ISMA* Technical Meetings

Milan, Italy

25-26 October 1949

In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).

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IE/156.

Group I. (R,

August, 1949.

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This paper will be presented at the Technical Meetings in Milan on October 25th and 26th, 1949. It must not be published prior to that date and, in any case, it must not be published without the permission of the author.

NEW TRENDS IN THE MANUFACTURE OF SULPHURIC ACID.

by MONTECATINI Società Generale per l'Industria Mineraria e Chimica.

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Summary.

The three systems in general use for the manufacture of sulphuric acid, namely, the lead chambers, tower and contact systems are taken into consideration.

Following a short description of the pyrites and sulphur burners employed in the three systems, improvements effected in the chambers are described and an account is given of the apparatus and equipment used in the tower and catalytic plants.

Finally a comparison is made between the three systems, indicating the convenience of the tower plants in the manufacture of fertilisers and how the contact plant fulfils the demand for a pure and high grade acid and for long distance transportation.

It is the object of these notes to cover briefly the industrial methods for the manufacture of sulphuric acid, to compare results, and, without going too deeply into the details of the most recent theories, to give some idea of practical trends.

Plants may be grouped in three major classes:

Lead chambers,
Towers,
Contact.

We will begin with a short consideration of the various kinds of burners common to all types of plants.

Burners and roasters.

In Europe, usually for economic reasons, it is preferable to produce sulphuric anhydride from pyrites. We refer, however, to the different types of sulphur burners more frequently found in use.

The Glen-Falls melted sulphur baths and rotary kilns of a capacity of 10 tons per day have been employed largely also in Italy.

In other types of burners the melted sulphur becomes atomised in a combustion chamber as usually practised in the case of oil, the sulphur being previously melted by steam.

The Monsanto Company in ~~hte~~ the U.S.A. makes use of a burner having a stack of refractory bricks upon which the melted sulphur falls and, spreading in a thin film, burns instantaneously.

The Montecatini Company was one of the first in Italy to adopt mechanical systems, patenting a furnace on the lines of the multiple hearth, a furnace which by its simplicity presents still to-day a certain interest.

In passing to the pyrites roasters we must mention first the multiple hearth furnaces still used in the majority of plants. These roasters are of very varied capacities some having as many as twelve hearths or trays fitted with an insulated column to permit access to fix the joints; they have a capacity of 25 tons per day and upwards.

The Lurgi horizontal revolving roaster of a minimum capacity of 40 tons per day, is used mainly in Germany in catalytic plants. A feature of these furnaces are the air inlets distributed all along the roaster in order to control the temperature at many points along the cylinder.

Among the roasters for pulverised pyrites we must mention the Nichols Freeman type which has a capacity of 40 tons per day and which works according to the princip of coal dust burners. Very finely crushed pyrites are injected and carried by a flow of air into a huge combustion chamber. With this type of furnace a Forster Wheeler boiler is used.

Generally in Italy, multiple hearth furnaces of small and medium tonnages are normally used. Among these a furnace patented by the Montecatini Company has found wide use. It has a capacity of 6 to 15 tons per day according to diameter; it is an extension of the normal multiple hearth roaster improved by the principle of "multiple circuits".

Until combustion has reached its maximum intensity the pyrites are distribute on several hearths working in parallel both as to the direction of the mineral and the gas. These hearths in parallel are followed by a single series working on semi-roast pyrites. Excessive temperatures are avoided in some of the hearths in this way and th yields are higher than in any other types of roasters having the same surface.

Dust boxes.

On leaving the roasters the sulphur gases normally pass into static dust box after which, especially in tower and contact plants, is placed the electro-static precipitator.

In the latest plants the static boxes are substituted by a simple metal pipe leading to the electro-filter.

At this stage begings the process of oxidation of sulphur dioxide and the formation of sulphuric acid, according to various systems.

Lead chamber plants.

In order to withstand competition from the more modern tower and contact plants, this process has had to evolve, in the course of time, along the lines of experience and in the light of the latest theories pertaining to the manufactuse of sulphuric acid.

Only by constant revision and adjustment of all its parts and operation can it hope to meet the competition of other methods and in certain cases still be advantageous.

It is now ascertained that reaction is accelerated by the liquid film flowing down along the walls of the chambers; standard lead chambers of low height and large volume scarcely profit by this acceleration.

In the intensive chambers where the surface volume ratio approaches 1, the contact of gas and liquid being promoted, a considerable increase in the yield per volume is obtained.

Compensation for the deficiency in volume which facilitates re-oxidation has been obtained by increasing the concentration of the nitric oxides and in practice by increasing the bulk of circulating nitrous products.

The theoretical amount of 36° Bé nitric acid required for 100 kg of 50° Bé sulphuric acid is 152.2 kg, the equation being:

$$SO_2 + N_2O_3 + H_2O = H_2SO_4 + 2NO$$

In the lead chamber process, in pradtice, considerably smaller quantities of nitric acid are effectively introduced into the system. Depending upon the size of the chamber and the intensity of the apparatus, more or less of the nitric acid is re-oxidised.

As a result, the more intense the production per volume unit, the greater must be the quantity of nitric acid in circulation for every 100 kg of acid produced.

By increasing to the utmost the contact surface between liquid and gas, as in tower plants, it is necessary to circulate about the stoichiometric quantity of acid.

The average yield of 50° Bé sulphuric acid from about 6 to 8 kg per cubic meter in the old standard chambers has reached 20 to 25 kg in the new intensive chambers having a surface-volume ratio approaching or even above one unit.

In addition to these two factors (the maximum contact of the liquid film on the walls and the increase in the concentration of the nitric oxides by enforced circulation) other physical means of intensifying the speed of reaction may be considered:

(a) Chambers from 12 to 20 and more metres in height with limited sections allow hot gases to generate, especially in the first chambers, with a strong upward flow in the centre and a downward flow in close proximity to the walls;

(b) A system of many chambers of small volume (from 6 to 12 for each plant, each chamber measuring 400 to 500 cubic metres) avoids the slowing down of the reactions and the acceleration in the pipes between the chambers;

(c) Very often the chambers are placed in two series and arranged in parallel accordin to the gas flow. This increases the chemical action in the first chamber after the Glover tower mentioned under point (a).

By the construction of chambers having a minimum of width in relation to height, savings have been attained due to the reduction in the size of the buildings.

The necessity, however, of having a larger amount of nitrous products in circulation has brought about an opportune improvement in the Glover and Gay-Lussac towers. These have been proportioned to proper dimensions to allow for adequate circulation of nitric acid and a corresponding production of sulphuric acid.

The last thirty years have seen the setting up of numerous plants for the production of sulphuric acid following various schemes for intensive systems.

We mention some of the best known:-

Moritz chambers.

Installed in France and Italy for more than thirty years, they are characterised by a small horizontal section; usually 5 x 5 metres; the height is btween 20 and 25 metres; the surface-volume ratio approximates to one; operating costs are low and production rises to about 16 kg or more to the cubic metre. An enlargement of the Gay-Lussac has increased production to 20 kgs per cubic metre.

Mills-Packard Chambers.

Installed in 1929 at Oldbury, England, and also in general use in other countries including Italy. They are cone-shaped chambers, sprayed with water, and have a surface-volume ratio of 0.75/0.80; they are set in the open air and give a production of about 20/22 kgs per cubic metre or 30 kgs per square metre of exposed surface. The elimination of buildings effects a great saving in the cost of installation.

Gaillard-Parrish Chambers.

These are cylindrical towers where the cooling of the gases is carried out by atomisation of the acid inside the chambers by suitable Gaillard sprayers. These plants were installed in Europe immediately after the war.

A further outstanding feature is the elimination of the Glover and Gay-Lussac towers packing this being replaced by an identical sprayer for the atomisation of the circulating acid.

The surface-volume ratio of such tower chambers is about 0.60/0.65; the production of acid is 22 kgs per cubic metre (26 kgs per m^2).

Such types are to be found in France and Spain, etc. but none have been installed in Italy.

Other similar types might be mentioned, all based on the principle of obtaining the maximum yield from apparatus of limited dimensions, with the aim of effecting a saving in installation and working costs. Also in Italy a certain number of those plants has been erected in order to obtain savings in installation and operation.

The results so far obtained have for the most part been encouraging.

For instance, in the most recent plants erected in Italy, chambers have been adopted of very reduced horizontal sections, about 2.5 x 3 x 6 metres, having 20 metres or more in height and a relative surface-volume ratio greater than one; the chambers are set in two series at a convenient distance from each other in order to allow ventilation of the walls.

The connections between the chambers are made only by means of pipes at the bottom of the chambers: this patented system has achieved considerable results in providing stability and ease of operation and has effected a vofy definite saving in lead.

The building housing the chambers is usually a light structure of reinforced concrete, the walls and roof of lead being supported by light iron bands. With the reduced horizontal sections of the chambers, the building occupies a small area with consequent savings in construction costs.

The Glover tower, at the beginning of the system, is of circular form and is constructed with acid resisting bricks and the packing is of chemical stoneware rings of a convenient size.

Always striving for economy in lead, the tower is not lined in this case.

The Gay-Lussacs, normally three in number, are placed in the open, the packing being sometimes 25 mm Raschig rings. Because of the high contact surface which it is possible to obtain with this filling, there is a considerable decrease in the dimensions of the towers and again a substantial saving in lead.

For the circulation of nitrous acid, the most up-to-date systems employ a vertical centrifugal type pump having a reduced space requirement instead of the old style reciprocating pumps of special metal. Such pumps force the acid direct to the top where a sprayer in the inside of the towers assures a perfect distribution of the circulating acid.

Acid tanks and the complex distribution equipment are no longer necessary on top of the tower this being another item of saving in lead.

The intensive chamber methods necessitate the use of effective coolers in order to eliminate the heat of the circulating acid; for this purpose outside lead pipe coolers for spraying water can readily be operated and maintained.

Small, special steel fans have taken the place of the old cumbersome lead fans usually placed between the last two Gay-Lussac towers. Instead of the nitric acid, nitrous gases are frequently used nowadays being obtained from small perfected catalytic ammonia oxidisers which give a lower cost per nitrogen unit.

Apart from the saving in capital and interest charges the efficient, easy and steady working of the new installations cannot help having an all round benefit of a reduction in working costs.

As an example, the consumption of 36° Bé nitric acid, whilst maintaining a high sulphur yield, can be kept down to even less than 0.5 kgs per 100 kgs of acid produced.

The rationalisation and the mechanisation of the handling of the raw materials and cinders has also permitted a reduction in labour costs.

In short, plants of this kind can still, in some cases, hold their own in competition with the more modern tower plants.

A point against them is that they cannot always produce the whole of the acid at a concentration of about 58° Bé and this may prove a severe handicap in areas where a higher concentration of acid is required; also in the manufacture of phosphatic fertilisers, the latest processes require a highly concentrated acid.

However, we must point out that with those foregoing intensive systems, if they are operated at the normal capacity, they can concentrate in the Glover tower almost all of the acid up to the desired 58° Bé concentration, but, unfortunately, this cannot always be if for unforseen circumstances the plant cannot run at its full capacity.

Tower processes.

Among all the reactions occuring in the chamber plant the slowest is certainly the dissolving of the SO_2 in sulphuric acid.

As mentioned, this depends, other things being equal, upon the liquid gas contact surface. Consequently, in order further to increase the production per volume unit compared with that of the intensive chambers, systems have been adopted whereby the wet surface, in contact with sulphurous gases, might reach limits unattainable in the lead chambers.

We take no heed of the ~~mechanised~~ mechanical apparatus such as the Schmiedel reaction box and similar appliances, as they have not found any great effective use because of difficulties in operation and complex mechanism.

The tower installations, however, have gradually acquired an importance chiefl on account of the following advantages:

(a) All towers and relative equipment can be set out-of-doors eliminating the cost of building;

(b) Such towers require the minimum use of lead - a considerable factor related to its present high cost;

(c) Constant production of all the sulphuric acid at about 60° Bé.

(d) Possibility of utilisation of cold weak gases and also at variable concentratio thus resolving a need of the industry such as the utilisation or sulphur dioxide from a metallurgical installation;

(e) Being able to work with cold gases it is possible to adopt steam boilers to recover the heat held by the sulphur gases coming from the pyrites roasters or even add to the system at its beginning a concentrating tower producing a certain quantity of acid at about 66°Bé.

It is worth while pausing for a moment upon the installation of the steam boiler by which, burning common pyrites 0 - 10 mm in size it is possible to obtain 1 kg and more of steam for every kg of sulphur burnt.

If, however, one uses very finely granulated pyrites in injection roasters having the boiler incorporated, it is possible to reach and surpass 2.5 kgs of steam per kg of sulphur. In many works, including those producing superphosphate, the steam has an economic use.

In these circumstances, the tower system can reach a level of steady and economic production, and, in recent years, manufacturers of sulphuric acid to be employed for superphosphate, have given preference to this method.

We shall mention here only the most well known types of tower plants:-

OPL Towers.

These consist of eight towers built with acid proof bricks, lead lined and filled with selected metallurgical coke.

The flow of gas is as follows:- Through two towers set in line, after which it is diverted in parallel with two towers in each circuit to be linked up again through the last two towers set in line. The circulating acid, separated in three circuits, is atomised on the ceilings of these towers after a sufficient cooling. The production of acid at 50° Bé appears to reach 60 kgs and more per cubic metre of tower. Water and nitric acid are added in the central towers to compensate the losses. If we are not mistaken, these OPL towers have become obsolete.

Multiple tower process (Kaskaroff).

This process is in common use in some countries. It consists of one tower divided into sectors but we will do no more than mention it as it will be fully described by Prof. Guareschi who is attending the Congress.

Petersen towers.

The Petersen system has been the most successful.

It consist of five towers built with acid resisting bricks and the gases are passed through them in a series. Each tower, except the re-oxidation towers, is spraye by the appropriate circulation of 58 - 60° Bé sulphuric acid, with nitric acid contents variable from tower to tower.

The first tower works as a Glover and the last is the second Gay-Lussac, both forming the so-called outer ring.

The inner ring is formed by the production tower and the first Gay-Lussac with the oxidation tower in the middle. The first and second towers produce, the middle tower oxidises and the last absorbs the nitrous gases.

The circulation of the nitrous acids is connected between the first and fifth and between the second and fourth tower.

The considerable heat carried by the sulphur gases entering the Glover and produced by the oxidation of the SO_2 and by dilution at 60° Bé of the produced acid is removed from the acids coming out of the Glover tower and from the production tower by means of efficient water coolers.

Strong circulation of the acids is maintained by centrifugal pumps.

A much less intense circulation of acid with low nitrous contents passes through the outer ring (Glover and second Gay-Lussac) so that the work of the former is so much eased that in consequence it is much smaller in comparison with the lead chamber installations and, as already mentioned, it may be fed by cold gases.

This tower in fact need no longer provide for the concentration of the acid as in the chamber process and it functions merely to de-nitrate and to produce.

These towers are constructed with acid resisting stone or chemical ware bricks and we can foresee the partial use of stainless steel with the assistance, in that event, of water spray cooling.

Most important and more so than in the lead chambers, is the purification of the gases from the pyrites cinders since the towers are fitted with small rings and it is essential to avoid chokage, the first tower being specially subjected to this danger.

Catalytic plants.

The speed of reaction in the catalytic oxidation of sulphurous anhydride increases with the temperature of the reaction; the speed of dissociation, very low up to a certain temperature, the increases rapidly becoming predominant in the speed of formation. The equilibrium constant depends upon the concentration and temperature of the gases, and rapidly decreases with a raising of the latter.

These facts are taken into consideration in the construction of convertors by bringing about the reaction in two steps. In the first the reaction is at a high temperature thus permitting a conversion rate of nearly 80% with a moderate quantity of catalyst; in the second, the reaction is at a much lower temperature with a low rate of conversion but with a equilibrium raised to 98 - 99%.

In the U.S.A. most of the catalytic plants use sulphur as a raw material so that the need for purification of the gases does not arise. This means a much simpler plant.

Generally, in such plants the air is dried before being introduced into the sulphur furnace; the sulphur becomes purified by liquefaction, decantation and filtration and the sulphur gases go direct to conversion after being cooled in a heat recovery boiler.

Despite the simplicity and low cost of the sulphur burning plants in Europe, in the majority of cases, pyrites are used. Though economical to obtain, its use involves a greater complexity of plant for the purpose of purifying and washing the sulphurous gases. These gases contain particles of ash, sulphuric acid mists, arsenious anhydride and water vapour. For the elimination of these impurities use is made of an electro-filter placed between the roasters and the converter; the ash is precipitated by a system of cooling, washing and spraying; a second electro-filter throws down the sulphuric acid mists and the arsenious anhydride whilst a drying-tower eliminates the water vapour.

We will now deal briefly with the improvements introduced into the plants recently put up in Italy. With the electro-filter for hot gases good results have been obtained by the automatic and periodical percussion of both types of electrodes. A three phase type of rectifier is normally employed giving an almost constant current or also used is a static type based on metallic oxides, of small size and dependable performance.

Before the electric filter it is possible to place an appropriate boiler which, besides recovering the heat, protects the filter itself from excessive temperatures harmful to metallic parts, and allows a saving to be effecte in the following cooling equipment.

The washing and cooling towers, combined in one, results in an advantage both in installation costs and in running, one circulation pump only being employed. The lead coolers are of the water spray type, very efficient and connected direct with the pump.

The acid settlers are constructed with conical bottoms and the cinder sludges which are deposited may be meachnically removed.

In the cold gas electro-filter the adoption of a three phase rectifier ensures a more even distribution of the gas or better still one of the static type which permit a reduction in the seize of the filter. This latter ensures a safe and regular run and has permitted the elimination of spare filters.

In the drying and absorbing towers the distribution of the gas and the spraying of the acid have been improved; the circulation acid tanks has been abolished, the bottom of the tower being used for that purpose. Cast iron coolers are of the water spray type. Recent research encourages the installation of towers without packing and coolers incorporated in the towers themselves.

It has been found preferable to circulate the acid in the towers independently in order to minimise the loss of SO_2 through the stack.

The circulation in the drying tower is kept at the required concentration (about 95%) by the continuous addition of acid coming from the absorbing tower. The towers are constructed with steel and lined with acid proof material.

For the production of fuming oleum at 105%, an additional absorption tower is placed after the usual one and from which it is supplied. To obtain acids of a greater concentration, oleum of about 105% is distilled by the hot gases coming from the catalysis and containing pure SO_3; an acid of any strength desired can be produced. The distilled acid returns to circulate in the oleum tower.

The vanadium catalysts which are the only ones in practical use reach a greater activity in the latest types having a larger percentage of vanadic anhydride. This allows of a reduction in the size of the equipment. New converters are now constructed with four layers of catalyst against seven formerly used.

The heat exchangers have been considerably improved by increasing the speed of the gas and improving a more uniform distribution and permitting a substantial reduction in weight.

The solid or liquid fuel gas pre-heaters, costly and cumbersome, have been replaced by an electric type, and a new type is actually being studied which should reduce considerably the power consumption.

The considerable heat of the gases coming from the catalysis is utilised to distil pure SO_3 from oleum, as mentioned above, or to pre-heat the feed water for the waste heat boiler.

Pumps for the circulation of the acid are of the immersed vertical type which avoids all likely loss.

The plants are also furnished with automatic instruments for a continuous recording of temperature, concentration, output and levels, thus making for a smooth easy working and control.

As to the capacities of these plants, they produce in the U.S.A. as much as 500 tons a day in some units. In Italy, the daily average is about 50 - 100 tons.

Technical developments continue and it is quite probable that within the next few years there will be still further modifications.

At one time all apparatus were housed in buildings but modern plants, except kilns, electric filters and heaters are not under cover thereby saving building costs.

To conclude, the improvements and simplification constantly being undertaken in these plants, and those envisaged, have succeeded or will succeed in reducing working costs which in the early plants were specially high. The cost of production by this means is not far short of that reached by other systems but with the quality of the product notably enhanced.

The catalysis system, while not yet a suitable one for utilising acids for the production of fertilisers, is preferable for the manufacture of acids required for other purposes.

An economic comparison of the three systems for the manufacture of sulphuric acid - Lead chambers, towers and catalysis.

Advantages of the tower system over the lead chambers.

- Economy of area and building.
- Economy of lead, less than one quarter being used than in the chambers.
- Taking 100 units as the cost of the chamber plant, to tower runs at about 85 units.

- Produces all acid at 60° Bé.
- By the addition of a concentration tower it can be made to yield a third of the acid at 66° Bé and the remainder at 60° Bé. A steam boiler may be installed to take advantage of the heat given off by the gases.
- All acid is carried to an iron reservoir.
- It can work on cold gas with a very low but variable percentage of SO_2.
- The yield of the sulphur and the consumption of nitric acid is comparable to that obtained by the lead chamber.
- The working cost is slightly higher due to the greater use of electric power and water, than it is in the lead chamber.
- Nevertheless, due to cheaper installation costs, the acid is produced more cheaply than in the other way.

Advantages of the catalysis system over the towers:

- The quality of the acid is clearly superior to that produced by the other systems.
- It is capable of producing pure SO_2 and an acid of any concentration up to 100%.
- Acids of high concentration can be transported in iron drums at comparatively less cost.

Against these advantages enumerated, the system has its disadvantages, namely:

- Average cost of installation is about 1.7 times as great as the tower method.
- The cost of production, exclusive of amortisation, exceeds that of the tower process by about 10%.
- Including amortisation the cost is about 20 - 25% above the other.

Milan, June, 1949.

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