

critical range (700°C .) and cannot be said to have any definite strength at a red heat, and that the property of principal importance to the engineer who wishes to subject highly heated steel to stress is the equivalent of the viscosity of a fluid. For the solution of a problem of immediate practical importance, he has ascertained for each of a number of steels the temperature at which the rate of flow does not exceed a very small and practically negligible amount under a uniform stress of 8.5 tons per square inch. The particular problem was the manufacture of large catalyst tubes for a synthetic ammonia process. These tubes were to be maintained at a temperature of about 600°C . under an enormous internal pressure, a long life under these conditions being essential to the economic success of the process. After due consideration it was decided to make them of a nickel-chromium alloy which was known to possess high resistance to oxidation and deformation when under stress at high temperatures.

Laboratory tests were carried out on this alloy, on pure carbon steels, on a high chromium steel, and a high-speed steel. For details of the actual experiments the original paper must be consulted. It must be noted, however, that although the mechanical conditions chosen for the tests appear to have been considered with great care, there were considerable variations in the temperature of a given test-piece which amounted to as much as $\pm 25^{\circ}\text{C}$. from a mean figure. Tests of two kinds were carried out: (a) those at constant load and constant temperatures, and (b) those at constant load and uniformly rising temperature. The extension temperature diagrams of the (b) series show that up to 400°C . all the steels extended alike. Thereafter, however, the curves diverged, a considerable amount of flow taking place in each case, at temperatures well below that finally reached. The range of temperature investigated extended up to nearly 1000°C .

The diagrams of the (a) series present some remarkable results, of which perhaps the most striking was that of the test-piece of nickel-chromium alloy (Vikro), which extended continuously from the first day of loading (at 625°C .) but only broke after 36 weeks.

The diagrams bring out well the enormous influence of time in determining the temperature up to which each type of steel can support a given load (in this case $8\frac{1}{2}$ tons per square inch), and by implication a load which can be borne at any given temperature. As an example, a nickel-chromium alloy withstood the above stress under a rapidly applied load at 965°C ., whereas the same specimen cannot be expected to endure the same stress for considerable periods without suffering sensible deformation at a temperature exceeding 600°C . Working conditions such as those outlined demand a knowledge of the latter figure.

Mr. Dickenson concludes from his tests that the extension and eventual rupture of the test-piece under unvarying load is due almost entirely to viscous flow. Whether plastic flow affects the shape of the curves, and if so, whether the data will prove sufficient to enable the plastic to be separated from the viscous flow, is a question to which he has not yet found an answer. His curves are also interesting for the light which they throw upon the differing degrees of resistance to mechanical deformation at high temperatures, which the various steels exhibit. Moreover, in selecting material for resistance to stress at these temperatures, the nature of the stressing action must be taken into account.

In the second half of his paper, consideration is given to the very important factor of resistance to "scaling" exhibited by steels at the temperatures in question. It has been known for some time that remarkable resistance to oxidation is offered by certain nickel-chromium alloys, and, in a somewhat less degree, by high chromium steels. Mr. Dickenson has carried out systematic experiments on eight typical steels, in nine temperature ranges from 550°C – 600°C up to 1075°C – 1175°C . The best results were given by a nickel-chromium alloy called "Vikro." Interesting photomicrographs are furnished, showing the varying character of the scale in the various alloys. Mr. Dickenson's research will be welcomed by chemical and metallurgical engineers, for it contains valuable information for which they have long been waiting. It is much to be hoped that he will see his way to continue his experiments.

The Manufacture of Acids during the War.¹

By Prof. T. M. LOWRY, F.R.S.

THE three technical reports before us deal with the manufacture of sulphuric, nitric, and picric acids during the war. The reports are compiled on similar lines to those of the four earlier volumes which have already been reviewed in these columns (NATURE, April 29, 1922, p. 541); and since the methods and workmanship of Mr. W. Macnab are now well known, it is not necessary to describe in detail the type of information which they contain. It may, however, be of interest to review briefly the general situation as

regards supplies of acids which had to be met by the Department of Explosives Supply, and the way in which the problem was solved by the workers of that Department, as disclosed in these three reports.

NITRIC ACID.

Although oxidised nitrogen was the key of the supply-problem in explosives—both propellant and H.E. (just as chlorine was the basis of the supply-problem in gas-warfare in its successive phases of chlorine, phosgene, CCl_3NO_2 , $\text{S}(\text{C}_2\text{H}_4\text{Cl})_2$, or mustard gas, etc.)—the report on the manufacture of nitric acid is undoubtedly the least important of these three, since it is much to be hoped that this country will never again be dependent on overseas

¹ Ministry of Munitions and Department of Scientific and Industrial Research. Technical Records of Explosives Supply, 1915-1918. No. 5: "Manufacture of Sulphuric Acid by Contact Process." Pp. vi+128+plates. (London: H.M. Stationery Office, 1921.) 25s. net. No. 6: "Synthetic Phenol and Picric Acid." Pp. vi+97+plates. (London: H.M. Stationery Office, 1921.) 15s. net. No. 7: "Manufacture of Nitric Acid from Nitre and Sulphuric Acid." Pp. vi+86. (London: H.M. Stationery Office, 1922.) ros. 6d. net.

sources for its whole supply of fixed nitrogen. No more eloquent testimony to our unpreparedness in this direction could be given than the fact that, while a whole volume is devoted to the manufacture of nitric acid from nitre and sulphuric acid, there is no corresponding report on the supply of fixed nitrogen from the air, for the all-sufficient reason that there never was a supply to describe. Since, however, the two factories of Gretna and of Queen's Ferry alone were making during the war 1300 tons of nitric acid per week, and since, moreover, the loss by submarines of nitre ships from Chile was the cause of incessant anxiety, lest the whole output of explosives should be arrested by even a temporary stoppage of supplies, it was of very great importance that the utilisation of the nitre should be carried out with the highest degree of efficiency.

As usual, detailed attention resulted in economies which, in an earlier stage, would have appeared to be almost impossible. Striking evidence of the elaborate care that was called for in this very large-scale production is afforded by the fact that twenty pages of the seventh report are devoted to a description of the plant and process used for washing the sacks in which the nitre was brought from Chile! This resulted, not only in the saving of a substantial percentage of the precious nitre and in the elimination of a very serious fire risk, but also gave a higher value to the bags themselves; thus, whereas an unwashed bag could be sold for 2d., there were obtained, after washing, 60 per cent. of sound bags at 4½d. each, 39 per cent. of slit bags at 3d., and 1 per cent. of ragged bags at 9.25d. per ton of 1400 bags.

A more obvious source of loss arose from the decomposition by heat of a certain proportion of nitric acid into water, nitrogen peroxide, and oxygen, especially towards the end of the distillation. It is this factor which gives rise to the one important complication of the plant, namely, the provision of towers in which the nitrous fumes can be reconverted into nitric acid by contact with oxygen and water. Since this oxidation is relatively slow, it is essential to provide adequate space in the towers, in order that the gases may not pass through them too quickly. Another important point in manufacture is to secure as large a proportion as possible of nitric acid of high strength, since, as the distillation proceeds, more and more water comes over with the acid. In practice the acid was collected in two batches, the receiver being changed when the density of the distillate fell to 1.465, while the fire was extinguished when the density fell to 1.340, although a little more acid distilled over from the hot charge before the retort was tapped. In a typical case, a series of six charges gave 5.05 tons nitric acid in the form of 90 per cent. acid and 3.55 tons in the form of 83.3 per cent. acid, giving a total yield of 86.6 per cent. recovered by condensation; to this must be added, however, an estimated recovery of 5.5 per cent. in the absorption towers, giving a total yield of 92 per cent. The balance of 8 per cent. is due mainly to loss of gases from the towers, especially during the brief period of violent interaction which takes place at an early stage of the distillation; there is also a small loss of nitric acid in the nitre-cake, from which the last traces of acid cannot profitably be removed. In some instances,

however, a yield of more than 97 per cent. was reached, the total loss being therefore less than 3 per cent.

An interesting problem arose from the production as a by-product of vast quantities of nitre-cake. This was sometimes thrown away, *e.g.*, by dumping in the sea, since it was difficult to find a commercial outlet for it. It was therefore a profitable process, during an early period of the war, to neutralise nitre-cake with the poorer qualities of caustic soda, and to sell the product to the glass-makers as a substitute for salt-cake. At a later stage, however, manufacturers were persuaded to make more and more use of nitre cake in place of sulphuric acid, and the cake gradually acquired a market value, except at the more outlying factories. On the other hand, the direct-conversion process for the manufacture of ammonium nitrate from sodium nitrate and ammonium sulphate led to the production of vast quantities of sodium sulphate as a by-product, for which no sufficient outlet existed, with the result that two vast glistening pyramids were accumulated as a new object of interest to be seen by travellers on the G.W.R. just before reaching Swindon. As a result of these two factors, the neutralisation of nitre-cake was changed abruptly from a commercial operation, on which a useful profit might be earned, into one in which the product was of less value than the raw material. Under these conditions the infant industry was abandoned as abruptly as if the ashes of Vesuvius had fallen upon it and converted the plants into a modern Pompeii.

SULPHURIC ACID.

The manufacture of sulphuric acid involved a two-fold problem: first, the provision of sufficient supplies of chamber-acid, the manufacture of which was as well established as that of nitric acid from sodium nitrate; and, second, the manufacture of oleum, a far more difficult operation, which might indeed be compared with the fixation of nitrogen, except that the production of oleum had been carried on during many years (although on a restricted scale corresponding with the small normal demand for this material), while the fixation of nitrogen was an altogether novel enterprise in this country. Although several new chamber plants were constructed, they have not formed the subject of a report, perhaps because the production of chamber-acid was very largely left to contractors. On the other hand, new capacity for the manufacture of oleum on a large scale was provided in several Government factories, and the experience gained in constructing and working these plants is described in the fifth report of the series.

The oleum plants were of two principal types. The first plants (*e.g.* that at Oldbury) were constructed on the Mannheim system, in which the oxidation of sulphur dioxide to the trioxide is effected by the use of ferric oxide and of platinum in series. In the later plants platinum alone was used as a catalyst. The plants at Queen's Ferry, Gretna, and Avonmouth were constructed on the Grillo system, in which the platinum is supported on a base of calcined magnesium sulphate; but a plant on the Tentelew system, which is in some respects intermediate between the other two systems, since it employs platinum as the only catalyst, but in

the more familiar form of platinised asbestos, was also taken over and worked at H.M. Factory, Pembrey. The Mannheim and Tentelew plants were constructed to burn iron pyrites; in the large Grillo plants, sulphur was burnt, among other reasons, in order to reduce the size of the towers used to purify the gases. This purification has been from the beginning the most essential feature in the successful manufacture of sulphuric acid by the contact process, and is substantially the same in all the different systems. It was, however, found that, even after the most careful purification of the gases, the proportion of sulphur dioxide converted to the trioxide was lower in the Mannheim and Tentelew plants than in the Grillos, where the efficiency often reached 94 per cent. instead of something less than 90 per cent.

While, however, the report describes in detail many elaborate technical features which were essential in order to secure high yields and efficiencies, it is of interest to find that the apparently simple operation of burning the pyrites provided an opportunity for securing improved yields, that may be compared in its simplicity with the washing of nitre bags, since it was found that careful attention to the method of building up and raking the fires resulted in the reduction of the sulphur content of the spent ore from 8 to 2 per cent. This feature proved to be so important that, in addition to an accurate time-table specifying exactly when the fires were to be raked, charged, and dropped, there was actually drawn up at the Queen's Ferry factory a chart to show exactly how the prong of the rake should be dragged or pushed through the fire in order to produce the best results, and this diagram is regarded as of sufficient importance to be reproduced in the report. The report also contains a precise specification of the way in which the fire-bars must be moved in order to remove the burnt pyrites from the furnace. It was by attention to such details as these that the high efficiencies ultimately achieved in the different factories were reached.

Perhaps one reason why chamber plants did not receive more attention was that, even when T.N.T. could be manufactured without oleum, it was still found to be advantageous to supply in this form the sulphuric acid required to make up for the losses sustained during working, *e.g.*, in the form of fumes and in the various washing waters, since in this way it was possible to avoid the final stage in the concentration of the sulphuric acid, *e.g.*, from 92 to 96 per cent., which was also the most expensive and the most wasteful part of the process.

PICRIC ACID.

The manufacture of picric acid presented a third type of problem. At the beginning of the war this acid was the only approved filling for H.E. shells, for Land Service as well as for the Navy. The demand for the acid soon outstripped the available supplies of coal-tar phenol, and it therefore became necessary to make use of coal-tar benzene as the raw material. This could be converted into picric acid by passing either through monochlorobenzene and dinitrochlorobenzene or through sodium benzenesulphonate and synthetic phenol. In this country the latter

process was adopted almost exclusively. In France the chlorination process was also used, although in many cases the manufacture was arrested at the penultimate stage of dinitrophenol—a milder explosive, which gave rise to many fatalities before its toxic properties were realised and controlled with the help of proper physiological tests.

The manufacture of synthetic phenol lends itself to considerable variations in plant and process, and the sixth report contains diagrams illustrating five different variations worked out by different manufacturers. The subsequent conversion of the phenol into picric acid also included a considerable range of variants, which are set out fully in the report. It may, however, be of greater interest to refer briefly to the final chapters of the history of picric acid manufacture, in which the personal influence of the late Lord Moulton was a dominating feature. Convinced from a very early date that vast quantities of explosive would be required, he had laid down as a fundamental proposition the view that these could be obtained only by using ammonium nitrate as the main basis of the shell-filling programme. In this connexion the limited supplies of T.N.T. were of particular value, since this compound could be diluted with ammonium nitrate to five times its original weight, and even then gave an explosive mixture which was of greater power than, although not quite so violent as, T.N.T. or picric acid. The insensitiveness of this mixture, which ultimately became one of its most valuable properties, made it very difficult at first to secure effective detonation, and a maximum output of picric acid was therefore demanded in order to secure complete detonation of the largest possible proportion of shells. Many efforts were made to dilute picric acid in the same way as T.N.T., and in France (where picric acid was adhered to until the end of the war, in spite of its high cost) it was diluted with a wide range of other nitro-bodies; but the dilution of ammonium picrate with ammonium nitrate was never sufficiently successful to provide a service filling.

When, therefore, the detonation of the mixture of T.N.T. and ammonium nitrate had been improved until its equality with picric acid was at last established, there was no reasonable alternative but to abandon altogether the use of this acid, which cost three times as much, and, moreover, required nearly eight tons of imports, instead of less than two tons, in order to give one ton of finished explosive. Very severe criticism was levelled against Lord Moulton's action in spending more than a million pounds in erecting a factory for the manufacture of picric acid, which was abandoned almost as soon as it was finished; but this criticism was really only a proof of the ignorance of the critics, since the policy on which it was based was one that effected a saving of several million pounds per year, in addition to effecting a reduction of imports which was at the time of vital importance. In this, as in other problems, Lord Moulton saw clearly almost from the beginning what must be done to achieve success, and the closing down of the Avonmouth factory was the final vindication of the policy which he had adopted, and then followed persistently, in spite of all the obstacles that it had to encounter, until he had accomplished his purpose.