

CONTRIBUTIONS FROM THE CHEMICAL WARFARE SERVICE, U. S. A.

THE MANUFACTURE OF WAR GASES IN GERMANY

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When it was announced that the British and French military authorities had invited the American army to send representatives to investigate the chemical factories in the occupied zones along the Rhine, the chemists selected for this duty approached the work with unusual interest and enthusiasm. We had all heard of the famous plants and were familiar with their output. We expected to find not only works of great magnitude but to see examples of novel processes in chemical engineering and factory methods. The famous Bayer plant was at Leverkusen, near Cologne, and the huge works of the Badische Anilin und Soda Fabrik at Ludwigshafen. In addition, the factories of Kalle and Company, Meister, Lucius and Brünig, and a number of smaller companies were situated in the occupied territory.

While we saw much of great interest, most of us, I believe, were somewhat disappointed. Novelty was largely lacking. With the exception of the plant for the manufacture of ammonia by the Haber process and for the oxidation of ammonia to nitric acid, there was nothing strikingly new. Here and there we found some device of interest, such as an improved mechanism in a filter press, but, in general, no great advance in factory practice was noticeable. The plant for the Haber process, however, was considered by everyone to be a triumph of engineering ingenuity and skill. The \$25,000,000 spent on it made it possible for Germany to go to war. The investigation of this plant was under the direction of the Ordnance Department, and it is hoped that one of the representatives of the department who prepared a report on the plant will furnish an account of it for publication in *THIS JOURNAL*.

We were also disappointed and somewhat surprised at the lack of novelty in the methods used to prepare war gases. They were, in general, those described in the literature. It is a striking fact that the Germans did not invent a new gas for use in war. They selected with skill the most efficient substances for this purpose from the compounds known, but, as the result of the large amount of experimentation which must have been put on the problem, no new substance was used by them. It should be a matter of pride to American chemists to know that research carried out in the laboratory in Washington yielded two new compounds which were to be used by the American army. They had properties of great value from the standpoint of gas warfare, and served new tactical ends. Mustard gas, which was perhaps the most important gas of the war, was manufactured by the Germans by the tedious and expensive process described in the literature. New and simpler methods were discovered by American and British chemists, and these made it possible for the Allies to use great quantities of the gas. Dr. Duisberg, director of the Bayer Company, told the writer that a dud containing mustard gas fired by the Allies had been examined by their chemists. As the result of finding a substance in the shell contents, which was a by-product in the manufacture of the gas by the new method, the secret of the latter was discovered. A large plant was about completed by the Germans for the manufacture of mustard gas by this method when the armistice was signed. They quickly learned from us, and were about to discard their own cumbersome method.

We did find, however, in the German plants much to admire. The organization of the great works was marvelous. This was seen not only in the way the personnel was handled, but in the

lay-out of the plants as well. Efficiency was the secret of success. In the manufacture of war gases, for example, one chemist was in charge of the preparation of a particular gas and he gave his whole time to it. He was assisted by a foreman and the number of workmen required to do the work. Each man had a particular thing to do—and he learned his job well.

As had been anticipated, the value of research was greatly appreciated. Every plant had a laboratory for this purpose which was a source of pride. We were shown through the research laboratory of the Haber plant by Dr. Gaus, who was in charge of the works. He told us the building and its equipment cost \$2,500,000, and appeared prouder of it than of the great plant itself. Every facility for research in chemistry and physics was provided, and much money had been spent to make the building attractive in appearance. Tiled walls, hardwood finish, and expensive furniture gave the effect of display which the Germans seek in the offices and administrative rooms of their chemical plants.

As soon as the armistice was signed the chemical warfare services of the Allies took up with their respective governments the question of investigating the chemical factories in the occupied territory. After careful consideration it was decided to limit the investigations to the study of the manufacture of war products only. As a consequence, the Germans were ordered to furnish complete details as to the production of war gases, anti-gas material, explosives, and propellants. All the large factories were operated under the control of representatives of the British or French armies. There were no important chemical works in the territory occupied by the American army. Compliance with the order was made necessary by the fact that it was possible for the army authorities to close any factory at will.

The American army was invited by the British and French to send representatives to take part in the investigation of the factories in the zones occupied by them. The Chemical Warfare Service selected two officers to study the production of gases and anti-gas material—Lt. Col. James F. Norris and Major T. W. Sill. The Ordnance Department undertook to investigate explosives and propellants, and detailed for the purpose Lt. Col. C. M. Steese, Capt. R. D. McGrath, Capt. James W. Martin, Jr., and 1st Lt. H. T. Himmelein. Major Frederick Keyes, C. W. S., served with the ordnance officers in their investigation of the Haber plant.

The American party left Paris by automobile on January 30 and went to Cologne by way of Amiens, Cambrai, and Liège. They passed through some of the country that had seen the Hun at his worst, and were prepared in spirit to extract from him as much information as possible. Cologne was made the headquarters for the British and Belgian zones.

The British had taken over one of the best hotels near the cathedral and entertained the French, Belgians, Italians, and Americans who had been invited to take part in the investigations to be made. As it was contrary to orders issued by the occupying army to purchase food in shops or restaurants, the commission was supplied with food from the army mess. This was cooked by servants of the hotel and served in good form. Wine was plentiful, which could be bought, although the price was not what we had been used to. For ten days the twenty-five or more chemists lived together under the pleasantest conditions, and lasting friendships were made. Brig. Gen. Harold Hartley, formerly of Oxford University, whose work in chemistry is so well known, was in charge of the investigations.

He and his aides did everything to make our stay in Cologne profitable and pleasant.

We were all interested to see how a great German city had come through the war. We had heard of the hunger that had weakened the resistance of the German people, and we walked the streets in every quarter to observe. It was plain that food had been scarce. The fat, wabby men with wrinkled necks were not there. Faces were drawn and cheeks sunken, and a smile was rare. The children, however, appeared well fed and showed their old-time joyousness. We looked for the newly devised shoes lacking leather, of which we had heard, but saw none in use, although they were displayed in the shop windows. A search was made for the articles of clothing made from substitutes as a result of the lack of textile fabrics. A very acceptable fabric was made from wood pulp by converting it into paper from which a fine thread was manufactured. This was woven, dyed, and made into many useful articles. A shirt of this material could be bought for two marks. It was a little harsh and not much preferable to sackcloth, but one could not help feeling it was good enough. To replace rubber in suspenders, garters, etc., fine steel springs covered with a cloth made from paper were used. These were excellent for the purpose and with many other things, born as the result of the war, may find application when normal times return.

The shops of the city were doing a rushing business. Most of the purchasers were British soldiers, however, who were taking advantage of the depreciated value of the mark to buy very cheaply. Prices did not rise with the fall in the mark. Optical goods and photographic cameras were in great demand. Food, wearing apparel, and any articles made of leather were high in price, but other things were, in general, not much more expensive than in pre-war days.

The theaters and cafés were well patronized. We had the usual good music with our beer, which, however, recalled the olden days by being so unlike what we had known before. The people were very sober and quiet. Even in the cabarets there was no spirit of frivolity.

The attitude of the people toward America was very conciliatory. They were of the opinion that the coming in of America ended the war—not the battles we fought, but the potentiality of a rich nation with an almost unlimited supply of men. But they looked to America to help them out. A large photograph of the White House at Washington was displayed prominently in a shop window, with the legend "Where the fate of Germany will be decided." Many of the Germans had friends or relatives in America, and they felt that we as a people did not feel toward them as the British and French did. They hoped the "unpleasantness" would soon be over, and normal relations established again. Some of the chemists expressed this view. They hope to regain their trade and former industrial influence here. We may anticipate very soon the extension of the right hand of fellowship. They have goods to sell and they will be very agreeable.

The great advance that has recently been made in the United States in the manufacture of dyes has aroused the concern of the Germans. Several directors of chemical plants inquired about this and wanted to know if it was all true—if so much money had been invested as was reported. They were afraid of the competition of America, but did not appear to be concerned about what was being done in other countries. They knew that America had the money and men to organize great concerns that could stand against their own wonderful organizations. They were, indeed, quite worried over the future, as far as America was concerned.

Throughout the occupied zones there was perfect order. The managers of several factories agreed that the occupation of the territory was the best thing that could have happened. On the other side of the Rhine labor refused to work and de-

manded unheard-of pay—everything was topsy-turvy. In fact before the allied armies arrived revolutionary notions were growing rapidly along the Rhine. One director of a well-known chemical plant is said to have escaped by night with his life by way of the river, when his employees were especially menacing. When the British army came, he returned and is now at his old post.

All the chemical plants which manufacture war material in the zone occupied by the British were visited from Cologne. The members of the commission were divided into several groups, and the representatives of the American Chemical Warfare Service were assigned to the one delegated to study the production of war gases. The account which is given later will be limited to a consideration of gases and anti-gas material. While we had an opportunity to get a general view of most of the factories, it would be best to leave to others who prepared reports on the manufacture of inorganic compounds, explosives, and propellants, a description of these war materials.

The only place near Cologne where war gases had been made was Leverkusen at the color works of the Bayer Company. The plant is about 10 k. north of Cologne and is built along the Rhine, so that the river furnishes a convenient means of transportation. It was established a long time ago, but has been enlarged greatly in recent years. In normal times, we were told, there are employed about 1500 chemists, engineers, and office assistants, and 7500 workmen. This force was increased during the war, but when we visited the plant it had been reduced to a total of about 7000.

The British authorities controlled the supply of raw materials for the factory imported into the zone of occupation, and the export from the zone of manufactured products. As these were limited in amount the activities of the plant were much curtailed, in fact, but a small proportion of the normal output was being produced. Dyes and pharmaceutical and photographic chemicals were being made in addition to the usual inorganic compounds, but a large part of the personnel of the works was engaged in making repairs and improvements. The plant appeared to be in perfect condition, ready to work at maximum efficiency as soon as normal conditions are restored.

The arrangement of the many buildings is excellent. The storehouses for raw materials are situated along the river front. Next come the buildings for heavy inorganic chemicals, then the plants for nitration, sulfonation, and chlorination, and after these the buildings in which dyes and pharmaceutical and photographic chemicals are made. The last group of buildings consists of mixing houses for dyes, packing houses, the photographic paper plant, storehouses for finished products, and machine and carpenter shops. The experimental dyehouse, laboratories, printing and bookbinding buildings are grouped in the neighborhood of the central administrative building. The elaborate construction and decoration of the latter suggests a modern bank building, and creates an impression of prosperity and wealth. Around the walls of the directors' room was a beautifully painted and artistic frieze which pictured the various plants of the Bayer Company and their activities. Dr. Duisberg, the director, pointed out proudly to the Americans the view of the company's plant on the Hudson River. We were not surprised to see it, although anti-war advertisements had assured us at home that Bayer aspirin had been made on the Hudson for years by an American company. During the war an anteroom had been decorated in a similar way with pictures illustrating the activity of the plant in the preparation of war-gas materials. One saw how gas was made, shells were filled, and gas masks assembled. The work was done by an artist and has a permanent value. The fact that the thing was conceived and executed during the stress of war throws an interesting side light on German character.

The works contains a beautiful and perfectly equipped club-

house for employees. In fact, everything is done to keep the men in a contented state of mind. Frequent lectures are given by professors from the universities, and regular instruction in chemistry, including laboratory work, is provided for all who desire to learn. Provision has been made to give review courses to the chemists who return after five years of absence during the war. They were to be freshened up and all advances made during their absence brought to their attention—another example of efficiency.

The first visit to the Bayer plant was spent in a general inspection. The director furnished a plan of the works, and explained what processes were carried out in the several buildings. The more interesting ones only were visited by the whole commission, but a committee inspected later each building to verify the statements given, keeping a lookout for evidences of the production of war materials which might not have been disclosed.

In the general inspection of the plant we were shown the process for making rubber which had been put on a manufacturing scale during the war. We were given only a general outline of the process. Acetone was first reduced by aluminum and sodium hydroxide to pinacone, which was then distilled under pressure; as the result of the loss of two molecules of water a methyl butadiene was formed. The compound was placed in galvanized iron drums, which were sealed and then heated at about 60° for 4 to 6 months. At the end of this time the polymerized product was obtained as a tough, white, clear, transparent mass. The methyl rubber so formed had all the properties of the best caoutchouc. It was used in the making of automobile tires and other rubber goods. While the process was said to be expensive, hopes of its use after the war were expressed. A decrease in the price of acetone and better yields would probably make the process of commercial value.

The systematic examination of the processes about which information was sought was carried out by several groups. The writer was, as has been stated, a member of the group which looked into war gases, and anti-gas material. In getting the information a simple procedure was followed. A list of the products manufactured was furnished by the director of the plant. The chemist who had charge of the production of a particular gas was called before the committee and asked to describe fully the method and apparatus used, and to furnish figures in regard to output and raw materials. All members of the committee were given an opportunity to ask questions. Stenographers took down all statements made. A visit to the plant was next made where the operations had been carried out. The process was gone over again, the apparatus described in detail, and sketches made of the essential features.

A natural question is, "How did the Germans respond to this inquisition?" We had been curious ourselves on this point, and did not feel sure that we would be able to do more than inspect the apparatus. But they met the problem in the right way and gave the information freely. We reassured them at the start by saying that we were after facts in regard to war products only, and would not attempt to pry into secrets of commercial value in times of peace. We had to inspect every building, of course, to see if all statements in regard to their use were correct, but no questions in regard to details need be answered if by doing so commercial secrets would be disclosed. This reassurance established a more or less cordial relation between us. Of course we had no adequate way of checking up figures of production—the books in most cases had been removed before the occupation by the Allies—but these were of secondary interest. We saw in nearly every case the apparatus used, and, guided by its capacity and a knowledge of the process, we could figure what its normal output could be. With this check the production figures given seemed to be reasonable ones. I am of the opinion that the description of the processes fur-

nished, and the details given, were in the main correct. I had seen made in the laboratory nearly every gas about which we got information and was familiar with the details of the procedures. If a chemist tried to lead us astray by false information—and this happened but seldom—a statement that the information was evidently incorrect at a particular point, with adequate reasons for the view, put him on the right track again. For example, a chemist was describing the manufacture of ethylene and gave a false account of the preparation of the catalyst. As this had been studied in great detail in our laboratories at home, we were in a position to set things right. When an inspection of the plant was made later the chemist confessed his error, and did all he could to rectify it by going into great detail as to his experiments and results.

The products used in gas warfare manufactured at the plant of the Bayer Company at Leverkusen were as follows: Dichlorethylsulfide (mustard gas), diphenylarsenic acid for the production of diphenylchlorarsine, diphosgene (superpalite), phosgene, chlorpicrin, xylyl bromide, bromacetone, and charcoal for gas masks. The more important details in regard to the manufacture of these substances are given later in this paper.

The American party left Cologne on February 11, and went to the headquarters of our Army of Occupation at Coblenz. We had found by previous inspection of the territory that no war gases had been manufactured in this zone. There were but a few chemical plants and these made inorganic materials only.

We next went to Mainz, and were the guests of the French, who had laid out a program for our visit to the territory occupied by their army. General l'Heure, who was in charge of the party, divided the chemists into groups, and the method of inspection was similar to that used in the British zone.

At Mainz and Ludwigshafen we were billeted in German houses and thus had an opportunity to come in close contact with some of the people. Everything was done for our personal comfort by the Germans. In one home I was entertained by two elderly ladies who, on my arrival, made sure my bed was just to my liking. When I returned at night I found a warming pan had been put into it—the night was a bit frosty. The next morning I was mildly scolded because I had not set my boots in the hall to be polished, and a promise was extracted that I would do better in the future. At another house when I presented my billeting order the whole family—father, mother, two daughters, a son, and the maid—followed me to my room to look me over—an American army officer. Each one tried to do something for me. I was told how to work the electric heater in my room to get hot water whenever I wanted it, and the master of the household said his wine cellar was at my disposal.

In Mainz we were entertained at meals at the French Officers' Club and at Ludwigshafen our hosts had reserved for the use of the party a table in a large restaurant. There our food was what we had been accustomed to in the past in travel in Germany. There were no restrictions in the French zone in regard to the purchase of food, and, after our formal entertainment was over, we had a chance to see what it was possible for the casual visitor to buy in a restaurant. We were surprised to find that the variety of the food furnished and the prices charged varied but little from pre-war days. There were no regulations here against fraternization, and as a consequence we were able to learn the attitude of the people toward the war and its results. The views expressed served to corroborate those expressed in Cologne. The provisions for our entertainment and the inspection tour were carefully worked out by the French officers in charge of the party, and we were glad to express our hearty thanks for what had been done for us.

The principal works visited in the French area were Kalle and Company at Biebrich, Meister, Lucius und Brüning at Höchst-am-Main, and the Badische Anilin und Soda Fabrik

TABLE I—SHOWING PRODUCTION OF WAR GASES MADE IN THE GERMAN TERRITORY OCCUPIED BY THE BRITISH AND FRENCH ARMIES¹

Abbreviations used are B. for the Bayer Company, Leverkusen; M. L. and B. for Meister, Lucius and Brüning, Höchst-am-Main; K. for Kalle and Company, Biebrich; B. A. S. F. for Badische Anilin und Soda Fabrik, Ludwigshafen.

Gas	Made by	Production Started	Production Ended	Average Tons per Month	Total Production in Tons
Dichlorethyl sulfide (H. S.)	B.	July 1917	Nov. 1918	300	(4800)
Perchloromethyl formate (diphosgene)	B.	June 1915	Oct. 1918	300	(12000)
Perchloromethyl formate (diphosgene)	M. L. & B.	Sept. 1916	Nov. 1918	139 (Max. 266)	3616
Diphenylchlorarsine	M. L. & B.	May 1917	Nov. 1918	150 (Max. 300)	3000
Diphenylcyanarsine	M. L. & B.
Ethylidichlorarsine	M. L. & B.	Aug. 1917	Oct. 1918	78 (Max. 150)	1092
Phosgene	B. A. S. F.	Before war	288 (Max. 621)	10682
Phosgene	B.	Before war	Made now for dyes	30
Phenyliminophosgene	M. L. & B.	Mar. 1918	Jan. 1918	65 (Max. 124)	721
Dichloromethylether	M. L. & B.	Sept. 1917	May 1918	26 (Max. 51)	233
Dibromomethylether	M. L. & B.	Apr. 1917	Dec. 1917	7 (Max. 29)	69
Chlorpicrin	B.	Summer 1916	Nov. 1918	200	(6000)
Chlorpicrin	M. L. & B.	Aug. 1916	Nov. 1918	45 (Max. 101)	1127
Bromacetone	B.	Spring 1916	3 small batches made
Bromacetone methylethylketone	M. L. & B.	Apr. 1915	Sept. 1918	19 (Max. 45)	1069
Xylyl bromide	B.	Apr. 1915	Manufactured at intervals	50 to 60	(500)

TABLE II—INTERMEDIATE PRODUCTS USED IN THE PRODUCTION OF WAR GASES

SUBSTANCE	Made by	Production Started	Production Ended	Average Tons per Month	Total Production in Tons
Dihydroxyethylsulfide (for H. S.)	B. A. S. F.	Early 1916	Nov. 1918	319 (Max. 552)	7026
Phenylarsenic acid (for diphenylchlorarsine)	K.
Phenylarsenic acid (for diphenylchlorarsine)	B. A. S. F.	July 1917	100 (Max. 178)	1600
Diphenylarsenic acid (for diphenylchlorarsine)	B.	Aug. 1917	150-200
Phenyl mustard oil (for phenyliminophosgene)	K.	Early 1917	Nov. 1918	15 (Max. 60)
Ethylarsenousoxide (for ethylidichlorarsine)	B. A. S. F.	Apr. 1917	60 (Max. 90)	840
Charcoal	B.	Summer 1916	Nov. 1918	30	810

¹ The table is not complete on account of the fact that the information necessary was not available in all cases.

at Ludwigshafen. The latter plant was the largest we saw. It employed about 15,000 workmen, 3500 of whom were assigned to the nitrogen fixation plant at Oppau, which was connected with the main plant by a private electric railroad. About one-half of the 250 chemists employed devoted themselves to research and the rest to factory control. All the chemicals required for the production of the products manufactured were made in the plant. The production started with the basic raw materials of chemical industry.

The conclusions reached by all members of the party which had the unusual opportunity of inspecting the great German chemical plants were in the main, I think, the same. We learned no secrets of great commercial value. Here and there we observed a new device or a novel way of carrying out some operation. If more time had been available we would have learned more. By the program arranged for us we were allowed but half a day at the plant of Kalle and Company, about three-quarters of a day at Höchst, and less than two days at the works of the Badische Anilin und Soda Fabrik at Ludwigshafen and Oppau. The British and French are studying the factories under the best conditions, for they have placed in the plants in their respective territories chemists who have the opportunity to watch all operations day by day. It should be recalled that we had military orders to inspect processes for the preparation of war materials only and we all endeavored to carry out the spirit of our orders.

We did get, however, what we went for. The information as to the manufacture of gases covered the subject adequately. It lacks real military value, however, as it is probable that the only gases used by the Germans which will be employed in the next war are phosgene and mustard gas, and the American methods for making these gases are far superior to those of the Germans.

We learned a novel way of activating charcoal for gas masks, but it was probably not the one that yielded the efficient material used by the Germans toward the end of the war. The methods for making charcoal were developed in Austria, and most of it was prepared in that country.

We came to the conclusion that the great success of the German chemical industry was due to organization and the emphasis put on research. Many of their business methods were far from ethical. Secret combinations and agreements between the large concerns eliminated competition and made it possible to mislead the purchaser.

The condition of the factories at present is such that they can put vast quantities of their products on the market at once. We must be prepared to meet every kind of effort on the part of the Germans, honest and otherwise, to regain their hold on the American chemical trade. We have no reason to believe that the means used to get control of the market after the war will be based on higher moral standards than those used during the war. The most impressive scene of destruction that I visited in France was the sight of what was the great chemical plant at Chauny. This, the oldest chemical works in France, where Gay-Lussac did his famous work on the manufacture of sulfuric acid, where Courtois discovered iodine, and where plate glass was first made, had grown with the times, and was among the largest factories in France. Around it was a thriving town of about 13,000 inhabitants, with some excellent modern public buildings. When the Germans in their first retreat were forced to leave the place, they dismantled the factory and carried away everything that was portable. The fortunes of war brought them back, and before they left a second time a regiment of soldiers was put to work to destroy systematically the factory and the entire town. For a month they kept at work, and when they withdrew but a few bricks were left standing. Every boiler had been blown up with dynamite, and every tank too heavy to be carted away rendered useless. About half an acre was covered with chemical stoneware of all kinds; each piece had been broken with a sledge hammer. Nothing was too small or too large to escape destruction. And to make sure of a good job everything that would burn had been set on fire. Professor Moureu, with whom the wreck was examined, was speechless—there were no words, he declared, in the French language to describe what was before us, or to analyze the spirit in the soul of the man who ordered such an act. Destruction which results from active fighting—from mines and shell-fire—are a part of war, but such a sight as we saw—a whole city destroyed by systematic barbarism—was almost beyond comprehension. The men who inspired the utter demolition of the industries of Belgium and northern France are the same men with whom we are soon to do business.

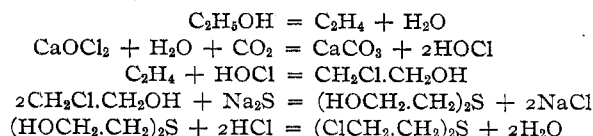
A technical account of the more important facts in regard to the manufacture of the war gases by the Germans follows. These facts will be of interest to the organic chemist and to the chemical engineer as examples of the ways in which exceedingly noxious substances can be handled on the large scale with the minimum amount of danger. The table of production which is

given covers only the places visited. Gases were manufactured elsewhere, but no information in regard to them could be obtained. Statements that were given to us everywhere showed that the government withheld as much information as possible from the men actually in charge of manufacture. At no plant was there knowledge of the source of the material used or the place to which it was sent. The production of war materials was directed from Berlin. When a product was ready for shipment directions were sent to the factory to send it to a specified station some distance away. From this point it was shipped to its proper destination. This was the case with intermediate products as well as finished gases. In some cases products had to pass through two or more plants before the final gas was obtained. For example, the Badische Company made the chlorhydrin which the Bayer Company converted into mustard gas, and neither firm evidently knew the other was concerned in the process. This policy may have been dictated by a desire for secrecy, or by the fact that the war ministry at Berlin assigned to each plant the manufacture of the compounds it was best prepared to handle.

The inspection was finished, the detailed report was written, and as a result of it all the conviction was definite that we had nothing to fear from German chemical industry. Given protection from unfair methods we could successfully compete with it. We all felt that as the result of the war German supremacy had disappeared. The myth of the superman had been buried.

β,β -DICHLOROETHYLSULFIDE (MUSTARD GAS)

This compound was prepared by the method originally described by Victor Meyer and later studied more fully in Emil Fischer's laboratory. The steps involved are represented by the following equations:



The process was carried through the preparation of the thio-glycol by the Badische Company, and this was converted into mustard gas at the Bayer Company plant.

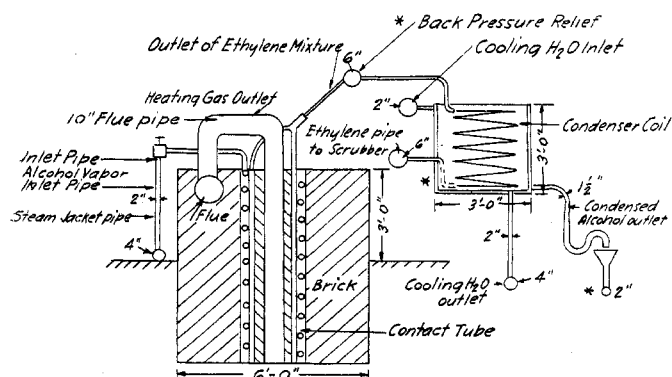


FIG. 1—PREPARATION OF ETHYLENE AT BADISCHE ANILIN UND SODA FABRIK. 60 UNITS

PREPARATION OF ETHYLENE—The gas was prepared by passing alcohol vapor over aluminum oxide at a temperature of 380° to 400°. The details of the construction of one of the furnaces are given in Figs. 1 and 2. The furnaces were very small and sixty units were required to furnish the amount of gas required. The tubes containing the catalyzer were made of copper and were heated in a bath of molten potassium nitrate. It was stated that the catalyzer was made according to the directions of Ipatieff, and that its life was from 10 to 20 days. The gas produced was washed in the usual form of scrubber. The

yield of ethylene was stated to be about 90 per cent of the theoretical.

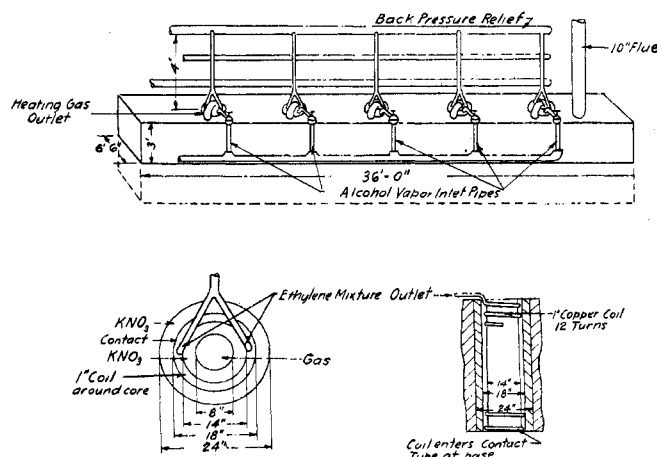


FIG. 2—ETHYLENE PRODUCTION AT BADISCHE ANILIN UND SODA FABRIK. 1 UNIT

PREPARATION OF ETHYLENE CHLORHYDRIN—The reaction was carried out in a cylindrical tank resting on its side. The tank was furnished with a stirrer and was insulated by means of cork in order to prevent the transfer of heat from the atmosphere to the inside. For details see Figs. 3 and 4. Enough chloride of lime was introduced into the tank to furnish 500 kg. of available chlorine, together with 5 cu. m. of water. At first, about 20 cu. m. of carbon dioxide were led into the mixture, next ethylene, and later carbon dioxide and ethylene simultaneously. The rate of absorption of ethylene was noted and when it slackened, more carbon dioxide was added. Fuller details as to the addition of the two gases were not given as it was stated that it was a matter of judgment on the part of the workman who was carrying out the operation. The reaction should be carried out at as low a temperature as possible, but it was found impossible to work below 5° with the apparatus employed in this factory. The temperature during the reaction varied between 5° and 10°. In order to maintain this temperature, the solution was constantly pumped from the apparatus through a coil which was cooled by brine. Details of construction will be seen in the diagram. When ethylene was no longer absorbed and there was an excess of carbon dioxide present, the solution was tested for hypochlorous acid. The time required for the introduction of ethylene was between 2 and 3 hrs.

The contents of the apparatus were passed through a filter press by means of which the calcium carbonate was removed. The solution thus obtained contained from 10 to 12 per cent of ethylene chlorhydrin. It was next distilled with steam and a distillate collected which contained between 18 and 20 per cent of chlorhydrin. The yield of chlorhydrin was from 60 to 80 per cent of that calculated from the ethylene used.

PREPARATION OF DIHYDROXYETHYLSULFIDE—To prepare the hydroxysulfide, the theoretical quantity of sodium sulfide, either in the form of the anhydrous salt or as crystals, was added to the 18 to 20 per cent solution of chlorhydrin. The reaction which takes place is as follows:



After the addition of the sulfide, the mixture was heated to about 90° to 100°. It was then pumped to an evaporator, and heated until all the water was driven off. The glycol was next filtered from the salt which separated, and distilled in a vacuum. The yield of glycol was about 90 per cent of the theoretical, calculated from the chlorhydrin.

PREPARATION OF DICHLOROETHYLSULFIDE—The thiodiglycol was taken from the rail to two large storage tanks and thence drawn by vacuum direct to the reaction vessel. Each reaction

vessel was placed in a separate cubicle ventilated both from above and below and fitted with glass windows for inspection (see Figs. 5, 6 and 7). The vessels themselves were made of $1\frac{1}{4}$ in. cast iron and lined with 10 mm. lead. They were 2.5 m. high and 2.8 m. in diameter. These tanks were jacketed so that they could be heated by water and steam, and the reaction was carried out at 50° . The hydrochloric acid coming from the main pipe was passed through sulfuric acid so that the rate could be observed, and passed in by means of 12 glass tubes of about 2 cm. diameter. The rate of flow was maintained at as high a rate as possible to procure absorption. The vapors from the reaction were led from the vessel through a pipe into a collecting room, and then through a scrubber containing charcoal and water, through a separator, and then, finally, into the chimney. These exhaust gases were drawn off by means of a fan which was also connected with the lower part of the chamber in which the reaction vessels were set, so that all the gases had to pass through the scrubber before going to the chimney. When the reaction was completed, the oil was removed by means of a vacuum, induced by a water pump, into a cast-iron washing vessel.

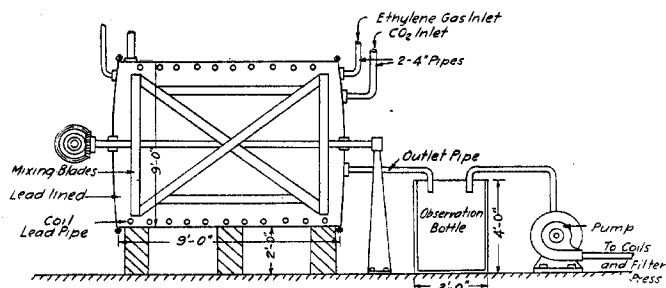


FIG. 3—CHLORHYDRIN REACTION KETTLE AT BADISCHE ANILIN UND SODA FABRIK. 16 UNITS

The hydrochloric acid layer was removed to a stoneware receiver also by vacuum. A glass enabled the operator to avoid drawing oil over with the acid. The pan was fitted with thermometer to the interior as well as to the jacket. For testing the material during reaction, provision was made for drawing some up by vacuum to a hydrometer contained in a glass funnel. The final test at this point read 126° Tw. Another portion could be drawn up to a test glass and hydrochloric acid passed through it in full view. A float contained in a glass outer tube served to show the level of the liquid in the vessel. The pans in which the operation is carried on, as well as those employed for washing and distilling the product, were of a standard pattern employed in many other operations in the works.

The washer consisted of a cast-iron vessel, lead lined, and was 2.5 m. in diameter, 2 m. deep, and fitted with a dome cover and stirring gear. Lead pipes served for the introduction of sodium carbonate solution and water. Similar pipes were fitted for drawing these off by means of a vacuum. A manhole on the cover, with a flat top, was fitted with light and sight glasses to which were fitted a small steam coil for keeping them clear. The washed oil is drawn off to a distillation still, which is a cast-iron vessel homogeneously lead coated, 1.5 m. in diameter and 2 m. deep, fitted with a lead heating coil and connected through a spiral lead condenser and receiver to a vacuum pump. The water is distilled from the oil at a pressure of from 62 to 70 mm. absolute pressure. When dried, the oil is sent by vacuum to a mixing vessel, similar in most respects to the washing vessel, in which it is mixed with an appointed quantity of solvent, which in this factory was usually chlorbenzene but occasionally carbon tetrachloride. The relative quantities varied with the time of year, and instructions were sent from Berlin on this point. Thence the mixture was passed to a storage tank and into tank wagons.

Gloves were used at first but were found unnecessary; more casualties resulted with than without their use. Operators were instructed to wash their fingers frequently and to make use of bleaching powder in doing so. They had very few casualties among their workmen—one case of pneumonia and no case of conjunctivitis or heart trouble.

PERCHLORMETHYLFORMATE (DIPOSGENE OR SUPERPALITE)

This compound was prepared at the Bayer Company plant and at Höchst. The method used at the former was as follows: The process employed consisted, in the first case, of the manufacture of methyl formate by heating 95 per cent formic acid and pure methyl alcohol together without any condensing agent in an iron still homogeneously lead coated and protected by a layer of porcelain tiles. The diameter of the pan was $2\frac{1}{2}$ m. and the capacity 12,050 l. Heat was applied by means of a copper coil. There was a fractionating column with a jacket made of copper and filled with porcelain packing. The ester was distilled and the pure ester placed in the chlorine reaction vessels. There were 33 of these vessels which were from 2 to 3 m. in diameter and 1.5 m. deep. (Fig. 8 is a sketch of a similar kettle used at Höchst.) They were made of cast iron homogeneously lead coated and lined with tiles, it being exceedingly important to prevent the least trace of iron from getting into the vessel. Chlorine was introduced by a number of glass tubes. Some of the vessels appeared to have six and some eight tubes. The chlorine merely bubbled from the end of them. The reaction was accelerated by means of high candle power lights. Osram filaments were found best and the greatest amount of light produced the most rapid reaction. Eight 4000-candle power lamps was the maximum light used on any vessel. Mercury vapor and carbon filament lamps were less effective. The quantity of methyl formate introduced in a charge varied from 1500 to 2000 l. and the time taken to complete the reaction was 8 to 14 days.

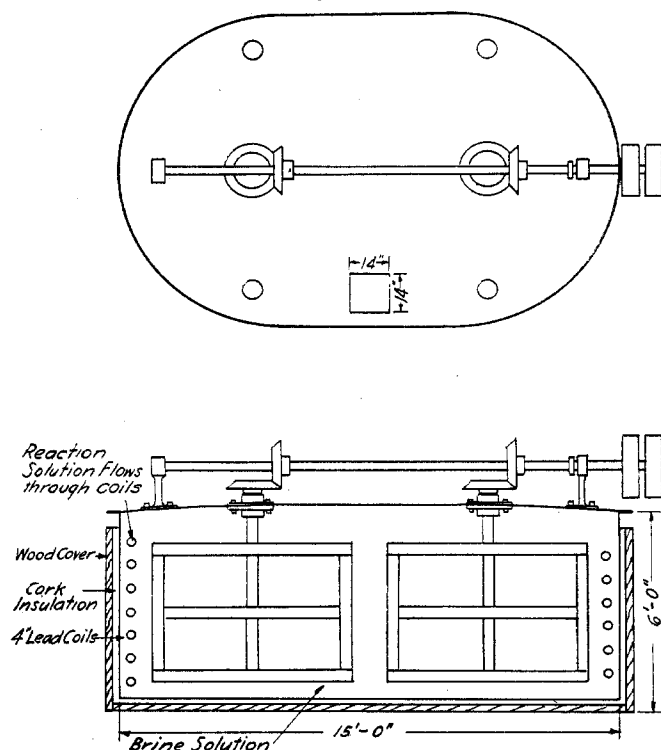


FIG. 4—CHLORHYDRIN COOLING TANKS AT BADISCHE ANILIN UND SODA FABRIK. 16 UNITS

The temperature of the reaction had to be controlled, at first by means of a water jacket and later by greater additions of chlorine which was bubbled through wash bottles containing

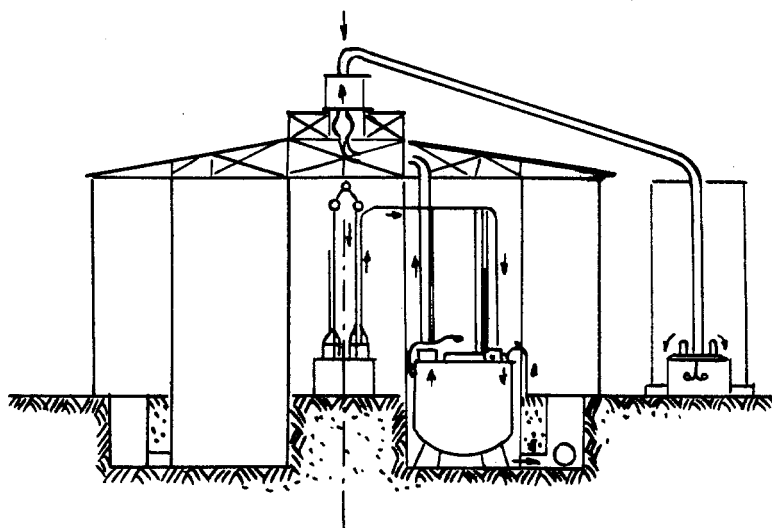
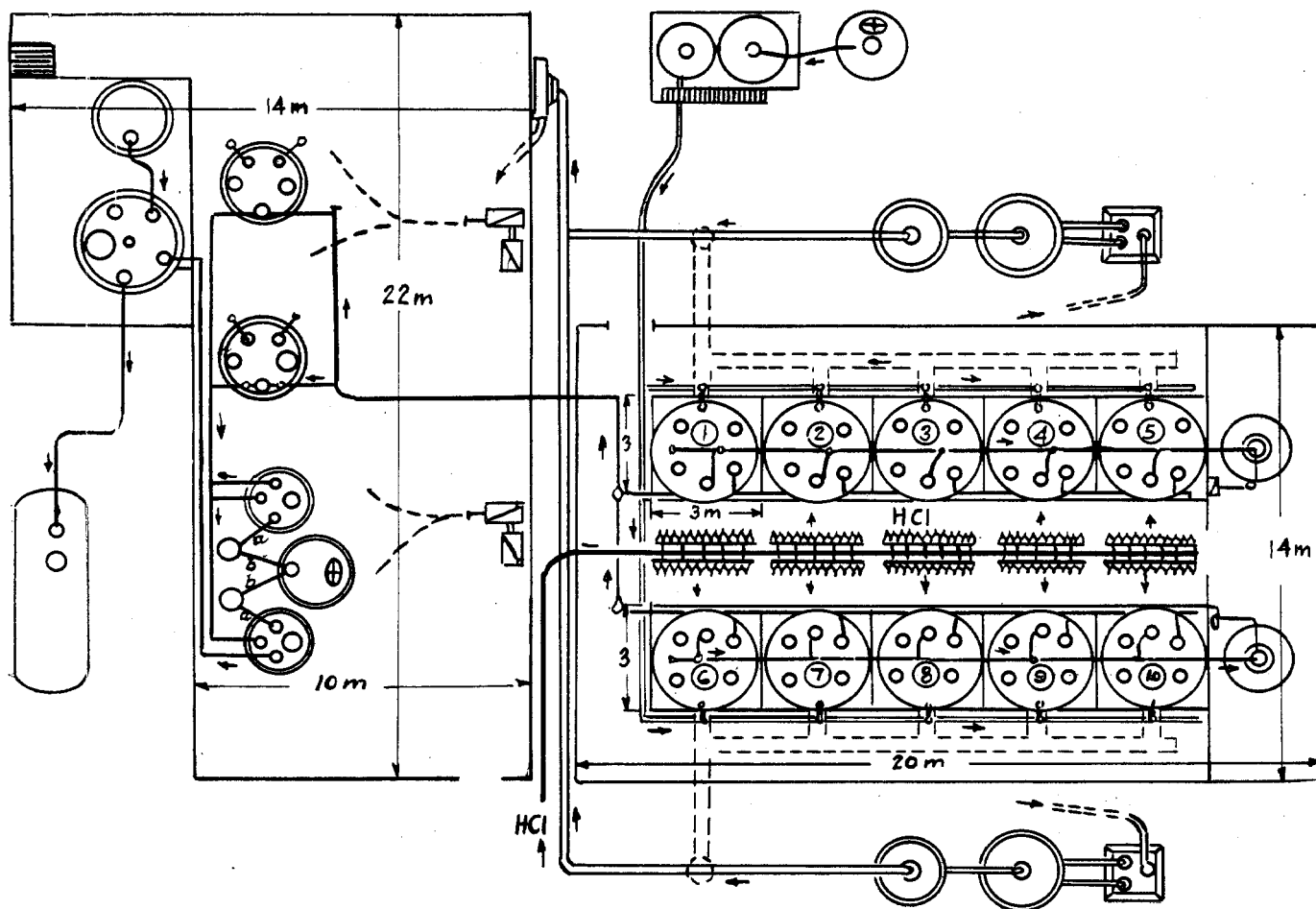


FIG. 5—H. S. MANUFACTURE AT LEVERKUSEN. LAYOUT FOR CHLORINATION OF THIODIGLYCOL

sulfuric acid. The temperature gradually rose finally up to 140° to 160°, as the percentage of chlorine product increased. Sunlight was found to accelerate the reaction, which was able to take place both in the liquid and gaseous phases. When the reaction was completed, the low-boiling fraction was recovered by distillation and the remaining diphosgene was transferred to the containers in which it was sent away.

The still was porcelain lined and fitted with a copper coil internally for heating (see Fig. 9). The diphosgene was tested

finally for its action on iron by measuring the volume of gas given off from a known volume of liquid in contact with iron after standing for 12 hrs. The methyl formate plant was part of the existing installation for the manufacture of other substances, but the plant for the chlorination and distillation was specially installed for the purpose.

In the early days they had several small explosions which were not serious. They had a large number of cases of poisoning among the workmen which also were not serious. All the

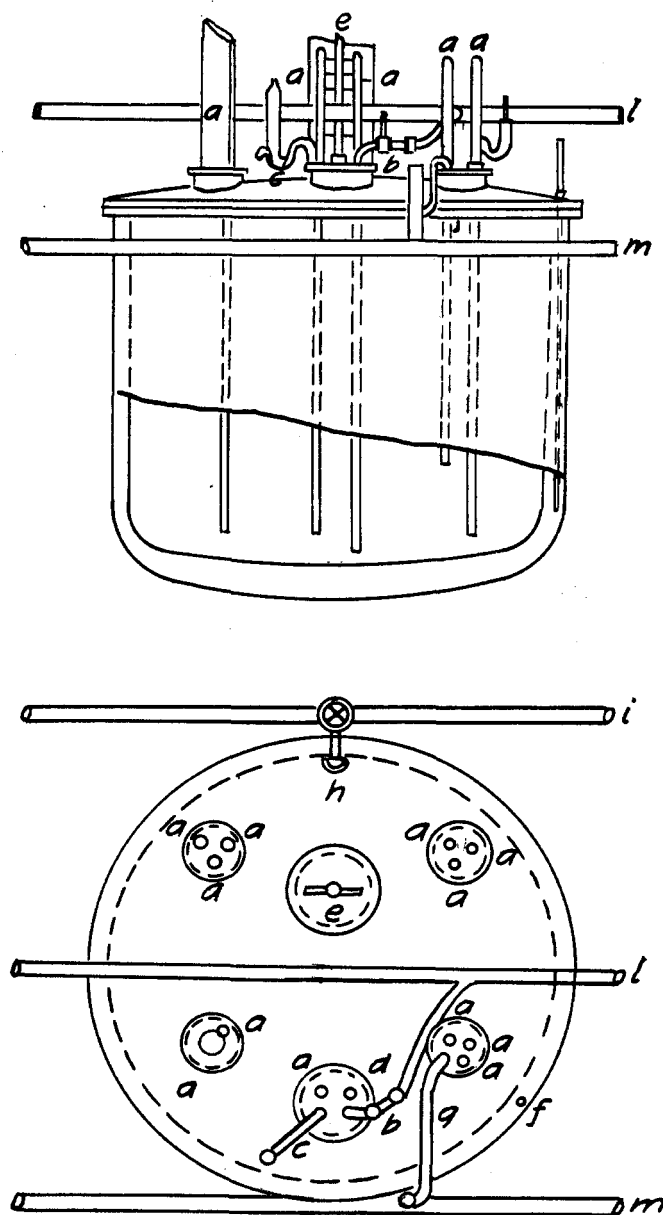


FIG. 6—H. S. MANUFACTURE AT LEVERKUSEN. DETAIL OF CHLORINATION KETTLE

workers were supplied with gas masks and put them on in case of emergency only. The workers suffered from chest and heart affections. Two or three died during the time though our informant would not admit that this was necessarily the cause of death. They sometimes had as many as one-third of the workers absent owing to sickness. The workers were not changed as they wished to retain those who could stand it. Only men were employed in the plant. The diphosgene was usually issued admixed with chlorpicrin. It was also admixed with phosgene.

At Höchst superpalite was prepared by chlorinating methylchlorformate prepared from phosgene and methyl alcohol. The final step was carried out in a way much like that used at the Bayer Company, and does not warrant description. An account of the first step in the process follows: The preparation of the methylchlorformate was carried out in an iron tank homogeneously lined with lead, and had a capacity of 2800 l. It was furnished with a lead stirrer and a lead coil, through which brine for cooling was passed. Phosgene, furnished by the Badische Anilin und Soda Fabrik in tank-wagons, was used. The methyl alcohol was a commercial dry material. In preparing the compound, phosgene and methyl alcohol were allowed

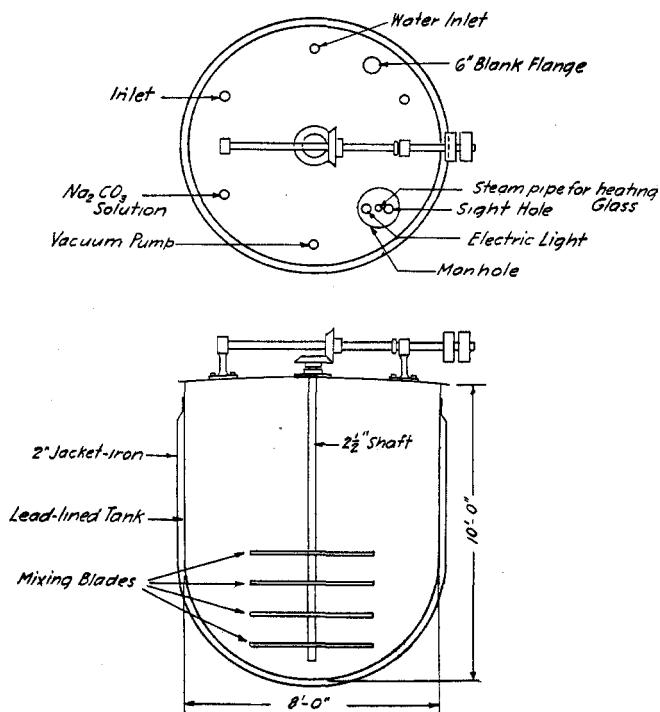
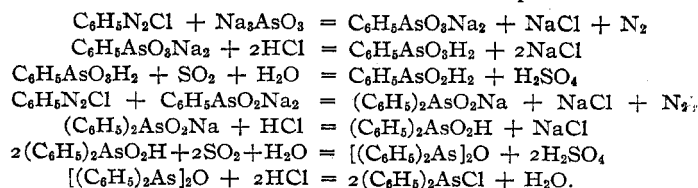


FIG. 7—WASHING KETTLE FOR H. S. MANUFACTURE AT LEVERKUSEN. 2 UNITS

to flow into the apparatus which contained a small amount of methylchlorformate. During the reaction, the temperature was kept below 0° . Between 5 and 10 per cent excess of phosgene over that required by the theory was used and enough of the materials so that at the end about 2000 kg. of the chlorformate were formed. The hydrochloric acid formed in the reaction was absorbed in towers. The kettle was so constructed that if explosions occurred no serious damage resulted. The product of the reaction was withdrawn from the apparatus and distilled, as long as anything came over, in a lead-lined distillation apparatus furnished with a lead coil. The yield of the methylchlorformate was between 80 and 90 per cent of the theoretical.

DIPHENYLCHLORARSINE

This substance (blue cross) was a favorite gas of the Germans and was made in large quantities. It produced sneezing and a disagreeable, temporary sickness, but it was not considered by the Allies to be very efficient. The method used by the Germans was different from the one worked out by the Allies, and on account of the fact that the German method could be carried out without specially designed apparatus and required as raw materials substances readily obtainable, it was probably preferable. It is doubtful, however, whether the Allies would have made this gas, for as the result of its use no fatalities were reported. The German process consisted in preparing phenylarsenic acid by condensing benzene diazonium chloride with sodium arsenite. The acid was next reduced by sulfur dioxide to phenylarsenous acid, which was, in turn, condensed with the diazonium compound to form diphenylarsenic acid. This acid was reduced to diphenylarsenous oxide, which with hydrochloric acid yielded diphenylchlorarsine. The chemical equations for the reactions will make clearer the steps involved.



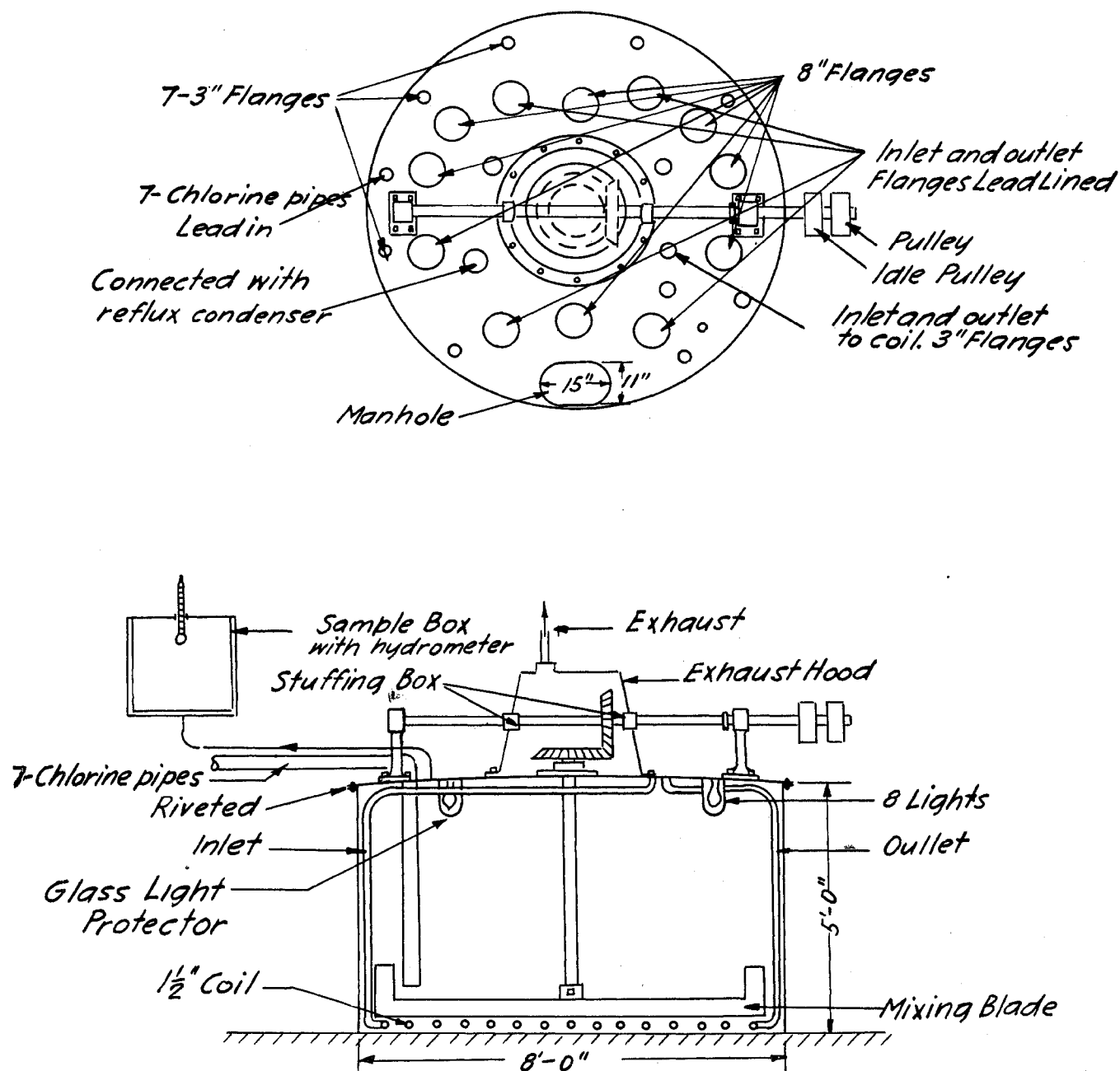


FIG. 8—SUPERPALITE PLANT AT HÖCHST-AM-MAIN. CHLORINATION TANK. 22 UNITS

The entire process was carried out at Höchst. Phenylarsenic acid was also made at the plants of Kalle and Company and the Badische Company. Diphenylarsenic acid was prepared by the Bayer Company. The processes at the several plants were similar. The method used at Höchst was as follows: In preparing the diazonium solution, 3 kg.-mols. of aniline were dissolved in 3000 l. of water and the theoretical quantity of hydrochloric acid. The temperature of the solution was reduced to between 0° and 5° and the theoretical amount of sodium nitrite added. The reaction was carried out in a wooden tank of the usual form for the preparation of diazonium compounds. A solution of sodium arsenite was prepared which contained 20 per cent excess of oxide over that required to react with the aniline used. The arsenous oxide was dissolved in sodium carbonate, care being taken to have enough of the alkali present to neutralize all of the acid present in the solution of the diazonium salt. To the solution of the sodium arsenite were added 20 kg. of copper sulfate dissolved in water, this being the amount

required when 3 kg.-mols. of aniline are used. The solution of the diazonium compound was allowed to flow slowly into the solution of the arsenite while the temperature was maintained at 15° . The mixture was constantly stirred during the addition which requires about 3 hrs. After the reaction was complete, the material was passed through a filter press in order to remove the coupling agent and the tar which had been formed. Hydrochloric acid was next added to the clear solution to precipitate phenylarsenic acid, the last portions of which were removed by the addition of salt.

The phenylarsenic acid was next reduced to phenylarsenous acid by means of a solution of sodium bisulfite, about 20 per cent excess of the latter over the theoretical amount being used. For 100 parts of arsenic acid, 400 parts of solution were used. The reaction was carried out in a wooden vessel and the mixture stirred during the entire operation. A temperature of 80° was maintained by means of a steam coil. Phenylarsenous acid separated as an oil. The aqueous solution was decanted

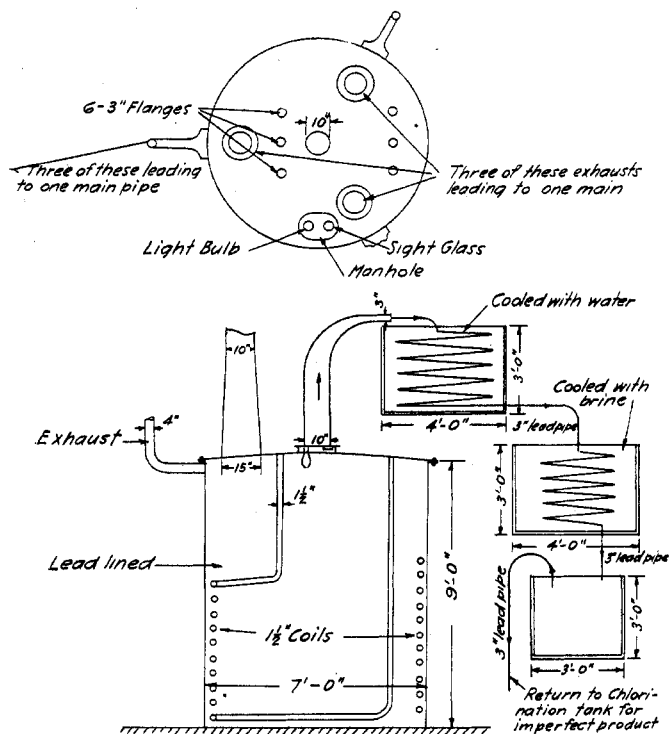


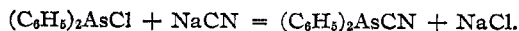
FIG. 9—SUPERPALITE PLANT AT HÖCHST-AM-MAIN. DISTILLATION KETTLE. 2 UNITS

from the oil, which was dissolved in a solution of sodium hydroxide, 40° Bé. The solution of the sodium salt of phenylarsenous acid was treated with water so that the resulting solution had a volume of 6 cu. m. when 3 kg.-mols. of the salt were present. Ice was next added to reduce the temperature to 15° and a solution of benzene diazonium chloride, prepared in the manner described for the first operation, was slowly added. After the coupling, diphenylarsenic acid was precipitated by means of hydrochloric acid. The acid was removed by means of a filter press and dissolved in hydrochloric acid, 20° Bé. For one part of diphenylarsenic acid, 3 parts of hydrochloric acid were used. Into this solution was passed 5 per cent excess of sulfur dioxide over that required for the reduction. The sulfur dioxide used was obtained from cylinders which contained it in liquid condition.

The reduction was carried out in an iron tank lined with tiles and a temperature of 80° was maintained. About 8 hrs. were required for the reaction. The diphenylarsenic acid on reduction by the sulfur dioxide was converted into diphenylarsenous oxide which, in the presence of the hydrochloric acid, was converted into diphenylchlorarsine, which separated as an oil. The oil was next removed and heated in the best vacuum obtainable until it was dry and free from hydrochloric acid. The compound melted at 34°. It was placed in iron tanks for shipment. The yield of diphenylchlorarsine calculated from the aniline used was from 25 to 30 per cent of the theoretical. No marked trouble was observed in handling the materials and no serious poisoning cases were reported.

DIPHENYLCYANARSINE

This compound was prepared by treating diphenylchlorarsine with a saturated aqueous solution of potassium or sodium cyanide.



Five per cent excess of the alkaline cyanide was used. The reaction was carried out at 60° with vigorous stirring. The yield was nearly theoretical.

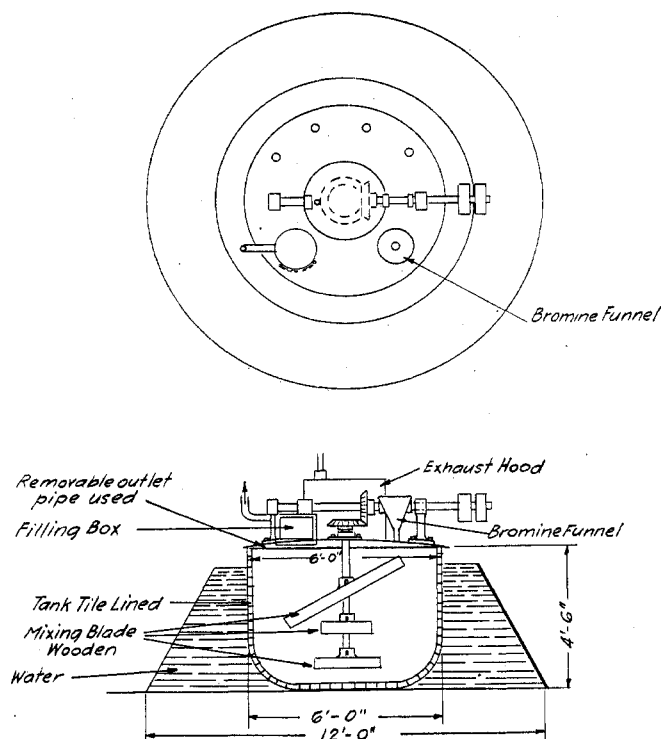
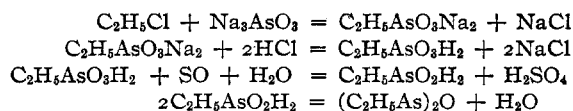


FIG. 10—BROMACETONE. 7 SMALL UNITS, 12 LARGE UNITS

ETHYLDICHLORARSINE

This compound was prepared at Höchst from ethylarsenous oxide which was obtained from the Badische Anilin und Soda Fabrik.

PREPARATION OF ETHYLARSENIOUS OXIDE—The compound was prepared by treating sodium arsenite with ethyl chloride under pressure. The resulting sodium salt of ethylarsenic acid was converted into the free acid and reduced by sulfur dioxide. The ethylarsenous acid formed in this way lost water and was thereby transformed into ethylarsenous oxide. The reactions involved are as follows:



The ethyl chloride used in the preparation was in part made in this factory, and in part received from other sources. As ethyl chloride is an important product used in peace time, it is not, therefore, essentially a war product and its preparation was not described.

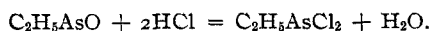
In preparing the solution of sodium arsenite, one molecular weight of arsenous oxide was dissolved in a solution containing 8 molecular weights of sodium hydroxide. The solution of the base was prepared from a 50 per cent solution of sodium hydroxide to which enough solid alkali was added to make the solution a 55 per cent one. In one operation 660 kg. of arsenous oxide were used. For 100 parts of arsenous oxide, 130 parts of ethyl chloride were used, this being the theoretical amount of the latter.

The reaction was carried out in a steel autoclave of about 300 l. capacity. The temperature was maintained at between 90° and 95°. The ethyl chloride was pumped in, in 3 or 4 portions, and the pressure in the autoclave was kept at from 10 to 15 atmospheres. The several portions of ethyl chloride were introduced at intervals of about 1 1/2 hrs. During the entire reaction, the contents of the autoclave were vigorously stirred. After all the ethyl chloride had been added, the ma-

terial was stirred from 12 to 16 hrs., at the end of which time the pressure had fallen to about 6 atmospheres. The excess of ethyl chloride and the alcohol formed in the reaction were next distilled off. At this point a sample of the solution was drawn off for testing. This was done by determining the amount of arsenite present in the solution. If not more than 20 per cent sodium arsenite had not reacted, the preparation was considered satisfactory. Water was then added to the contents of the autoclave in sufficient amount to dissolve the solid material. The product was next drawn over into a tank and neutralized with sulfuric acid. It was then treated with sulfur dioxide gas until there was an excess of the latter present. The mixture was then heated to about 70° when the ethylarsenous oxide precipitated out as a heavy oil. This was readily separated and shipped without further purification.

The yield of ethylarsenous oxide, from arsenic oxide, was from 80 to 82 per cent of a product which contained about 93 per cent of pure ethylarsenous oxide.

PREPARATION OF ETHYLDICHLORARSINE—The compound was prepared by treating ethylarsenous oxide with hydrochloric acid. The reaction is as follows:



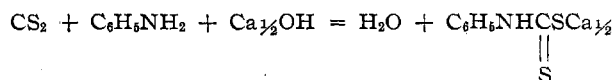
The operation was carried out in an iron kettle lined with lead, which was cooled externally by means of water and which was furnished with a lead covered stirrer. To the kettle, which contained from 500 to 1000 kg. of hydrochloric acid left over from the previous operation, were added 4000 kg. of ethylarsenous oxide. The gaseous hydrochloric acid was next led in. The kettle was kept under slightly diminished pressure in order to assist in the introduction of hydrochloric acid. The temperature during the reaction must not rise above 95°. When the hydrochloric acid was no longer absorbed and was contained in appreciable quantities in the issuing gases, the operation was stopped. This usually occurred at the end of from one to two days. The product of the reaction was drawn off by means of a water pump and heated in a vacuum until drops of oil passed over. The residue was passed over to a measuring tank and finally to tank-wagons made of iron. The yield of the product was practically the theoretical.

On account of the volatility of the compound and its poisonous character, the apparatus in which it was prepared was surrounded by an octagonal box, the sides of which were fitted with glass windows. Through this chamber a constant supply of air was drawn. This was led into a chimney where the poisonous vapors were burned. The gases given off during the distillation of the product were passed through a water scrubber.

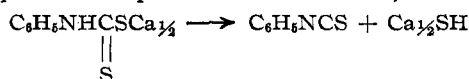
PHENYLIMINOPHOSGENE

The phenyl mustard oil required for this preparation was made by Kalle and Company and converted into the finished product by Meister, Lucius and Brüning at Höchst.

PREPARATION OF PHENYL MUSTARD OIL—In the preparation of the compound, carbon disulfide was allowed to interact with aniline in the presence of milk of lime, the reaction being as follows:



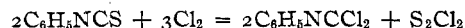
The resulting product was treated with zinc chloride and sodium hydroxide, as the result of which phenyl mustard oil and calcium sulfhydrate were formed. The product of the first reaction decomposes in the presence of the zinc salt, thus:



Six kilo molecules of carbon disulfide were mixed with the theoretical proportion of a 30 per cent milk of lime. To this mixture, which was contained in a closed iron tank, was added

a slight excess over 6 kg. mols. of aniline. The addition of the aniline required about 1 hour, while the mixture was stirred and kept cool by means of water circulating in the jacket. After the addition of the aniline, the mixture was stirred for about one day and the temperature maintained at about 25°. A solution of zinc chloride was next prepared in a wooden tank by dissolving enough zinc chloride to furnish 840 kg. of 100 per cent zinc chloride in the amount of water required to make a 50 per cent solution. To this solution were added 550 kg. of sodium hydroxide which was in the form of a solution of 40° Bé. strength. The product formed from the aniline and carbon disulfide was next pumped over into the alkaline solution of the zinc chloride and the resulting mixture was allowed to interact at a temperature of 30° to 40°. The mixture was then run into an iron still which was heated by a steam jacket and coil on the inside, and by direct steam. The phenyl mustard oil, which distilled over with the steam after passing through a condenser, was run into a series of three settling tanks from which the oil was drawn off. It was shipped without being further distilled.

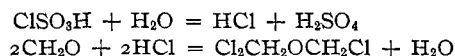
PREPARATION OF PHENYLIMINOPHOSGENE—The compound was prepared by the action of chlorine on phenyl mustard oil:



About 600 kg. of mustard oil were used in a single operation. This was contained in a lead-lined kettle of about 1000 l. capacity. The kettle was furnished with a lead stirrer and a lead coil through which cold brine was circulated. Chlorine was led into the coil and the temperature kept below 0°. When the specific gravity of the material was about 1.45, the reaction was complete, the time required being a little less than 24 hrs. The product was transferred to a lead-lined still which was furnished with a steam jacket, and the chloride of sulfur distilled off in a good vacuum. The residue was used without being distilled and always contained a small amount of chloride of sulfur. The yield of the phenyliminophosgene was about 90 per cent of the theoretical. The apparatus in which the operation was carried out was markedly affected by the chemicals used, and had to be frequently replaced.

DICHLORMETHYL ETHER

This compound was prepared by the action of hydrochloric acid on formaldehyde in the presence of sulfuric acid. As a source of hydrochloric acid, chlorosulfonic acid was used. The reactions involved are as follows:



The formaldehyde was used either in the form of paraformaldehyde or an aqueous solution containing 80 per cent of formaldehyde. The paraformaldehyde, however, is preferred.

The reaction was carried out in an iron kettle lined with acid-resisting tiles. It was furnished with a stirrer covered with lead, which had to be frequently replaced on account of the action of the acids upon it. The kettles were of 5000 l. capacity and were furnished with lead cooling coils.

In carrying out an operation, first, 1200 kg. of 70 per cent sulfuric acid, prepared from 85 per cent sulfuric acid recovered from a previous operation, were added to the kettle. Six hundred kilos of paraformaldehyde or an equivalent amount of a solution of formaldehyde were next added slowly while the mixture was well stirred. The addition of the aldehyde required from 3 to 4 hrs. Twenty-four hundred kilos of chlorosulfonic acid were next run in slowly, about 48 hrs. being required for this operation. The temperature maintained during the addition of the formaldehyde was between 5° and 10°, and that maintained during the addition of the chlorosulfonic acid was between 10° and 15°. During the whole operation, the contents of the kettle were thoroughly stirred.

At the end of the reaction, the kettle contains 2 layers: at the bottom, the sulfuric acid which contains the water formed in

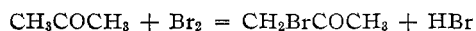
the reaction and on the top, dichloromethylether. The mixture is drawn from the kettle—first, the sulfuric acid and then the oil. The oil is run directly into tank-wagons of iron, care being taken to avoid the presence of any moisture. The dichloromethyl oxide contains free hydrochloric acid; but, in the absence of moisture, does not appreciably affect the iron tank. The yield of the oxide obtained was from 90 to 95 per cent of the theoretical.

DIBROMMETHYL ETHER

The process by which this compound was manufactured was identical with that used to prepare the dichlorether, except that ammonium bromide was added to the mixture of sulfuric acid and paraformaldehyde, instead of using chlorosulfonic acid. Six parts by weight of 70 per cent sulfuric acid were first added to the kettle. One part by weight of paraformaldehyde was then added. Ten per cent excess over two molecular quantities of solid ammonium bromide for each molecular quantity of formaldehyde was next added slowly. The time required for the addition of the ammonium bromide was 48 hrs., and the temperature was maintained at 15° to 20°. When all the substances had been added, the mixture was stirred for from 5 to 10 hrs. at 30°. The product formed was separated from the sulfuric acid and about 10 per cent removed by distillation in a lead-lined still. The yield of the residue, which was the compound sought, was between 70 and 80 per cent.

BROMACETONE AND BROMMETHYLETHYLKETONE

These two products were prepared by identical methods. About two-thirds of the product produced by the factory was prepared from methylethyl ketone which was obtained from the product resulting from the distillation of wood. The method employed was to treat an aqueous solution of potassium or sodium chlorate with acetone or methylethyl ketone, and then add slowly the required amount of bromine. The equation for the reaction in the case of acetone is as follows:



Ten kg.-mols. of acetone or methylethyl ketone were used in a single operation. About 10 per cent excess of chlorate over that required to oxidize the hydrobromic acid formed in the reaction was used. The relation between the water and the ketone was in the proportion of 2 parts by weight of the former to 1 part by weight of the latter. For 1 kg. mol.-wt. of the ketone, 10 per cent excess over 1 kg. atomic-wt. of bromine was used.

The reaction was carried out either in earthenware vessels or in iron kettles lined with earthenware (see Fig. 10). The kettles were furnished with a stirrer made of wood, and varied in capacity from 4000 to 5000 l. They were set in wooden tanks and cooled by circulating water. The chlorate was first dissolved in the water and then the ketone added. Into this mixture the bromine was allowed to run slowly while the solution was stirred and kept at a temperature of from 30° to 40°. The time required for the addition of the bromine was about 48 hrs. When the reaction was complete, the oil was drawn off into an iron vessel and stirred with magnesium oxide in the presence of a small amount of water in order to neutralize the free acid. It was then separated and dried with calcium chloride. At this point a sample of the material was taken and tested. The product was distilled to tell how much of it boiled over below 130° when methylethylketone had been used. If less than 10 per cent distilled over, the bromination was considered to be satisfactory. If, however, a larger percentage of low-boiling material was obtained, the product was submitted to further bromination. The material obtained in this way was found on analysis to contain slightly less than the theoretical amount of monobromketone.

It was finally transferred by suction or by pressure into tank-wagons. At first lead-lined tanks were used, but later it

was found that tanks made of iron could be substituted. In order to take care of the small amount of hydrobromic acid, which is slowly formed, a small amount of magnesium oxide was added to the material. The amount of the oxide used was approximately in the proportion of 1 part to 1000 parts of ketone. When the magnesium oxide was used, it was found that the bromketone kept without appreciable decomposition for about 2 months. The yield of the product from 580 kg. of acetone (10 kg. mol. wts.) was 1100 kg. The yield from 720 kg. of methylethyl ketone (10 kg. mol. wts.) was 1250 kg.

XYLYL BROMIDE

The process employed was to introduce xylene into iron or enameled stills fitted with a close-fitting stirrer and a coil for heating. The stirrer shaft had fitted to it a special lead-lined gland with a sulfuric acid seal. The xylene was heated to 115° and the bromine run in little by little. The hydrobromic acid gas was absorbed. The total amount of bromine employed was about three-fourths of the theoretical. Eight hundred kilos were used in each charge and there were six of these units. At the end of the reaction the xylene was distilled off in vacuum and the residual xylyl bromide packed without further treatment. The bromine was recovered from the hydrobromic acid by-product by means of chlorine and distilled off.

CHLORPICRIN

The process employed was to prepare an emulsion of bleaching powder and to add picric acid to it little by little, maintaining a temperature of about 30° by water-cooling. The chlorpicrin was distilled and the distillate drawn up to large tanks for separating the water. The reaction vessels consist of 6 units, 8 ft. in diameter and from 15 to 20 ft. deep. They were lead-lined and had coils on the side with a gate stirrer. During the reaction the manhole was closed by a glass cover to facilitate inspection.

PHOSGENE

Phosgene was manufactured in the works of the Bayer Company prior to the war. The plant is capable of producing about 30 tons per month. In the first instance, large quantities of phosgene were sent to the factory for filling and also for conversion into diphosgene. The method employed does not appear to be an economical one. The carbon monoxide is prepared by passing carbon dioxide, a by-product from the acidification of vat liquors, over wood charcoal contained in gas-fired muffles and the resulting carbon monoxide is washed with sodium hydroxide. The carbon monoxide and chlorine are bubbled through Wouff bottles and the speed regulated by inspection of these bottles and reading of flow meters. The mixed gases, at a short distance from where they were mixed, are passed downward through a layer of about 20 cm. of prepared charcoal contained in a cast-iron vessel 80 cm. in diameter and 80 cm. deep. The phosgene is led away by a lead pipe to which is attached a view pipe by means of which the color of the issuing gas may be watched. By regulating the mixture so that there is a slight excess of carbon monoxide, the phosgene is obtained with one-quarter to one-half per cent of chlorine. Stress was laid upon the method of purifying the carbon catalyst. Wood charcoal was washed with hydrochloric and other acids until perfectly free from soluble ash. It is washed and dried in vacuum. Animal charcoal is generally found better. The size of the granules was about one-quarter inch mesh. The life is about 6 months. The phosgene is liquefied by cooling with ice and salt. The phosgene plant remains intact ready for use. There are 14 units inside the building and 2 experimental ones outside.

CHARCOAL FOR GAS MASKS

In the first instance, the charcoal for filling the gas masks was supplied to the Bayer Company from Aussig in Austria.

but in the summer of 1916 the manufacture was started at Leverkusen. The average production was 30 tons per month.

The process consists of taking wood of even size, pieces of about one-fourth inch diameter, and soaking it in strong hydrochloric acid to which zinc chloride had been added. The acid was 20° to 40° Bé. in strength. The amount of zinc chloride added was indefinite and said not to be very much. The wood employed was generally pine wood but it made no difference what wood was used. The wood was soaked in the acid mixture for half an hour and upwards, a small quantity being mixed up at a time in lead-lined tanks. The acidified wood was packed into a closed muffle furnace lined with porcelain tiles and fitted with a stoneware flue pipe to a hydrochloric acid condenser plant. It is desirable that carbonization should take place slowly and very thoroughly.

The muffles were filled nearly full with a few inches of air space above. They were heated to a cherry-red and the heating continued for from 6 to 8 hours at least. It is most desirable to continue it long enough, otherwise the material would not be good. The muffle was about 24 in. square by 12 ft. long with an iron door through which the charge was introduced. The charcoal was washed with hydrochloric acid in lead-lined tanks 8 by 10 by 5 ft. The washing was continued until the soluble ash was reduced to a minimum and the finished charcoal contained about 0.01 per cent of zinc. It was finally washed free from acid. The time taken for washing was in all 2 or 3 days. The charcoal was next drained on a grill and transferred to a vacuum cupboard and dried at 70° or 80°. It was finally sifted on a rotary sieve to get rid of the dust.

The furnaces had a good life and lasted for about 2 years. The only replacements necessary were thought to be due to carelessness on the part of the workmen. No satisfactory test appears to have been arrived at but the charcoal was usually tested for its absorption of hydrogen or oxygen. They did not test it for absorption of phosgene. Berlin appears to have tested with phosgene and did not agree with the result obtained by the oxygen or hydrogen test. Experiments were made with sulfuric acid and with other salts, such as sodium chloride and calcium chloride, without good effects.

A visit was paid to the room in which the box respirators were packed but all the filling machines and test apparatus had been removed. We were, therefore, unable to get any information as to these. It was said that the number of respirators packed per day was 40,000.

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AN ARTILLERY GAS ATTACK

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Of all gas projectiles, artillery shell are most important either for producing casualties or for the purpose of assisting infantry operations. This fact is due to the long effective range of this weapon which makes its use less dependent upon wind and weather conditions than any other means of projecting gas.

The importance of this method of gas attack may be estimated from the fact that 90 per cent of the total gas casualties in the British army was caused by enemy artillery shell, and this in spite of the tremendous casualties incurred by the first unexpected use of cloud gas from cylinders in 1915 against troops wholly unprepared. Casualties in the British army due to gas artillery shell reached the appalling total of 170,000.

The use of toxic shell may be divided into three periods. During the first of these, from May 1915 to July 1916, only lachrymatory shell were used and while these lachrymators had considerable harassing power, no serious casualties or deaths occurred. The protection at this time consisted of goggles,

impregnated fabric helmets, such as the P. H., and cotton waste respirators.

Lethal shell came into use in July 1916 and from this time on until July 1917, in addition to the lachrymators, such shell were employed, containing phosgene, diphosgene, and chlorpicrin. At the beginning of this period only the fabric mask protection was available. The British box respirator was introduced in August 1916, and issue was completed early in 1917.

The third period began with the first appearance of mustard gas at Ypres in July 1917 and it was only during the latter part of this period that American troops came into the line. By this time a variety of chemical shell was being used by all the armies. The British army was completely equipped with the small box respirators and this form of protection was also adopted by the American forces. The French were using the so-called M₂ masks and a special Tissot mask for artillery and medical officers. It is only with this third period that this discussion will be concerned.

While the effect of H. E., or shrapnel shell, is ended immediately after the burst, that of a chemical shell has only just begun, and may continue, depending on the nature of the filling, up to a week or 10 days. Moreover, the effect is continuous over the limits of the area of spread; in the words of the trap-shooter, "There are no holes in the pattern." A bomb-proof shelter composed of barriers of concrete, steel, and earth, for protection against flying fragments, is of no avail against chemical shell, since the fumes can perfectly well pass around corners.

For these reasons, effects may be produced with gas shell which are impossible with others, but for the same reasons, the maximum effects can be produced only when the properties of the chemical are thoroughly known to those directing the operation. The behavior of the toxic cloud following the shell burst is dependent upon the physical properties of the chemical, upon the nature of the ground, temperature, wind and weather conditions, and the number, caliber, and kind of shell, as well as the rate and duration of fire; and the choice of shell is dependent upon the nature of the target and the end to be accomplished. From the standpoint of the artilleryman, chemical shell are divided into two great classes, depending on the purpose for which they are to be used. These may be called "lethal" and "neutralizing." With certain variations, it was the policy of all the armies to mark chemical shell on the basis of this difference in tactical use.

Lethal shell are used to produce casualties and this purpose immediately defines their manner of use. Such shell should be fired against occupied targets for surprise effect and, therefore, it is important that the greatest possible number of shell fall on the target in a minimum time. To accomplish this, all available batteries should be assigned and should maintain their maximum rate of fire until the required concentration has been built up. It is almost never profitable to fire lethal shell for more than a 2 or 3 minute period on one target since by this time the enemy masks would be adjusted and no further results could be expected. Chemicals used for this purpose are generally not persistent and the best example of this type is phosgene.

Neutralizing shell, on the contrary, are filled with chemicals which are persistent and vaporize slowly. As the name indicates, they are employed to interfere with the enemy activities by producing an atmosphere which is intolerable for unprotected troops. Suitable targets for such shell are lines of communication, camps, rest billets, important trench systems, cross roads, battery positions, or areas where supports or reserves may be concentrated. Instead of a burst of rapid fire, a slow searching fire should be maintained with such shell, scattered over the area to be neutralized. A low concentration of such gas gives just as good results as a high one, since it is desired only to force the enemy to wear respirators and thus cut down their efficiency in