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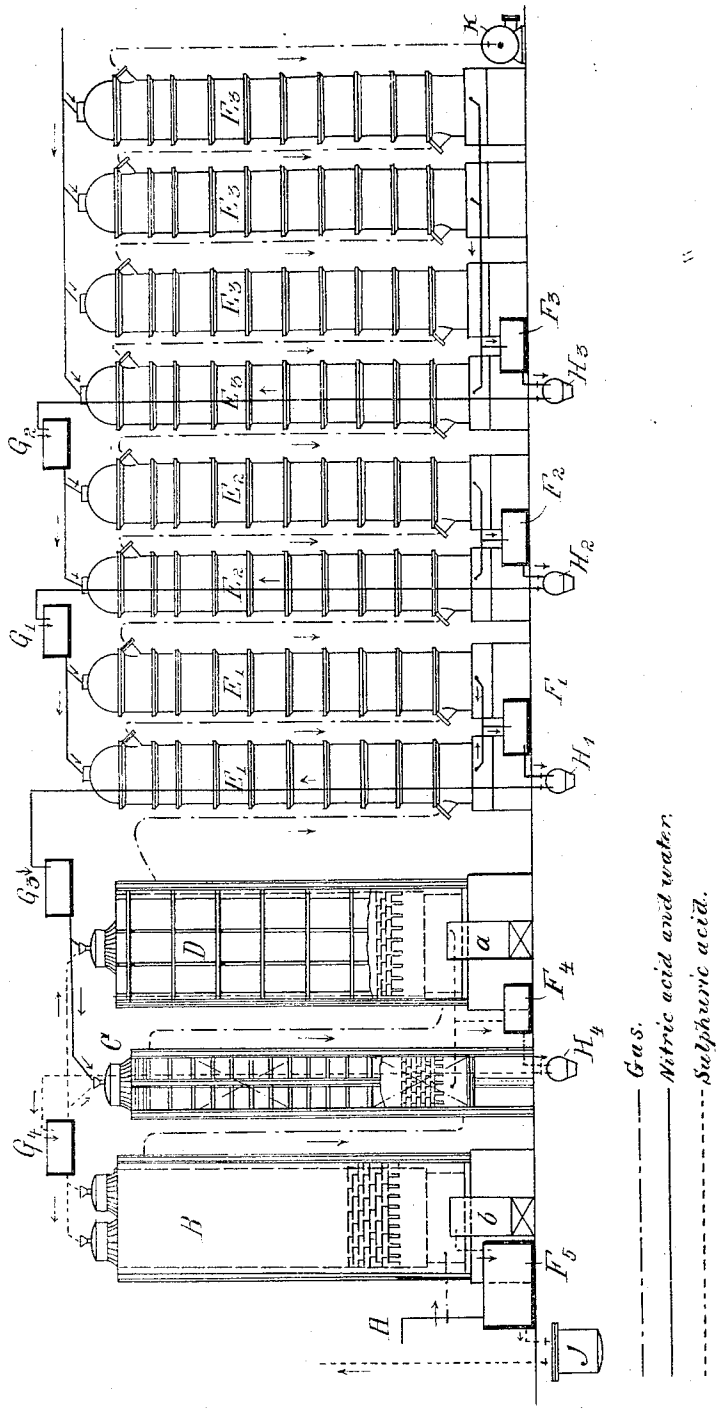
MANUFACTURE OF SULFURIC ACID.

APPLICATION FILED SEPT. 10, 1909.

1,048,953. Patented Dec. 31, 1912.



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UNITED STATES PATENT OFFICE.

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MANUFACTURE OF SULFURIC ACID.

1,048,953. Specification of Letters Patent. Patented Dec. 31, 1912.

Application filed September 10, 1909. Serial No. 517,112.

To all whom it may concern:

Be it known that I, WILHELM FULDA, a subject of the German Emperor, and resident of Griesheim-on-the-Main, Germany, have invented certain new and useful Improvements in the Manufacture of Sulfuric Acid, of which the following is a specification.

In the manufacture of sulfuric acid by means of oxidizing agents in the form of nitrosyl acid many proposals have been made to replace the costly lead chambers by towers, but hitherto these proposals have not proved successful. According to Lunge's statement (*vide* Lunge's *Handbuch der Sodaindustrie*, III edition, vol. 1, page 1005), the processes hitherto proposed have the disadvantage that they require too great a consumption of oxidizing agents. It has also been attempted to produce sulfuric acid by the use of nitric acid as an oxidizing agent, but this has not been successful, the losses of nitric acid being so high as to make the process practically unavailable, (*vide* Muspratt's *Technische Chemie*, IV edition, vol. VII, page 1293).

The manner in which according to my invention the loss of combined nitrogen is avoided will hereinafter be explained. I will only mention here the advantages of my new process over those hitherto known. These advantages consist in that the new process requires less reaction space and a more concentrated acid is obtained. A cubic meter of reaction space furnishes from 100 to 140 kilograms of acid of from 50° to 54° Baumé, or even 57° to 58° Baumé, as against 5 to 7 kilograms of acid of 50° to 54° Baumé in the case of lead chambers. In addition to this, the process according to this invention has the great advantage that it is not, (as is the case with the lead chamber and contact processes) confined to the use of a definite and uniform concentration of the SO_2 gases, as the concentration can vary within wide limits, so that with the process according to this invention it is possible to utilize sources of sulfurous acid which supply a current of gas of irregular composition. Such sources of SO_2 are, for instance, certain ore roasting processes and other processes in which gases containing SO_2 are evolved. Further in the process in accordance with this invention, it is possible to obtain acids of greater concentration than those hitherto obtained in the lead chamber process and the nitric acid used as oxidizing agent can be recuperated as such, that is in the highest, and consequently most active, state of oxidation of nitrogen.

To successfully carry out the process according to this invention, it is necessary to observe a number of essential points, some of which have already been taken into consideration, but which, combined together in a special manner, secure the desired result. As is known it is essential that the sulfurous acid should come directly into contact with nitric acid in excess, so that the conversion into H_2SO_4 is almost instantaneous. Such instantaneous oxidation is necessary in order that a complete and easy separation as regards time and space of the two reactions under consideration may take place, namely, the oxidation of the SO_2 to H_2SO_4 and the reconversion of the NO resulting from the oxidation into higher oxids and HNO_3. A quantitative separation of the two reactions as regards both time and space is essential for if such separation is not effected the complete conversion of the nitric oxid into higher oxids is impossible owing to the constant presence of SO_2 and great losses of oxidizing agents occur. In the lead chamber process enormous spaces are required to avoid these losses. Further in order to obtain an acid of 58° Baumé, care should be taken that an acid of about 56° to 58° Baumé should flow down through the oxidation towers C and D. An acid with a higher concentration than 58° has not proved practical as such acids can only be fully denitrated with difficulty if only cold SO_2 gases are available.

The necessity of a quantitative separation is pointed out here in an express manner for the first time. Processes are indeed known (for instance, that disclosed in the specification of the British Patent, No. 972 A. D. 1871) in which separate apparatus are used for the oxidation, of the sulfurous acid and the regeneration of the nitric acid. But it is in this specification nowhere mentioned that care should be taken that this separation actually takes place, although the economical success of the tower process depends upon this separation. This fact is explained by the low reaction power possessed by di-

lute cold gases which, when no quantitative separation takes place, results in the production of NO down to the very end of the apparatus; this NO not being capable of becoming completely oxidized is therefore lost.

The three special features which differentiate this invention from other tower processes are first the use of such a large excess of nitric acid as oxidizing agent, second the separation of the process of formation of sulfuric acid from the recuperation of the nitric acid and third that sulfuric acid of from 56° to 58° Baumé is constantly sprayed into the oxidation towers C and D along with the nitric acid.

We will now deal with the second reactions, namely, the reconversion of the nitrogen oxids into nitric acid. As the reactions occurring in the conversion of the nitrogen oxids into HNO_3 require much time for their completion, care must be taken that the gases remain a sufficiently long time in the apparatus. It has been found that for the perfect oxidation to nitric acid at least four minutes are required. Such a long time and correspondingly large space are necessary because the reactions in the highly diluted gases containing nitric oxid which are dealt with proceed at a very slow rate. A pyrites furnace containing a charge of 10,000 kilograms supplies, per minute, 40 cubic meters of gas. It has been found that the space required for the regeneration of the nitric acid should be equal to at least 4x40=160 cubic meters. In none of the tower processes hitherto known has this point been taken into consideration. It is further necessary to provide as large an absorption surface as possible for the absorbing liquid. Moreover, the temperature of this liquid should not be much above 30° centigrade. It has been ascertained that special care should be taken to maintain as low a temperature as 30° C. in the last 40 or 50 per cent. of the absorption space. In none of the processes hitherto known was any value attached to the maintenance of this low temperature. On the contrary it was even proposed to use warm water for the absorption.

It has been found that a most important factor for the perfect conversion of the nitrogen oxids into nitric acid is the amount of HNO_3 in the absorption liquid of the last parts of the apparatus; this amount should not be more than from 12 to 13 per cent. in the last 40 to 50 per cent. of the space, otherwise a considerable amount of nitrogen oxids will be lost.

The main points which are to be observed in the reconversion of nitrogen oxids into nitric acid are therefore: (1) each particle of gas should remain at least 4 minutes in the apparatus; (2) the absorption liquid, and consequently the gases, should be kept as cold as possible, and (3) the HNO_3 contents of the absorption liquid in the last 40 or 50 per cent. of the absorption space should be below 13 per cent.

As already stated, the absorption liquid should present as large an absorbing surface as possible

The accompanying drawing illustrates, more or less diagrammatically, an apparatus adapted for carrying out the improved process.

In the drawing the course of gas through the apparatus is indicated by a dot-and-dash line, the path followed by the nitric acid and water is indicated by a solid line and the course of the sulfuric acid by a dotted line.

The sulfurous acid produced by the action of a roasting kiln A is conducted through a Glover tower B having a cooler *b* and sprinkling devices *b'*. From the tower B the gases are conducted through a tower, or towers, (or tower-like chamber, or chambers) of any suitable construction, such as C, into which a spray, of a mixture of nitric acid of from 30° to 35° Baumé and sulfuric acid of 56 to 58° Baumé is sprayed in. This tower or these towers and the succeeding tower or towers need not necessarily be filled with material. They can if desired be empty and the liquids be injected by means of nozzles preferably arranged in the roof, or cover. In the oxidation tower C or towers C and D the oxidation of the sulfurous acid to sulfuric acid takes place almost instantaneously. The mixture of nitric and sulfuric acids is thereby denitrated down to 1 per cent. and the concentration of the sulfuric acid of the mixture in the towers C and D is again raised to 56 to 58° Baumé. This acid is pumped again partly into the oxidation towers and partly de-nitrated and concentrated in the Glover tower, or other in a special apparatus.

The gaseous nitric oxids liberated in the Glover tower B enter the tower C, or towers, into which nitric acid of from 25° to 30° Baumé, or a mixture of nitric and sulfuric acids, of from 25° to 30° Baumé is sprayed. The proportions of nitric acid and of sulfuric acid in this mixture are 95 liters nitric acid and 5 liters sulfuric acid respectively and the degree of concentration of each of the acids, which is necessary to obtain the mixed acid of from 25° to 30° Baumé is as follows: nitric acid 24° to 29° Baumé, sulfuric acid 50° to 57° Baumé. In the nitric acid tower, or towers E_1, the acid is raised to 30°, or 35°, Baumé and then used in the oxidation towers C and D. Thereupon the gases enter the tower E_2 for the conversion of SO_2 into H_2SO_4. The space required for this part of the absorption apparatus is about 20 per cent. of the whole space. Thereupon the gases enter a tower D or towers into which nitric acid of from 10° to 25° Baumé is sprayed whereby

the acid is enriched. The space required here is about 30 per cent. of the whole space. In the remaining 50 per cent. of the total space the gases containing the nitric oxid come into intimate contact with an acid containing from 0 to 13 per cent. HNO_3.

In the apparatus shown in the drawing three sets or groups of towers, E_1, E_2 and E_3 are shown. F_1, F_2, F_3, F_4 and F_5 indicate acid receptacles arranged below the level of the several towers and G_1, G_2, G_3, and G_4 are similar receptacles arranged at a higher level than said towers. A series of pressure tanks H_1, H_2, H_3 and H_4 are connected with the lower series of receptacles F_1 to F_4 respectively and a tank J into which sulfuric acid may be drawn is connected with the tank F_5. The several groups of towers and the tanks are connected so that the acids and water will circulate through the apparatus in the manner indicated, a fan K being provided for drawing the gas through the several towers as represented by the dot-and-dash line.

It will be seen that water is sprayed into the towers E_3 and the mixture of water and nitric acid is then circulated through the towers E_2, E_1 and oxidizing towers C and D. In the actual practice of the invention it will be understood that it is necessary to cause the acid to circulate several times through the same tower in order to obtain the desired strength.

In order to maintain the temperature of the absorption apparatus as low as possible, the absorption liquid circulating in the tower or towers is cooled. For the purpose of conversion into sulfuric acid of the sulfurous acid supplied by a pyrites furnace taking a charge of 10,000 kilograms and producing 40 cubic meters of gas per minute, and for the purpose of converting the nitrogen oxids formed thereby into nitric acid of from 30° to 35° Baumé, only about 200 cubic meters space is necessary in accordance with the hereinbefore described process. Of these 200 cubic meters, about 30 cubic meters are needed for the oxidation of the sulfurous acid by the towers C and D, the remainder being utilized for the regeneration of the nitric acid. The amount of space thus required can be reduced by about 40 per cent. (=50 per cent. of the regenerating space) if the last remnants of the nitrogen oxids be absorbed by sulfuric acid of at least 59° Baumé, instead of by water. The nitric acid regenerating space still amounts to 90 cubic meters, in which over 90 per cent. of the nitric acid used is recuperated as such. If more than 50 per cent. of the regeneration space be replaced by this mode of absorption by means of sulfuric acid, it is no longer possible to oxidize the NO to such an extent that it will be fully taken up by the sulfuric acid. Besides this, the required quantity of nitric acid is no longer obtained. The nitro-sulfuric acid is freed from nitrogen oxid compounds in the Glover tower as aforesaid. The nitrogen oxids come again into the oxidation tower, or towers, and that, or those, for the formation of sulfuric acid.

Having thus described the invention, what is claimed is:

1. The method of manufacturing sulfuric acid from sulfurous acid by means of nitric acid, comprising the oxidation of the sulfurous acid and the regeneration of the nitric acid, the time and space of the regenerating operation being so proportioned that each particle of the gas remains at least four minutes in the regenerating apparatus.

2. The method of manufacturing sulfuric acid from sulfurous acid by means of nitric acid, comprising performing the regeneration of the nitric acid in a series of chambers comprising 20 per cent., 30 per cent. and 50 per cent. respectively of the whole space, and subjecting the nitrogen oxids in said chambers, to acid of 25° to 30° Baumé, to acid of 10° to 25° Baumé, and to acid of 0 to 13 per cent. respectively.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

WILHELM FULDA.

Witnesses:

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ERWIN DIPPEL.