The History of Vitriol Making in England

BY

H. W. Dickinson, Past President

(*Read at the Imperial College of Science, London, December 15th*, 1937).

Oil of vitriol, or shortly " O.V.," essentially the chemical that we know to-day as sulphuric acid, is the most important and useful acid known, since it is at the basis of, or ancillary to, so many industrial processes. Its history may be said to be representative of that of industrial chemistry as a whole, and affords a striking instance of development: the march from a drug sold by the ounce to a chemical sold by the ton; methods of manufacture owing much to happy inventions as well as to trial and error; processes modified or superseded as the result of experience; and lastly the application concurrently of chemical knowledge and research.

The word vitriol occurs in the thirteenth century when it was applied, in the first instance to sulphate of copper, presumably because of the glassy appearance of the crystals (*i.e.*, Low Lat. *vitriolum*, dim. of Lat. *vitrum* = glass). The word was applied to other sulphates, *e.g.*, that of iron, hence they were distinguished by their colour—" blue vitriol " for cupric sulphate and " green vitriol " for ferrous sulphate. Oil of vitriol got its name because it was prepared from these vitriols, the word " oil " being used because the concentrated acid pours like oil and resembles oil in adhering to the sides of the vessel containing it. It is to be borne in mind always it was for medicinal purposes exclusively that vitriol and its compounds were originally prepared and used.

There are three processes, in order of date, used commercially for the preparation of oil of vitriol: First, the distillation method, from green vitriol (ferrous sulphate rendered anhydrous), the product being essentially " fuming " vitriol or strong sulphuric acid in which sulphur trioxide is dissolved; Secondly, the combustion method from sulphur assisted by nitre, producing a comparatively pure acid; and Thirdly, the modern " contact " or catalytic process, producing the purest acid of all.

In this paper we shall not concern ourselves with the first process—its product was known to the alchemists as early as the thirteenth century and is still, under the name of " oleum," used for making explosives—nor with the third, which it will surprise most chemists to know is a century old, for it was patented in 1831 by Peregrine Phillips.[1] It is the combustion process, and its development in England more particularly, whose history we are now about to trace.

To understand how the process originated, we have to go back as far as the sixteenth century, when we find that a chemical which went under such names as "spirit of sulphur," etc., and which was essentially sulphurous acid,

FIG. 3. THE BELL OR PER CAMPANAM METHOD OF MAKING SPIRIT OF SULPHUR. From Le Fevre, *Compleat Body of Chymistry*, 1664.

was being made by the combustion of sulphur in the presence of water vapour in a covered vessel. The reaction seems to have been known to the alchemists, *e.g.*, Andreas Libavius in 1595, but J. R. Glauber (1604-1668) is the first from whom we get anything like a clear description of the reaction and of the apparatus used. Other descriptions could be cited; one of the best, showing

[1] Eng. Pat. Mar. 25th, 1831. [No. 6096], *cf. Nature,* Vol. 117, 1926, pp. 419-21.

incidentally that it was being made on the commercial scale, is that given by Nicholas Le Fevre or Le Febure,[2] because it is accompanied by a copperplate (see Fig. 3), which is almost self-explanatory. A few words may be added, however: a is a grey earthenware pan with some water and an iron "trefoot" or support in the bottom. A glazed dish dd. holding brimstone melted at a low heat, is placed on the support and the sulphur set on fire with a red-hot iron (it is noted that a horseshoe is most proper for this purpose!) A glass bell c is at once placed over the pan. When the brimstone is spent, another dishful must be ready to replace it. "The Artist may place as many earthen pans and bells under a chimney as it can hold, to advance the more his work . . . above all times chuse that of the two Aequinoxes, vernal and autumnal, to work this Spirit."

It is true that a certain small amount of sulphuric acid is produced in this "bell" reaction as Lunge remarks:[3] "Besides SO_2, a little SO_3 is always formed and also H_2SO_4 more or less diluted with water. Moreover, an aqueous solution of sulphurous acid in contact with air gradually changes into sulphuric acid. . . . The reaction is very slow. . . ."

It seems that the distinction between this spirit of sulphur and oil of vitriol was well-known; for example, Denis Papin, who was trying an improved method of making this spirit, says in a letter, dated 25 November, 1697, to Leibniz:[4] "L'esprit de souphre chez les auteurs de Medecine et de chymie est preféré à l'esprit de vitriol et aussi il est bien plus cher et plus difficile à préparer par les voies ordinaires." George Ernest Stahl in 1702 shows that he was well aware of the difference between the two acids.

Sulphur does not burn too readily and sometimes it went out, with bad effects on output, so that some person had the brilliant idea of adding a little nitre to the brimstone with the idea of promoting combustion. Thus, unwittingly, he hit upon a most important reaction, for it is now usually explained as a catalytic one—*i.e.*, the oxides of nitrogen evolved act as carriers of oxygen from the air to the nascent sulphur dioxide, forming sulphur trioxide but are not themselves consumed. From the practical point of view the effect was most important for instead of sulphurous acid, sulphuric acid was produced. In this fortuitous way the foundation of a world-important chemical industry was laid.

As is the case in many of our greatest inventions, it is not known whose idea it was to add nitre, nor when nor where it occurred. It has been credited to Cornelis Drebbel (1572-1633), the Dutch chemist and inventor, but the

[2] Eng. trans. *A Compleat body of Chymistry,* 1664, p. 342.
[3] Lunge, G. *Manufacture of sulphuric acid & alkali,* Rev. ed. 1923, Vol. I, p. 7.
[4] Gerland, Ernst. *Briefwechsel mit Papin,* 1881, p. 227.

evidence rests on a slender foundation. Robert Dossie says[5] " and though the practise of this art was, on his [*i.e.*, Drebbel's] death discontinued, yet I can produce the model of an apparatus for extracting the acid spirit from sulphur by means of nitre which was made a considerable time before that patent [*i.e.*, Ward's *see infra*] was applied for." Dossie describes the bell method, with and also without the use of nitre. On the other hand, the latest writer on Drebbel[6] does not mention any invention of his concerned with vitriol.

From the writings of Nicholas Lémery (1645-1715) we can narrow down to the end of the seventeenth century the date at which the use of nitre became generally practised. In the 9th edition of his well-known *Cours de Chimie*, 1697, p. 420, he introduces a paragraph describing this addition of nitre to the bell method but without stating that there is anything novel about it. The paragraph is headed " Autre préparation d'Esprit de Soufre " and he says: " Cette operation est l'acide du soufre separé par le moyen du feu & du salpetre." He gives as the best proportions a mixture 4 lb. of sulphur and 4 oz. of saltpetre. In his *Remarques* he recommends horseshoes for setting the sulphur alight, not from any magical power but because " they are more proper than of another shape to place on the saucer, one being made red-hot while the other is in use." This paragraph does not occur in the 5th edition, 1685. A legitimate inference is that the process came to Lémery's notice about 1690 and may have originated in the Netherlands, Germany or France. From the shape of the apparatus employed the acid so produced was known as oil of vitriol " made by the bell " or " *per campanam*." It should be borne in mind that the acid was still being produced for medicinal purposes and that its use in industry was only beginning.

The credit for the introduction of the process into England, is always given, and perhaps rightly, to Joshua Ward (1685-1761), a quack doctor famous for his " drop and pill," the efficacy or otherwise of which excited heated controversy (See Pl. VI). Ward had tried to enter Parliament irregularly in 1717, and had been obliged for this and other offences to flee the country. He went to St. Germain, but returned to this country and in 1733 was pardoned; here he waxed fat on a credulous public with his potions and pills that he had concocted abroad. Ward, it may be supposed, needed vitriol to make his nostrums—to judge by contemporary comment they were of the drastic order with which we are not unfamiliar to-day—hence it would be convenient to him to have his own laboratory to make the vitriol; this laboratory he established possibly as early as 1736. He carried on the manufacture at Twickenham; it is said that the stench from his works caused intense annoyance to the residents

[5] [Dossie, Robert] *Elaboratory laid open*. 1758. p. 162.

[6] *cf.* Tiere, Dr. G. *Cornelis Drebbel*, 1932.

in that district. It may be that it was the stench that led to the removal of the laboratory, *c.* 1740, to Richmond, then a more retired place than Twickenham.

For some reason, possibly the one which we shall suggest later, Ward abandoned secrecy and patented the process in England and Wales (Pat. June 23, 1749, No. 644). The patentees were "Joshua Ward, Esq., of the Parish of St. Martin-in-the-Fields and John White, of Twickenham, in the county of Middlesex, Gentleman." They recite that they have "with much study, labour and at a very great expence, found out, invented & made . . . a certain Acid Spirit of Sulphur with Sulphur & Saltpetre which in all Things answers and in some Excells Oyl or Spirit of Vitriol. . . . The said acid spirit of sulphur is made by powdering and mixing a proportionable quantity of rough stone or flour of brimstone and saltpetre and putting the said mixture into a glass vessel and setting the said mixture on fire, which, by burning, afterwards condenses into an acid spirit of sulphur; the just quantity of sulphur & saltpetre cannot be ascertained, more or less of one or other being required, not only according to the quality of the sulphur and saltpetre, but according to the various seasons of the year & different weather when the air has at various times so extraordinary effect that without proper alterations the matter yields not above half the quantity of spirit as at other times; for which changes it is impossible to give any general rules, nor is it to be known but by observations and experience."

What the role played by John White[7] was is not altogether clear, probably technical, for among the controversial pamphlets that appeared at the time of the vogue of Ward's remedies[8] there appears the statement that "Mr. White is the Ingenious Chymist who carried on the Great Vitriol Works at Twickenham for Mr. *Ward* and was employed by him in other Chymical Preparations." Someone would be needed, naturally, on the spot, for Mr. Ward was too busy in town gulling the public, to have time to attend to the laboratory. Much is made in the specification, it will be observed, of the state of the atmosphere, *i.e.*, the amount of moisture present in the air, and as to the proportion of brimstone to nitre. This was commented on by Lémery and possibly indicates some connection with his description. The notion about the influence of the atmosphere persisted to quite modern times: Lémery was the first to show that its influence was negligible.

The method of operation was as follows. Glass globes as large as could be blown with safety, with wide necks, capable of holding 40 or 50 gallons (say

[7] He may be the "John White of St. Margaret's, Westminster," who was married by licence from the Bishop of London at Twickenham 21 June 1733 to Elizabeth Flitcroft of Hampton.

[8] Page, John. *Receipts for preparing and compounding the principal Medicines of the late Mr. Ward,* 1763 p. 14. Ward left his book of secrets to Page.

26 in. to 28 in. diam.) were placed in a double row on a bed of sand. A few pounds of water were poured into each, a stoneware pot introduced through the neck and on this was placed an iron saucer previously made red-hot. In this by a ladle was placed the mixture of brimstone and nitre, the mixture ignited by a red-hot iron and the neck closed by a wooden stopper. When combustion was over, the saucer with withdrawn and the vapours suffered to condense in the liquid. The same operation was carried out in each globe successively so that when the workman had got back to the globe he had started upon, it was ready to receive a fresh charge. This action was repeated till the resultant acid attained the desired strength. The acid so produced was still known as " oil of vitriol made by the bell " although the bell had long been discarded, and it was sold at the same price per lb. as it had formerly been sold at per oz., *viz.*, 1s. 6d. to 2s. 6d.

It is obvious that, until the art of blowing these large glass globes had been perfected, the process could not have been so far improved. Again, glass bottles to store and transport the acid must likewise have been available. The bottle—now known as the carboy, padded with straw in a wicker-work or a hoop-iron basket—is the counterpart in shape and size of the older glass globe.

Gabriel Jars, on one of his journeys in England, which took place in 1758, 1765, 1766 and 1767,[9] describes the English method of making vitriol. The laboratory was " Sur la route de Londres à *Wensworth* " [which may mean at Battersea]. Welsh women were employed, the greater number of whom could only talk a few words of English. This, he thought, was a precaution to prevent the process being divulged but as he appears to have got into the laboratory by himself pretty easily, there seems little ground for this statement. He describes the distillation of nitric acid and the making of sulphuric acid " by the bell." There were more than 100 glass globes about 2½ ft. diam. and 4in. or 5in. diam. of neck, in rows the full length of the laboratory. They were buried to the depth of 6 in. in sand on a bench. There was a spring stopper which would act as a safety valve if the pressure inside should rise. The acid was very weak and was concentrated by distillation.

Not only was the new method of manufacture known in England before the date of Ward and White's patent of 1749, but a far-reaching improvement in the manufacture, *viz.*, the use of leaden chambers instead of the glass globes, the frequent breakages and cost of which were constant sources of trouble, had

[9] *Voyages Métallurgiques*, Tome III, 1781, p. 309. Jars has this interesting comment, " In imitation of the English, the Liége people have formed an establishment for making of oil of vitriol of which we shall give an account: the process differs somewhat from that we have just described . . . It was not pointed out to me that the method by which the sulphur burned was by mixing nitre with it; the entrepreneur was ignorant without doubt that the English made use of it, for he appeared astonished when we apprised him of it."

been introduced in Birmingham about the year 1746, by the enterprise and technical knowledge of John Roebuck (1718-1794) who is best remembered as the first partner of James Watt in developing the latter's steam engine. It was known that lead would resist acid, but he must be credited with being, if not the first then one of the first, to make practical application of this knowledge. Roebuck was a physician (he studied chemistry and medicine at Edinburgh and was a M.D. of Leyden, 1743), who, attracted by the growing importance of Birmingham, and an opportunity presenting itself to acquire a practice there, settled in the town in 1745. He was interested more in technical chemistry than in medicine and eventually in partnership with Samuel Garbett (1715-1803), established a chemical laboratory. Besides making vitriol and nitric acid, they refined and recovered gold and silver for the local "toy" trades, and produced corrosive sublimate and hartshorn; in addition they acted as consulting chemists—the first of that race. The laboratory and acid works were in Steelhouse Lane. Thus it can be said with truth that Birmingham was the cradle of the manufacture on the commercial scale of oil of vitriol in England.

It may occasion surprise that Roebuck did not secure protection, as he might have done by patent, for his leaden vessels, but he appears to have relied instead, like Ward and others, on secrecy. Nevertheless, what Roebuck was doing came to the ears of Ward, and the latter was much annoyed, so that possibly his patent was the reply. In this way he took the wind out of Roebuck's sails, for in the then state of patent law interpretation, Ward's patent might possibly have been construed to include the use of leaden as well as glass vessels. However that may be, there is no trace either of a patent application by Roebuck or of an action for annulment of Ward's patent on the ground of prior disclosure. Besides there was really no need for Roebuck and Garbett to take action for they could afford to sell their acid at one-fourth of the price of that "made by the bell." Another thing was that the ease of transporting the raw materials as compared with the difficulty of transporting the heavy product, coupled with its dangerous character, rendered the manufacture largely a local affair controlled by economic needs, as we shall see later.

We have an interesting side-light on the Birmingham firm and the price they charged for acid, in the papers of John & Nathaniel Philips, tape manufacturers, of Tean, Staffs.[10]

"Aug. 21, 1767. Sent Messrs. Saml. Garbett and Co., Birmingham, 5 Vitriol Bottles to be filled with the best Oil [of] Vitriol by John Smith's waggon. They agreed with Bro. Natt [*i.e.*, one of the partners] to deliver it here at 4½d. per lb. Credit."

[10] Communicated by Miss J. de L. Mann.

"May 10, 1769. Ordr. of Sam. Garbett and Co. by John Smith's next waggon with[t] Fail 6 bottles of the best Oil of Vitriol."

It should be noticed how the price had fallen.

In 1749, Roebuck and Garbett established an acid works at Prestonpans in the county of Haddington, 8m. S.E. of Edinburgh, noted since the twelfth century for its saltpans. The process carried on there differed in no respect from that employed by them hitherto, except in the scale of operations and in the size of the chambers, which were now 10 ft. sq. Why the partners went to Scotland may be explained by the fact that Ward's patent only covered England and Wales, so that the partners were safe in Scotland from interference if Ward had been inclined to be obstructive. However, we hear no more of Ward, except that he left a fortune at his death, and when his patent expired in 1763, vitriol-making was open to anyone. "Acid by the bell" gradually disappeared from the market, its place being taken by the cheaper chamber acid which Roebuck and Garbett continued to make with great success and profit to themselves. They supplied Great Britain and Ireland and established an export trade to the Continent, where the acid became well-known and esteemed under the name of "English vitriol."

After Roebuck went bankrupt in 1773, the laboratory seems to have passed into the sole possession of Garbett. As the town grew in size, Steelhouse Lane would become unsuitable for the manufacture of acid and probably the leaden chambers were removed elsewhere, perhaps to Prestonpans.

The laboratory itself at Garbett's death in 1803, seems to have passed into the hands of Alston & Armitage.[11] They were succeeded by James Alston & Sons, whose name continued to appear in the Birmingham directory as "refiners and manufacturing chemists" at 17, Steelhouse Lane, till 1847, but disappeared before 1852, by which time the firm seems to have gone out of business.

Before taking leave of Roebuck and Garbett, we ought to mention that they applied for and obtained, August 9th, 1771, a patent for Scotland for making acid in leaden chambers. No improvement is specified and it is difficult to understand what was the object of the partners in applying for the grant. The wording of the specification is as follows:—

"The said acid spirit of Sulphur is made by providing and mixing a proportionable quantity of Role, Rough, Stone or flour of Brimstone & Saltpetre and putting the said mixture into a vessel or vessels of Lead and setting the said Mixture on fire which by burning occasions Fumes, Vapours or Steams to arise and which afterwards condenses into an acid spirit of Sulphur. The exact quantity of the Sulphur & Saltpetre cannot be ascertained more or less of

[11] Prosser, R. B., *Birmingham Inventors*, p. 16.

one or of the other being required not only according to the quality of the Sulphur and Saltpetre but also according to the various seasons of the year and different weather when the air hath at various times so extraordinary an effect that without proper alterations the mixture will yield very considerably less quantities of spirit than at other times for which change it is impossible to give any general rules, nor is it to be known but by observations and experience, and the acid spirit thus made is rectified & purified by heat in vessels of Lead over a fire, but the proper degrees of heat or of fire cannot be described but can only be known by experience. The vessels of Lead may be of many different forms and of different magnitude according to the quantity of materials used at any one time or according to the quantity of weak spirit extracted from the said Mixture of Sulphur and Saltpetre and put over a fire to rectify and purify. The material discovery being the use of Leaden Vessels instead of Vessels of Glass in all or any part of the process."

A marked consonance of language with that of Ward's specification is observable; even the idea of the influence of the atmospheric conditions is trotted out, although long previously exploded. The patentees, it will be noticed, were careful to give nothing away and there is no hint that there had been any improvement since 1749, such as in the method of burning the mixture of brimstone and saltpetre, in introducing steam instead of water, or in the construction of the chambers, any one of which would have been good subject-matter for a patent.

An action was brought for annulment of the patent in January, 1772, the respondents alleging that Roebuck had carried on the manufacture for twenty years (*i.e.*, since 1751), and that the process was practised in England. The Scottish Courts pronounced the patent bad for want of novelty, as indeed it was, and this decision was upheld in the House of Lords in 1774,[12] who found that making of oil of vitriol in vessels of lead was practised in England before the date of the patent. In this connection Bridgnorth and Bewdley, as seats of manufacture, are mentioned and to these we must now turn. By this time oil of vitriol was, owing to its reduced price, finding extensive employment in the distillation of nitric acid, as a solvent for copper, in pickling metals and in dyeing.

In 1756,[13] a workman who had absconded from Roebuck's employment at

[12] *House of Lords Journal,* 34, pp. 76 and 217.

[13] Parkes, Samuel—*Chemical Essays,* 1815, II, 398, whence much of this early history is derived. It would seem that he can be relied upon because his knowledge was first hand. He says (p. 387): "From my connection with the family of one of the principal original manufacturers, I am in possession of some facts which I am desirous of communicating to the public." He says further (p. 473): "I had an intention of giving an ample detail of the methods to be pursued in erecting a lead-house for the manufacture of sulphuric acid, having preserved every necessary document and registered every precaution which appeared to be needful should I have occasion to superintend the business," but he found his "Essay would have extended to a length quite inconsistent with the plan of these volumes."

Birmingham, a native of Bridgnorth, induced a Mr. Rhodes, seed-crusher of that town, to embark in the business and it was carried on for many years, although the workman did not stay with him long but engaged with Samuel Skey (1726-1800), of Bewdley, drysalter, a prominent industrialist and canal carrier, who had just begun making vitriol on a large scale at Dowles nearby. Skey's chambers had been erected under the direction of a man discharged from the Prestonpans works, of whom Skey heard by accident. The chambers were 10 ft. sq. This Samuel Skey was succeeded by his son, also named Samuel (1759-1806), after whose early death the works were carried on by Trustees till well into the nineteenth century. The present Bewdley Gas Works occupy part of the site.

The first acid works using leaden chambers, close to London, were established at Battersea, in 1772, possibly on the site of the laboratory described by Jars, by Messrs. Kingscote & Walker, druggists. They had 71 circular chambers 6 ft. diam. by 6 ft. high; they also had 4 cubical chambers 12 ft. side (1728 cub. ft. capacity). This works was unproductive of profit, was shut down and the plant sold.

In 1783, a nephew of one of these partners established a works at Pilsworth Moor, near Eccles and Manchester, under the name of Baker, Walker and Singleton. The firm had four chambers 12 ft. sq. and four others 10 ft. sq. by 45 ft. which gives an indication of how the scale of operations was being enlarged. This is claimed as being the first works in the South Lancashire area. As regards Yorkshire, Bradford appears to have been the first place to have works and tradition gives the date as 1750. The first definite record, however, is in a Directory of 1792 where the entry is " Rowson, Benjamin, proprietor of Vitriol and Aquafortis Works " and when describing the works in the town the Directory says " Here is a large still-house for aqua fortis and spirits of vitriol by Mr. Rowson." These works, it is interesting to record, are still carried on in direct succession by Mr. H. K. Burnet at North Brook, under the style of Leather's Chemical Works.[14] Surely this must be the oldest chemical works in the world? By degrees other works were established in different parts of the country. A well-known works in London was that of Thos. Farmer & Co., at Kennington Common, established 1778, which lasted well into the present century. By 1820 there were 23 factories in England alone, of which 7 were in or near London.

The stimulus given to the manufacture by the application to bleaching of the discovery of Berthollet of chlorine in 1785-7, led to a greatly increased use of acid. It is stated that the first vitriol in the West of Scotland was made by Charles Tennant (1768-1838), at St. Rollox, Glasgow, for the purpose of carry-

[14] Information from H. K. Burnet, Esq.

ing out the manufacture of dry bleaching powder, the patent for which he took out in 1799. This gave a renewed impetus to the manufacture. It was with plans supplied by his firm that Messrs. Doubleday & Easterby erected their first chamber between 1809 and 1810, at Bill Quay, Newcastle-on-Tyne.[15]

A number of descriptions of the way in which the leaden chamber process was carried on about this time are to be found. One that may be considered typical is a "description of the method then in use at Messrs. Bealy, Radcliffe, near Manchester,[16] in 1799," given by Mr. James Mactear. There were six chambers 12 ft. by 10 ft. sq. (1200 cub. ft. capacity) roofed like a cottage and placed under cover. Each had a door to introduce the charge and a water-luted valve on top for ventilation between the burnings. The charge was 8 lb. of a mixture of 7 lb. of pounded brimstone to 1 lb. of nitre (at that time the commercial article contained about 70 per cent. of KNO_3). This was placed on double iron trays of which there were 2 to each chamber, 3 lb. on the lower tray and 1 lb. on the upper tray every 4 hours (*i.e.*, 1 lb. mixture to 300 cub. ft. chamber space). The lower tray was first ignited, then the upper and the door closed. The burning occupied an hour, and 2¾ hours were allowed for absorption in the water which covered the floor of the chamber to a depth of 8 in. to 9 in. Door and valve were opened ¼ hr. before the next charge was introduced. The campaign lasted 6 weeks, one chamber being drawn each week. The total amount burnt in 6 weeks was 1386 lb. brimstone and 198 lb. nitre, indicating that a double-shift 5½-day week was worked. In 6 weeks the O.V. attained a sp. gr. of 1.25 and was run off for concentration to 1.37 when it was sold commercially.

The costs were as follows:—

	£	s.	d.
1386 lb. brimstone @ £22 per ton	13	12	3
198 lb. nitre @ £64 per ton	5	13	1½
Labour	1	1	0
Wear and tear	1	1	0
	21	7	4½
Drawback of customs duty on the brimstone, £6 12s. 8d. per ton	4	2	0½
Product, 1800 lb. O.V. cost	17	5	4

equal to 2.3d. per lb. or £21 9s. 9d. per ton.

[15] *Industrial Resources of the Tyne, Wear and Tees,* 1864. p. 161.

[16] *Proc. Glasgow Phil. Soc.,* Vol. 13, 1881, pp. 409 *et seq.* in a valuable paper: "History of the Technology of Sulphuric acid," but he does not say whence his information came. Bealy's works originated in 1683 as bleachworks, began making O.V. in 1791 and lasted till 1901 or later.

The charge for labour shows that there could not have been more than 6 men employed on the double shift. Mr. Mactear gives the figures for Prestonpans[17] at about the same date for the production of 112 lb. commercial O.V. as follows:—

100.8 lb. brimstone @ 7s. per cwt.	6	3
13.06 lb. nitre @ 36s. per cwt	4	2
Expenses	10	7
	£1 1	0

equal to 2¼d. per lb. or £21 per ton.

It is curious that the cost of the product at the two places should agree so closely while the prices of the raw materials were so different—sulphur about three times and nitre nearly twice the price at Manchester as at Prestonpans.

Much light is thrown upon the conduct of the manufacture at the end of the eighteenth century and beginning of the nineteenth by an illustrated MS.[18] of recipes and experiments by W. E. Sheffield, of Birmingham. Among other items is an account of the manufacture of acid there. He gives " the exact definition of Mr. Garbett; he has 30 [chambers] in one room, each lies him in [*i.e.*, costs him] £8." The " lead-house " is 6 ft. wide, 4 ft. broad and 8½ ft. high (204 cub. ft. capacity). The bottom was made of 9 lb. lead and the sides and top of 3½ lb. lead; the top was slightly convex and " bresting over the sides." The lead sheets were rivetted together with lead rivets; (ordinary soldering will not do because, in the presence of the acid, electrolytic action is set up between the lead and the spelter, resulting in corrosion); there must have been leakage and perhaps it was stopped with cement. The " lead-house " rested on sand under cover. At 8 in. from the bottom was a hole 10 in. diam. to admit the charge. Many further particulars are given but the account does not differ sufficiently from that already given to deserve reproduction here. The chamber acid was concentrated in open leaden pans 6 ft. long, 2 ft. wide and 1 ft. deep to a sp. gr. of 1.5—further " retorting " was done in glass vessels. Data are given as to cost. The acid was sold at £35 per ton (3¾d. per lb.) on 4 months credit or £37 6s. 8d. (4d. per lb.) on 6 months credit leaving a profit of 25 per cent.

Parkes gives a plan[19] of a "Sulphuric Acid Manufactory " (see Fig. 4),

[17] *op. cit.* p. 423.

[18] Brought to light by Oscar Guttmann and described by him in a valuable paper " The early manufacture of sulphuric and nitric acid." *Journ. Soc. Chem. Ind.* 31, Jan. 1901, Vol. XV, to which the writer is greatly indebted. Unfortunately the MS. cannot now be found. Could this Mr. Sheffield have been the source whence Dr. Parkes drew his information?

[19] *Chemical Essays,* Vol. II, 1815. Plate XII, p. 477.

which may be taken as representative of good practice in 1815. The premises occupy a space 200 ft. by 125 ft. completely walled in.

There are four chambers A, A, A, A, 50 ft. long by 20 ft. wide; B is a weak acid reservoir 12 ft. by 8 ft. of any convenient depth in the ground; C a lead lined trough to take the acid by siphon from A to B; D a leaden pump to supply evaporating pans E, E, E, E, E; F are pillars supporting the open-fronted shed which houses the evaporating pans; G a concentrated acid reservoir; H, the retort room, 50 ft. by 20 ft., where the acid is concentrated in

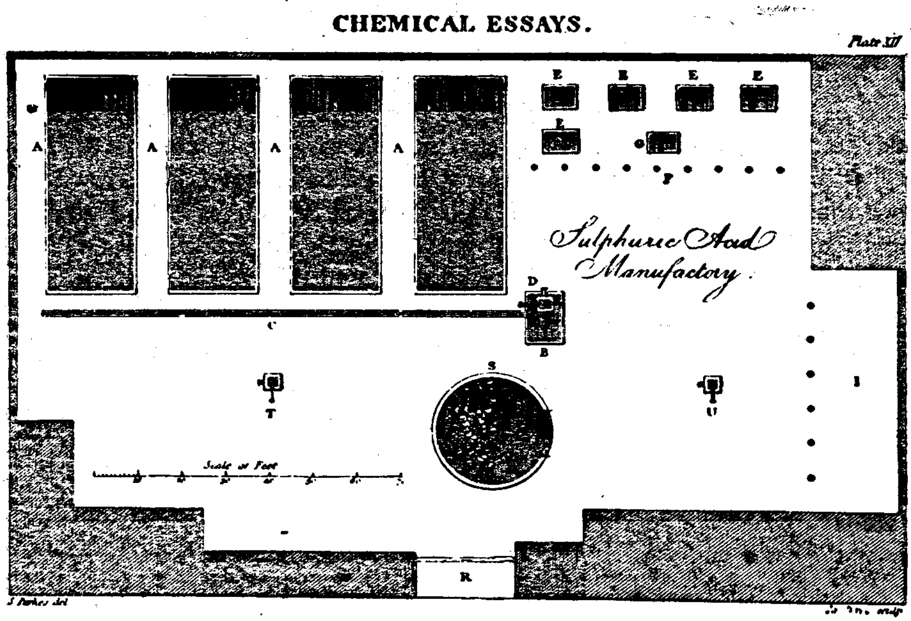

FIG. 4. SULPHURIC ACID MANUFACTORY.
From Parkes, *Chemical Essays*, 1815.

glass vessels; I an open-fronted shed, 56 ft. by 20 ft., for filling carboys; K, the warehouse for carboys; L the office; M, the saltpetre store; N, the brimstone store; O, the pounding room where sulphur is mixed with nitre; P, the stable and cart shed; Q, the laboratory; R, the main entrance; S, the coals store; T, the pump for supplying chambers; U, the pump for washing water; V, the general store.

The concentration of chamber acid in leaden vessels has the drawback that a certain amount of lead goes into solution after the acid has reached a sp. gr. of 1.7, so that about 1820 platinum vessels or stills were introduced.[20]

[20] Parkes, *op. cit.*, 2nd ed. 1823; 535.

A still to hold 30 gallons cost then about £300, *i.e.*, platinum about 14s. per oz., the then price.

A step of considerable importance, suggested, it is believed by Chaptal, was to burn the sulphur and nitre in a furnace external to the chamber. According to Mactear[21] this was effected in 1803 at St. Rollox, Glasgow. At first it would appear that the object was to use up the sulphur and nitre left unconsumed in the "sulphur ashes," of which there was a large accumulation, but about 1811 it became the general practice to burn new materials in this way, one furnace being applied to two chambers, so that one could be charged while the other was absorbing.

Another most important step in progress was the introduction of steam instead of water into the chamber keeping the latter warmer and promoting the production of stronger acid. This step is said to have been taken at Rouen in 1774[22] by De la Follie, but whether persisted in or not is not clear. It is known that the step was taken in 1813 or 1814 at St. Rollox,[23] and about the same time the process was rendered continuous. In neither case does the importance of the step appear to have been recognised.

Brimstone is an expensive material and it was natural that attempts should be directed to utilize cheaper sources of sulphur. It was known that sulphides, such as iron and copper pyrites, would on roasting, give off their sulphur as sulphur dioxide. The first use of pyrites for replacing brimstone is attributed to Thomas Hills of Bromley-by-Bow in 1818;[24] it is stated[25] that he believed that it was necessary to add coal to the pyrites to help it to burn (although nothing of this is mentioned in the specification) and this proved detrimental to the formation of acid in the chamber owing to the diluent carbon dioxide and soot introduced from the combustion of the coal; hence the use of pyrites was discontinued.

The merit of successfully introducing pyrites is credited to Messrs. Perret & Fils, of Chessy, France, in 1835,[26] who were, however, primarily interested in getting rid of the sulphur in the pyrites in order to smelt the copper. As far as this country is concerned, Thomas Farmer, of Kennington, London, was the first, in 1839, to employ pyrites on a large scale. This innovation was largely precipitated by economic pressure. The Neapolitan Government

[21] *op. cit.*, p. 423.

[22] Auden, W. A. *Sulphuric acid and its manufacture*, p. 5.

[23] Mactear, *op. cit.*

[24] British Pat. Spec. A.D. 1818 No. 4263 of Thomas Hills and Uriah Haddock who claim to be the first to use pyrites.

[25] Lunge, *loc. cit.*, 2nd ed. p. 28.

[26] French Patent, Claude Perret No. 1094, dated 2 Feb. 1836, "Pour le perfectionnement de la fabrique de l'acide sulfurique par l'emploi des pyrites."

granted in 1838 a monopoly of the export of Sicilian brimstone to the house of Taix, Aycard et Cie., of Marseilles, and the monopolists raised the price from £5 to £14 per ton. Although the monopoly collapsed in 1842, it had lasted long enough to spread the conviction that brimstone was not a *sine qua non* for vitriol making; by 1852 brimstone had quite gone out of use in Lancashire. Both the roasted iron pyrites—" blue billy "—and the roasted copper pyrites, are valuable raw materials for their respective industries. It is interesting to observe that with the discovery of large deposits of sulphur notably in the United States, brimstone has since 1914 largely recovered its ground so that to-day the proportions used are 23.7% brimstone and 46.3% pyrites.[27]

With the introduction of the continuous process, the mixed gases with steam and diluent air are drawn by chimney draught slowly through the chamber or chambers—for the important fact was realised as early as 1834 that two or three in series were better than one. One result of this was the loss of nitrous fumes with consequent expense and with nuisance to the public. This loss was overcome by the introduction, in 1827, by J. L. Gay-Lussac (1778-1850), of the tower named after him, in which just before reaching the chimney the upward current of waste gases meets a descending trickle of concentrated chamber acid over coke in a glazed tile-lined tower. This acid has the property of absorbing nitrous fumes with the formation of nitro-sulphonic acid which breaks up again on contact with hot sulphur dioxide.

It was found difficult to utilize this " nitrated " acid and the Gay-Lussac tower did not come into extended use till John Glover (1817-1902), of Newcastle-upon-Tyne, in 1859, after working on the problem since 1848,[28] introduced the tower known by his name, to use " nitrated " acid. He found that not only could his tower break up the nitrated acid but chamber acid could also be deprived of water and thus save some part of the expense of the after concentration of the acid. The Glover tower is situated between the pyrites burners and the first chamber. It is filled with flints and the upward current of hot gas meets a trickle of the nitrated acid together with chamber acid in given proportions. The nitrated acid parts with its nitrous fumes and the chamber acid with some of its water; concentrated acid flows into a reservoir at the base of the tower, while the nitrous fumes and the steam pass into the chamber to take part in the reactions going on there. The gases sweep on into a second chamber meeting with more steam and then into a third where by this time the sulphur dioxide is completely absorbed. The saving in the consumption of nitre was 4 per cent. on the weight of sulphur burnt. It may be remarked that neither the Gay-Lussac nor the Glover tower was patented.

[27] Auden, W. A., *Op. cit.* p. 7.

[28] *Journ Soc. Chem. Ind.*, Vol. 15, p. 511, *cf.* Lunge, *loc. cit.* I, 421.

Subsequent improvements in vitriol-making have been largely matters of detail.

The size of chambers has varied very greatly but there has been a progressive increase. In 1750, their capacity was about 360 cub. ft.; in 1799, 1,200 cub. ft.; in 1815, from 1,500 to 15,000 cub. ft., although an exceptional one of 96,000 cub. ft. is mentioned. Since 1834 it has been the practice to use two or more chambers in series, and the size of each has been moderate—38,000 cub. ft. in 1884 and about 50,000 at the present day.

The construction of leaden chambers made rapid progress after the invention attributed to Debassays de Richemond in 1838, of "lead burning"[29] or autogenous soldering of the lead sheets—a skilled operation—thereby obviating electrolytic action mentioned above. The outside appearance of vitriol chambers is distinctive and readily recognizable.

The chamber process is used to the extent of two-thirds and the contact process to the extent of one-third of the output which in 1936 amounted in England and Wales to the enormous total of 867,000 tons. As indicating where all this acid goes, it may be said that two principal uses are in the production of artificial fertilizers—superphosphate—and in gas works, etc., to make ammonium sulphate: another large use is for electric batteries.

I have to thank Mr. Rhys Jenkins, Past President, and Mr. A. A. Gomme, Member of Council, for help in the preparation of this paper.

The paper was illustrated by an engraving of the *per campanam* process, 1664, which is reproduced in Fig. 3.

Discussion.

Mr. F. O. Beckett and Mr. R. Wailes commented on (p. 45) the proper time to be chosen for making "spirit of sulphur" being that of the two equinoxes, and said that the idea still persisted in other directions.

Mr. Dickinson said there was possibly something in it. The amount of moisture in the air at the equinoxes might be the most favourable for the reaction being about a mean of that during the year. In reply to a question he said he had written to Imperial Chemical Industries enquiring for the Guttmann MS. but nothing was known about it.

Correspondence.

Dr. H. A. Auden submitted a number of valuable notes on the history of vitriol-making together with a list of patents *in re*, also two portraits of Joshua Ward. The notes prefaced by a reference to the page to which they are germane are printed below; the list of patents has been omitted; the portraits have been reproduced on Pl. VI).

[29] Fairlie, A. M., *Sulfuric acid manufacture,* 1936, p. 23.

NOTES.

p. 43. In the time of Dioscorides 2nd cent. A.D., the production of fumes when the metallic vitriols were roasted was noticed, but the condensation of the fumes does not seem to have been attempted.

p. 43. It is proable that sulphuric acid is referred to by Jabir ibn Haijan, 8th cent. A.D., when in his *Invention of Verity* he speaks of "solutive waters" obtained by distilling green vitriol and of a spirit possessing solvent power obtained when alum is strongly heated.

p. 43. The Arabian author, Al Qazwini, in the 13th cent. records that the thick fumes produced when vitriol is roasted give rise to heat when brought into contact with water.

p. 43. In a MS. entitled *Buch der Dryvaldigkeit*, composed 1414-8, oil of vitriol is mentioned.

p. 43. In Jerome Cardan's *De Subtillitate*, 1553 edition, the distillation of dried "chalcanth" or "misy" is mentioned. The "very sharpe and burning oil" so obtained causes wounds and "is like a hot iron to the tongue."

p. 44. Mayow, in 1681, showed that sulphur was a constituent of oil of vitriol. In 1779 Lavoisier showed that this was the correct view.

p. 44. Glauber, in 1648—then residing at Amsterdam probably—taught the mixture of nitre with the sulphur for producing the acid.

p 45. Evelyn, in his *Diary* under date Nov. 7, 1657, writes: "I visited Sir Kenelm Digby . . . I showed him a particular way of extracting oyle of sulphur." But what this was he does not say.

p. 46. The function of the nitric fumes was shown in 1793 by Nicolas Clément-Desormes (1779-1842).

p. 46. Dossie (d. 1777) was an apothecary in London, and a skilful chemist; he was a friend of Dr. Johnson and is mentioned by Boswell.

p 46. This *per campanam* method is mentioned in the *Treasure of Euonymus* (Eng. trans. by "Peter Morwyng felowe of Magdaline College in Oxforde" 1565, p. 304). Euonymus was the pseudonym of Conrad Gesner, born at Zurich in 1516 in poor circumstances, studied at Strasburg, Bourges and Paris, later at Basel, Lausanne and Montpelier. He was a man of great ability and diligence and was known as the German Pliny. He died in 1565.

p. 46. See *Gent. Mag.* 1734, pp. 387 & 658. He was known as "Spot" Ward from a mark on his face. A statue of him by Agostino Carlini is in the Hall of the Royal Society of Arts and was presented to the Society in 1792 by Ralph Ward, his grand-nephew.

Plate 5 of Hogarth's *Harlot's Progress*, 1732, represents two quacks arguing about the merits of their respective nostrums while their patient dies. The quack on the left is "Spot" Ward.

For these portraits, see Pl. VI.

p. 47. A search in the rate books of Richmond for 1741 and an exhaustive search in the Library has not revealed anything local relating to Ward or his laboratory.

p. 52. Samuel Skey was a native of Upton-on-Severn and was apprenticed to a grocer named Church in Bewdley. At the time when he finished his apprenticeship, a relative left him £1,000 and with this sum he began business as a grocer and drysalter in Bewdley. Later he erected works in Dowles chiefly for the manufacture of sulphuric and nitric acids. About 1790 he purchased the Manor. The tramway and canal that he constructed, leading to his works, where the present gas works stand, can still be traced. His enterprises succeeded and he became a wealthy man. He was buried at Dowles.

p. 52-3. Mactear (*Brit. Assoc. Rep., Glasgow*, 1876) mentions 23 acid factories existing in 1820 of which 7 were in London. He describes Bealy's plant as worked in 1799; he had 6 chambers 12 ft. by 10 ft. by 10 ft. Roebuck at Prestonpans had 108 chambers 14 ft. by 4 ft. by 10 ft. high, and at Burntisland 360 chambers 8 ft. by 4 ft. by 6 ft.

p. 55. The first crucible in platinum was made by Achard in 1784. Guttmann says: "Mr. Sellon of Messrs. Johnson & Matthey has no knowledge of a platinum vessel for sulphuric acid having been made before 1804."

p. 56. Mactear states that pyrites kilns were at first difficult to work. Lighting from the top as now practised was discovered accidentally by a workman of Todd's in Cornwall.

p. 57. Although Gay Lussac had suggested in 1827 the use of absorption towers supplied with strong sulphuric acid, they do not appear to have been adopted generally for various reasons till about 1860; one early example was erected in 1842 at Chauny and another in Glasgow, 1844.

STATUE OF JOSHUA WARD AT THE ROYAL SOCIETY OF ARTS.
Courtesy of the Society.

CARICATURE OF WARD in the engraving of Hogarth's *Harlot's Progress*, 1732.