

French Chemical Industry during the War.

IN the November-December issue of the *Bulletin de la Société d'Encouragement pour l'Industrie nationale* Prof. Haller gives a detailed and interesting account of the way in which the requirements of the fighting forces in munitions were met, and of the activities of French chemists in extending, improving, and creating processes for the manufacture of the necessary materials on the large scale.

The official policy before the war was to lay in stocks of explosives sufficient, in the judgment of the military authorities, to last out a "short, sharp war." The phenol required was obtained from Germany. In the middle of September, 1914, the use of explosives by the artillery was exceeding very considerably the amount estimated by the military authorities, and it was necessary to provide daily 40,000-50,000 75-mm. cartridges and to make schneiderite and ammonium perchlorate for trench mortars. The need for explosives continually increased, and it became evident that the character of the war was not at all like that for which the country had been prepared. A great national effort was required, and the part which the chemists of France played in this can be appreciated from the following table, giving the requirements of the Army in metric tons per day:

	Propellants	Nitrogenous explosives	Chlorate and perchlorate explosives
Mobilisation	24	0	0 ¹
January 2, 1915	80	100	—
June 6, 1915	104-135	125-195	—
October 19, 1915	238-313	351-654	109-135
December 25, 1916	441-550	728-936	150-159
June 25, 1917	484-640	859-940	124-148
February 28, 1918	444	625	—

Provided in stocks accumulated.

After April, 1918, the requisitions for explosives amounted to about 390 tons per day.

Sulphuric Acid.—Before the war there were 87 scattered works for the manufacture of sulphuric acid, producing 13,500,000 tons of 53° Bé. acid, of which 975,000 tons were used for the manufacture of superphosphates and the rest concentrated to 66° acid. This output was reduced by 15-20 per cent. by enemy occupation of territory. The production of explosives called for large quantities of concentrated acid, and steps were taken to force the production of the chambers from 5-6 kg. of acid per cu. m. to 7-8 kg., and to increase the Kessler and Gaillard concentrating plant in the ratio of 1 to 20. The use of acid was also restricted in industry, and nitre-cake began to be used in August, 1915. The Volvic lava of Puy-de-Dôme proved invaluable in the construction of concentrating apparatus. In addition, there were needed for the transport of acid 2000 20-ton tank wagons, 600 platforms for which were made in England and Spain.

Oleum containing 20 per cent. of sulphur trioxide was exclusively used, the consumption amounting

to 1.5-1.9 tons per ton of nitrocellulose, and 2.2 tons per ton of trinitrotoluene. The oleum was, at the outbreak of war, made in a few works only, one of which, at Thann (Alsace), came under fire in 1914, and was transported by night to Saint Denis, where it was re-erected and came into operation in 1916. All the common processes (Tentelaw, Grillo, and Mannheim included) were used, and a monthly output of 21,000-22,000 tons was secured. New works were put in hand, and in the meantime oleum was imported from America. The monthly consumption of sulphuric acid and oleum was as follows, in metric tons:—

	66° Bé. acid	20 per cent. oleum
February, 1915	6,000	1,000
January, 1916	42,000	5,000
January, 1917	80,000	20,000
January, 1918	60,000	19,000
June, 1918	40,000	18,000

Nitric acid was produced before the war almost exclusively from Chile nitre by the retort process, and during the war great extensions of these plants were made. The stock of nitre at the end of 1915 amounted to 90,000 tons; it increased during 1916, but from the beginning of 1917, when the submarine campaign was begun, the stocks of nitre diminished. In 1917 numerous ships laden with nitre were torpedoed. On account of the large amounts of raw material (coal, pyrites, and nitre) required in the manufacture of explosives, necessitating great shipping demands, it was decided in 1917 to ask the American Government to supply explosives ready-made. A programme was agreed upon, but the actual deliveries from America fell far short of the promises. Help was also given by Great Britain. The consumption of nitre and nitric acid (calculated as sodium nitrate) in metric tons per month was as follows:—

January, 1915, 3,600	March, 1916, 25,000
August, 1915, 9,600	July, 1917, 42,000

On account of the transport and storage difficulties it was decided to produce nitric acid by synthetic methods. These had an additional advantage, *i.e.* the economy in sulphuric acid which would otherwise be required in decomposing the nitre, which was even more important than the nitric acid. Before the war synthetic nitric acid was made by the Pauling arc process at La-Roche-de-Rame at the rate of 2 tons of 50 per cent. acid per day. This was continued, but a new factory on the Birkeland-Eyde principle was erected by the Société norvégienne de l'azote at Soulom, utilising 12,000 kw. from the hydro-electric installation in the Hautes Pyrénées of the Compagnie des chemins de fer du Midi. This works delivered 300 tons of nitric acid a month, partly as nitrates. The ammonia oxidation process was also largely used, the ammonia being derived from cyanamide. The first works was installed at the Poudrerie nationale d'Angoulême. Carbide was imported

from Switzerland and converted into cyanamide by the Société des Produits azotes, nitrogen being obtained by the Claude process at Martigny, Notre-Dame de Briançon, and especially Bellegarde. From 2650 to 3500 tons of cyanamide per month were delivered at Angoulême. The first oxidation plants were operating in the autumn of 1916, and the whole was in operation in 1917. The programme was much enlarged in 1917 on account of the submarine warfare, and it was then decided to erect factories for making 500 tons of nitric acid and 150 tons of ammonium nitrate per day by the oxidation of ammonia. This programme required 800 tons of calcium carbide per day and 125,000 kw. Water-power from the Pyrenees, Central France, and the Alps, and even central steam-power plants at Nanterre and Carmaux, were brought into requisition. The most important works was at Lannemezan (50,000 kw.), and new oxidation works were installed at Toulouse, Bassens, Sorgues, and Saint Chamas. Toulouse and Bassens had begun to operate at the armistice, and the others were nearly finished. These works would have supplied all requirements in nitric acid and ammonium nitrate.

Alcohol was used, apart from minor requirements in the purification of trinitrotoluene and xylite, for the manufacture of ether for the gelatinisation of gun-cotton. Great economy was effected during the war in the latter process, the quantity of alcohol per ton of Poudre B being reduced, by solvent recovery, from 20 hl. to 8 hl. A sixty days' stock of alcohol had been accumulated and arrangements made with distillers for the regular supply of 550 hl. per day, sufficient for the estimated need of 24 tons of Poudre B. As the war proceeded, new supplies had to be obtained from the distillation of beets, molasses and cider, the saccharification of grain, horse-chestnuts and sawdust, and by recovery from stocks of confiscated absinthe and from liqueurs. Before the war the production of alcohol in France was 2,000,000 hl. per annum, with 6000 hl. of brandy per day, and was principally obtained from beets cultivated in the Département du Nord. The German occupation deprived the nation of this source, and there were labour difficulties. In August, 1915, the distilleries and stocks were requisitioned, and forced production was begun. From absinthe 40,000 hl. were obtained, 10,000 hl. from apples mixed with beets, and 500,000 hl. were imported from Canada and the United States. Experiments were made on synthetic alcohol from acetylene, with encouraging results. The total consumption of alcohol to (and including) 1918 was 4,713,607 hl.

Ether was made at the rate of 74 tons per day in 1915, 119 in 1916, and 166 in 1917, mostly in Government factories.

Aromatic hydrocarbons (benzene, toluene, and xylene) were used in large quantities, and their provision was one of the most difficult problems to be solved. The pre-war annual production of crude benzol from coking plants did not exceed 16,000–18,000 tons, the rest being imported from

England and Germany. The yield from coking plants in occupied territory was a considerable loss during the war, and not more than 3–4 tons per day could be expected from the remaining plants, although 50 tons in 1915, and later as much as 250 tons, per day were required. Needs were supplied by the requisition of stocks, imports from England and (to a less extent) from America, the re-starting and erection of recovery ovens, extraction from town gas and from Borneo petroleum. The use in private factories was restricted, and every available means of rectification was brought into requisition. From one-third to one-fourth of the weight of crude benzol was recoverable as toluene, although the English supplies had been detoluated previous to export. Borneo petroleum was an important source (35–40 tons per day). Three fractions were obtained. The benzene fraction boiled at 80–81° C., the toluene fraction at 110–112°, and the xylene fraction at 130–132°. These fractions were nitrated and the unattacked hydrocarbons distilled off. The mononitrotoluene and mononitroxylene were converted into trinitrotoluene and xylite, the nitrobenzene being sent to the aniline factories for conversion into diphenylamine for use as a stabiliser. The production of trinitrotoluene rose from 10 tons per day in 1915 to 50 tons in 1916 and 60 tons in 1917.

Phenol and *metacresol* were used for nitro-explosives. Before the war all the phenol had been imported from Germany, and a large amount of work was necessary before the production from benzene (by fusion of sodium benzenesulphonate with caustic soda, and 2–3 tons per day from aniline by diazotisation) was in operation. The supplies of synthetic phenol (excluding relatively unimportant American imports) rose from 200 tons in 1914 to a maximum of 52,747 tons in 1917.

After the explosion in the *Liberté* in 1911, large quantities of gun-cotton were thrown into the sea outside Toulon. This was recovered in excellent condition and utilised. The two State factories of Angoulême and Moulin-Blanc were developed for the manufacture of propellants. New factories were later erected at d'Empalot (Toulouse) and Bergerac. The maximum productions of gun-cotton per day reached 120 tons at Angoulême, 38 tons at Moulin-Blanc, 140 tons at Toulouse, 100 tons at Bergerac, and 35 tons from private firms. Cotton cellulose was exclusively used. The preliminary washing and extraction of grease were carried out mainly at Angoulême, and to a less extent in paper- and dye-works. More than thirty works supplied 240 tons of cotton daily, sufficient for 360 tons of gun-cotton, which was brought up to 433 tons in 1916 by American importation. Nitration, with a mixture of nitric and sulphuric acids, was before the war carried out in pots. This method required much less apparatus than the new methods of Selwig and Thomson, which were introduced only when a crisis in the supply was feared. Pots were used at Toulouse, Angoulême, Bracqueville, and Bergerac. Angoulême later installed a Selwig

plant for 60 tons, and replaced a pot installation by one using the Thomson process. The same change was effected at Bracqueville, and a Selwig plant was installed at Bergerac. The nitro-cotton, after washing, was stabilised by boiling with water, pulped, and dried to 30 per cent. moisture. Two varieties were made, CP₁ with 11 per cent. of nitrogen, soluble in a mixture of alcohol and ether, and CP₂ with 13 per cent. of nitrogen, insoluble in that mixture.

Poudre B was made by masticating the requisite proportions of these two varieties with a mixture of alcohol and ether, pressing into filaments, and drying. This was carried out at Le Bouchet, Pont-de-Buis, Ripault, Saint Médard, Sevran-Livry, Bergerac, and Toulouse. The maximum productions in tons per day from these works were 10, 48, 60, 140, 35, 60, and 130 respectively. Private industry furnished a maximum of 20 tons of ballistite (gelatinised nitro-cotton with nitroglycerin). The total production of Poudre B in France from 1914 to 1918 amounted to 306,693 tons, and 117,000 tons were during this period imported from America.

The manufacture of nitro-explosives was accompanied by strenuous endeavours to improve the methods of production and to replace these substances by others less difficult to produce. The 75-mm. shells, for example, were filled with ammonium nitrate and dinitronaphthalene; chlorates and perchlorates were introduced for filling hand grenades; and experiments were made with liquid air for charging aeroplane bombs.

The nitro-bodies picric acid and trinitrometa-cresol could be manufactured by known methods, but the production of trinitrotoluene, xylite, dinitrophenols, and mono- and di-nitronaphthalenes was introduced during the progress of the war. These explosives were used both alone and in the form of mixtures.

Three methods are available for the manufacture of picric acid (trinitrophenol): nitration of phenol in presence of sulphuric acid by nitric acid or sodium nitrate; chlorination of benzene, transformation of monochlorobenzene into dinitrochlorobenzene 1, 2, 4, saponification of this with formation of dinitrophenol, and trinitration of the latter; direct oxidation and nitration of benzene with nitric acid and mercury. The method of direct nitration alone was used. The second method was in use in Germany prior to the war, but as it required the use of pure chlorine it was not suited to French needs. Nevertheless, 1000 tons of chlorine were ordered from America in order to commence production in France. After the German gas attack of April 22, 1915, on the Belgian front, this chlorine was devoted to experiments on the new method of warfare. In the meantime the production of phenol had increased, and there was no longer any point in making use of the method of chlorination. The yield by the third method was poor (140 of picric acid per 100 of benzene, as compared with 190 with phenol), and the recovery of the mercury was difficult. The latter was important in view of the pressing need of mercury

for the manufacture of fulminate. Picric acid so prepared may also contain small amounts of mercury picrate, which renders it very sensitive to shock.

There were three picric acid factories in operation before the war. Several chemical and dye factories in the Lyons district were requisitioned, including one of the Badische firm. State factories were also erected. Some of these factories were destroyed by explosions. The total productions of picric acid and trinitrotoluene, in tons per day, were as follows:—

Production of Trinitrotoluene in metric tons per day.

August, 1914, 0·31	January, 1917, 66·71 (maximum)
August, 1915, 8·93	January, 1918, 24·02
August, 1916, 55·87	

Production of Picric Acid in metric tons per day.

August, 1915, 0·50	July, 1917, 166·1 (maximum)
January, 1916, 11·95	January, 1918, 58·86
January, 1917, 145·47	

Lack of cresol led to the use of dinitrophenol, made by nitrating phenolsulphonic acid. Picric acid was also formed, but as a mixture of the two substances was finally used, this was immaterial. The preparation by the nitration of chlorobenzene led to the installation of electrolytic chlorine apparatus producing 20 tons of chlorine per day.

The explosive *schneiderite* was used in large quantities, and was prepared by triturating in mills a dry mixture of 88 parts of ammonium nitrate and 12 parts of dinitronaphthalene. The ammonium nitrate was prepared to some extent by double decomposition of accumulated stocks of Norwegian calcium nitrate (for agricultural purposes) with ammonium sulphate, by neutralising nitric acid with ammonia solution, and by the interaction of ammonium sulphate and sodium nitrate according to a process worked out by M. Fosse, of Bordeaux, and by M. Danne, of Gif. Nearly all the ammonium nitrate, however, was imported from Norway at the rate of 200 tons per day.

Chlorate and perchlorate explosives were also manufactured. Paraffined ammonium perchlorate was tried for filling 75-mm. shells, but proved too sensitive to shock. It was, however, extensively used for trench-mortar bombs, hand grenades, and aeroplane bombs. Sodium chlorate and a mixture of 61·5 parts of ammonium perchlorate, 30 of sodium nitrate, and 8·5 of paraffin were used. The chlorates and perchlorates were made electrolytically at Cheddes, Vonges, Castres, and Grenoble, the production being 79 tons of ammonium perchlorate and 77 tons of sodium chlorate per day.

Many new products were made. Mustard gas, known as "yperite," was produced at the rate of 6 tons per day at the signing of the armistice, and plant for the manufacture of 12 tons per day was ready to be put into operation. A daily production of 24 tons was planned. Liquid nitrogen

peroxide was produced at the rate of 70-80 tons per day at Angoulême, and of 25-30 tons at Basens. It was used with a hydrocarbon in the manufacture of "anilite" for aeroplane bombs.

Switzerland, Italy, and Spain delivered machinery and raw materials of various kinds; Chile furnished millions of tons of sodium nitrate; and Norway supplied more than 200,000 tons of ammonium nitrate. England supplied benzene,

naphthalene, and coal, and America sent raw materials and finished explosives.

The tremendous strides made during the war may be appreciated from the following table, giving the productions in tons per day:—

	Before 1914	July, 1917
Poudres B	15	370
Nitro-explosives	6	700
Chlorate explosives	4	176

War-time Archæology.¹

THE volume before us might truly be described as a "war number," for it represents not only the published work of the British School at Athens for the first regular session after the armis-

of Archæology who lost their lives during the war, and the school's distinguished and learned librarian, F. W. Hasluck, who died early in 1920 of a malady caused or aggravated by war service in Greece, are appropriately commemorated, and a brief summary shows the war work which fell to other students. It is a striking and varied record. If the school had done nothing beyond training for eventual public service in Greece and the Near East so large a body of men accustomed to observe accurately, handle native labourers tactfully and economically, and act with expert knowledge and executive efficiency, it would have earned many times over the miserable allowance which

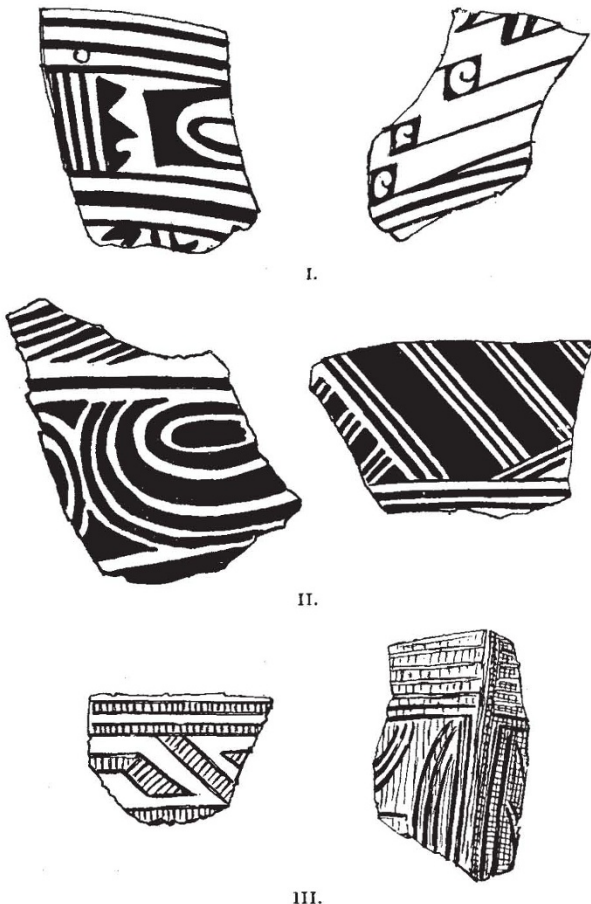


FIG. 1.—Specimens of prehistoric pottery from Dikilitash. I. Dimeni ware; fine reddish biscuit, surface usually bright chestnut; patterns, a mixture of geometrical and curvilinear figures in dull brown paint. II. Black or red biscuit; patterns, geometrical designs, parallel lines in sets of threes, and rows of concentric circles, in dull white paint. III. Coarse black or red biscuit; patterns, similar to those of I. and II. filled in with cross-hatching or painted; specimen on right is painted and incised. From "The Annual of the British School at Athens."

tice, but also mainly the results of observations made while on duty by actual and former students. The seven students of the British School

¹ "The Annual of the British School at Athens." No. xxiii. Session 1918-19. Pp. xvi+260+xvi pls. (London: Macmillan and Co., Ltd., n.d.) Price 30s. net.



FIG. 2.—Wall of ruined fort near Kato Kastelli, in ancient Doris. From "The Annual of the British School at Athens."

it receives annually from the Treasury. Special mention is made in the annual report and in a letter of thanks from the Secretary of State for Foreign Affairs of the services of the director, Mr. A. J. B. Wace, who was attached to the British Legation at Athens during the war while carrying on the school as a hostel for British officers in transit or on duty in Greece.

The greater part of the volume is devoted to the publication, by Prof. E. A. Gardner, Messrs. Carson, Welch, Woodward, and others, of sites, inscriptions, and other antiquities discovered during the British occupation of Salonica. This district was previously very ill-explored, but numerous finds were made in trenching operations and military surveys. The contents of the museum formed at British G.H.Q. have now been presented by the Greek Government to the British