Platinum Catalysts in Ammonia Oxidation

OPERATING CONDITIONS IN FISONS NEW NITRIC ACID PLANT

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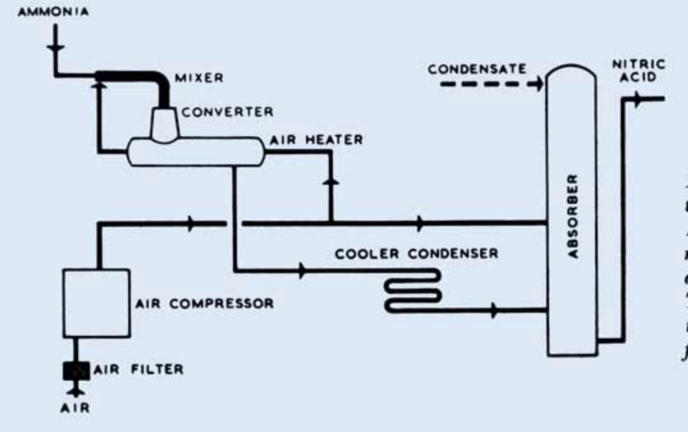
At their new factory in Stanford-le-Hope, Essex, Fisons Fertilizers Limited began in 1959 the manufacture of ammonium nitrate for use in Fisons compound fertilisers. This salt provides nitrogen, one of the three essential elements of all plant food, in a highly concentrated form, with resultant advantages to the farmer. As a starting material for the manufacture of ammonium nitrate, anhydrous ammonia of high purity (99.9 per cent minimum, with an oil content of 15 p.p.m. maximum) is used, and is purchased from an adjacent plant operated by Shell Chemical Company Ltd at Shell Haven. Here ammonia is made synthetically from the nitrogen of the air and from hydrogen obtained from oil by the Shell gasification process, and is delivered to Fisons by pipeline as a liquid under pressure.

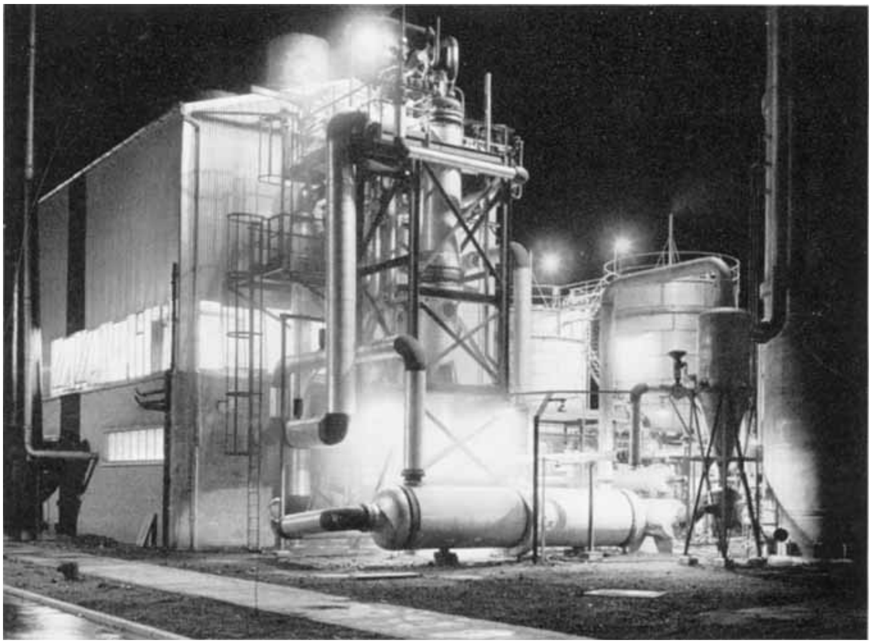
The ammonia is stored on the Fison site in a 2,000-ton insulated spherical tank, the largest of its kind in Europe, at 55 p.s.i.g. and 4°C. The raw material is converted by two processes into ammonium nitrate—first, by catalytic oxidation followed by absorption to form nitric acid, and second, by neutralisation of the acid with further ammonia to produce a hot concentrated (88 per cent) solution of ammonium nitrate in water, which is despatched by road and rail to Fisons compounding factories in various parts of the country. We shall be concerned here only with the catalytic process for making nitric acid.

The Principle of Nitric Acid Manufacture

The principle of the catalytic oxidation of ammonia to produce nitric oxide has long been known, and the discovery was in fact



A simplified flow chart of the Fison nitric acid plant. Pre-heated air and ammonia are fed to the mixer and then to the converter. The nitric oxide produced is absorbed in water to form nitric acid



A night-time view of the plant, showing the waste heat boilers and tail gas pre-heater with the nitric acid storage tanks in the background

made about 1839 by Kuhlmann, who passed an air/ammonia mixture over heated platinum, forming oxides of nitrogen which produced nitric acid when absorbed in water. Ostwald repeated these experiments in 1900, and by 1909 the principle became a commercial project when a factory started production in Germany. Since then many changes have taken place and many improvements have been made. Various processes are in use today, the main difference being in the pressure at which the reactions take place.

In the earliest commercial plants the process was carried out at atmospheric pressure; later high pressure (8 atmospheres), medium pressure (3 to 4 atmospheres) and a combination of low pressure conversion and higher pressure absorption, have all been employed. All have certain advantages. At Fisons, a modification of the American du Pont (8 atmospheres) process is used in a plant supplied by the Chemical & Industrial International of Nassau, Bahamas. The main advantages of this type of plant are low capital cost, since at high pressure smaller burners and smaller absorption towers are used with resulting savings in stainless steel, and improved absorption efficiency at the higher pressure, with a higher acid concentration. The principal disadvantages are lower conversion efficiency at the catalyst and greater loss of catalyst material when compared with the atmospheric pressure process. These factors make it important to strive for the optimum conversion conditions with this type of plant, particularly so since raw material cost constitutes about 75 per cent of the total plant operating cost.

Catalytic Conversion

At the converter, various reactions may take place, depending upon the conditions. These may be as follows:

$$\begin{array}{llll}
4\,NH_3 + 3O_2 & \rightarrow & 2\,N_2 + 6\,H_2O & (1)\\
2\,NH_3 + 2\,O_2 & \rightarrow & N_2O + 3\,H_2O & (2)\\
4\,NH_3 + 5\,O_2 & \rightarrow & 4\,NO + 6\,H_2O & (3)\\
4\,NH_3 + 7\,O_2 & \rightarrow & 4\,NO_2 + 6\,H_2O & (4)\\
2\,NH_3 & \rightarrow & N_2 + 3\,H_2 & (5)\\
6\,NO + 4\,NH_3 & \rightarrow & 5\,N_2 + 6\,H_2O & (6)
\end{array}$$

The choice of a suitable catalyst favours the desired reaction (3) to the exclusion of the others, and particularly of (1) and (5) which give degeneration to nitrogen. Insufficiency of air would obviously also give rise to reaction (1) to some extent. Reaction (6) is the result of incomplete conversion at the catalyst, possibly due to excessive velocity, the nitric oxide produced by oxidation reacting further with unconverted ammonia.

Experience over a number of years has shown that the best results, in terms of completeness of conversion to nitric acid, are obtained with a rhodium-platinum alloy gauze, a 10 per cent rhodium content being commonly used. The presence of rhodium increases the conversion efficiency and also improves the mechanical properties of the gauze, giving lower catalyst losses than with pure platinum.

Reaction gas temperature, which increases to an optimum for a given pressure, reaction pressure, gas velocity and gas composition are all factors that influence efficiency of conversion or loss of catalyst.

Raw Material Requirements

Compressed air and vaporised ammonia are mixed and fed into the reactor where conversion to nitric oxide takes place. Exclusion of impurities likely to cause loss of efficiency or of catalyst is of the greatest importance. For best results, oil in ammonia should not exceed 5 p.p.m., and if oil in the supply is greater than this, a filter or adsorber must be provided. Dust or pipeline scale in the air stream will likewise cause contamination of the catalyst and reduction of efficiency, and filtration of the air both before and after compression is provided. The catalyst itself must be clean and free from all contamination, and this is achieved by pickling in hot hydrochloric acid (constant boiling mixture) before use.

The Platinum Gauze Catalyst

The catalyst at Stanford-le-Hope consists of hexagonal gauze sheets, 36 inches in diameter, woven by Johnson Matthey from rhodium-platinum wire of 0.003 inch gauge into an 80 mesh screen. A total of 36 of these gauzes, fused together in pads of three to improve mechanical strength, is employed in a complete charge, the total weight of a charge being approximately 500 ounces troy. The catalyst is held in position by a nickel-chromium alloy supporting ring, the converter itself being constructed of 18/8 titanium-stabilised stainless steel.

Operating Conditions in the Converter

To start the reaction an electrical igniter is employed, with a nickel-chromium wire loop at its end in contact with a point on the catalyst gauze. The air/ammonia mixture is fed in at the top of the converter after passing through a baffle plate mixer. During operation the air, at 120 p.s.i.g., is preheated to approximately 270°C by the hot process gases in a heat exchanger. The ammonia is vaporised, initially by steam in a heat exchanger, but by process gases once operating conditions have been established. It is then superheated by steam to 155°C and thence fed to the mixer at approximately 150 p.s.i.g.

Control of ammonia percentage is important, the explosive mixture range under the operating pressures extending down to about 11.5 per cent NH_3 by volume, and explosive conditions are avoided by maintaining a maximum of 10.3 per cent NH_3 in the mixture. Periodic sampling and analysis of NH_3 in the gas mixture checks the composition. Control is achieved by temperature rise across the gauze, 1 per cent ammonia in the mixture being equivalent to about 70°C rise in temperature.

Automatic alarm and shut down are also provided to protect the catalyst against increase of temperature beyond prescribed limits.

On energising the igniter and feeding in the gas mixture, reaction begins to take place at the point of contact between igniter and

The converter and control panel. The converter contains the catalyst, consisting of a pack of 36 hexagonal gauzes woven from rhodium-platinum alloy wire

gauze, observed by glowing of the catalyst. This gradually spreads to the edges of the gauze, when the igniter is no longer required and may be withdrawn from the gauze. Ammonia burns on the catalyst to form a gaseous mixture containing about 9 per cent nitric oxide.

The highly exothermic reaction that takes place between ammonia and oxygen maintains the required temperature on the gauze. The heat evolved in the reaction is employed to raise steam for process use and also to provide energy for a gas turbine which operates on tail gases from the process and drives the process air compressor. The plant is thus virtually self-sustaining once operating conditions have been reached.

Reaction actually begins at temperatures of 600°C and upwards, but the optimum temperature with this plant is about 940°C. This is somewhat higher than with atmospheric plants, and this contributes to the greater catalyst loss due to some volatilisation of the metal and consequent mechanical breakdown.

Catalyst Performance

Once initiated, operation can continue until conversion efficiency falls to an uneconomic level due to catalyst loss. On a plant of this type this will be after three to four weeks running at design rate (250 short tons/day of 100 per cent HNO_3). Initially the conversion efficiency will be relatively low (93 to 94 per cent) but after two or three days will rise to a maximum of 95 to 96 per cent. This is the result of increased catalyst activity caused by the exposure of a greater area of metal to the reacting gases. The smooth wires at first become etched, then "sprouts" appear on the surface, indicating the effect of the reaction on the catalyst, though the mechanism is not known with certainty. At this stage maximum activity is achieved; later, losses occur as these "sprouts" break off and ultimately the weakening of the gauze structure and loss of platinum makes it necessary to shut down and renew the catalyst. Removal of a catalyst charge and replacement with a spare pack, already prepared, involves a shut down of about four hours.

Catalyst Recovery

Considerable care is necessary to recover the maximum possible weight of metal displaced from the gauze. First, a canister type filter with fibreglass as the filtration medium, held in position with stainless steel mesh, is installed in the system between the converter and the absorber, and will trap platinum dust carried forward with the process gas stream. The filter element has to be renewed every few months. Platinum dust will also accumulate in the vessels between the converter and the filter, and must be carefully recovered when the vessels are opened up for maintenance purposes. In units not provided with a filter, the dust will gradually accumulate as a sludge in the nitric acid storage tanks and may be recovered at a suitable shutdown.

When the catalyst pack is removed from the converter, dust remaining inside the converter is recovered by means of a vacuum cleaner, specially fitted with a paper bag which retains the metal and can afterwards be burnt off. On examination of the gauze, the top few sheets will be found to be so brittle and weakened that they have to be removed from the pack. The rest of the pack is then pickled in hydrochloric acid to remove catalyst poisons, particularly ferric oxide which will have accumulated on the gauze during operation, in a special room set aside for the purpose. After washing with distilled water, then drying and carefully treating with a hydrogen flame to reduce to the metal any rhodium oxide formed during operation, the pack is finally made up to weight with new catalyst which is added at the bottom of the pack. The life of an individual gauze will be about three to four months of operation, involving several picklings during this period.

Platinum remaining in the pickling acid is recovered by evaporation, and the walls and equipment in the pickling room are vacuum cleaned. The whole of the scrap and residues are returned to the refiners, Johnson Matthey & Co., Limited, who also supply the finished catalyst gauzes, for recovery. Overall, the suppliers of the nitric acid plant (C & I.I.) claim that a total loss figure as low as 0.0055 troy ounces per ton of 100 per cent acid produced is attainable, but limited experience so far as Stanford-le-Hope indicates a performance at present of about double this figure.

Fume Elimination by Catalytic Reduction

One other important application of the platinum metals in a nitric acid plant is demonstrated in the fume eliminator at Stanford-le-Hope. A feature of all ammonia oxidation plants is the effluent gas containing oxides of nitrogen which are difficult to remove. Absorption in water or alkali will always regenerate nitric oxide,

$$3\ NO_2+H_2O=2\ HNO_3+NO$$

and some brown discoloration due to NO_2 will always be observable at the exhaust stack. An effluent containing less than approximately 0.26 per cent nitrogen oxides, measured as NO_2, is regarded as acceptable by the Alkali Inspectorate. At Stanford-le-Hope the problem is overcome by the use of catalytic reduction of the oxides in the tail gas, with refinery gas as the reducing agent,

$$CH_4+2\ NO_2=2\ N_2+2\ H_2O+CO_2,$$

thus producing a harmless and practically colourless effluent. The catalyst in this case, supplied by Catalytic Combustion Co. of Detroit, is a mixture of platinum metals deposited on a crimped nickel-chromium ribbon, compressed into pads through which the gaseous mixture passes. The reduction of NO_2 is initiated at the catalyst at about 480°C, this temperature being achieved by control of the oxygen content of the tail gas. The refinery gas burns in the oxygen, thus raising the temperature to the point where reaction can begin between the refinery gas and the oxides of nitrogen. The heat liberated at the catalyst is utilised to generate steam for process use.