemical Research Section.

Canisters are tested on men and on machines. Multiple machines have been developed which will test eight canisters simultaneously at continuous flow of the gas-air mixture or at intermittent flow. The continuous flow machines are the easiest to construct and were made first. Since the man breathes through the canister intermittently, the results with the intermittent flow machines resemble more closely those encountered when masks are actually worn in gas. The intermittent flow machines are capable of wide variation both as to volume of air passing through and as to number of oscillations per minute. They can therefore be adjusted to simulate any type or rate of breathing. Comparison tests on men have shown that the intermittent machines give results in excellent agreement with man tests, are easier to run, and are much more accurate



APPARATUS TYPE B FOR TESTING CANISTERS AGAINST CHLORINE.

NAME	M.C. Jaeger	58A
NO.	616	
DATE	3-27-10	A.C. Fieldner

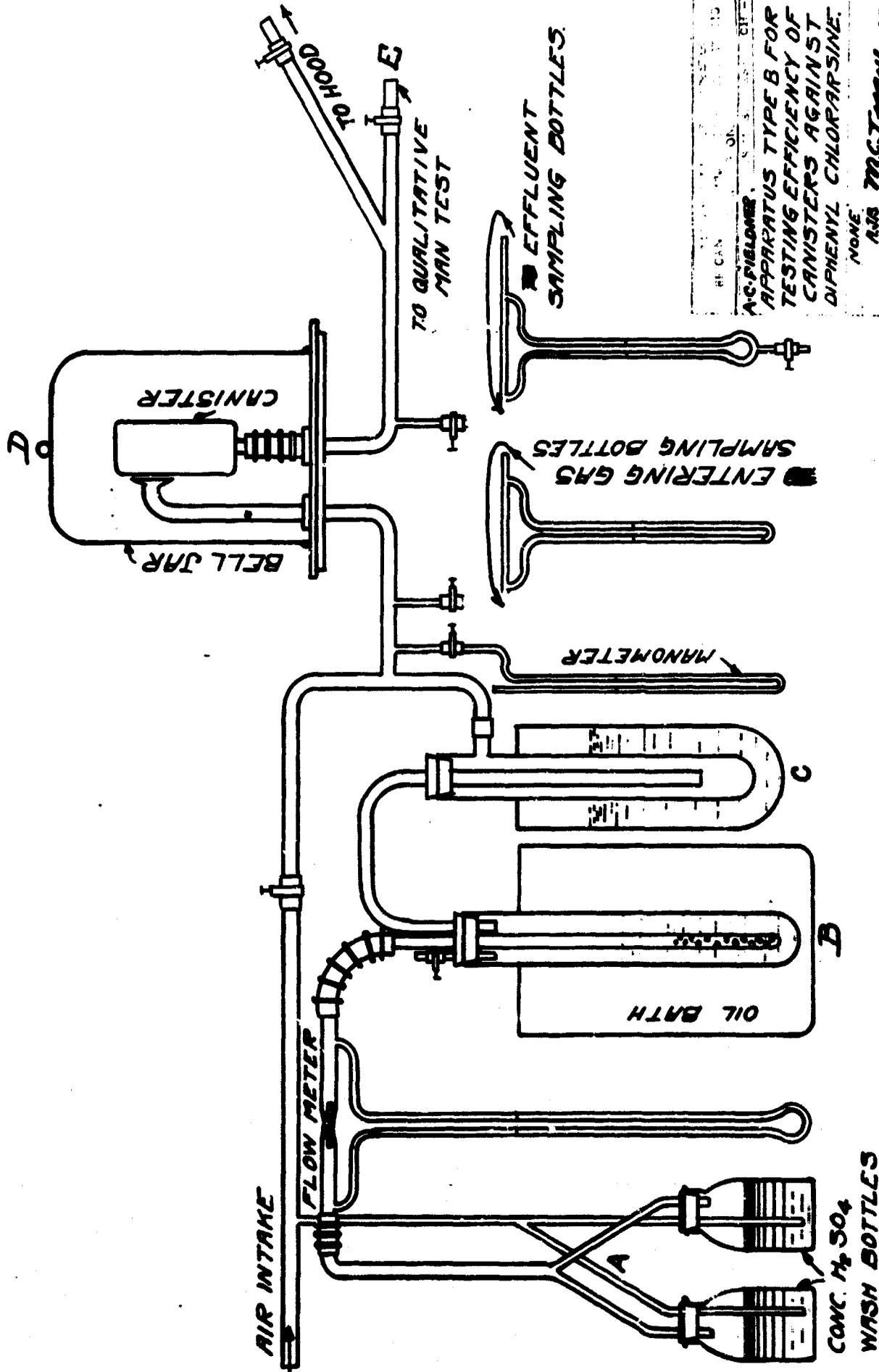


APPARATUS TYPE D FOR  
 TESTING EFFICIENCY OF  
 CANISTERS AGAINST  
 CHLORPICRIN.

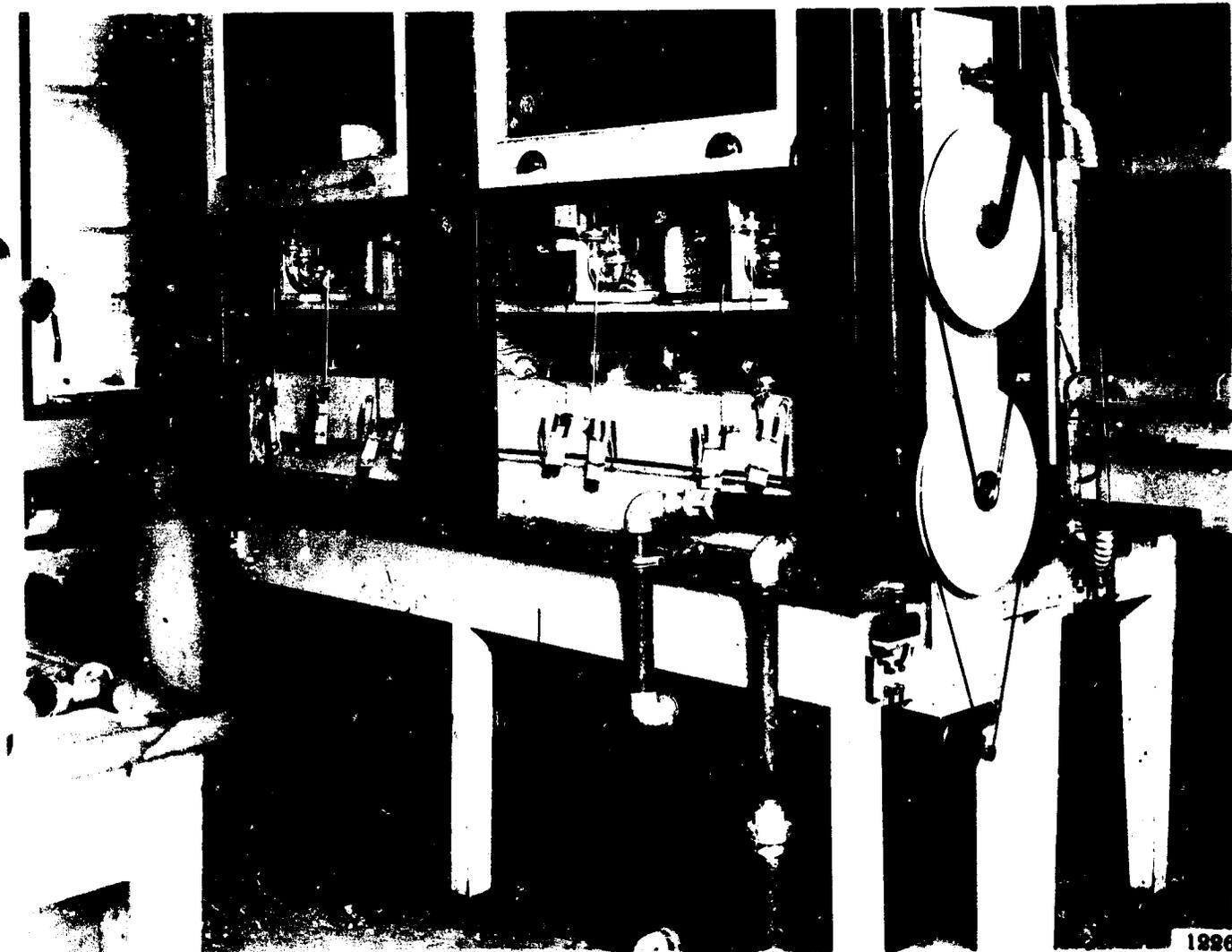
MADE BY  
 THE  
 U.S. ARMY  
 CHEMICAL WARFARE  
 CENTER  
 DURHAM, N.C.

61A  
 1944





RE. CAN. ... OF ...  
 A.C. FIELONER  
 APPARATUS TYPE B FOR  
 TESTING EFFICIENCY OF  
 CANISTERS AGAINST  
 DIPHENYL CHLORARSINE.  
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 A. C. FIELONER  
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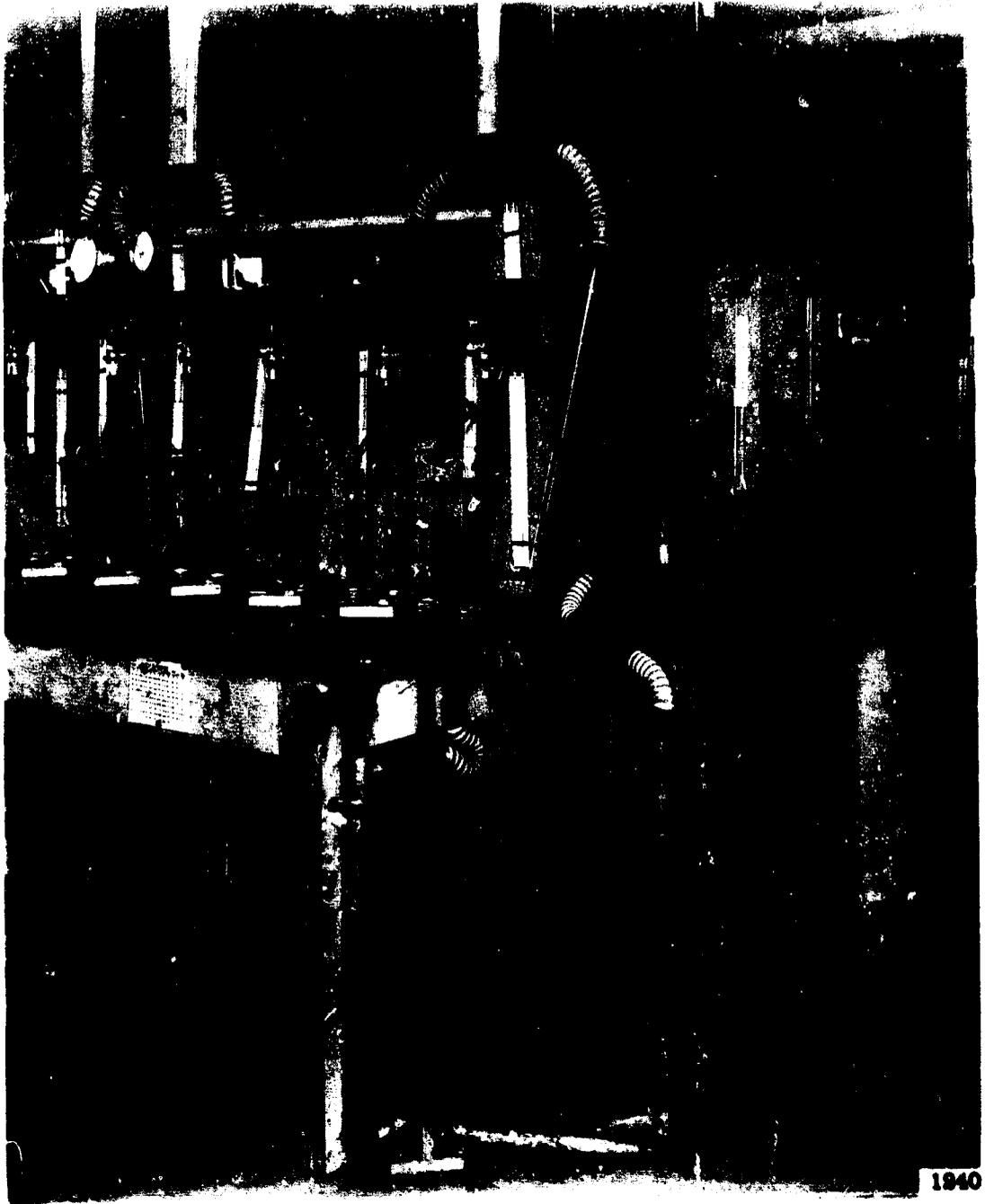


A NEW MULTIPLE MACHINE FOR TESTING CANISTERS

WITH INTERMITTENT FLOW

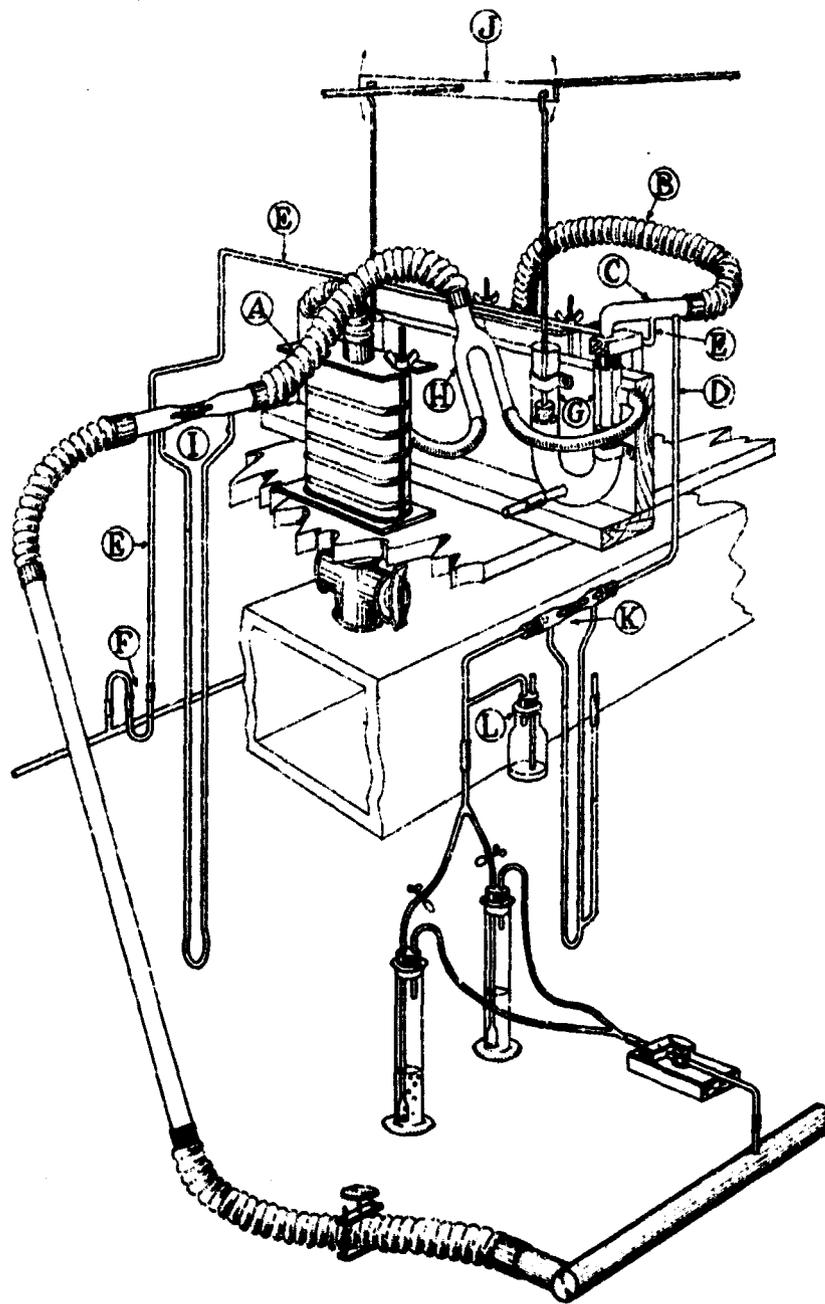
(Rear View)

PLATE XV



A NEW MULTIPLE MACHINE FOR TESTING CANISTERS  
WITH INTERMITTENT FLOW  
(End View)

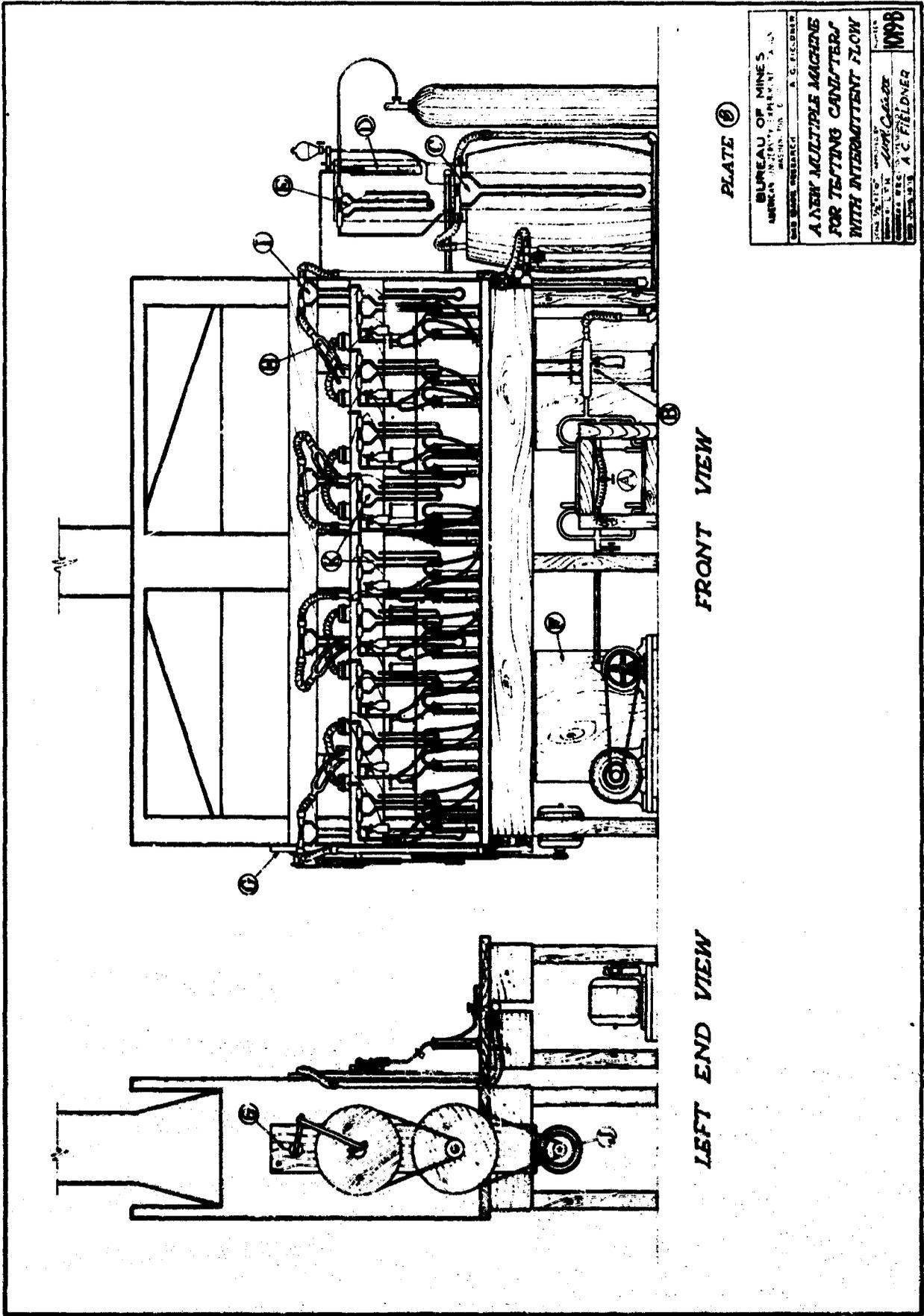
82



DETAIL OF ONE UNIT

PLATE 4

BUREAU OF MINES	
DEPARTMENT OF THE INTERIOR	
WASHINGTON, D. C.	
Geological Survey	Division of Mines
A NEW MULTIPLE MACHINE FOR TESTING CARBIDES WITH INTERMITTENT FLOW	
Author	A. C. FIELDNER
Editor	A. C. FIELDNER
Printer	1919

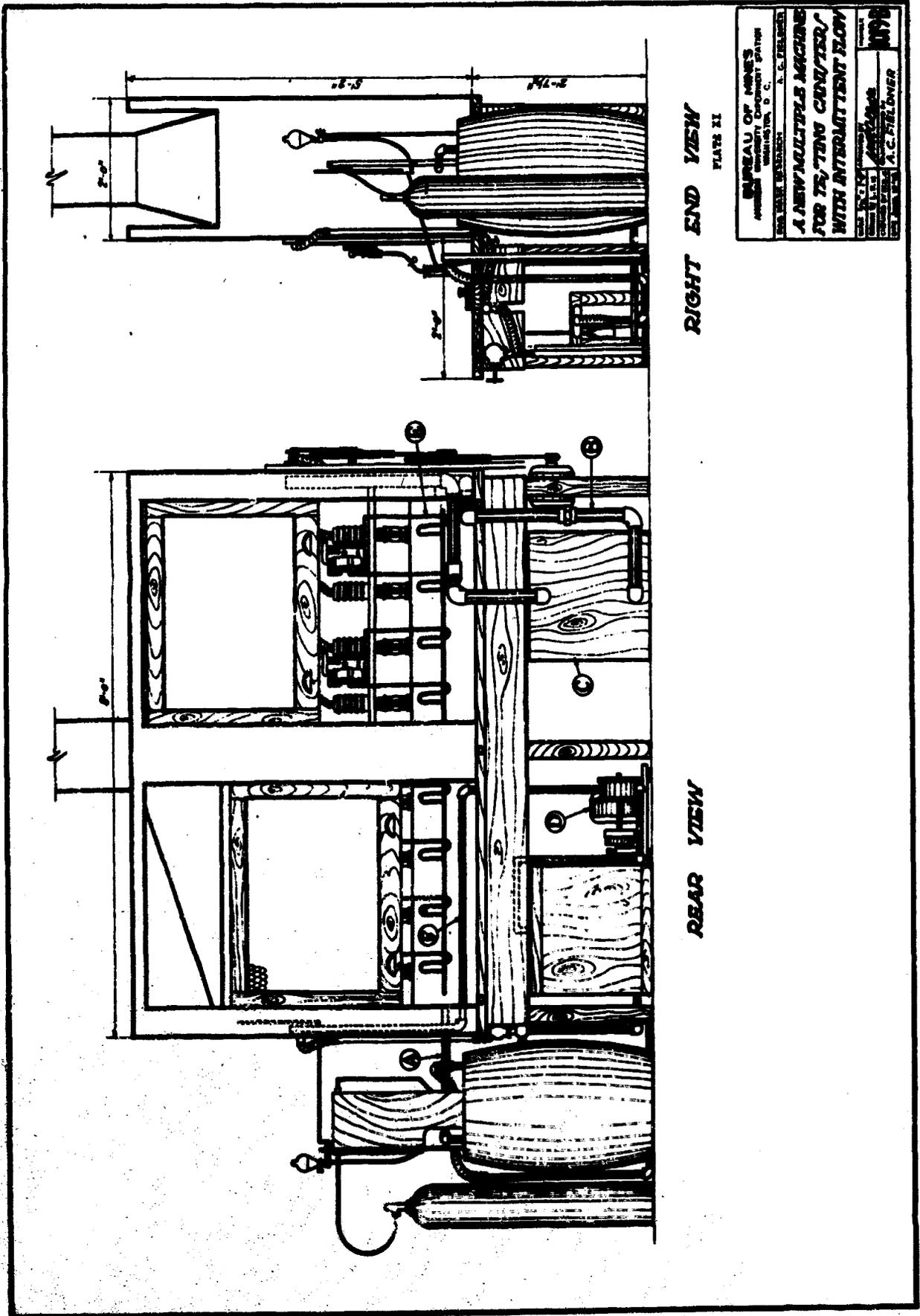


FRONT VIEW

LEFT END VIEW

PLATE 8

BUREAU OF MINES  
 AMERICAN INDIAN PRESENT  
 WASHINGTON, D. C.  
 GAS ENGINE SUBJECT A. C. FIELDNER  
 A NEW MULTIPLE MACHINES  
 FOR TESTING CAPACITORS  
 WITH INTERMITTENT FLOW  
 DRAWN BY  
 J. C. CASPER  
 CHECKED BY  
 A. C. FIELDNER  
 10998



RIGHT END VIEW

REAR VIEW

PLATE XI

BUREAU OF MINES  
 UNITED STATES DEPARTMENT OF THE INTERIOR  
 WASHINGTON, D. C.

DESIGNED BY  
 A. C. FRIEDLBERGER

DATE  
 1918

A NEW MULTIPLE MACHINE  
 FOR TESTING CONDUITS  
 WITH INTERMITTENT FLOW

2.

because they do away with the personal idiosyncrasies of the men. This does not mean that man tests should be abolished. They must always be kept to provide for unexpected contingencies but they can be reduced to a minimum with a great saving of time and friction.

In the earlier man tests the men were sent inside a gas chamber; but afterwards the canisters were connected by tubing to the gas chamber and the men sat outside the chamber. This made it possible to run more tests simultaneously and had the further advantage that the man in charge of the testing could determine for himself whether any given canister had broken down or whether the report was due to nervousness on the part of the subject. All the toxic gases can be detected at concentrations which do no harm to the individual. There are two extremes to be guarded against. The man who is testing the canister may imagine that gas is coming through when that is not the case, or he may be so anxious to avoid giving a false report as to continue the test too long and consequently get gassed slightly. With the men accessible outside the chamber, it is a comparatively simple matter to guard against both these possibilities.

The man test is only run until gas is detected coming through the canister; but the machine test can be run farther. It is customary to designate the time at which gas can be detected coming through the canister as the "breakdown". Up to then all the gas was removed by the materials in the canister. The 99%, 95%, 90% points, etc. are the points at which 99%, 95%, 90%, etc. of the gas is stopped and 1%, 5%, 10%, etc. of the gas in the air comes through.

~~Trained observers can detect mustard gas by smell at 0.1~~

25.

25a

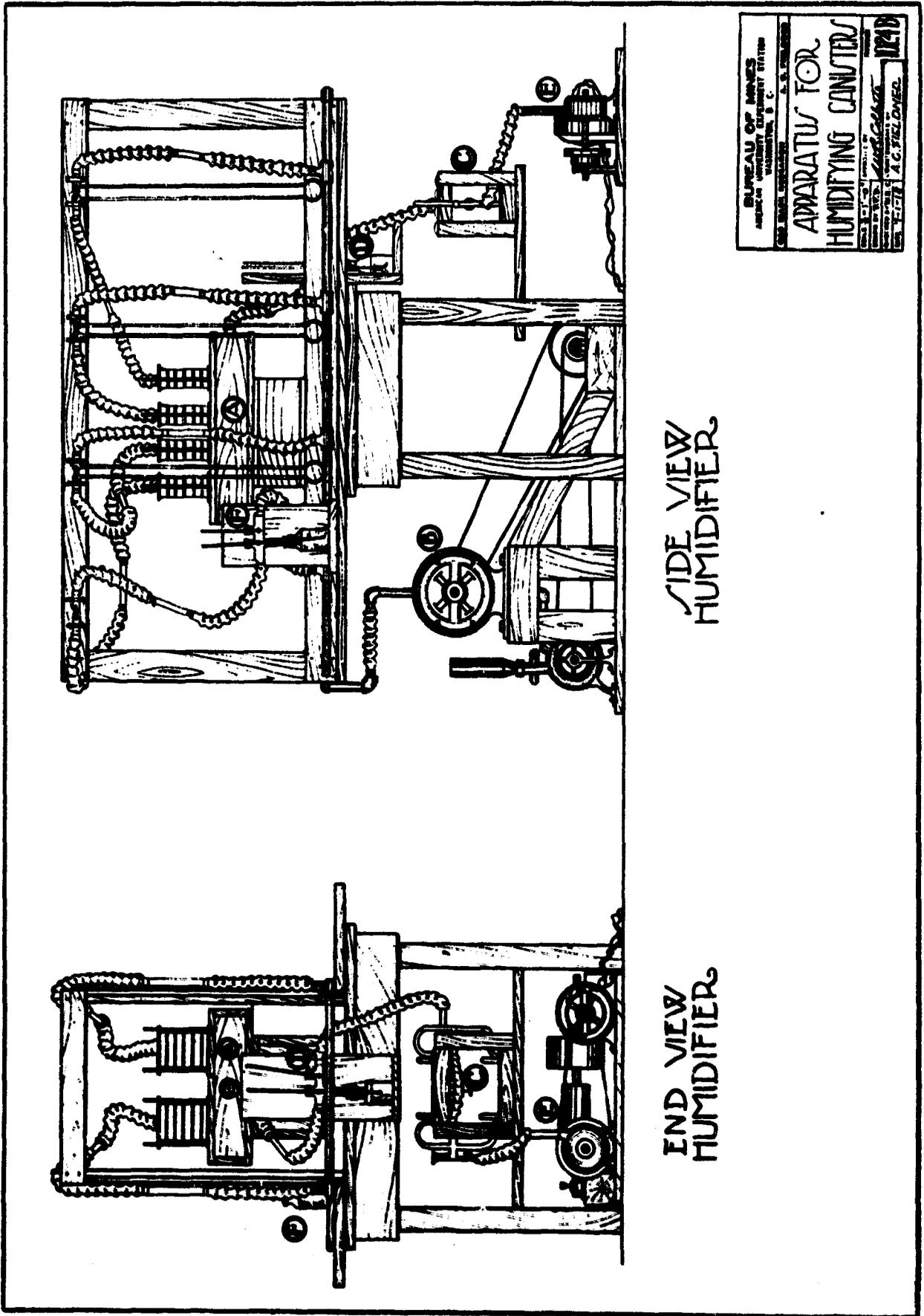
When testing the variations in absorbents, the absorbent is filled into a sample tube, of specified diameter, to a depth of 10 cm. by the standard method of filling, and gas passed through under definite conditions. The following summary of conditions for standard tube tests on absorbents were adopted as official by the Research Division and the Defense Production Division.

<u>Gas</u>	<u>Conc.</u> <u>p.p.m.</u>	<u>Rate per</u> <u>cm<sup>2</sup>/min.</u>	<u>Depth</u> <u>cm.</u>	<u>Diam.</u> <u>cm.</u>	<u>Relative</u> <u>Humidity</u>
Chlorpicrin (1)	7,000	1,000	10	1.41	0
Chlorpicrin	1,000	500	10	2.0	50
Phosgene (1)	10,000	500	10	2.0	50
Superpalite	1,000	500	10	2.0	50
Arsine	1,000	500	10	2.0	50
Hydrocyanic Acid	1,000	500	10	2.0	50
Cyanogen Chloride	1,000	500	10	2.0	50
Chlorine	10,000	500	10	2.0	50
Sulphur Dioxide	10,000	500	10	2.0	50

(1) Accelerated test.

If only one point is reported, it is assumed to be the copper flame break-point in the case of chlorpicrin and the 99% efficiency point in all <sup>other</sup> cases.

When testing variations in the quality of charcoal, the standard chlorpicrin test with a concentration of 1,000 p.p.m. was for a long time the only one in use. As the charcoals improved, the time necessary to make a test became too long. Laboratory charcoals have stood up for 1200 minutes or more against chlorpicrin. To enable more tests to be run, the accelerated chlorpicrin test was introduced using



SIDE VIEW  
HUMIDIFIER

END VIEW  
HUMIDIFIER

BUREAU OF MINES  
 UNITED STATES DEPARTMENT OF THE INTERIOR  
 WASHINGTON, D. C.

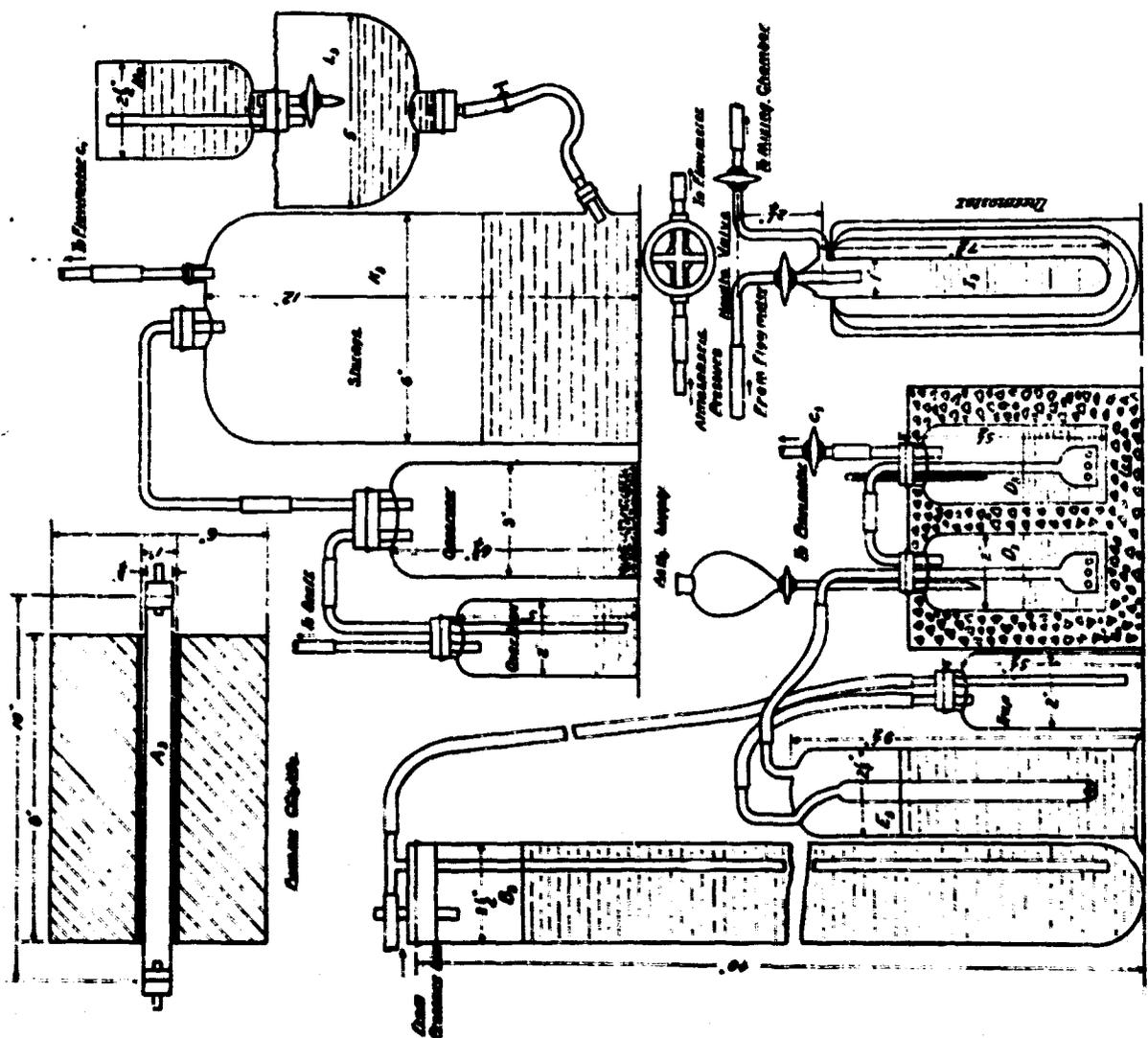
APPARATUS FOR  
 HUMIDIFYING CANSTERS

DESIGNED BY  
 JAMES C. HARRIS

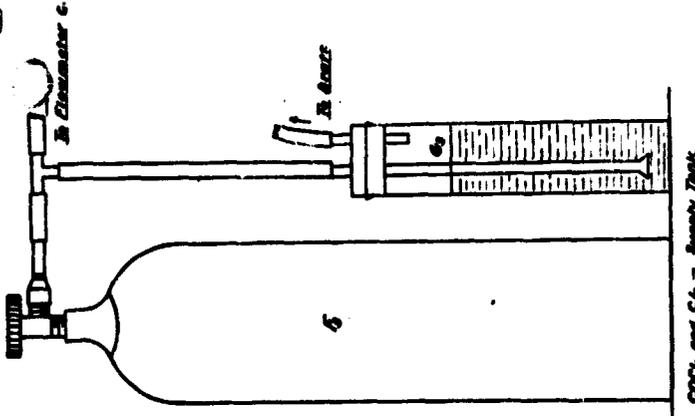
FILED  
 A. C. STELLINGSMA

1924

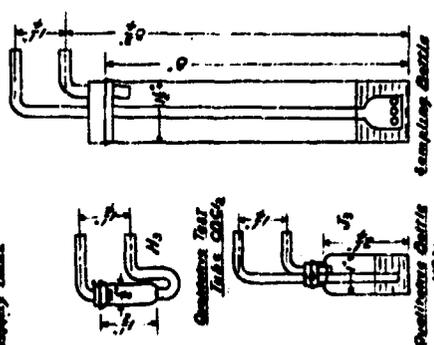
Velocity Chamber



Cal. 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280, 300, 320, 340, 360, 380, 400, 420, 440, 460, 480, 500, 520, 540, 560, 580, 600, 620, 640, 660, 680, 700, 720, 740, 760, 780, 800, 820, 840, 860, 880, 900, 920, 940, 960, 980, 1000



CO<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> - Supply Tank



Purification Chamber  
MCA  
CCl<sub>4</sub> Ag.  
Sampling Bottle

ARMY AND NAVY  
WAR GAS INVESTIGATION  
AMERICAN UNIVERSITY  
EXPERIMENT STATION  
Bureau of Mines, Washington, D.C.  
Series 7-8  
17-1208  
STANDARD TWO TUBE  
ABSORPTION APPARATUS  
Copyright 1918  
A-3

End View of Chamber

FIG II

G-41 APPARATUS

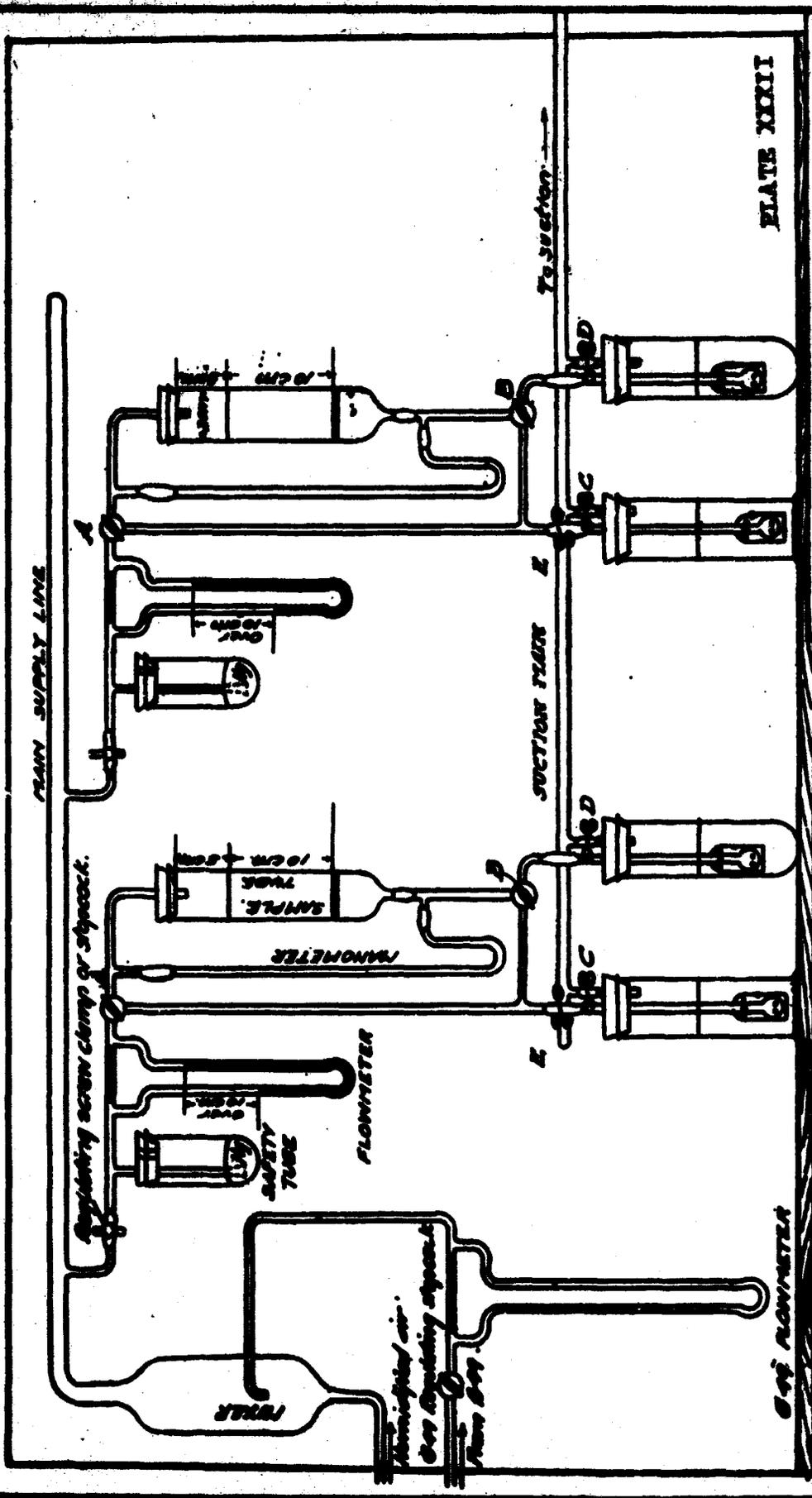


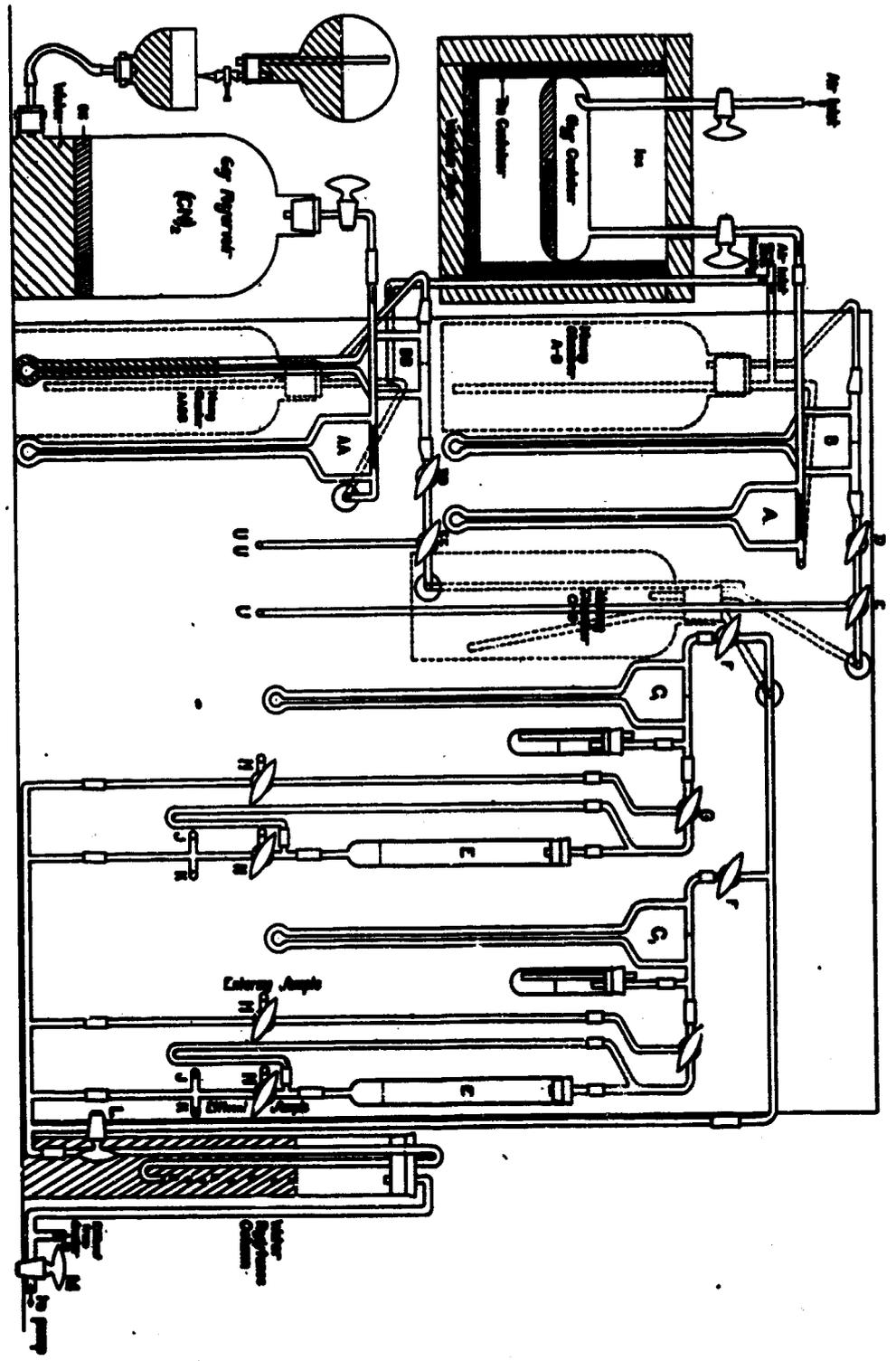
PLATE XIXII

BUREAU OF MINES - MINE GAS INVESTIGATIONS  
 GAS DEFENSE SERVICE  
 COMMITTEE ON TESTING GAS MASK ABSORBENTS

QUANTITATIVE  
 TUBE

Date June 22, '19  
 Drawn by J.S.M.

Checked by  
 Approved by

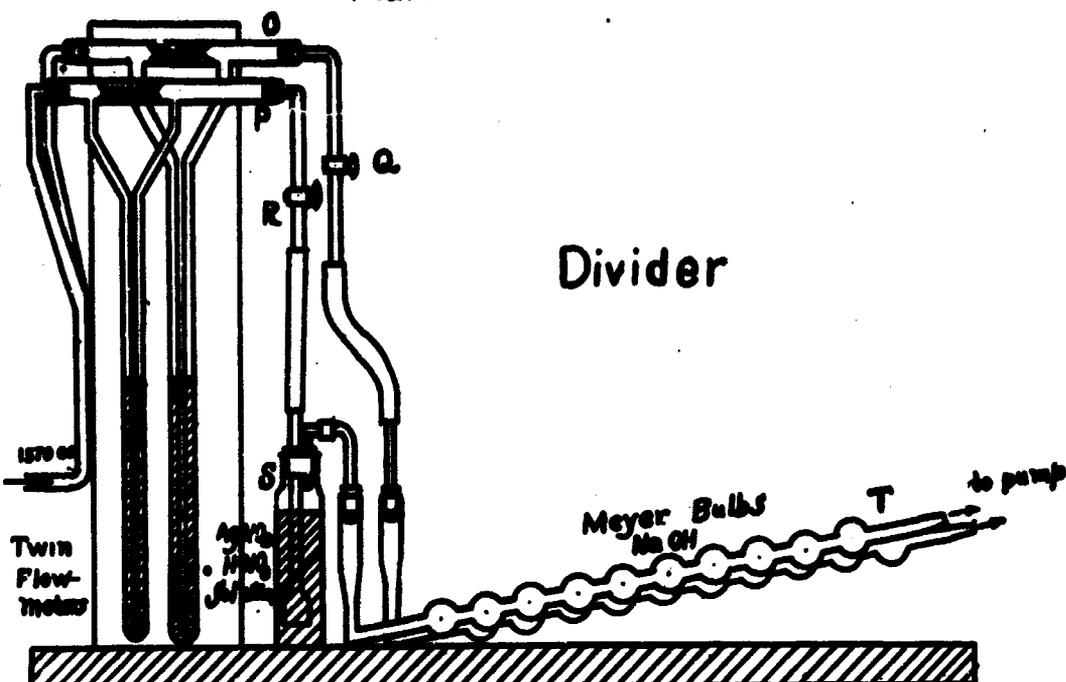


Front of Board (Partial top view indicated on back)

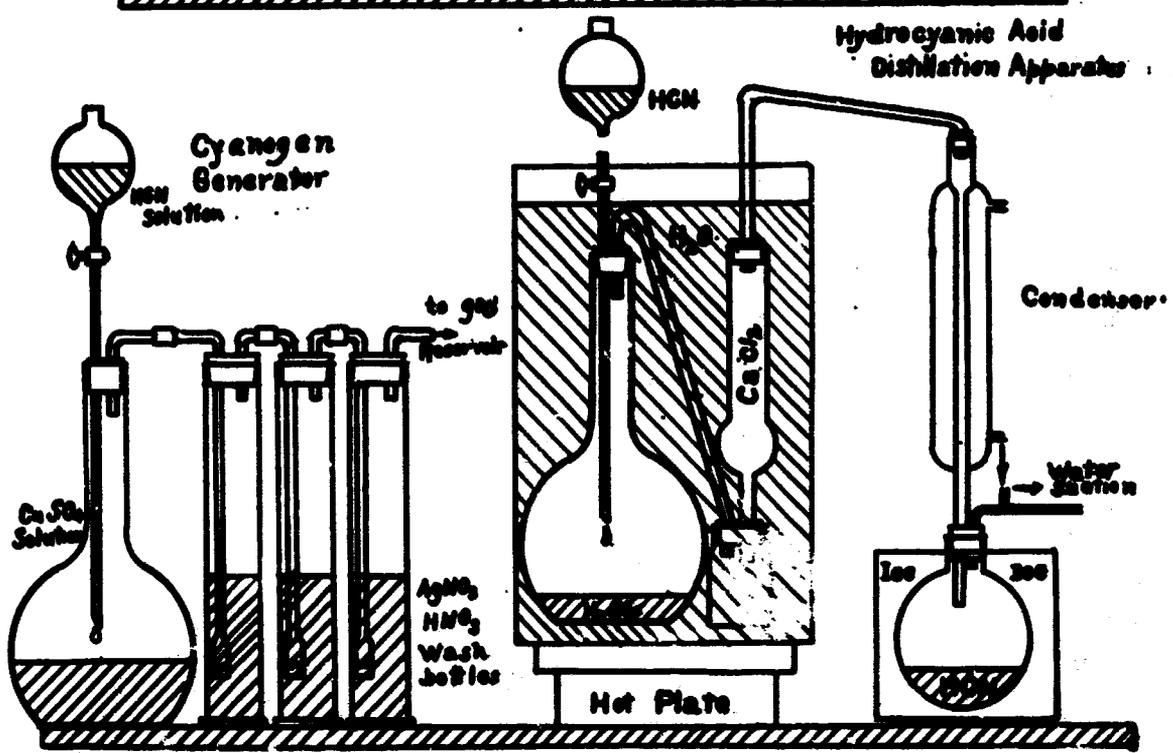
SCALE 1 2 3 4 5 6 7 8 9 10

THE TUBE ARRANGEMENT FOR  
 TESTING ADVANCED TYPE  
 RANGE OF MATERIALS  
 THE TUBE ARRANGEMENT FOR  
 TESTING ADVANCED TYPE  
 RANGE OF MATERIALS  
 THE TUBE ARRANGEMENT FOR  
 TESTING ADVANCED TYPE  
 RANGE OF MATERIALS

Plate I



Divider



Hydrocyanic Acid Distillation Apparatus

Cyanogen Generator

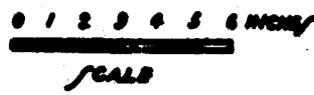


PLATE XXVI  
 BUREAU OF MINES  
 U.S. DEPARTMENT OF THE INTERIOR  
 GEORGE W. BRIDGES, CHIEF  
 A. C. FLEMING  
**ACCESSORY APPARATUS**  
 FOR  
**MIXTURE MACHINE**

REPORT SL-251.118-D

FIG 2.

CO<sub>2</sub> BOARD

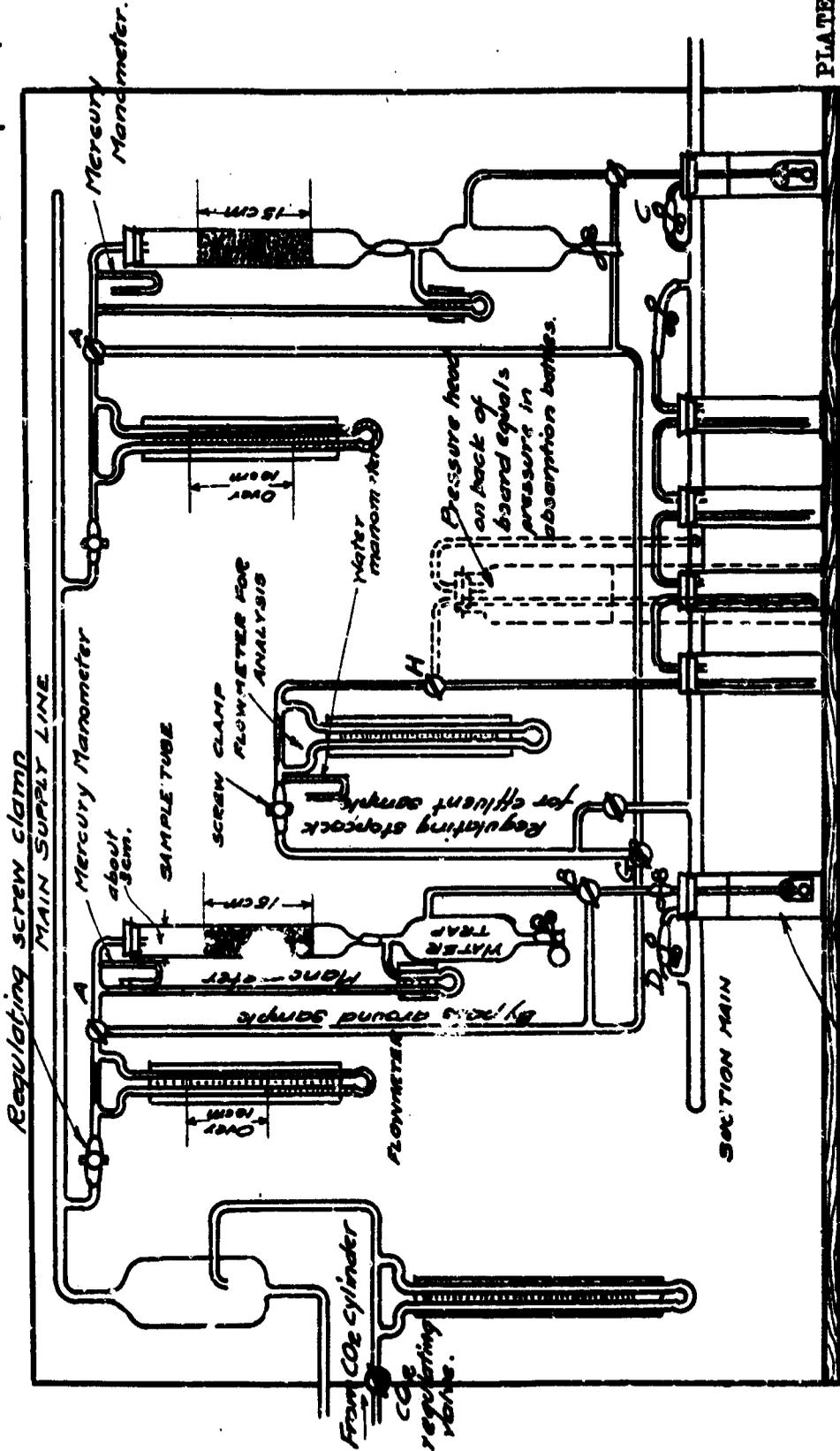


PLATE XXXIX

QUALITATIVE TEST  
ABSORPTION TUBES  
FOR QUANTITATIVE ANALYSIS

WAR DEPARTMENT  
 CHEMICAL WARFARE SERVICE      RESEARCH DIVISION  
 SODA LIME UNIT                      DEFENSE SECTION  
 EXPERIMENT STATION, AMERICAN UNIVERSITY, WASHINGTON, D. C.  
 Checked by Frank H. McComb Date Nov 14, 1918  
 Approved by C. W. Parsons      Drawn by J. S. Miller.

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a concentration of 7000 p.p.m., decreasing the diameter of the tube, and doubling the rate of flow. The outgoing gas passes over a copper spiral heated by a burner. The appearance of a green flame is taken as the end-point. Just before the green flame is visible there appears a preliminary orange color which may be used as a warning. It is not known whether the appearance of the orange flame would make a more sensitive end point or not.

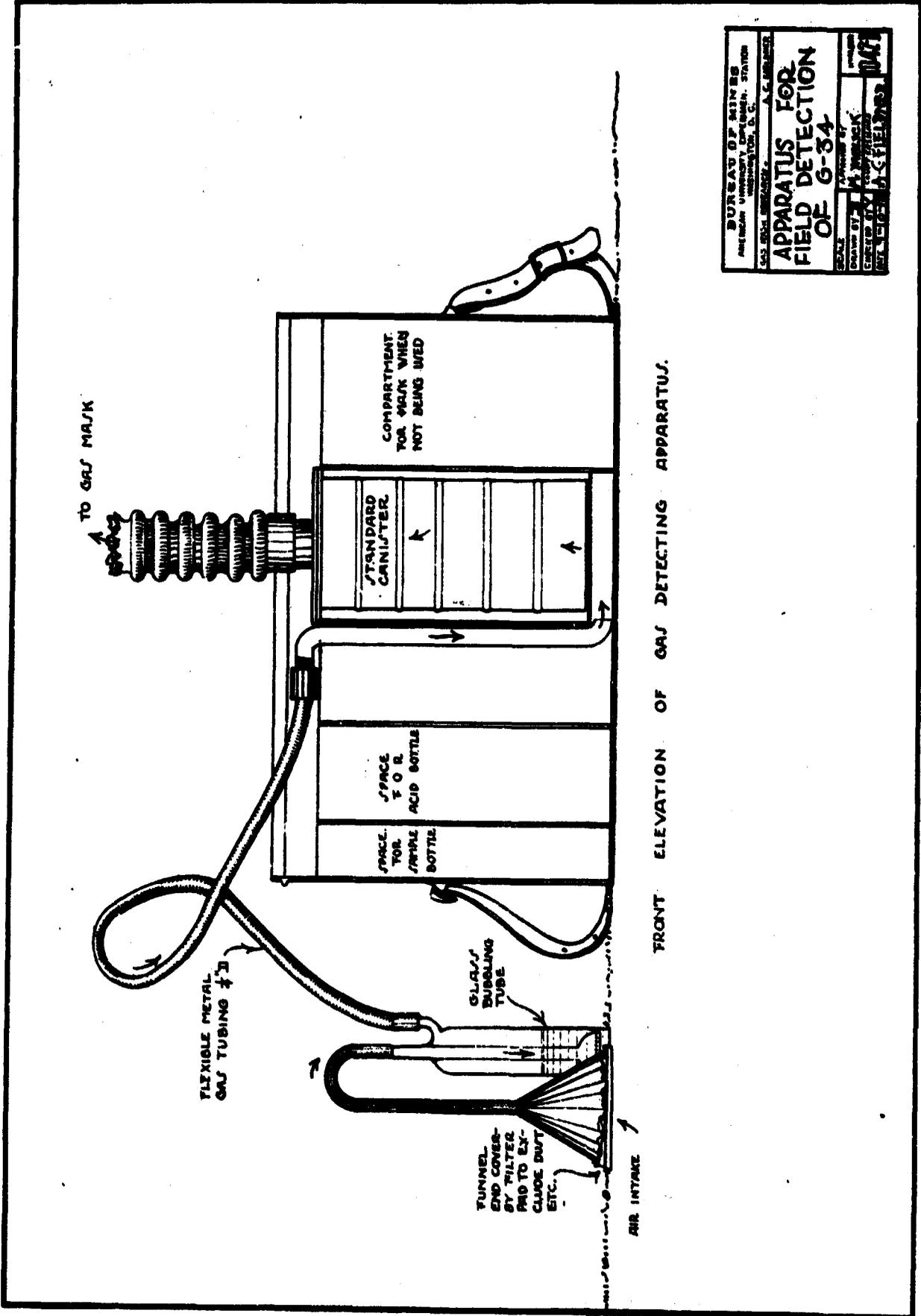
It is usually assumed that the service times with the standard method are fourteen times those with the accelerated method, and this factor is often used. There are two sources of error here. The air is run through moist in the standard test and dry in the accelerated test. It is quite possible, though not proved, that the relative effect of moisture might vary with different charcoals. The second source of error is a real one. It has been shown by Dr. Patrick that with the high concentrations of chlorpicrin used in the accelerated test, there may be actual condensation of liquid chlorpicrin in the pores of the absorbent. This chlorpicrin is held loosely and will be given up readily when air passes over the charcoal. This actually occurs with the German charcoal. When this is run to the break-point with the accelerated chlorpicrin test, and then dry air is passed over the charcoal, 70% of the chlorpicrin is removed, whereas only 10% is lost by the American charcoal under the same conditions. An absorbent with a low absorbing power, but with a fine-grained structure may show up very well on the accelerated test and not well at all on the standard test. Since the concentrations of the standard test are more nearly those of the battlefield, the results with the standard test are the ones to be trusted.

Trained observers can detect mustard gas by smell at 0.1

3.

p.p.m. (0.0007 mg. per liter); but only for the first minute or two of exposure. Low concentrations of mustard gas vapors, when in contact with a dilute solution of selenious acid, produce an orange-colored colloidal suspension of selenium which gradually increases to a deep brick-red color in time if the concentration of mustard gas is sufficient. The test is sensitive to about 1 p.p.m. (0.0007 mg. per liter). This method is not specific because arsine gives a similar precipitate in less time than does mustard gas, and other compounds such as diphenylchlorarsine and butyl mercaptan give positive results. As against this, chlorine, hydrogen chloride, phosgene, chlorpicrin, and superpalite give a negative test even when present in fairly high concentrations.

While the copper flame test is not sufficiently sensitive to permit of direct detection of low but toxic concentrations of mustard gas, it has been found possible to modify the method so that one can detect 0.1 p.p.m. (0.007 mg. per liter) or even 0.01 p.p.m. under special conditions. The method consists in passing air containing mustard gas through a quartz tube over a fine ~~coiled~~ <sup>wound</sup> cylinder of copper gauze about four inches long, which fits snugly into the tube and which is heated at the tip at the inlet through the tube by a small flame. As the mustard gas passes over the heated tip of the copper gauze, it is broken down and the halogen is absorbed by the cooler portion of the gauze beyond. After a period of accumulation, the gauze is moved slowly into the flame and heated directly, the presence or absence of a green color being noted. The principle has been embodied in a portable field apparatus. The method is really one for halogens and is not specific for mustard gas. Its usefulness



FRONT ELEVATION OF GAS DETECTING APPARATUS.

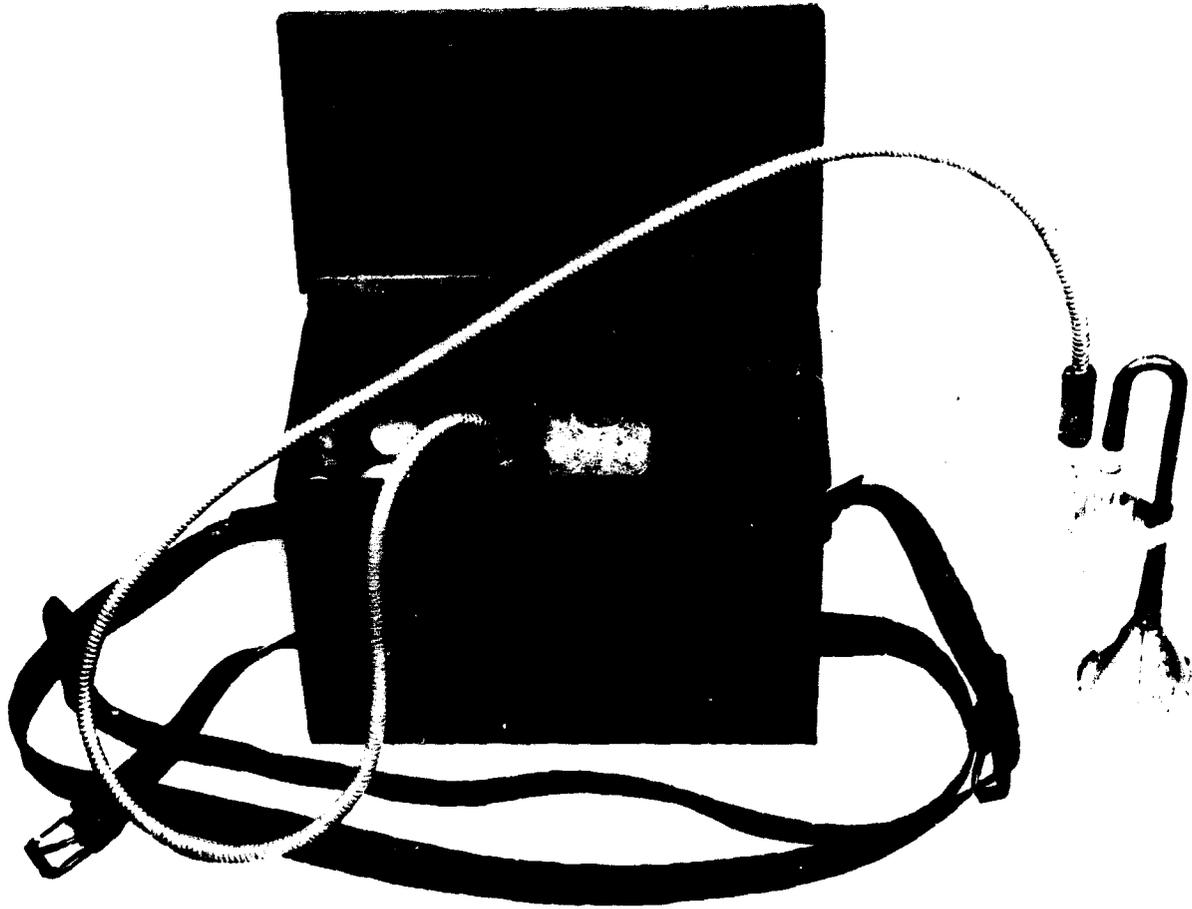
BUREAU OF MINES  
 AMERICAN UNIVERSITY EXPERIMENTAL STATION  
 GAS ANALYSIS  
 WASHINGTON, D. C.

**APPARATUS FOR  
 FIELD DETECTION  
 OF G-34**

DESIGNED BY  
 H. J. HARRISON  
 CHECKED BY  
 H. J. HARRISON  
 DATE  
 10/15/34



FIELD DETECTOR FOR G.34 IN USE.



FIELD DETECTOR FOR G-34

4.

in the field in questionable.

Experiments with snails and slugs showed that these animals were exceptionally sensitive to mustard gas and other toxic gases, moving their horns in different ways in different gases. It was found that a skilled observer could utilize these animals to detect mustard gas at concentrations as small as one part in three million and other toxic gases at even greater dilution. A trained observer could distinguish between the various toxic gases with considerable certainty at low concentrations and with entire certainty at higher concentrations. The variations of sensitivity are considerable with different individuals and in all cases the susceptibility disappears pretty completely on prolonged exposure. It is therefore doubtful whether this special test would have anything more than a confirmatory value in the field. <sup>P</sup> A lacquer enamel paint has been devised which can be used on shell to tell whether they leak or not, there being an instantaneous color change of one kind in contact with liquid mustard and a color change of another kind in contact with arsenicals, thus making it possible to use the same paint in two different kinds of shell. The enamel consists of <sup>m</sup>chrome yellow as pigment, a mixture of 85% of Oil Scarlet and 15% of Rhodamine B in small amount as the sensitive agent, and a lacquer vehicle which is essentially a solution of nitrocellulose in amyl acetate. Both the Oil Scarlet and the Rhodamine B turn crimson red in presence of liquid mustard; but the Rhodamine B is much the more sensitive. On the other hand the Oil Scarlet turns deep purple to dark green in presence of arsenicals. The paint is not affected by such other substances as chloropicrin, phosgene, superpalite, and butyl mercaptan.

5.

Similar effects can be obtained with a linseed oil paint instead of the lacquer enamel, the contrasts being more marked with the paint but the enamel reacting more quickly. The paint has been tested thoroughly for the effect of sunlight, moisture, time and high temperature. The color is entirely stable before exposure to mustard gas and the red color produced by the mustard gas is equally stable under all conditions of weather. It is immaterial whether the paint is used on shell steel, tin copper, wood, cloth, or paper.

In order to get some idea of how long mustard gas may be dangerous in the field, a study of the persistency under field conditions was made by the Research Division in the summer of 1918. ~~The necessary testing equipment, and the rather extensive equipment for protection of the operators, as well as meteorological instruments were borrowed from the Weather Bureau, and installed in the vacant dwelling place on the farm.~~ Some hundreds of plots, varying from 20 feet square to 100 feet square, were sprayed with mustard gas and other toxic materials. This was very dangerous work and required the utmost precautions and the maintenance of strict discipline. Few of the men escaped various burns; but, so far as is now known, no permanent injuries resulted. Successful prosecution of these measurements required the development of a very accurate, quantitative method for the determination of minute traces of mustard gas and the other gases in the air. This was finally secured by a considerable development of the nephelometric method of Richards. It was found possible by this means to determine mustard gas with an accuracy of about 10% <sup>at</sup> concentrations as low as 0.0006 mg. per liter (1 part in 14 million) within a 14 liter air sample.

The concentration of mustard gas over an area 20 x 20 feet sprayed with 20 cc of mustard gas per sq. ft., which corresponds to an intense shell-hole, amounts to 0.04 mg. per liter in clear calm weather (68° Fm.) and a slight breeze. At one foot from the ground, it is only 0.008 mg. per liter and at 3 feet 0.002 mg. per liter. A man standing erect in this area for any length of time would therefore be burned severely about the legs, irrespective of the temperature of the soil itself, and eventually on exposed portions of his body. The concentration is much higher on a man

days and lower on cold ones, but the percentage of decrease in concentration at increasing distances from the ground is practically identical for all temperatures. Thus, at 4" the concentration is 40%, at 12" 30%, and at 36" 8% of that at the surface of the ground. The variations in horizontal concentration were in part as expected and in part unexpected. Thus, as would be expected, at 4" from the ground the concentration reached its maximum at or near the leeward side of a sprayed area. However, it decreased with very great rapidity beyond this. For instance, in clear, moderate weather, and with a slight wind blowing the concentration at 1" from the ground is about 0.04 mg. per liter at the leeward edge. Ten feet beyond this, it dropped to 0.004 mg. per liter and at 50 feet beyond to 0.001 mg. per liter. The diluting effect of the wind is evidently surprisingly great as has indeed been the universal experience in our warfare. The toxic area does not extend more than about 100 feet beyond the sprayed area under ordinary conditions. A further and even more unexpected discovery was the very great turbulence of the air, even in apparently steady wind conditions. Simultaneous samples collected over a considerable area to the leeward of patches showed decided variations in concentration at identical heights and distances from the sprayed ground. Localized pockets of low concentration and islands of high concentration were observed.

The effect of temperature on concentration is, of course, pronounced. Thus, on a clear day of moderate temperature, the concentration on the leeward edge of a patch at 4" from the ground is 0.045 mg. per liter, on hour after spraying. On a warm day (70°F.) it was 0.064 mg. per liter,

and on a cold day (44°F.) it was 0.006 mg. per liter. These figures are approximately proportional to the vapor pressures of mustard gas at the respective temperatures. The effect of sunshine was surprisingly marked. The moment the sun went behind a cloud, an immediate drop in concentration could be observed. This drop often amounted to as much as 75% or 80%.

Curves of solar radiation taken on a recording pyrheliometer ran substantially parallel to curves showing the change in concentration with the time, though this parallelism was more or less confused if the clouds were small and scattered, due to the fact that the recording instrument was located nearly one-half mile from the patches.

The change in concentration with time was studied with particular care. Immediately after spraying, the concentration close to the ground approaches saturation at the leeward edge of the patch. On a warm day, a very rapid decrease with the time takes place, so that, after an hour, the concentration at 4" above the ground will have dropped to about 0.060 mg. per liter and in five hours to 0.010 mg. per liter; the next day it will be only 0.004 and the second day 0.0002 mg. per liter, etc. At greater distances from the ground the concentrations will be correspondingly lower.

On a moderate day, the initial concentration is, of course, much lower, but the decrease will be much less marked, so that five hours after spraying there is little difference in the actual concentrations on a warm and a cold day. On the second day, the concentration at moderate temperatures is even greater than after the first day, and this difference becomes even more marked after three days. The curves rather strikingly illustrate the

of the mustard <sup>gas</sup> to evaporate during the first five hours that the concentrations become low on this account. In hot weather, therefore, the concentration of the vapor over a sprayed patch is very high, and, hence, dangerous during the first day; but is only slightly dangerous on the second and third days, and is negligible thereafter. In cool weather, however, the air remains dangerous for a week or even more, and is particularly dangerous on a warm day following a cold one.

The nature of the soil was found to have no appreciable effect on the gas concentration. Spraying a larger amount of liquid per square foot of area increases the gas concentration, but not in proportion to the increased amount. When the amount used is less than what is required to wet the surface of dry soil, the gas concentration is found to be very low. In other words, the soil has a noticeable adsorptive power.

The effect of varying the size of patch was found proportional to its linear extent in the direction of the wind.

Windy weather was found to affect the persistency of mustard gas in two ways. First, the heat received by radiation during such weather is so small that the concentration of mustard gas is very low on this account. In the second place, the capillaries of the soil become filled with water so that under such conditions the variation in the amount of mustard gas sprayed per square foot of area has no appreciable effect on the concentration of the gas in the air.

The topography exerts an appreciable effect on persistency. Where the contaminated soil is on a steep slope in a protected place, the gas tends to collect in the bottom of the slope in pockets, especially on the contour of the ground. The liquid also evaporates less readily from

ground in the woods.

The ability to detect the odor of mustard gas under varying conditions, and at low temperatures was found to be subject to considerable individual variations and to depend on the amount of experience in such work. Many of the men acquired decided skill so that they could detect the odor at a foot from the ground over patches that had been sprayed with 20 cc of liquid to a square foot ten days' after spraying. Over patches that had been sprayed with 1 cc per square foot they could detect the odor after three days under normal summer conditions. In the summer time soil contaminated with mustard gas will cause skin burns after fifteen minute application for at least four days. After four days, the danger is relatively slight, depending no doubt on the amount of material originally applied to the soil and on the intervening weather conditions.

The work on protective clothing by the Research Division and the Medical Division has been chiefly with reference to protection against mustard gas and has included a study of fabrics intended for use in the following forms: gloves; over-all suits; underclothing; footwear; dugout blankets and screens; masks for horses and dogs; boots for horses. The ordinary materials such as cotton, wool, linen, leather, and rubber are penetrated by irritant gases in a relatively short-time, partly because of their porosity and partly because of solvent action, this latter being the important factor in the case of rubber. O.D. issued clothing protects from saturated vapor of mustard gas for 5-7 minutes. Untreated glove leather resists penetration by liquid mustard gas for 35 minutes; untreated buff horse-hide and split cow-hide for four and five minutes.

PROTECTIVE GLOVES

Six different types of gloves have been tested. They are

1. Leather gloves impregnated with softened linseed oil.
2. Canton flannel gloves with leather palm, impregnated with boiled linseed oil and stearine pitch.
3. Rubber gloves.
4. Cotton gloves, waterproofed and coated on the inside with a gelatine-glycerine-formaldehyde composition.
5. Gloves sewed from oiled fabrics.
6. Flannel gloves coated with cellulose-nitrate.

The first type was made from thick leather impregnated with a mixture of boiled linseed oil, castor oil and paraffin. They give protection against liquid mustard gas for two to five hours. The disadvantages lie in the scarcity of leather, the tendency of the glove to shrink somewhat,







the necessity for oxidizing the linseed oil during the drying process and the tendency of the glove to stiffen with ageing.

Gloves of the second type give protection of one hour on the fabric part and four hours on the leather palm. The time required for drying and the tendency of the glove to stiffen are its weak points.

Acid proof rubber gloves (the third type) are available in the market. Samples which contain zinc oxide in the composition resist liquid mustard for 15 to 45 minutes. The high price makes this type unsuitable for anything but special use.

A gelatine-glycerine-formaldehyde impregnation (type four) was tried out, with a waterproof coating outside to protect the water-soluble impregnation. Gloves thus made are more flexible than any other type and more resistant to mustard gas. The necessity for the outside waterproofing introduced complications into the manufacturing process which were not sufficiently under control to give this glove standing as the best developed.

The fifth type consists of an oiled-skin fabric sewed into a glove. This material was used largely by the French, and is the most resistant to mustard gas as such; it loses this distinction when used in gloves, however, because of the tendency to break at the joints. Difficulties in resin, the stiffness and non-elasticity of the material are additional disadvantages.

The sixth type of glove was found most suitable for large scale production and for general military use. The fabric selected as having sufficient strength, flexibility, and a smooth surface suitable for treatment is a medium weight well woven cotton fabric, known as 1.50 micron. This is run over cylinders carrying short wire brushes which pull out the fibre on one side, forming a soft napped surface like the ordinary cotton flannel.

The material is treated on the smooth side with a coat of cellulose nitrate to form the outer layer. After drying it is cut by dies and sewed with the treated side out into a glove with the thumb and first finger in separate divisions, the remaining three fingers forming a mitten. The glove is then put on a wooden form and dipped repeatedly into a solution of cellulose nitrate softened with rape-seed oil and dissolved in ether, benzol, methyl salicylate and alcohol. After drying in ovens, these gloves protect against liquid mustard for 30 to 60 minutes, depending upon the number of coatings. The gloves become softer rather than stiffer upon ageing, and show no tendency to crack at temperatures as low as  $-12^{\circ}$  C.

In response to a request from the War Defense Division for recommendations for producing 2,000,000 pair of protective gloves at a rate of 250,000 per month, the cellulose-nitrate glove was recommended and production started. About 1800 pairs had been completed when work was stopped by the signing of the armistice.

#### PROTECTIVE SUITS.

Protective suits of three types were experimented with. The classification adopted is as follows: impermeable suits, in which the textiles have been thoroughly impregnated (with tarry oil) so that the fabric is gas-tight and water-tight; semi-permeable suits, in which the impregnating materials are used so as to render the fabric gas-tight but permit passage of water by its solubility in the impregnation; and permeable suits, in which the fabric is impregnated with non-tarry oils in such a way that the interstices remain open for ventilation.

### A. Impermeable Suits.

The Air-Lined Suit was developed for especial use in factory production of poison gas. It comprises a suit covering the whole body, a helmet, gloves, shoes and air supply hose. The helmet is an aluminum cylinder ten inches in diameter with a hemispherical dome top, being supported by a fabric band resting on the head like a cap. A rectangular window is in front beneath which the air supply enters. The suit is made of oil-skin fabric made up as a union suit, buttoned at the back and tied at the wrists, ankles and around the helmet. The gloves and footwear are not distinctive. Air is pumped into the helmet at a rate of 200 liters per minute, giving a constant current from the inside of the suit, outward through the seams and openings. In a 30 minute test in the gas chamber containing phosgene (1000 p.p.m.) no gas could be detected in any part of the suit. There was no discomfort reported due to gas.

The Oil-Skin Suit. The material of this suit is a specially prepared oilcloth. As a fabric, sheeting is used; a 64 x 64 (count) sheeting gives a high tensile strength, which is very desirable. This is coated with three coats on each side of a so-called "rub," and then with two coats of varnish. The composition of the mixture is as follows:

<u>Finished Rub</u>	<u>Stock Rub</u>	<u>Stock Pigment.</u>			
Stock Rub	55.16%	Linseed Oil	46.4%	Raw Umber	16.64%
Stock Pigment	5.74%	Raw Umber	0.116%	Yellow Ochre	33.28%
Martins (54 20)	11.3%	Motor Oil	35.4%	Prussian Blue	0.26%
Motor Gas	27.8%	Naptan (500)	3.24%	Linseed Oil	49.32%
		Motor Oil	9.24%		

122



1187

**AIR LINED HELMET AND SUIT**

**Front View**

**Showing suit inflated.**

123 ~~122~~  
~~122~~



IMPERVIOUS OVERALL SUIT FOR  
PROTECTION AGAINST H2O.

front view.

124  
~~123~~

5.

<u>Varnish</u>		<u>Stock Varnish</u>	
Stock Varnish	79.13%	Linseed Oil	59.33%
Stock pigment	6.66%	Litharge	0.241%
Naphtha (54°Ce)	3.33%	Cobalt (?)	0.593%
Paraffine wax	6.32%	Caster Oil	5.93%
Gasoline	4.56%	Gasoline	33.90%

The cloth is dried in hot festooning chambers between the coatings. It is then cut and sewed into a one-piece overall garment, following in general the French design, but with changes permitting greater freedom of movement of the legs. After being sewed up, the suits are coated over the seams with a quick-drying mixture of the following composition.

- 5 part cellulose nitrate
- 1 part butyl acetate
- 1 3/16 part blown rapeseed oil.

Samples from factory production show protection against liquid mustard gas from 60 to 90 minutes on the physiological test, which is distinctly higher than tested samples (recent old) of French protective fabric, (25 to 75 min). In use in several types of exposed work here, they protected from body burns in every case. They are open to objection on the ground of comfort, since they permit no evaporation of perspiration or ventilation.

An order for 1,000,000 suits of this type was in process of being filled for the U.S.A., with hostilities closed. About 500 suits were completed for the War Reliance Division.

Nitrocellulose suit. Experimental work on this type of fabric was conducted, in connection with the earlier work. No suits of this material were prepared. The material prepared was highly resistant to mustard gas.

6. Semi-permeable Suit

A type of fine-glycerine-formaldehyde impregnation resistant fabric resistant to mustard gas, but permeable to perspiration. This is a...

23. 36

ter of such importance in reducing the discomfort due to accumulation of perspiration in the impermeable suit. The cotton fabric is treated by means of a "doctor knife" with a mixture of glue and glycerine (with 1% zinc sulphate as preservative), and is then hung in an atmosphere of formaldehyde until the glue is thoroughly set. For indoor use, the glue becomes insoluble in water, but the glycerine is leached out by water, rendering the fabric stiff after drying. For outdoor use this point is of no importance; for field use, the fabric is rendered more resistant to rain by including in the impregnating mixture <sup>oil</sup> linseed oil emulsified in water by ammonia, which, upon drying, retards the leaching effect of water.

When care is exercised to avoid pinholes in the material, the protection against liquid water for up to 50 minutes, and is held to be superior to that afforded by the impermeable suit. Evaporation of water vapor occurs freely; the amount in unit time varies from 57% to 80% of that occurring through untreated section. The gain in comfort over the oil skin suit is very marked.

C. Permeable Suits.

The flexene suit consists of 1/16" thickness of Cambium fabric, the inner acting as lining and the outer carrying an impregnation of flexene b, which is composed of 45% resin and 55% resin oil. This is taken up largely by the fibres, leaving the interstices open for evaporation of water and for ventilation. The cloth is impregnated in a machine, passed between rollers and dried 48 hours before cutting and sewing. It is made up into one piece overall with hood, hem at the wrists and elbows.

126 ~~123~~  
~~124~~  
~~125~~

The suit is designed to meet the need of a front line fighting suit, in which the comfort of the individual will be sufficient to permit of strenuous exertion, which has not proved possible with the impermeable suit. It permits evaporation of water with substantially no decrease from the rate through untreated fabric, and permits passage of air with almost totally no pressure drop. It is somewhat sticky, and stiffens somewhat upon lengthy exposure. It is not intended for protection against liquid mustard, but has been found in field tests to mitigate burns from liquid mustard. Against saturated mustard vapor, it gives protection at 20° for 15 minutes; 20 minutes protection is given at 9° C.

About 1000 of these suits were made up and several hundred taken to the field for tests. These were but partially completed when hostilities ceased. The general conclusion reported is that it is thought the protection afforded by this suit might enable one to work for about 1 hour without serious danger on open ground contaminated with mustard gas; to walk for half an hour through thick woods which have been heavily shelled with Vello. Cross, or for a longer time if the woods are open or have been lightly shelled. If a man wearing the suit should be heavily splattered with mustard gas, or if the fabric becomes seriously wet with mustard from any cause the suit should be removed as soon as possible.

The Emulsoid Suit is composed of two layers of Camburg fabric, both impregnated with an emulsion of the zinc soap of cotton-seed oil with cylinder oil, equal parts of each being used. In order to gain higher protection than that of the Simplexone suit, 8 ounce and 9 ounce Camburg were used as fabrics, which take a heavy load of solvent (25 mgrs per sq cm) and

127-157  
128

leave the interstices of small dimensions. In factory impregnations, the fabrics must be passed over hot cylinders until all chemical action involved in the formation of the soap is at an end, to avoid danger from later heating up. The material is then sewed into overall suits, following the design of the Simplexene suit. Compared with a summer suit of issued army clothing, it permits evaporation at a rate 70% as rapid, the pressure drop on passage of air is practically the same, and the heat conductivity distinctly better. Against saturated mustard vapor, it affords protection for 45 to 75 min.

About 75 of these suits were made up. They were not tested in the field. They appear to be less cool for summer wear than the Simplexene, but much cooler than the impermeable or semi-permeable suits; they lack entirely the stickiness and tendency to stiffen which the Simplexene suit shows, and afford protection at least twice as great.

It is shown that the emulsoid process (setting of the impregnation upon the fibre from a zinc soap emulsion) is applicable to any oil, the one quoted being selected because of its cheapness. No essential difference between the various oils has been established as to their protective value. The general instruction is made that drying oils (linseed, etc) should be avoided, either free or in the soap, in order to reduce liability to spontaneous combustion, and that volatile and resin oils should be avoided on account of their tendency to stiffen. The critical points in the making of a permeable suit are that the oil used should be free from the two disadvantages mentioned and should be put on in such form as to obviate stickiness and tendency to run, and most important of all, that the permeable fabric be selected with great care so that the interstices shall be reduced to a minimum size, such as in the case of other non-cooking fabrics

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worn as conventional outer suits. With fabrics of a degree of openness comparable to that of usual suitings, a protection of 45 to 75 minutes is attainable; with open fabrics such as used in the Singapore suit, the protection drops to 10 to 20 minutes.

PROTECTIVE UNDERCLOTHING

Protective underclothing has been tested, on the theory that a small amount of protecting material might have a maximum value if used directly over the skin. Cotton drilling impregnated with oils or with oils and soaps give substantial protection for short time exposures (8 to 12 minutes) against saturated mustard vapor; the pressure drop is increased somewhat, but is still so low as to offer no serious impediment to ventilation and the rate of evaporation of water is almost unaffected.

TESTS UPON PROTECTIVE UNDERCLOTHING.

Impregnation	%	mg per sq cm	Pressure Drop	Rate of Evap- oration	Physiological Protection for 8-12 min.
(none)	--	--	1.00	1.00	0
Albasol	11	2.0	1.00	1.00	57%
Mg linoleate	28	5.0	1.70	1.03	61%
Sulphonated Castor Oil	22	4.0	1.00	.92	61%
Castor Corn Oil	20	3.6	1.50	1.03	75%
Ointment #60	33	6.0	2.20	.96	83%
Castor Oil	20	3.6	1.00	1.03	77%
Ointment C.F.	27	4.9	5.00	.86	90%
Ointment #32	45	8.1	2.30	.96	93%
Ointment #16	28	5.0	1.00	.93	93%
Ointment #66	47	8.5	1.50	.79	97%

Impregnations running up to about 40% in weight can be worn with no discomfort and with no sensation of oiliness; with heavier impregnations,

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the sensation is disagreeable. Fabrics treated by the Emulcoid process with oil-soap impregnations up to 70-80% give very little sensation, and protect (by machine test) for 24 to 40 minutes. A 90% impregnation with rosin oil mixture containing iodine pentoxide shows 99% protection for 16 minutes, but is too oily for use. Tests with underclothing impregnated with cils and dichloramine-T or chlorazene give high protection, but the fabrics are not lasting, owing to the instability of the active reagents.

#### FOOTWEAR

Rubber boots and a special boot made from pyroxylin fabric were used as foot protection in experimental work in ground spraying with mustard gas. Special study of these articles was not made.

#### DUGOUT CURTAINS

The research was directed toward finding materials which would give a flexible curtain, impermeable to war gases (air also being excluded, since sufficient ventilation is assumed to occur in dug-outs through the soil), as free from stickiness as possible and as uninflatable as possible. The work has included the development of a suitable blanket, suitable impregnating oil, and a machine for impregnation.

Specifications for all-cotton blankets have been based upon a study of the suitability of all available blanket materials. A tensile strength of 50 lbs. per inch in the warp and 95 lbs. per inch in the filling is necessary to prevent such stretching during use as will break the oil film and lower protection. The most suitable material for impregnation consists of 85% of heavy steam refined mineral oil, with 15% boiled linseed oil. On the blanket the linseed oil dries slowly and makes

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an outer surface which is but slightly oily to the touch, while the inside core remains fluid and flexible. The impregnated blanket protects from chlorpicrin (400-600 p.p.m.) for 5 to 48 hours and from liquid mustard gas for 100 to 400 minutes (machine-test). It is not ignited by cigarette butts or lighted matches thrown upon it. It remains flexible enough to unroll under its own weight at 18° F, and at 6° is easily unrolled by applying force. The tendency to drain is negligible.

A field impregnating apparatus has been devised, consisting of a galvanized iron tub for holding the oil mixture, which is heated to about 70° C by a gasoline torch or other available means. In there the blankets are dipped singly, and drawn out through a scraper to remove excess oil. The desirable impregnation is about 300%, or about 14 lbs. of oil per blanket. About 191,000 blankets were manufactured by the War Service Division following these recommendations.

HORSE MASKS

The first horse mask developed made use of Patrick's "Komplexone" mixture soaked into a flannel-like bag to be worn over the nostrils. The impregnating mixture is of the parts, having the composition:

<u>A</u>	<u>B</u>
100 parts hexamethylene tetramine	30 parts sod. carbonate
250 " water	100 " water.
95 " glycerine	
70 " nickel sulphate (hydrated)	

Upon mixing these at 35° C or below, a fine suspension of nickel pyrazine is produced. The mask shows a high resistance to air, for this reason it is regarded as unsuitable, as tests with mustard gas have shown.

A second type of mask has been developed, in which a very low air resistance is obtained by use of a special type of acetate; description is

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secured by use of 12 layers in the bag. The mask is 12 inches wide and 18 inches long, having a total area of about 400 sq. inches. In order to secure absorption of as large a variety of gases as possible, the mask is made of two parts; the inner four layers are impregnated with Komplexene, as in the first mask, and the outer eight layers with a new solution known as Simplexene, consisting of 80% resin oil and 20% paraffine oil. This mixture was selected after careful testing out of a large number of oils and mixtures of oils and soaps. The time to penetration of this mask by various gases at 50 liters per minute is as follows:

<u>Gas</u>	<u>Concent.</u>	<u>Time to Penetration</u>	<u>Active Absorbent</u>
Mustard	100 p.p.m.	80 min.	Simplexene
Phosgene	1675 "	130 "	Komplexene
Chlorine	1300 "	65 "	Simplexene
Chlorpicrin	1500 "	2 "	neither

The mask affords excellent protection against three of the four gases. It was adopted by the War Defense Division, after it had been shown by tests at Fort Meyer that horses could run for two miles with the mask on, without showing evidence of exhaustion. Contracts for 1,500,000 masks were drawn (using, however, two additional layers treated with Komplexene), and 577,981 were completed.

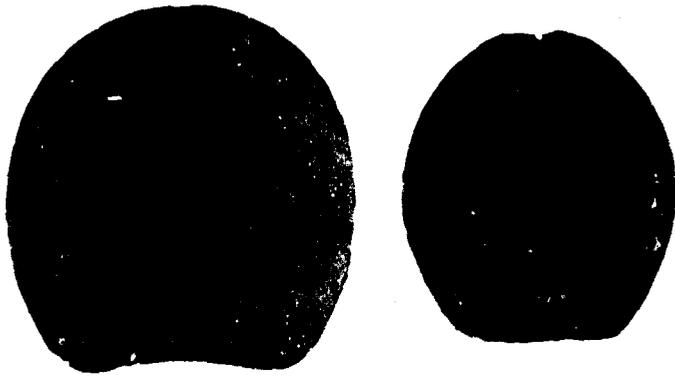
#### HOUSING

Protection of horses in the under portions of the roof of horse barns against mustard gas has been provided for by a tent which covers the legs from the hoof to a line just below the knee, and a special roof, etc.

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IMPERVIOUS BOOTS AND PADS TO PROTECT HORSES' LEGS & HOOFS AGAINST HB.  
1714, 1716, 1807,





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Tests showed that wearing the boot and hoof-pad for nine days and nights consecutively caused no lameness to the horse; it is recommended, however, that the boot be removed and cleaned whenever the animal is in stable. They are good for six weeks use on rough roads.

#### THEORY OF PROTECTION BY IMPREGNATED FABRICS.

All protection by impregnated fabrics so far is either purely mechanical or physical, dependent upon solution of gas. In the case of linseed oil fabrics, it is probable that mechanical exclusion of gases is what occurs, the penetration being effected through microscopic holes in the film. However, it is possible that oxidized linseed oil (like unoxidized oil) is a solvent for some of the gases, and that slow solution occurs in the exposed film, after which the dissolved gas passes by diffusion into the interior of the fabric and finally to the inner surface, from which it diffuses. Experiments are not at hand throwing light upon this point.

In the various oiled fabrics (dugout blankets, Simplexone suit, Emulacid suit, protective underwear, horse and dog masks) it is obvious that solution is the mechanism by which the gas is taken up. It has been demonstrated by parallel experiments that the gas is present in the oil with a detectable vapor tension; fabrics exposed to mustard vapor for a short period and allowed to remain upon the skin will not cause a burn, while <sup>they</sup> ~~it~~ will cause a severe burn if cupped after the same exposure so as to prevent evaporation.

During the exposure of such an oiled fabric to gas, it will be gaining in concentration of dissolved gas on the exposed surface until equilibrium with the gaseous phase is reached. The time at which penetration

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occurs, however, may be entirely independent of the rate at which this outside equilibrium is reached and is probably due to diffusion of dissolved gas in the body of the impregnation through to the inner surface, from which it will at once begin to evaporate, there being no opposing vapor pressure upon that side. The plausibility of this explanation is shown by the fact that the highest degree of resistance to penetration was found, by a number of independent investigators, to be shown by the most highly viscous oils, in which this diffusion would be slowest - cylinder oil, rosin oil, castor oil, etc.

The penetration of hydraus materials such as the gelatine-glycerine impregnation, in which most gases are insoluble, may be due in part to pin-holes (macroscopic or microscopic) or in part to transport in which the water plays a part. The amount of water present in such fabrics has been shown to influence the rate of penetration; with three fabrics (untreated heavy duck, gelatine-glycerine fabric, and oil-cloth) it has been shown that increase in moisture content up to about 5% increases the amount of mustard penetrating per unit of time, higher amounts than 5% reducing the amount of penetration. The explanation advanced for this is that water may play a double role; it may act (presumably when its amount is large) as an absorbent, dissolving the gas and eventually destroying it by hydrolysis, but may also (when its amount is small) facilitate passage of gas by preventing surface adsorption on the fibre or impregnation and by passing the gas through the interstices or pores of the fabric by means of capillarity.

For protection of the skin against mustard gas, an ointment was developed, consisting of a mixture of petrolatum, lanolin, linseed oil, and zinc oxide, which served primarily to delay the penetration of mustard gas to the skin, thus giving more time for evaporation to take place. This

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ointment was known as Sag Paste, and was shipped to the Western Front in large quantities. The majority of the reports were quite favorable though of course the paste was only used at the front for a limited time. It was later found possible to improve this ointment greatly by sprinkling bleaching powder over the skin after the ointment had been applied, the bleaching powder serving to destroy the mustard gas.

*The question of the physiological problems involved in the production of the gas mask has been studied in great detail by Major Pearce at the Lakeside Hospital in Cleveland. No 9*

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We can now come back to ~~some of~~ the defense research work. ~~Starting with that~~ on the absorbents, of which the most important is charcoal. It had been known for a long time that charcoal would condense in its pores or adsorb certain gases, holding them very firmly. It was also known that certain charcoals were very effective in decolorizing sugar solutions for instance; but that was about all. It was known that in general so-called animal charcoal was the best for decolorizing sugar charcoals, that wood charcoals were the best for adsorbing gases, and that coke had very little adsorbing or decolorizing power; but nobody knew why and nobody could write a specification for charcoal. It had been found by Hunter more than fifty years ago that cocoanut charcoal was the best for adsorbing gases and this was the charcoal usually used in scientific laboratories. In 1912 two Germans, Hempel and Vater, claimed to have made a better charcoal than cocoanut charcoal by mixing a special animal charcoal to a stiff paste with ox-blood diluted with water and charring at 6000. This was not very much in the way of information and even this was <sup>not</sup> necessarily applicable. The scientific work on adsorption had to do with the equilibrium relations of pure gases while the war problem was to remove mere traces of toxic gases from air in a very short interval of time. For instance, with a rapid stream of air through the canister, the modern charcoal will reduce 7000 p.p.m. of chlorpicrin to a negligible concentration in about 0.03 seconds. The magnitude of the task is more evident when we remember that the pre-war charcoal scarcely stopped chlorpicrin at all.

Some experiments by Professor Lemon at the University of Chicago had shown that the adsorbing powers of cocoanut charcoal could be varied

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a great deal by suitable treatments. Small amounts of air were taken up by the charcoal at low temperature and then the charcoal was heated to some specified temperature and as much gas as possible removed by pumping out the vessel. If this were done a number of times at 600°, the charcoal was improved a great deal. If its temperature was raised to about 800° the charcoal became worse. No satisfactory explanation for this phenomenon had been developed at the time the United States went into the war.

It was therefore necessary to develop a war charcoal without any real knowledge of how to do it and to develop it very quickly. *NOTE*

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The first problem was to get a charcoal which would stop chlorine. After ~~testing~~ carbonizing all sorts of materials in all sorts of way, the National Carbon Co. succeeded in making a charcoal from red cedar which stood up very well against chlorine, lasting 150-200 minutes as then tested. In order to improve the charcoal still further, it was desirable to have some theory as to the way the charcoal acted. Everybody was agreed that fine pores were essential; but nothing was known in regard to the other factors. Some people said that the presence of certain hydrocarbons were essential. This was in line with the view that nitrogenous material is of the greatest value in charcoals that are used for decolorizing sugar solutions. Mr. Chaney of the National Carbon Co., took up the opposite view, that carbon had very high adsorbing power and that the important thing was to remove the hydrocarbons which he assumed still to be there after the carbonization. He believed that one great difference between different raw materials was the difference in the hydrocarbon residues, some of which were driven off more easily and more completely than others. To prove this some of the red cedar charcoal was heated in a bomb connected with a pump which drew air through the bomb. Although this charcoal had been carbonized at 800°C, various gases and vapors began to come off at 300°C and some of these vapors condensed when cooled to crystalline plates.

This not only proved the existence in the charcoal of compounds containing hydrogen but also showed that one way of removing the hydrocarbon film on the active carbon was to treat with an oxidizing

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agent. A process of activation by oxidation in air was developed rapidly and the regular cedar charcoal which had lasted 150-200 minutes against chlorine then lasted 400-500 minutes.

If the true cause of the inactivity of various charcoals was the presence of adsorbed hydrocarbons, it was evident that two methods of activation were possible. The charcoal could be heated for a long time at a temperature high enough to decompose or drive off the hydrocarbon. It could also be oxidized either wet or dry. Both these general methods give some degree of activation. The first one was employed by the British and the French. It was abandoned in this country because it was found that high-temperature cracking of the hydrocarbons gave rise to a somewhat graphitic carbon which was not active.

One puzzling fact was encountered in regard to air oxidation. Samples of cocoanut shell charcoal had been made which were even better than the red cedar charcoal; but they did not respond to air oxidation under the conditions which had improved red cedar so much. This proved to be because the critical oxidation temperature of cocoanut charcoal was considerably higher than that of cedar charcoal. By increasing both the temperature and the time of oxidation, the cocoanut charcoal improved even more than the cedar charcoal, changing from a service time of 200-400 minutes against chlorine to one of 1500-1800 minutes, or up to thirty hours.

About this time it was discovered that the 180-200 minute cedar charcoal did not stop chlorpicrin at all, lasting two to three minutes at the most. Since chlorpicrin was then being used by the

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Germans, all orders for red cedar charcoal were cancelled. Fortunately, it turned out that the activated coconut charcoal lasted 200 minutes against chlorpicrin which was a wonderful showing at the time, though such a charcoal would not <sup>now</sup> be considered fit to use. The production of this charcoal on a commercial scale was turned over to Mr. (later Colonel) Dorsey of the Nela Park Laboratory at Cleveland, who started a plant at once at Astoria, Long Island, for the Gas Defense Service, later the Defense Production Division. The commercial development will be discussed in the chapter on the Development Division. The product as turned out at Astoria was called Dorsite. Before the Astoria plant was built, the National Carbon Company succeeded in making a coconut charcoal which lasted 400 minutes against chlorpicrin.

Chaney believed that only part of the activation was due to the removal of the hydrocarbon and that another function of the oxidation was to dig out channels through the carbon thereby increasing the active surface. If this is the case, different oxidizing agents might easily act differently, a weak oxidizing agent acting selectively, while a powerful one might burn the carbon away uniformly, or might enlarge existing pores instead of developing new ones. With this in mind a careful analysis of all possible methods of oxidation was made. All oxidation processes involving liquids were discarded in favor of oxidation by gases because the latter type of oxidation seemed cleaner and cheaper, and could be completed in a single operation, there being no need of washing, filtering, drying, etc. The following gaseous oxidizing agents seemed to be worth studying:

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1. Air
2. Chlorine
3. Oxides of nitrogen
4. Steam at water gas temperatures
5. CO<sub>2</sub> at high temperatures
6. Sulphur Dioxide.

The first experiments were made with chlorine and were not encouraging because the results were practically the same as with air. It was thought that the reason for this was that the charcoal had to be heated in air afterward to drive out the chlorine and that any especially fine structure produced by the chlorine might be burned up by the air. To avoid this, superheated steam was passed over the charcoal to drive out the chlorine, the temperature being kept too low for the steam itself to react. The product improved steadily and reached a life of 800 minutes or four times the life of the first air-treated cocoanut charcoal. With rising temperature the product kept on improving until at 900°C it was found that treatment with steam alone was just as effective as the chlorine treatment. While working with steam at 900-1000°C is not the easiest thing in the world to do, it is a much simpler problem than working with chlorine at that temperature. A semi-commercial continuous process, steam-treating unit was then built, in which the charcoal was fed into the top and removed at the bottom. This furnace was electrically heated and yielded about 24 pounds of charcoal a day.

The results were so good that men were sent from the American

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University Experiment Station to help in the work. By the time of the signing of the Armistice the detachment consisted of thirty Chemical Warfare Service men. At Astoria, Mr. Dorsey at once started large scale production, using a nichrome metal central tube instead of a clay one and firing by flameless combustion instead of using electrical heating.

The rapid development of the steam process was not due <sup>to the fact</sup> merely that it gave the best charcoal. The air-treatment was much cheaper and gave a product which was several times as efficient as that then in use by the British and French. The great advantage of the steam process was that it worked well with all kinds of charcoal. With the air process it was not possible to make charcoal from other sources which was as good as the air-treated <sup>cocconut</sup> charcoal, whereas inferior material, when treated with steam gave charcoals as good as, or better than, the best air-treated charcoal. <sup>through not as good as the best steam-treated cocconut charcoal.</sup> This was very important because not over 100 tons of raw cocconut shells per day could be counted on. Since this meant only eight tons of charcoal finished per day, it was very necessary to find a substitute for cocconut charcoal.

Arrangements were made by the Defense Production Division to import <sup>USA</sup> ~~cocconut~~ nuts from South America and Central America, and to collect peach stones, etc., from all over the United States, and the National Carbon Company started developing charcoals from anthracite coal, bituminous coal, lamp-black, wood, cocconut fines, etc.

The first experiments were made with a special anthracite coal which gave service times up to 560 minutes as against 360 <sup>minutes</sup> for air-treated cocconut charcoal and 800-900 <sup>minutes</sup> for steam-treated charcoal.

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This product was called Batchite after Mr. H. D. Batchelor. When the Gas Defense Service tried to activate anthracite on a large scale in vertical gas retorts at Derby, Connecticut, the attempt was a failure. They carbonized at 900° and then turned on the steam with the result that the steam-treated coal had a slightly greater density than the untreated, which was wrong, and had a shiny appearance in parts with roughened deposits in the other parts. When the hydrocarbons are decomposed at high temperatures, the resulting carbon is somewhat graphitic, is itself inactive, is not readily oxidized, and impairs or prevents the activation of the normal carbon upon which it is deposited. This discovery made it possible to treat anthracite successfully. The conditions must be such as to minimize high-temperature cracking, to carry off or oxidize the hydrocarbons as fast as formed, and especially to prevent the gases from cooler portions of the treater coming in contact with carbon at a much higher temperature. With these facts in mind, Mr. Batchelor of the National Carbon Company was able to build a plant at Springfield which produced 10 tons a day of 150-300 minute charcoal from raw anthracite. This was one-third of the total production at that time and was mixed with the nut charcoal made at Astoria, thereby preventing an absolute shortage of canister-filling material in October, 1918.

The effects of high-temperature cracking, or gas treating as Chaney calls it, explain why it is impossible to activate retort coke satisfactorily and also why samples of lighting carbon made with lamp-black flour might activate well if taken from one part of the furnace,

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and not at all if taken from another part of the same furnace. It is all a question of the temperatures in the different parts of the furnace.

It was next shown that the cocoanut charcoal fines resulting from grinding and screening losses with the cocoanut charcoal, and amounting to 50% of the product, could be ground, mixed with binder, and baked like ordinary carbon products. By avoiding gas-treating in the bake, the resulting charcoal is nearly as good as that from the original shell. A recovery plant for treating the cocoanut fines was built at Astoria. The product was called "Coalite."

The great advantage of cocoanut shell as a source of charcoal is that it is very dense and consequently it is possible to convert it into a mass having a large number of fine pores, whereas a less dense wood, like cedar, will necessarily give more larger pores, which are of relatively little value. The cocoanut charcoal is also pretty resistant to oxidation which seems to make selective oxidation a more simple matter. By briquetting different woods, it is possible to make charcoal from them which is nearly equal to that from cocoanut shell.

By heating lamp black with sulphur and briquetting, it was possible to make a charcoal having approximately the same service time as cocoanut charcoal. At the Cornell Laboratory a charcoal was made by emulsifying carbon black with soft pitch, which gave the equivalent of 400 minutes against calcipicrin before it had been steam-treated. This looked so good that the plans were drawn for making a thousand pounds or more of this product at Washington so as to give it a thorough test. This was not done on account of the stopping of all research work. The possible advantage of this product was the more uniform distribution of binder.

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The National Carbon Company ~~also~~ studied the production of charcoal from bituminous coal and made a 600 minute charcoal from this material. Instead of steam-treating anthracite coal direct, the National Carbon Company also pulverized it, mixed it with binder, and baked it into rods which were then ground and activated with steam. The resulting material, which was known as Carbonite, had somewhat less activity than the lamp-black mixes but was very much cheaper. A plant was built to bake 40 tons a day of this material, which would yield 10 tons a day of active carbon after allowing for grinding losses and steam treatment. The plant was guaranteed to furnish an absorbent having a life of 600 minutes against chlorpicrin (40 minutes on the accelerated test).

After the armistice was signed, Mr. Chaney took up the question of how the Germans made their charcoal. The German charcoal was made from a coniferous wood and was reported to be as good as ours, in spite of the fact that they were using inferior materials. Inside of a month Mr. Chaney had found out how the German charcoal was made, had duplicated their material, and had shown that it was nothing like as good as our charcoal. The Germans impregnated the wood with zinc chloride, carbonized at red heat, and washed out most of the zinc chloride. When this zinc chloride was found in the German charcoal, it was assumed that it had been added after the charcoal had been made. It was therefore dissolved out with hydrochloric acid, thereby improving the charcoal against chlorpicrin. The German charcoal was then tested as it stood, including the fines, against American charcoal, 8-14 mesh. The most

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serious error, however, was in testing only against a high concentration of chlorpicrin. The German charcoal contains relatively coarse pores which condense gases at high concentrations very well but which do not adsorb gases strongly at low concentrations. The result was that the German charcoal was rated as being four or five times as good as it really was.

The general theory of adsorbent or "active" carbon has been outlined by Mr. Chaney something as follows:-

1. Active carbon is a form of amorphous carbon deposited at relatively low temperatures (below 600°C) by chemical or thermal decomposition of carbon compounds. It is substantially free from adsorbed hydrocarbons and from the inactive forms of carbons deposited by thermal decomposition of hydrocarbons at relatively high temperatures, as in so-called "gas-treating".
2. Primary carbon is active carbon plus adsorbed hydrocarbons. Destructive distillation of hydrocarbons at low temperatures, as in the charring of woods, burning of oils to lamp-black, and distillation of coal, results, in general, in the deposition of active carbon, which adsorbs a certain amount of the hydrocarbons, thus forming what is called primary carbon. The adsorbed hydrocarbons are stabilized thereby so that they resist cracking and volatilization at very much higher temperatures than they would if not adsorbed.
3. Activation consists in removing the adsorbed hydrocarbons from the active carbon and in securing the proper porosity.

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The removal of the hydrocarbons is a difficult matter owing to their being stabilized by adsorption. Increasing the surface of the active charcoal means increasing the adsorption. Increasing the porosity and, therefore decreasing the density is of benefit only so long as it increases the surface. A first-class charcoal, may have an apparent density of 0.4 while the true density of the carbon is over 1.8.

The specific oxidizers found of most value were air at 350-450°C and steam or CO<sub>2</sub> at 800-1000°C. The success of the method lies in the fact that the hydrocarbons are more susceptible to oxidation than active carbon and may therefore be removed with only the loss of carbon essential to proper porosity of the granular absorbent.

4. Gas treating is the decomposition of hydrocarbons at high temperatures, in general above 600°C. The product is inert, non-absorbent, and resistant to oxidation. When deposited in the pores and on the surface of active carbon, it renders the latter inactive, and partially or wholly incapable of re-activation, depending on the extent of the gas treatment. The inferiority of the British and French charcoal is due to the inactive carbon formed as a result of prolonged, high-temperature distillation.

The essential feature in the manufacture of active carbon is to avoid gas-treating both in the preliminary carbonization and in the subsequent processes of removing hydrocarbons from active carbon. While retort carbon, ordinary bituminous cokes, and various manufactured carbons are inactive and incapable of activation, this is not a necessary characteristic. <sup>u</sup>Going to the method of coking or baking, such products have received a severe gas-treating. When this is avoided, active carbon may be manufactured from any carbonaceous material.

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The manufacture of a satisfactory soda-lime was a difficult problem. The first soda-lime had too much caustic soda and was too soft and too deliquescent. Captain (afterwards Major) Dudley brought over the formula for the British soda-lime and this was taken as a starting point. It was necessary to strike a balance between a number of desirable qualities: absorptive activity, capacity, hardness, resistance to abrasion, chemical stability, low breathing resistance, etc. The development of a satisfactory soda-lime involved, as a preliminary, a careful study of the raw materials and the development of standard specifications and of methods for testing. The method of manufacture is in some respects more important than the exact composition of the product. Details therefore had to be worked out for mixing, slabbing, drying, and grinding. The method of manufacture was also improved by devising a process for spraying sodium permanganate upon the granules after they were dried. The final product consisted essentially of a mixture of lime, cement, kieselguhr, sodium permanganate and sodium hydroxide, the last two being present in very small proportions. The caustic soda-gives the activity, the lime the capacity, the kieselguhr the porosity, and the cement the hardness, while the permanganate is added to take <sup>care of</sup> ~~off~~ certain oxidizable gases which the Germans might have used but did not. The final product was better than the soda-lime made by any of the other belligerent countries.

A great many experiments were also made to find better binding agents, better activating agents, or special reagents which might improve the absorbent with reference to some particular gas. It was quite easy to produce better results in any one direction; but these were usually counter-balanced by a corresponding disadvantage. If the hardness was increased,

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for instance, the absorptive activity always decreased and vice-versa. The following materials seemed fairly promising however: copper oxide, which improved the soda-lime greatly against hydrocyanic acid; ferric hydroxide, which helped against cyanogen chloride; and finely ground charcoal, which tended to activate the soda-lime against all gases.

The successful production of a satisfactory soda-lime for the Army led to a request by the Navy for the development of a more satisfactory soda-lime to absorb carbon dioxide in submarines. A material was developed which gave distinctly better absorptive efficiency and enormously better mechanical properties than any CO<sub>2</sub> absorbent previously used by the Navy and permitted submergence for eight times the periods which had been possible previously. A soda-lime was also developed for the Navy to be used in a self-contained oxygen respirator apparatus for the absorption of CO<sub>2</sub> from the lungs.

Since the absorbents are placed in the canister at least two or three months before they are used and may be in use for several months before they are replaced, the question of deterioration is a serious one. The prevention of deterioration of soda-lime was found to be largely a question of keeping the various raw materials as pure as possible. The chief difficulty is the decomposition of the permanganate, which can be prevented if the alkali content is kept low and all the materials are free from reducing agents or soluble salts. A low alkali content also prevents deterioration due to deliquescence of the absorbent.

The only method by which sodium permanganate was made before the war gave a product which was entirely unsatisfactory for use in soda-lime because not sufficiently pure. New methods for oxidation and evaporation were

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therefore developed. An electrolytic method of preparing sodium permanganate was developed. The work was begun at the Johns Hopkins laboratory, carried further at the Washington laboratory, put on a large-scale laboratory basis at Columbia University, and tried out on a semi-plant scale at the works of the National Electrolytic Company, Niagara Falls. The experiments were entirely satisfactory and a much purer permanganate was obtained than by any other method. It was estimated that the cost by the electrolytic process would only be about one-third that by the chemical process.

As soon as the soda-lime problem was fairly well in hand, investigation was begun of a great number of other types of possible absorbing materials. It was soon found that the most promising of all types of absorbents were impregnated charcoals, since they retained the absorptive action of the charcoal and yet could react chemically with certain gases, depending upon the nature of the impregnating agent. Charcoals have been impregnated with practically all the metallic hydroxides, with a great many inorganic salts, with organic compounds, with oxidizing agents, etc. The best material was a copper-impregnated charcoal to which the name of Whetlerite was given. It was made by introducing copper sulphate into charcoal and ~~by~~ reducing with finely divided iron. This absorbent is a consistent all-round improvement over the corresponding <sup>un</sup>impregnated charcoal and was to have been put into large-scale production by the Gas Defense Division. The material gave an average increase in service time of 500% against arsine, 100% against hydrocyanic acid, 60% against phosgene and other acid gases, and 10 - 40% against other gases.

Another very promising new type of absorbent was the so-called iron gel or ferric hydroxide absorbent which was made by precipitating ferric hydroxide in a very finely divided form, washing, drying very slowly, and grinding into granular form. All these operations must be carried out under carefully

42 60

defined conditions. The final product is a better absorbent for all gases than charcoal in a dry atmosphere; but it showed a great tendency to take up moisture rather than the poison gases. It seems possible that the ideal mixture for a canister may consist of 70% Whetlerite and 30% iron gel.

\* Another very interesting absorbent was the silicon<sup>a</sup> gel developed at the Johns Hopkins University. This had great absorpti~~on~~<sup>ve</sup> power especially against high concentrations, but did not hold the gases sufficiently when they were present in low concentration.

Special determinations on the effect of the size of the particles of the different standard absorbents on their efficiency against different gases showed that the increase in efficiency with decreasing size of grain is very great with soda-lime, less with Whetlerite, and least of all with charcoal. Experiments were also made to determine the best combination of size of granules, depth of layer, and area of cross-section to give the maximum efficiency and the lowest pressure drop through the canister. These experiments led to a radical change in the design of the 1919 canister, giving it a very large cross-section area, a shallow layer of absorbent, and fine-meshed particles.

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5.

The Navy wished a special absorbent to stop carbon monoxide and Col. Lamb's Section succeeded in developing two which were satisfactory. The first consisted essentially of iodine pentoxide and fuming sulphuric acid mixed with pumice. This reacts with the carbon monoxide oxidizing it to carbon dioxide. Some experiments along this line were ~~carried out~~ <sup>made</sup> by the French; but they did not carry the idea through to a successful finish. The second and better absorbent consisted of a mixture of suitably prepared oxides which act catalytically under certain conditions and cause the carbon monoxide to react with the oxygen of the air. This is the one that has been put into large scale production. Since there are color changes connected with the iodine pentoxide reaction, it has been possible to develop this so as to serve as a detector for carbon monoxide, sensitive to 0.001% CO.

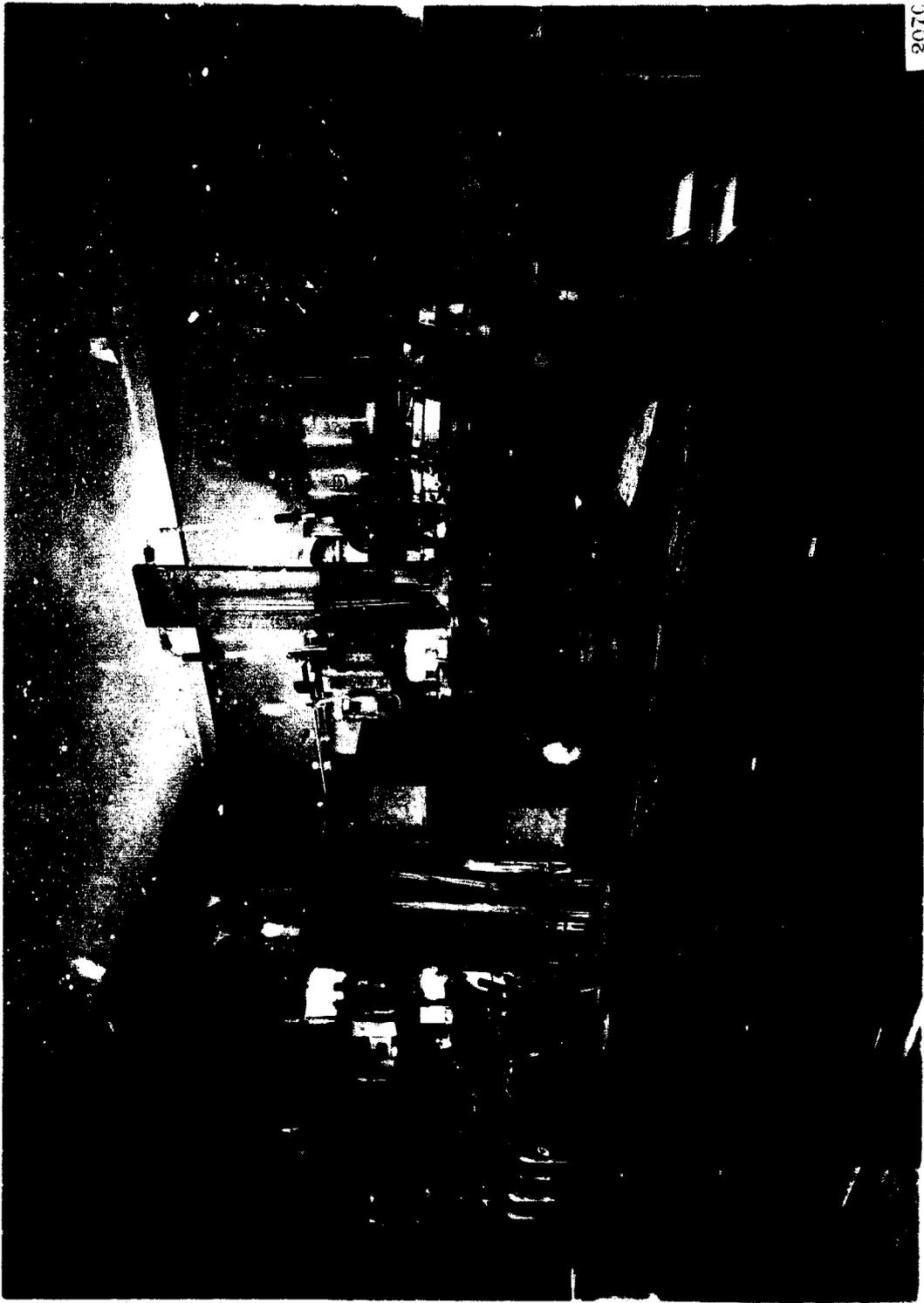
*the Research Division developed*

The Navy also wished an ammonia absorbent and a successful one ~~was found in~~ <sup>called</sup> Kupramite which consists of pumice impregnated with its weight of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . With 44 cubic inches <sup>of this material</sup> in the standard Army canister, men at rest have complete protection against 3% ammonia for four hours and against 5% ammonia for 2.5 hours. With men doing severe exercise the life against 5% ammonia is over 25 minutes. At a rate of flow of air of 85 liters per minute, the resistance is less than 50 mm. of water.

*44. 62*

The development of the canister and of the face-piece of the mask was connected so intimately with the production that it seems better to take up these two general questions in the chapter devoted to the Defense Production Division in spite of the fact that a great deal of work was done by the Research Division. Certain points in regard to the canisters and the eye-pieces cannot be discussed here, <sup>fact</sup> however.

44a 63



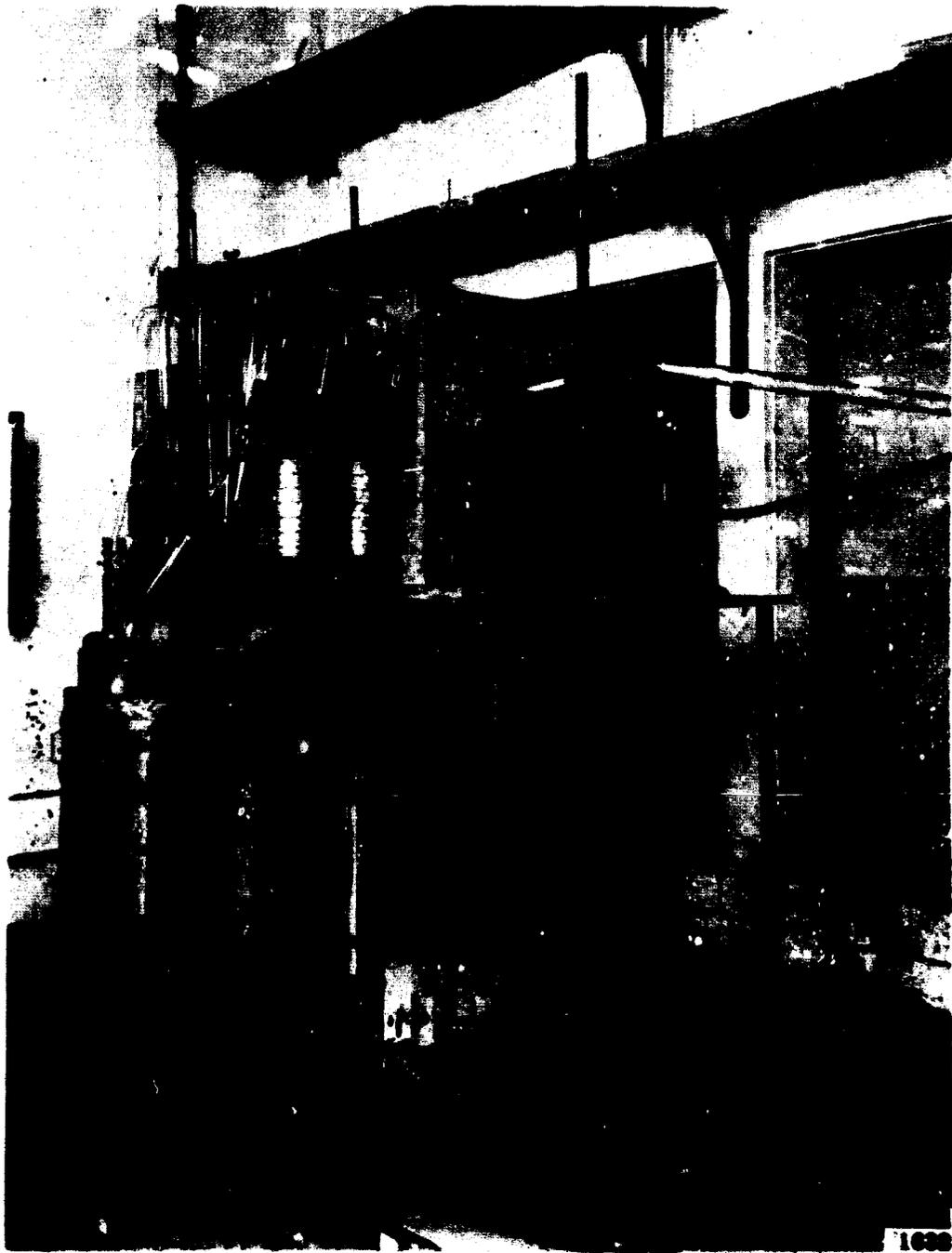
207C

Assembly of Optical Penetrometer.

Plate XII.



A DUPLEX MACHINE FOR STUDYING THE COURSE OF  
GASES THROUGH CANISTERS.  
(Side View)



A DUPLEX MACHINE FOR STUDYING THE COURSE OF  
GASES THROUGH CANISTERS  
(End View)

The general development of the canister has been along two general lines: decrease in volume as better absorbents were obtained and reduction of resistance to breathing. The absorbents used in filling the first canisters consisted of wood charcoal and a soda-lime containing a high percentage of caustic soda and colored green by sodium manganate instead of pink by sodium permanganate, as should have been the case. The gases that were considered at that time were chlorine, phosgene and hydrocyanic acid. Early experiments showed that with 50 cubic inches of absorbent in the canister, two parts of soda-lime to three of charcoal was as low as one could cut down the amount of ~~charcoal~~ <sup>soda-lime</sup> and still have adequate protection. This ratio was adopted because it was desired to keep the amount of charcoal as high as possible. The charcoal in use in June 1917, did not stop chlorine and the soda-lime was a distinctly inferior product. The wood charcoal was replaced by coconut charcoal as soon as possible and the quality of the latter was improved continuously. The improvement in the soda-lime was equally marked and no change in the relative amounts of soda-lime and charcoal was ever made. On the other hand it was soon found that better results were obtained by mixing the charcoal and soda-lime, rather than <sup>by using</sup> them in separate layers. It was also easier to fill the canister with the mixture than with the two substances separately, so this change was adopted.

There is always a tendency for the incoming air not to pass uniformly through the mixture. Special experiments showed that this channelling, as it is called, could be reduced to a minimum by introducing a wire down the bottom of the canister, this serving to spread the air more uniformly. As might be expected, the channelling up the sides of the canister is less the lower the rate of flow and is less for intermittent flow than for



2133

TOBACCO SMOKE MACHINE FOR FLANGE TESTING OF FILTERS  
ILLUMINOMETER SET-UP ATTACHED

continuous flow. The tendency to channel varies with the packing of the canister and the experiments on channelling led to an improved method of packing. The original method of packing experimental canisters had been to pour the absorbents into the canisters and bump them down with a wooden block. This method packs the center harder than the sides causing the gas to channel up the sides. The improved method consisted in filling the canister with absorbents and then inserting the top screen and springs. The canister with the spring pressure applied, is then jolted on a machine designed to give the canister a one-inch drop one hundred and fifty times per minute. This settles the absorbents evenly and decreases irregular channelling to a great extent. With the latest type of canister, having a central breathing tube, it is absolutely necessary to jolt the canister with the spring pressure applied in order to avoid channelling.

When stannic chloride began to be used as a source of smoke, it was necessary to place in the canister two cotton wadding pads, consisting of two or three layers each, between the canister and the soda-line stops smoke effectively. Tests showed that the best protection was obtained with one pad one-third of the way from the bottom of the canister and the other two-thirds of the way, though it is also true that for the same filtering material, a vertical height of the filter is more important than a horizontal width, when the apparent amount of gas surface or the position of the pad in the canister.

The filter used can be a standard -line with wire protection, a coarse screen material; but the use of a standard pressure drop. The standard used was 14 for charcoal and 8-14 for soda-line. Tests were made to see whether there could be any advantage in using the standard screen and placing them in layers in the canister. The results were that no increase in life is produced by placing the standard screen in the canister and the filter material at the top; also that there is a slight increase in efficiency by using fine charcoal and coarse soda-line or coarse charcoal and fine soda-line.

46 2. b5

With falling temperature the life of the canister increases against phosgene, hydrocyanic acid, and cyanogen chloride while there is practically no change with the temperature when the canister is tested against chlorpicrin. The differences may be quite marked. Thus a charcoal which lasts 17.5 minutes against phosgene at 40°C will stand up for 54 minutes at -13°C. The difference is not so great with soda-lime, so that the life of a canister against phosgene at -13°C is only about 70% greater than at 40°C instead of about 200% greater as would be the case if the filling were entirely charcoal. With hydrocyanic acid the variation with the temperature is very marked for the soda-lime and relatively little for the charcoal. Thus the life of the canister is more than doubled when changing from 40° to -13°C while the increased life with charcoal alone is only about 20%. Against cyanogen chloride the life at the lower temperature is six times what it is at the higher temperature.

With increasing humidity the life of the canister against phosgene increases because the phosgene is hydrolyzed more rapidly, while with chlorpicrin the life is less because the water cuts down the absorption of chlorpicrin. If a canister is stored for six months, there is an increase in efficiency against phosgene and a decrease against chlorpicrin. This is due in part <sup>to</sup> a transfer of moisture from the soda-lime to the chlorpicrin. As a first approximation the life of the canister varies inversely as the concentration of the gas, though it is more accurate to use a formula  $C^2T = \text{constant}$  where  $T$  is the time in minutes to the breaking point,  $C$  is concentration in parts per million and  $n$  is a constant in any given set of conditions varying between 0.9 and 1.5.

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1.

One great difficulty with the mask is the dimming of the eye-pieces. The French met this to some extent by using eye-pieces made of 'cellophane', a hydrated cellulose acetate. This material takes up water but lets it diffuse through. The eye-piece remains non-dimming provided the condensation of moisture is not too rapid. The Germans used a gelatin-coated eye-piece which could take up a certain amount of water before dimming, after which another eye-piece must be substituted. The British used a glass eye-piece upon which they rubbed an anti-dimming mixture called glasso, which kept the water from forming in drops on the surface. In the French Tissot Mask the air which comes through the canister passes over the eye-pieces and cuts down the dimming very much.

The Research Laboratory of the Eastman Kodak Company succeeded in producing a gelatine which was distinctly superior to that manufactured by the Germans. The fatal defects of this material as compared with glass are its poorer initial optical qualities, its softness when moist making it liable to scratching, and the tendency of the eye-piece discs to warp during the absorption of moisture or during drying.

The French 'cellophane' eye-piece is essentially viscose, so the actual making of the material is easy, but the difficulty is to obtain discs in a sufficiently transparent and optically satisfactory form. The Viscose Company succeeded in obtaining material equal to that made by the French and in thicker sheets, but it was still distinctly inferior to the hydrated cellulose obtained in other

48. 67

ways. Denitrated cellulose nitrate gives a still better product but it proved impossible to denitrate completely sheets as thick as were desired. This work was done at the Delta Laboratory of the DuPont Company at Arlington, N. J. Cellulose acetate proved to be the best substance from which to prepare transparent cellulose. The Chemical Products Company of Boston found that with alcoholic or aqueous ammonia it was possible to hydrolyze sheets containing very little softener and which were thicker than those to be obtained from any of the other materials. The product was distinctly superior to the French 'cellophane' both in hygroscopic and optical properties. Like the other forms of hydrated cellulose it is subject to cockling and shrinking on repeated drying, so that it frequently pulls out of its holder. Though its <sup>initial</sup> optical properties are surprisingly good, they are inferior to glass and the material is easily scratched when moist.

One other material studied was a hygroscopic glass. Glass lenses were actually secured which did not dim readily; but the material had not the required degree of permanency.

While these experiments were being carried on, work was also being done to improve on the anti-dimming materials used by the British. The material finally adopted was made by heating a mixture consisting of 100 parts of 85% Turkey red oil, 15 parts of caustic soda, 5 parts of syrupy water glass, and 5 parts of paraffin, then drying the mixture to about 10% water content. This material was manufactured on a large scale by Colgate and Company in the form

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3.

of small round sticks. Ten million of these anti-dimming sticks had been contracted for by the Gas Defense Production Division.

With the introduction of the Tissot type of mask, the problem changed somewhat. With this type there is much less dimming, because the inhaled air passes over the eye-pieces. Dimming does take place intermittently when the man exhales and this is of course more marked the colder the weather. Experiments showed that the anti-dimming stick developed for the S. B. R. mask was not absolutely satisfactory for the Tissot type of mask, but a slight change in the formula met this difficulty and four million of the new type of anti-dimming sticks were ordered by the Gas Defense Production Division.

It seemed possible to eliminate all dimming with the Tissot type of mask by changing the design somewhat. All the forms developed for this purpose made use of a sponge-rubber dam fitting tightly across the face over the nose and cheeks thus dividing the air space within the mask into two chambers, one for the eyes and the other for the mouth and nose. In what seemed to be the best of the four types the air from the eye chamber passes through a single, large, low-resistance valve to the breathing chamber. It is not practicable to place this valve in the rubber dam and it must in general be included in an external tube. With a valve placed at this point, the corresponding valve on the base of the canister can be omitted. This arrangement prevents the backward flow of moist air into the eye-chamber and yet does not involve any serious effects in mask resistance even at high rates of breathing.

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## 4.

Masks of this type have stood up most successfully under very rigid tests. The one essential is that they shall fit well. On the other hand the question of fit can be determined easily by the soldier himself. If the eye-pieces dim, the mask does not fit and should be changed.

In connection with this work experiments were also carried out to determine the effect on the soldier of varying visibility. Eye-piece materials which are optically inferior when the illumination is good become relatively very much more inferior with poor illumination. While good definition is important in bright light, it becomes extremely important in poor light. For military use, eye-pieces should therefore have the best possible defining power. The effect of decreasing visibility on the accuracy of rifle sighting was tested thoroughly with good illumination. No serious impairment occurs until the definition is reduced to about 30% of normal, the decrease in visibility evidently being counteracted largely by an increase in the effort of attention. Different results would probably be obtained with tired men. Discrimination in a limited time between a gray object and a white background was also tested with varying illumination and it was found that there was not much impairment in the power of discrimination until the defining power dropped below 50%. With poor light the difference became noticeable much sooner.

G

The glass used in the mask eye-pieces ~~was~~<sup>is the</sup> so-called triplex glass

consisting of two layers of glass cemented together by a layer of pyralin, which is a special celluloid. For a long time the output of the Super-Glass Company was only 20000 eye-pieces per day with 60% Rejections. These rejections were due largely to 'let-goes' (in which case the glass separates from the pyralin layer), cracks, 'squeeze-outs', and dry spots. Most of these difficulties were caused by insufficient curing of the pyralin and by improper methods of cutting and pressing the layers used in the eyepieces. The Research Division was able to suggest improvements which brought the production up to as high as 50000 lenses per day with 10% rejections.

5/27/51 5.

169  
by the Dispersion Section

Research Division

by the Dispersion Section

has been

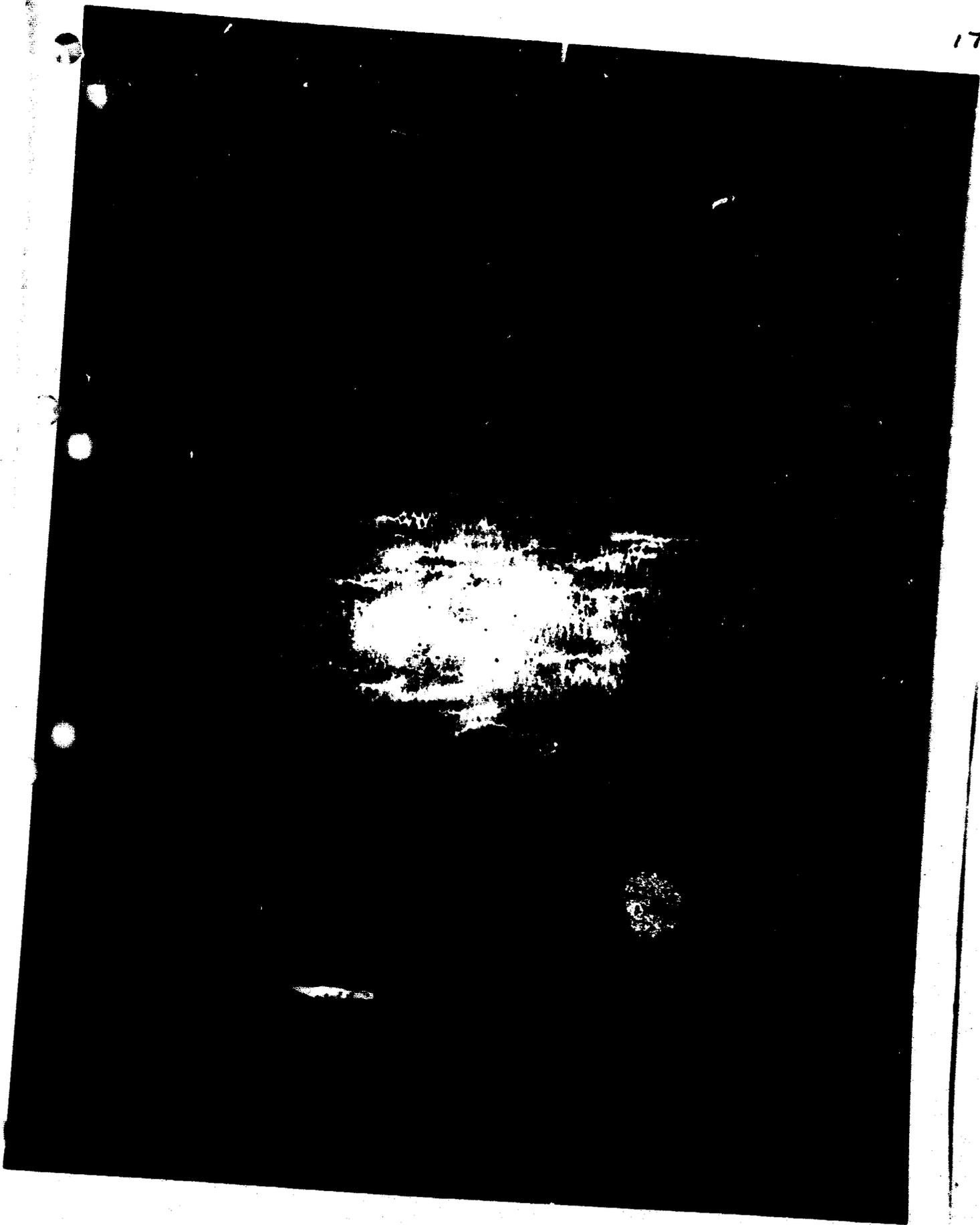
A very careful study of the theory of smokes <sup>has been</sup> made. The concentration of the smoke was determined by precipitation in a modified Cottrell apparatus consisting of a central wire cathode surrounded by a cylindrical aluminum foil anode about 1/1000 inch in thickness. A 15000 volt rectified direct current was used and complete precipitation was obtained with fairly concentrated samples of smoke even when drawn through the apparatus <sup>at a rate</sup> of about five liters per minute. The aluminum foil and adhering smoke were then weighed. Microscopic examination showed whether the smoke particles were liquid or solid. The size of the particles in a smoke can be determined ultra-microscopically with fair accuracy by measuring the velocity of a charged particle in an electric field of measured intensity, photographing the path of the particle while the direction of the electric field is reversed regularly by a rotating commutator whose speed is known accurately. When the convection due to the source of light is perpendicular to this motion, a zigzag line is obtained. Since about one-third of the smoke particles are charged electrically, photographs of these oscillations show simultaneously the behavior of a large number of particles, thus simplifying the study of size distribution. For the more rapid study of smokes an instrument called the Tyndall meter was devised which measured the brightness of the Tyndall beam set up in the smoke to be examined. For low concentrations of smoke the brightness of the beam increases with the concentration and the degree of opacity of the smoke material, so that if either factor remains practically constant the readings give a measure of the variation of the other.

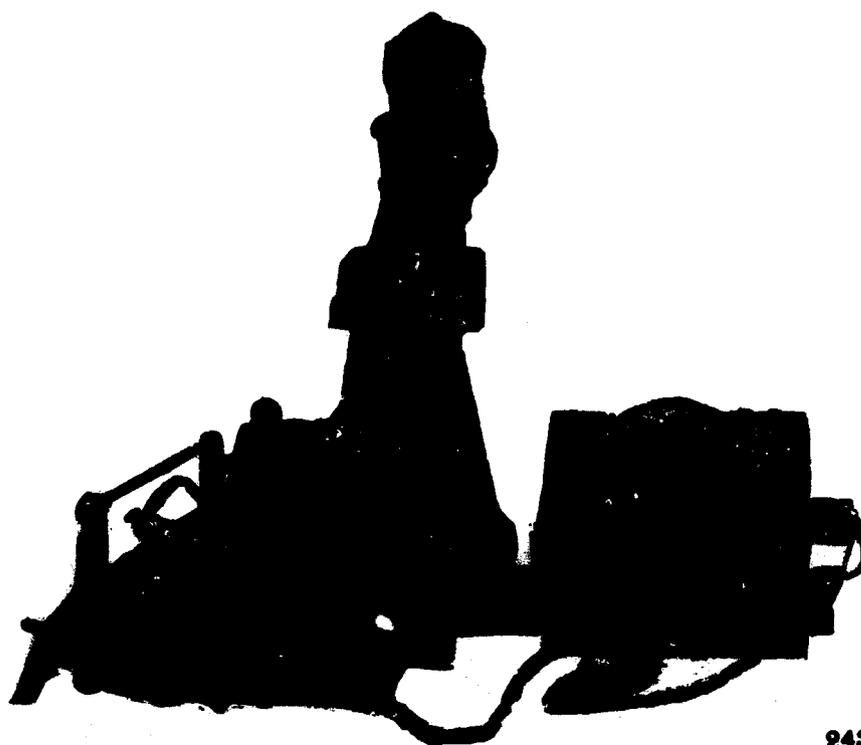
Toxic smokes are prepared by condensation, disintegration, or some combination of the two. The condensation or thermal method consists essentially in the volatilization of a substance having a sufficiently low vapor pressure, followed by a recondensation of the vapor when the temperature has fallen

1. 55 72



Ultramicrograph showing zig zag path of Charged Smoke Particle  
subjected to a Rapidly Reversing Electrical Field.

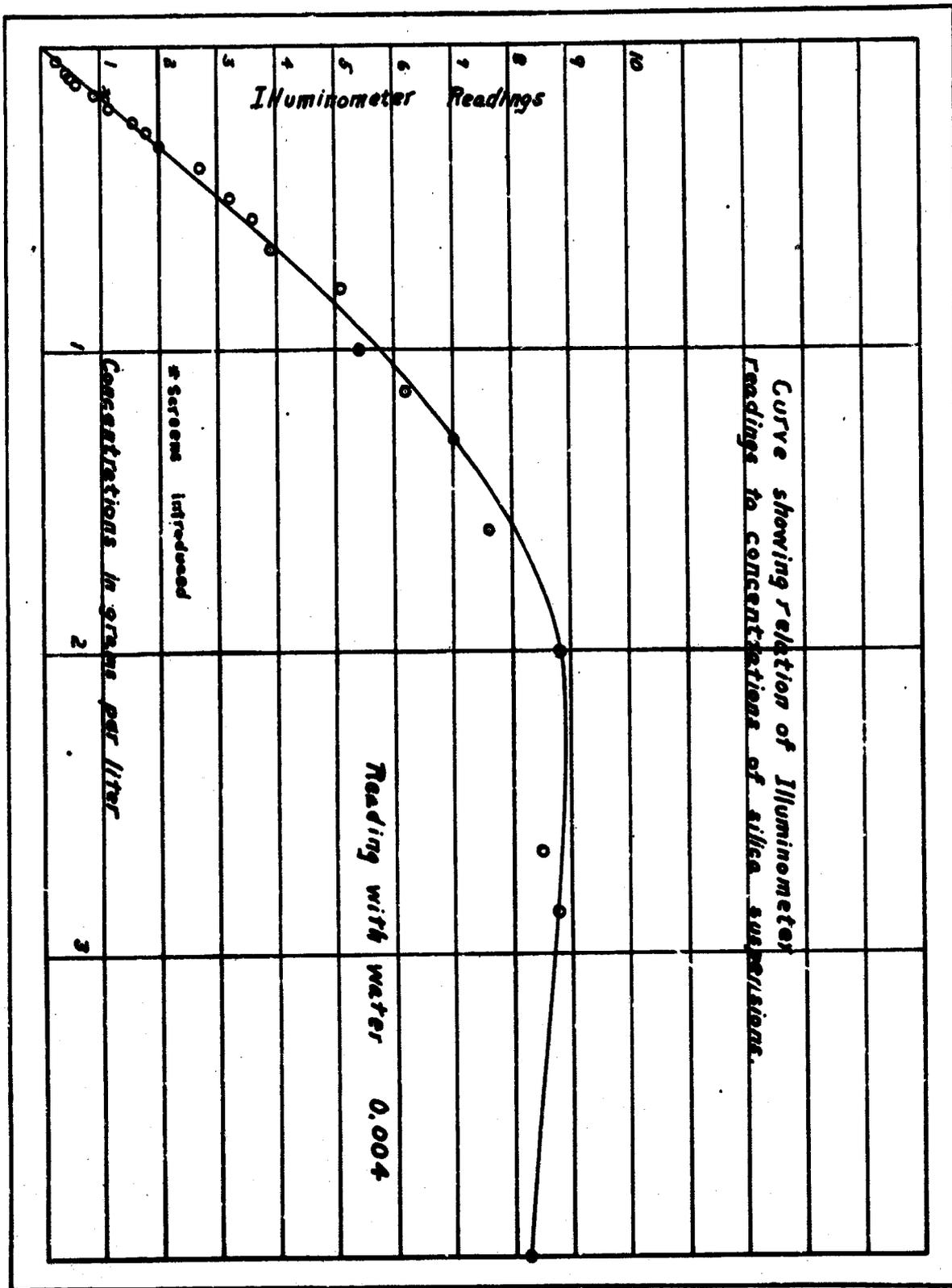


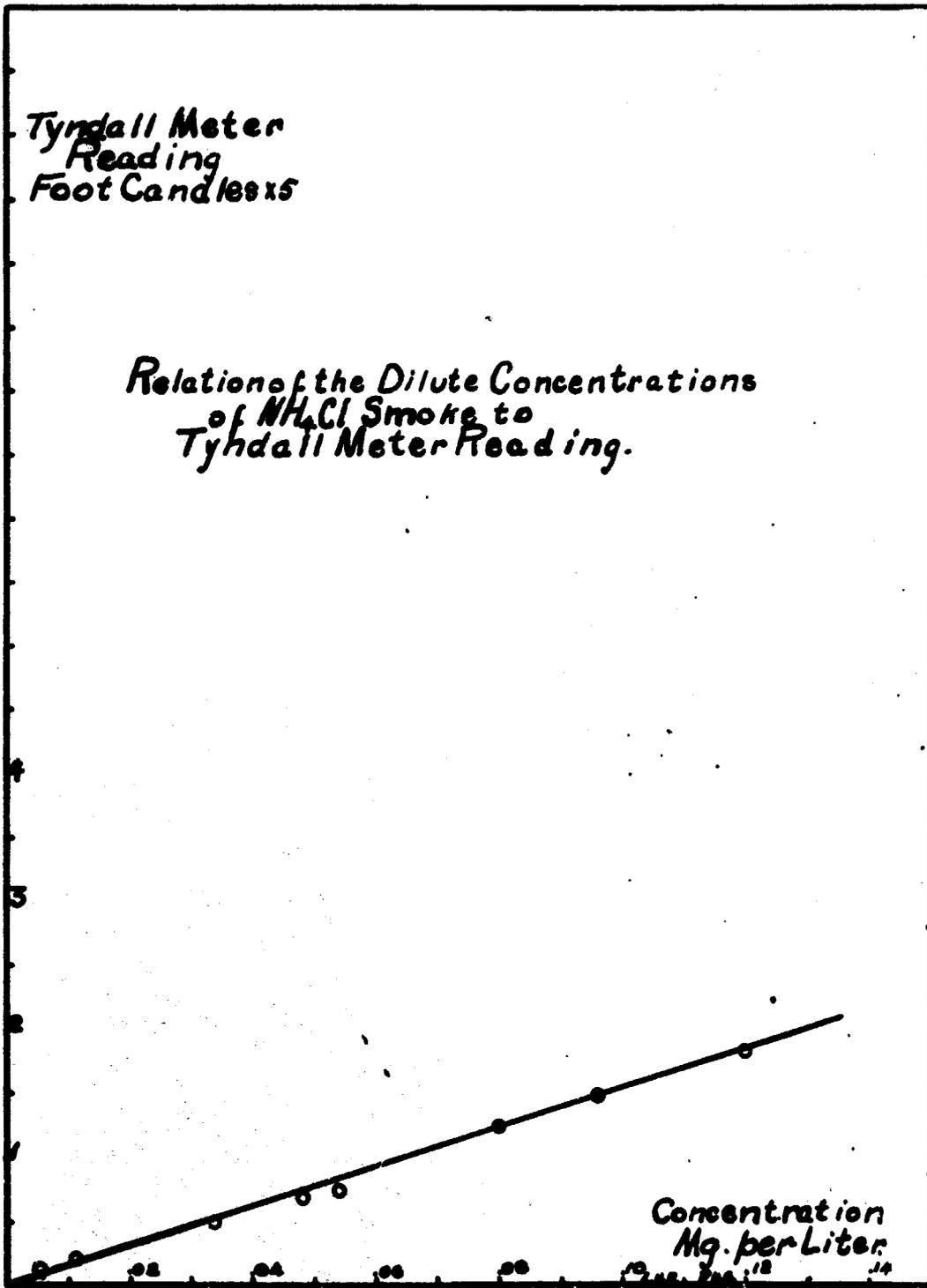


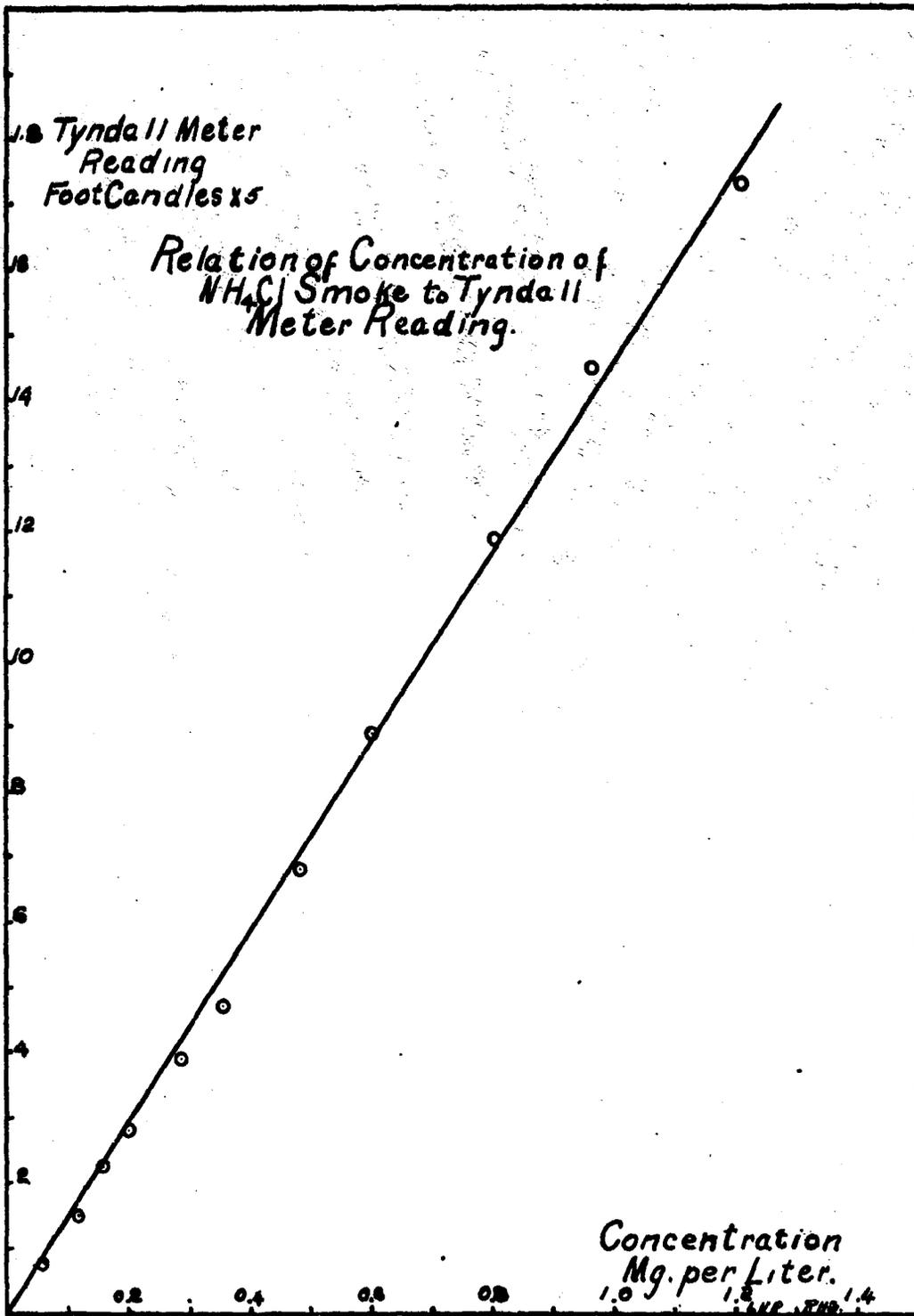
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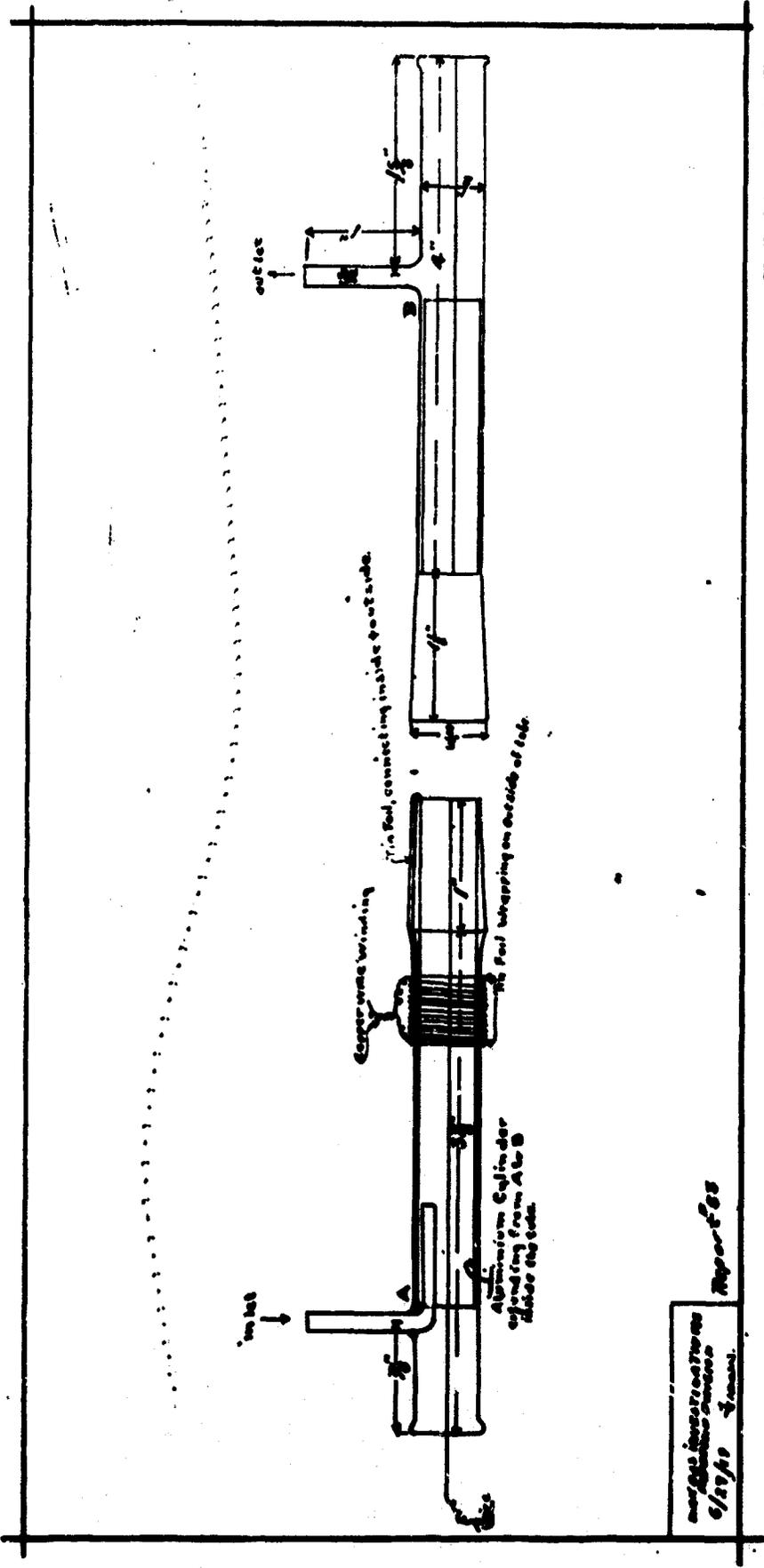
TYNDALL METER AND AUXILIARY APPARATUS

PLATE V

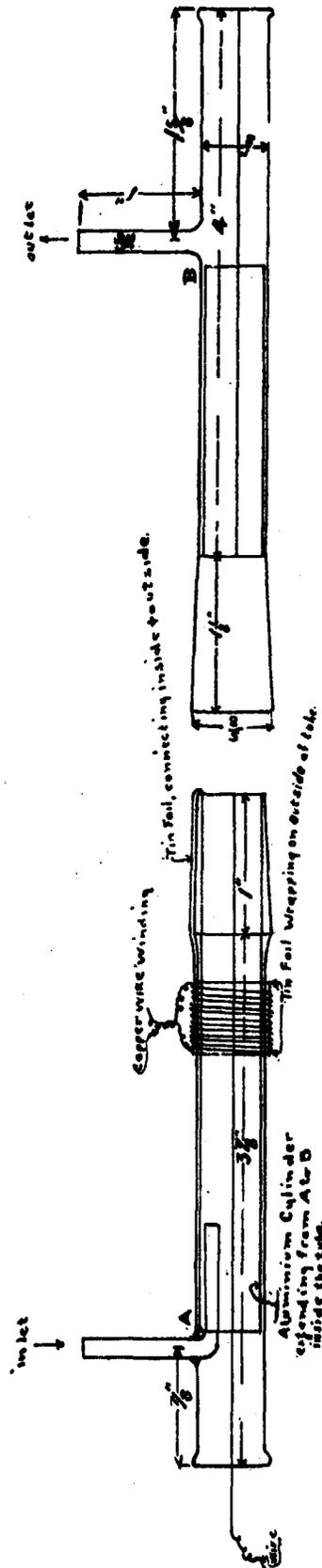






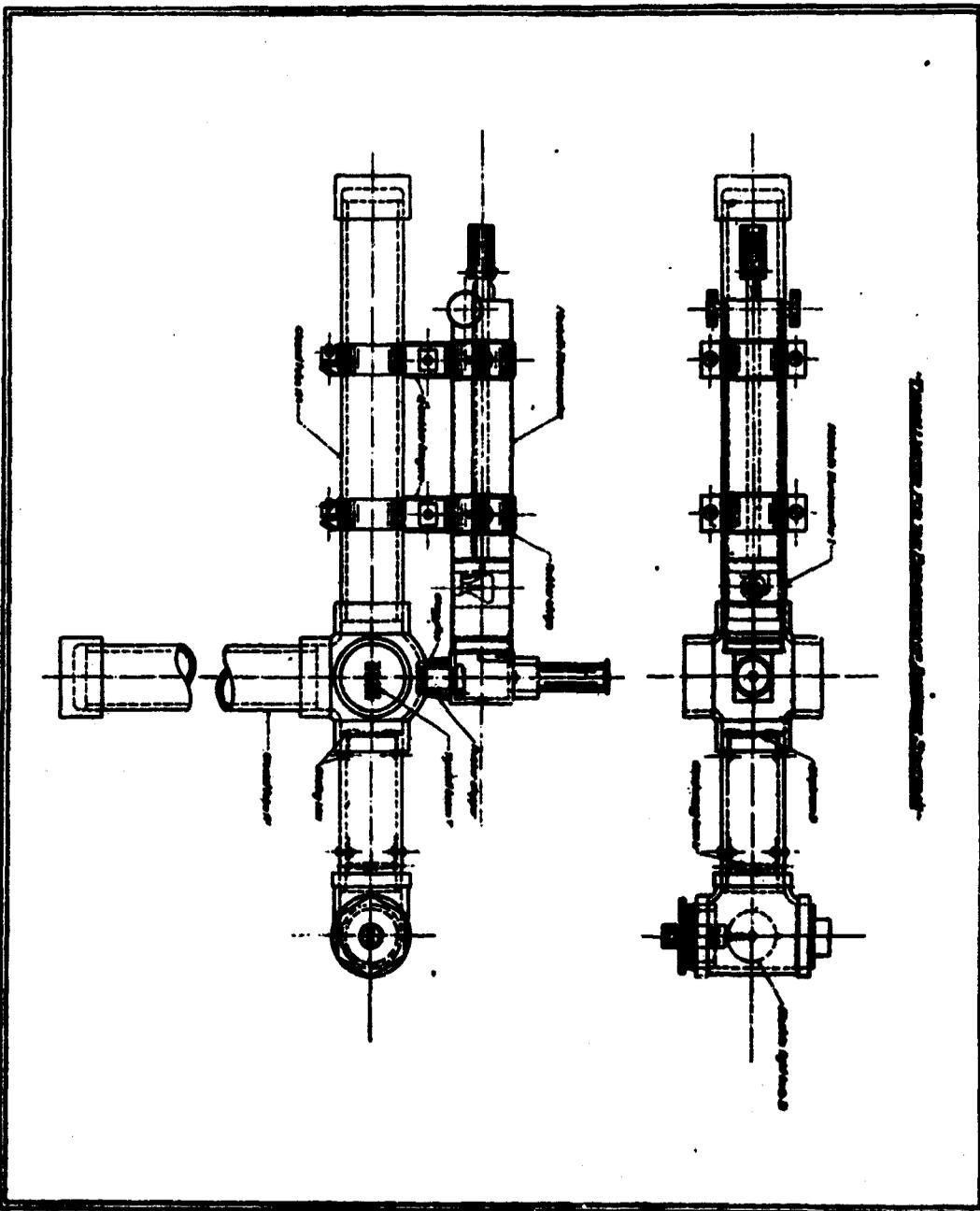


THE ENGINEERING TOOL COMPANY, INC., NEW BRUNSWICK, N. J.



METEOR INVESTIGATIONS  
 UNIVERSITY OF CALIFORNIA  
 6/29/53  
 Report 53  
 Yaman.

THE HORNBY PETERS CO. PASADENA, CALIF., MANUFACTURERS U.S.A.



ASSEMBLY DRAWING OF METAL VALVE

sufficiently. The smoke consists of relatively large particles if the rate of condensation is low as when vaporization takes place in an open container from which the condensing vapors pass slowly into the air without being diluted sufficiently. Each particle remains an appreciable time in contact with saturated vapor and consequently increases very rapidly in size. On the other hand relatively small particles will be formed if the vapor is swept away by a current of hot gases under pressure because it is then diluted before supersaturation occurs. The possibility of the very small particles coalescing is also less at high dilutions.

In the disintegration or explosive method we have the partial mechanical shattering of the material owing to the shock of the explosion and a partial vaporization of the shattered material due to the heat of explosion. The full violence of the mechanical shock is not utilized since the smoke material does not possess sufficient inertia to receive the full force of the shock; and the effectiveness of the heat of the explosion is reduced greatly owing to the very brief <sup>time during which</sup> ~~duration~~ <sup>is</sup> of a particle in the heated zone. Consequently the explosive method does not give so many finely divided smoke particles as does the thermal method. Starting with a powder of about 0.1 mm in diameter, the explosion will shatter these more or less completely into particles <sup>of an average diameter of</sup> about 0.001 mm. The heat produced will vaporize some of these particles which will then precipitate in a finer form; but the percentage having diameters 1 - 0.01  $\mu$  is very much less than when the thermal method is used. With the substances studied, very few particles are obtained having diameters less than 0.01  $\mu$ , apparently because the very small particles are too unstable.

Some substances give good smokes by ~~the~~ <sup>the</sup> explosion <sup>method,</sup> while others do not. The important factors are the vapor pressure, the latent heat of vaporization, the melting-point, and the strength of the crystalline forces. The vapor pressure should have a medium value at ordinary temperatures; if it is too high, recondensation does not take place sufficiently rapidly and if it is too low, a very fine state of subdivision cannot be obtained on explosion and the temperature must be raised too high in the case of the thermal method. This objection is serious with combustible smokes and does not apply of course to phosphorus pentoxide for instance.

If the latent heat of vaporization is low, vaporization by the heat of explosion is facilitated and a cooling of the supersaturated vapor is obtained more easily. If the melting point is low, the substance will melt on slight heating and the cohesive force of a liquid is generally less than that of the corresponding solid. With any given solid, disintegration will take place more readily the lower the cohesive force and the ductility. If the smoke material is a solid it should be comparatively dry and should be ground very fine. As a rule liquids, semi-solids, and relatively low-melting solids give much better smokes than high-melting solids.

Particles of a diameter 1 - 0.01  $\mu$ , such as are found in good, relatively permanent smokes, are small compared with the capillary diameter of the smoke filters. Consequently, the filter does not act primarily like a sieve. The actual mechanism of the filtering consists in the sticking of smoke particles to the wall of the capillary when they are brought in contact with it. Particles are brought in contact with the wall by brownian movements, by direct collision when the stream of air carrying the particle turns a sudden corner, and by gravitational settling.

3. 58 74

With a given filter the percentage penetration of smoke decreases during a run partly because of clogging of the filter and partly because of coagulation of the smoke with time. For the same sized particles the percentage penetration is practically independent of the concentration. At very low rates of flow the penetration is practically zero. With increased rate of flow there is increasing penetration, beyond which the percentage penetration varies very little with the rate of flow. The shape and position of the penetration curve depends of course on the smoke and on the filter.

This study of the theory of smoke production made it possible to devise methods of using smoke which would undoubtedly have had great military value had it not been for the signing of the armistice. Large-scale production of the new devices was already under way.

A study was also made of the possibility of rendering the German masks valueless by coating the charcoal with a material which would prevent its absorbent action, or by clogging the smoke filter thus making breathing through it difficult. Since part of the improvement in the charcoal consists in removing hydrocarbons, experiments were made with kerosene, benzene, etc. testing the charcoal against ammonia. It was found that exceedingly large quantities of these materials were necessary in order to impair the absorbing power of the charcoal appreciably and consequently this method was discarded. It would apparently be feasible to clog the German smoke filter with a titanium chloride smoke; but <sup>toxic</sup> smokes penetrate the German mask so readily that an attack with these seems more promising than one with titanium chloride.

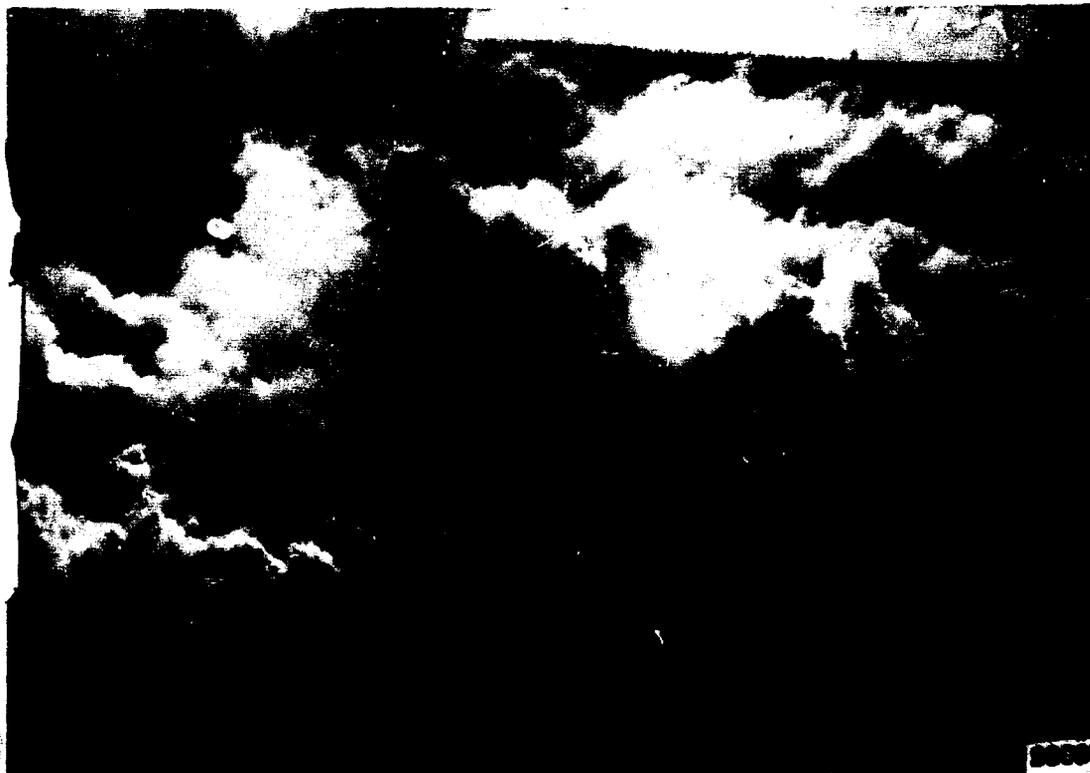


**TOXIC SMOKE CLOUD FROM 500 D.M. CANDLES (Second Test)**

**(Arrangement of Candles Similar to that in First Test)**

The cloud drifted over the Garrison nearly three miles from the origin causing unprotected men severe burning in the throat and lungs, accompanied by coughing and in some cases vomiting. The smoke was detectable to an irritating degree in Lakehurst, N.J. which is about 4 1/2 miles from the origin of the cloud.

**Test at Lakehurst Proving Grounds.  
Dec. 12, 1918.**



**TOXIC SMOKE CLOUD FROM 500 D.M. CANDLES (First Test)**

The candles were placed in 5 parallel rows which were 2 yards apart, each row containing 100 candles on a 100 yard front. The rows of candles were ignited in succession, the total time of active smoke emission being 23 minutes.

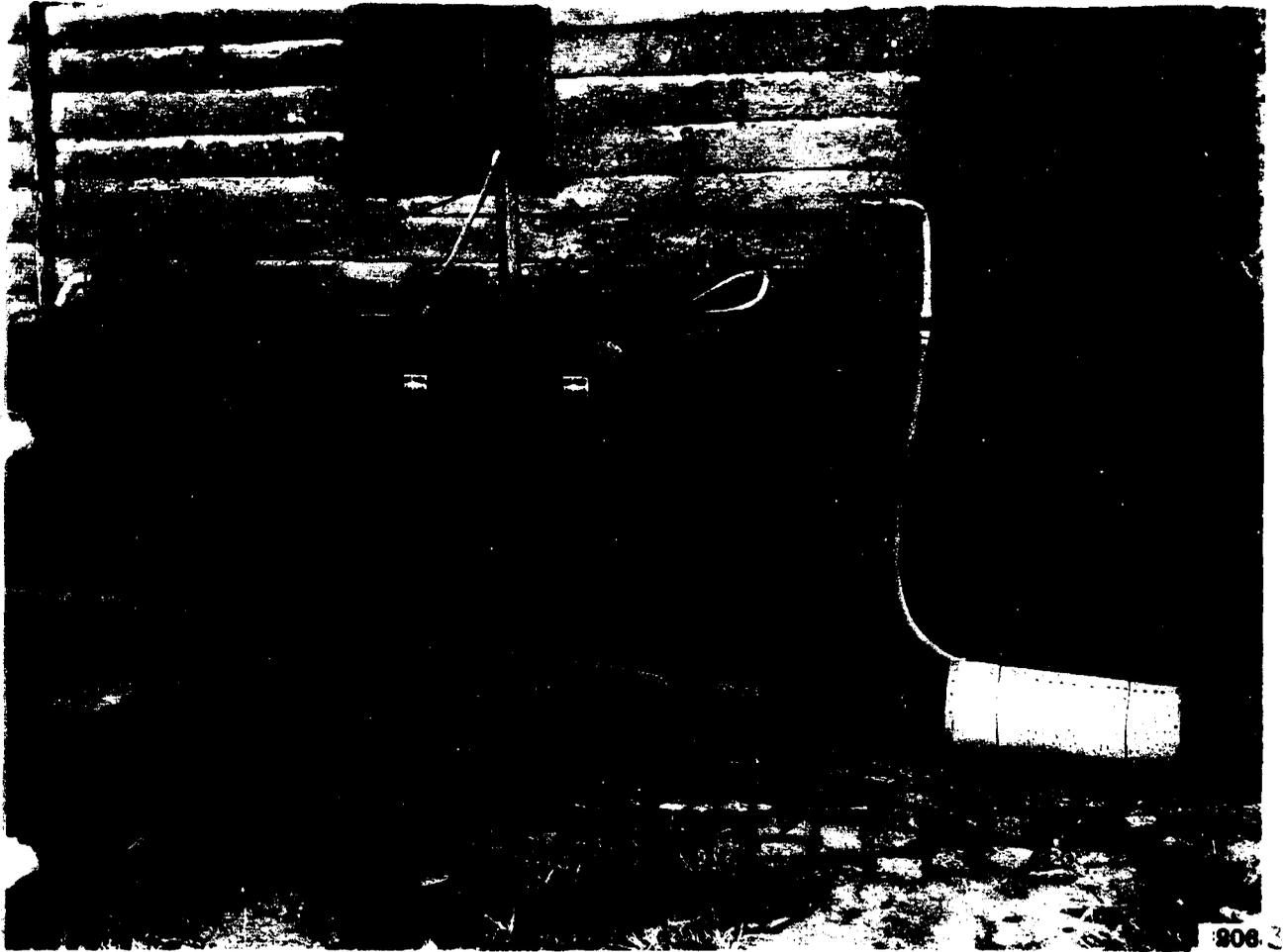
Practically all German and U.S.D.R. Canisters were penetrated unbearably to a distance of 1800 yards. Logan Felts slightly penetrated up to 1000 yards.

Lakehurst, N.J. Proving Grounds  
Dec. 12, 1918.



2005

VIEW FROM BEHIND ORIGIN AFTER IGNITION OF  
THIRD ROW OF CANDLES.



PENETRATION APPARATUS USED TO TEST  
THE SMOKE FROM TOXIC CANDLES.

PLATE LXXXI



8084

PENETRATION APPARATUS IN ACTION

All the filters devised for stopping smokes introduced a very high resistance to breathing. The Defense Chemical Research Section therefore tackled the problem of electrical precipitation. They succeeded in developing a portable electrical precipitation apparatus of the Cottrell type, weighing about four to five pounds which removed smokes completely and introduced only an inappreciable resistance. While the cost and complication of the special apparatus would undoubtedly prevent the general use of such an ~~apparatus~~ <sup>instrument</sup> on the battlefield, it might be of considerable value in special cases and might well be used for a variety of industrial purposes. It was found, for instance, that the electrical precipitator removes bacteria completely from the inhaled air.

Best Available Co

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DEPARTMENT OF THE ARMY  
US ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND  
EDGEWOOD CHEMICAL BIOLOGICAL CENTER  
5183 BLACKHAWK ROAD  
ABERDEEN PROVING GROUND, MD 21010-5424

REPLY TO  
ATTENTION OF:

APR 14 2015

RDCB-DPS-RS

MEMORANDUM THRU Director, Edgewood Chemical Biological Center (ECBC),  
(RDCB-D, Mr. Joseph L. Corriveau), 5183 Blackhawk Road, Aberdeen Proving Ground,  
MD 21010-5424

FOR Office of the Chief Counsel, US Army Research, Development and Engineering  
Command (RDECOM), (AMSRD-CCF/Ms. Kelly Knapp), 3071 Aberdeen Boulevard,  
Aberdeen Proving Ground, MD 21005-5424

SUBJECT: Operations Security/Freedom of Information Act (FOIA) Review Request

1. The purpose of this memorandum is to recommend the release of information in regard to request to RDECOM FOIA Requests FA-14-0054.
2. ECBC received the request from Ms. Kelly Knapp, the RDECOM FOIA Officer. The request originated from [REDACTED] gathering information on the Chemical Warfare Service.
3. The following documents were reviewed by Subject Matter Experts within ECBC:
  - a. History of Research at Yale University, dated 20 Nov 1918, 11 pages.
  - b. Bancroft's History of the Chemical Warfare Service in the United States, by Lt. William Bancroft; AD-495049; dated 31 May 1919, 206 pages.
  - c. A Historical Sketch of Edgewood Arsenal, by Lt. William McPherson; AD 498494; date unknown, 20 pages.
  - d. The Diary of Jet Parker; C390D1; dated Sep - Dec 1918, 26 pages.
  - e. American University Technical Reports, Bureau of Mines, War Gas Investigations (WGI) Monographs, date unknown.

RDCB-DPS-RS

SUBJECT: Operations Security/Freedom of Information Act (FOIA) Review Request

4. ECBC has determined that all of the reviewed documents are suitable for release, however, all documents must have the classification/distribution changed through the Defense Technical Information Center prior to any release.

5. The point of contact is Mr. Ronald L. Stafford, ECBC Security Manager, (410) 436-1999 or [ronald.l.stafford.civ@mail.mil](mailto:ronald.l.stafford.civ@mail.mil).



RONALD L. STAFFORD  
Security Manager