# Knitted Gauze for Ammonia Oxidation

## NEW INDUSTRIAL RHODIUM-PLATINUM FABRIC CATALYST

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Nitric acid is used in the manufacture of fertilisers, explosives, plastics and other chemicals, and its production has been the subject of substantial technical development since its inception on an industrial scale at the turn of the century. Thus, a modern manufacturing plant is as different from its early predecessors as the computer is from the abacus. The exception to this is the catalyst, the design of which differs little from that used in the early years of this century. An early patent filed by Karl Kaiser in 1909 suggested the use of a platinum gauze (1), and he settled on "a thickness of thread of 0.06 millimetres, and netting of about 1050 meshes per square centimetre...". Today the vast majority of nitric acid plants use 1024 mesh gauze of 0.076 mm and/or 0.060 mm diameter wire.

Nitric acid production plants can be broadly classified into two types according to the reaction process:

(i) A single pressure process carried out at either medium pressure (4 – 6 atmospheres) or high pressure (7 – 14 atmospheres)

(ii) A dual pressure process where ammonia oxidation is carried out at medium pressure, and the absorption stage is completed at high pressure.

The overall chemical reaction sequence in both processes is described by the following equations:

$$4NH_3 + 5O_2 = 4NO + 6H_2O \quad \text{ammonia}$$

$$2NO + O_2 = 2NO_2 \quad \text{oxidation}$$

$$3NO_2 + H_2O = 2HNO_3 + NO \quad \text{absorption}$$

The ammonia oxidation stage utilises a catalyst pack of up to 36 platinum group alloy gauzes, the number being dependent on the pressure in the plant, and the make-up of the pack is designed to maximise the efficiency of the reaction.

The process is fast, but during the reaction contact between the gas and the catalyst is required for times of the order of $10^{-4}$ seconds in order to maintain process efficiency. The catalysts employed have a typical service life of 50 – 300 days, depending upon the pressure of the system. Conventional woven rhodium-platinum catalyst gauzes fulfil the requirements of the plant quite successfully.

Initial work on catalyst development was performed using flat gauzes (2), and has progressed by the almost exclusive use of woven gauzes. Woven gauzes, however, restrict catalyst development, because only alloys with mechanical properties that satisfy the requirements of the weaving loom can be considered for use. Gauze and catalyst pack designs, therefore, have evolved together from the initial concept, rather than the concept driving the development.

### Why Develop New Gauzes?

Since very little has changed in the design of catalysts from almost the start of the industrial ammonia oxidation process, it appears that this could be an area for potential improvement. There are numerous pressures on the fertiliser manufacturing industry, not least of which is concern for the environment which has increased in recent years. A reduction in the rate of application of nitrogen-based fertiliser seems inevitable, and this in turn could result in a decline in industrial output. There are many indications that the industry is already streamlining itself for this eventuality.

One of the major costs of the nitric acid production process is the catalyst. In a typical plant, the catalyst could consist of 25 kg of 10 per cent rhodium-platinum, which at present metal price levels (platinum £6860/kg and rhodium £90,000/kg) would cost approximately £350,000. Fluctuations in metal prices and especially the recent high cost of rhodium further increases the need for the nitric acid producers to make optimum use of this asset. With the widespread adoption of the "just in time" philosophy, pressure is being put upon the catalyst gauze manufacturers to improve further their response to the needs of the catalyst users. The process of weaving gauze is, however, inherently inflexible, since it ties up large amounts of metal for long periods of time, to the possible financial detriment of both the supplier and the user.

As previously stated the catalyst used for ammonia oxidation must fulfil several needs. Lowering the amount of rhodium in a catalyst will substantially reduce its cost, but then it will not be able to meet its full requirements. Changing the alloy composition and seeking to develop new alloys would be difficult also, under such constraints. A compromise is needed between cost and requirements, and an appreciation that any benefits from alternative alloys, such as higher conversion efficiencies and longer life, will be more difficult to instigate.

An alternative flexible catalyst manufacturing system was therefore believed to offer solutions, providing that the resultant catalyst was able to meet specification. Knitting was identified as a possible method of manufacture. No one, however, had been able to successfully knit the relatively low tensile strength platinum group alloys used for ammonia oxidation catalysts, beyond laboratory scale.

## Gauze Manufacturing Trials

Initial attempts to produce knitted gauzes on a commercial knitting machine proved difficult, the wire breaking frequently. Sufficient material was produced, however, to enable basic catalyst proving trials to take place. This knitted material was found to be significantly lighter than the same area of conventionally woven catalyst gauze.

Trials were carried out in a high pressure ammonia oxidation development reactor built by Johnson Matthey (3). The initial trials were restricted due to the limited availability of material, the catalyst pack consisting of 16 knitted gauzes backed up with 4 woven catalyst gauzes. The results, however, were encouraging. As the knitted catalyst, shown in Figure 1, was 75 per cent lighter than the conventional gauze, four knitted catalysts were used as a substitute for one woven gauze, thus maintaining the weight of the catalyst charge. The resulting ammonia conversion efficiency was recorded as being 3 per cent higher than normal, and the light-off characteristics were also improved. Subsequent examination of the surface of the knitted gauzes by scanning electron microscopy revealed a well-developed, faceted structure, comparable to that observed on used conventional gauzes. It was found that no reaction occurred on the surface of the woven gauze, indicating that any improvements could be attributed to the knitted material.

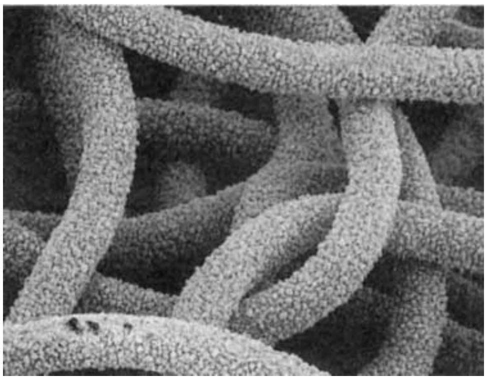

**Fig. 1 Initially, gauze produced by knitting was significantly lighter than the same area of woven gauze, and this was allowed for by using four knitted gauzes as a substitute for one woven gauze. During use knitted gauzes developed a faceted appearance, comparable to that of conventional woven material × 80 approx.**

Additional fabrication work was undertaken, but this did not produce a knitted gauze having a 1:1 weight ratio with the woven gauze. Encouraged by previous success, however, further pilot plant catalyst trials were carried out at both medium and high pressures using various industrial pack simulations. Every permutation gave improved plant performance, Table I. The make up of the packs and the test conditions are given in Table II.

In view of the novelty of the concept and the lighter weight catalyst fabric, a continuous 4 day trial at medium pressure was undertaken to assess

**Table I**

## Results of Pilot Plant Trials

| .Conditions | Pack construction | Run number | Campaign hours | Ammonia range, per cent | Inlet temperature, °C | Reactor temperature, °C | Average conversion efficiency, per cent | Pressure drop, iwg |
|---|---|---|---|---|---|---|---|---|
| Medium pressure | Standard | 85/34 | 10.5 | 9.9→10.1 | 267→272 | 741→748 | 90.4 | 1.0 |
| | Standard | 85/35 | 12.5 | 9.9→10.2 | 269→271 | 737→743 | 89.3 | 1.0 |
| | 50% knitted | 87/16 | 13.3 | 9.8→10.1 | 287→298 | 733→740 | 94.5 | 2.7 |
| | 100% knitted (a) | 88/9 | 9.8 | 10.0→10.2 | 273→280 | 765→795 | 94.5 | 0.2 |
| | 100% knitted | 88/11B | 26.5 | 9.5→10.3 | 259→267 | 730→769 | 94.7 | 1.2 |
| | Reduced weight* (b) | 88/11A | 9.8 | 10.2→10.4 | 259→272 | 747→760 | 87.7 | 0.8 |
| High pressure | Standard | 87/5 | 10.8 | 10.5→10.9 | 268→270 | 825→845 | 91.6 | — |
| | Standard | 88/22 | 6.5 | 10.2→10.5 | 275→283 | 850→863 | 90.4 | — |
| | 40% knitted | 88/17 | 9.5 | 10.2→10.9 | 272→273 | 824→874 | 93.3 | 3.5 |

* 100% knitted pack but with 28 (7 weave equivalent) rather than 32 (8 weave equivalent) knitted gauzes

**Table II**

**Test Conditions and Pack Construction for the Evaluation of Knitted 10 Per Cent Gauze Catalysts**

| Pack construction | Targeted operating conditions |
|---|---|
| **Medium pressure trials** | |
| Standard pack<br>8 × 1024#/0.076 mm<br>50% knitted pack<br>16 × 260#/0.076 mm knit<br>4 × 1024#/0.76 mm knit<br>100% knitted pack<br>32 × 260#/0.076 mm knit (a)<br>28 × 260#/0.076 mm knit (b) | Loading 12 tonnes/day $NH_3$<br>Pressure 56 psi<br>Percentage of ammonia 10.0<br>Inlet temperature 270°C<br>Reactor size 1.25" dia |
| **High pressure trials** | |
| Standard pack<br>21 × 1024#/0.076 mm<br>40% knitted pack<br>32 × 260#/0.076 mm knit<br>13 × 1024#/0.076 mm knit | Loading 78.9 tonnes/day $NH_3$<br>Pressure 135 psi<br>Percentage of ammonia 10.5<br>Inlet temperature 270°C<br>Reactor size 2.0" dia |

the durability of the knitted catalyst. The results confirmed those of the short term trials.

Some possible explanations for the improved efficiency of the knitted catalyst could be its open weave, or a feature associated with it, coupled with the increased number of gauzes required to provide the equivalent weight. Scanning electron microscopy showed that the reactants had penetrated to greater depths than normal, presumably because the gas needed to travel further before finding a reaction site, thus increasing contact time. However, an important feature of the knitted material is that, unlike woven gauze, the crossover points of the wires are more accessible to gas impingement. The loss of catalytic area on a woven gauze due to masking at crossover points is 10 per cent of the total area theoretically available. Therefore, it was postulated, if equivalent weight knitted catalysts could be manufactured, then fewer gauzes would be required to fulfil the same function. Alternatively, lighter weight packs could be used to achieve the same result.

To ensure initial acceptance by the chemical industry, the production of a knitted gauze of equivalent weight to the conventional woven gauze was considered desirable, although not essential to ultimate performance. Using the experience gained, a knitting machine believed to be suitable for producing such a fabric was identified; this being a commercially available 6 inch diameter circular knitting machine with a single feed. The single feed system reduced the need to carry large stock levels of wire during the development stages, although multiple feed units were available for the knitting machine, and could be used to scale up the operation and increase the flow of knitted material from the machine. With such a feature it is possible to commence knitting as soon as wire of the

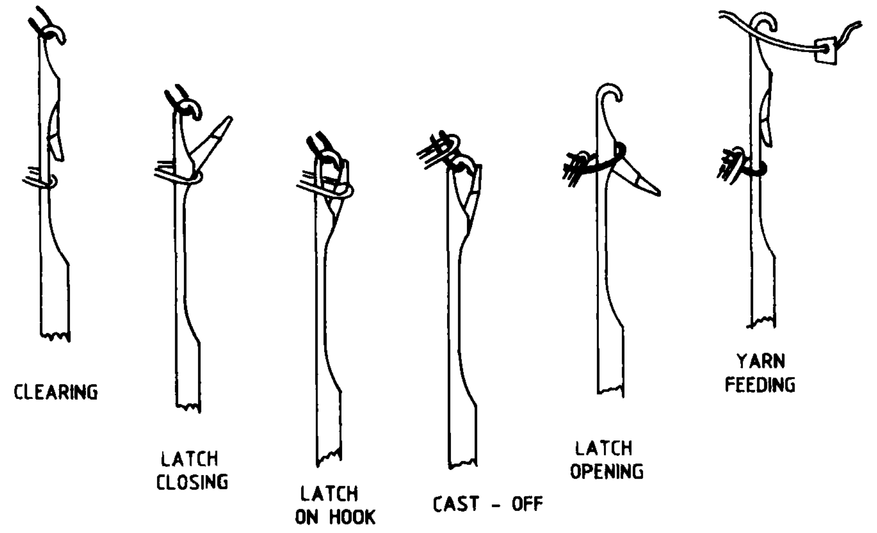

**Fig. 2 The knitting process imposes severe distortions on the metal feed wire, but co-knitting a polyester yarn gives support to the wire and reduces friction at the needles**

correct diameter and with the necessary mechanical properties, becomes available. It soon became apparent that, due to the relatively low tensile strength of the alloys being used, and to the surface friction generated, the wire could not withstand the severe deformation it was subjected to. Therefore changes to the basic design of the knitting machine were made and special features were developed to assist in the production of knitted noble metal gauzes.

The knitting process is shown in Figure 2. Here the degree of deformation, as well as the mechanical operations that produce it, are shown. To overcome the problems resulting from such severe distortions, a polyester yarn was added to the metal wire feed. This had the effect of wrapping the wire, giving it support, and also reducing friction in the needles. After fabrication the co-knitted polyester is removed. Furthermore, the mechanical properties of the rhodium-platinum wire being knitted were optimised by varying the annealing conditions, so as to produce properties which were more amenable to the high degree of deformation experienced by the wire during the knitting process. To reduce further the friction forces, several lubricants were investigated and the optimum one identified. Using a knitting head with 370 needles (19 per inch), a fabric was produced with an effective weight of 590 g/m$^2$, the same as for typical woven gauze. During trials it was found that by careful adjustment the machine could be made to produce fabric with a weight tolerance of ± 25 per cent. Thus, a flexible manufacturing technique was successfully developed enabling fabrics of different cloth densities to be produced, using noble metals and alloy wires of various diameters, including rhodium-platinum and rhodium-palladium-platinum.

## Commercial Trials

An industrial plant operated under atmospheric conditions with a production capacity of 160 tonnes per day of nitric acid was used for the initial trials, the campaign lasting for 75 days. An examination of the catalyst pack by scanning electron microscopy again revealed excellent surface development, and also showed that activation had occurred in the areas of potential masking, see Figure 3. This may be compared with the woven gauze shown as Figure 4. The results of an EDXA (energy dispersive

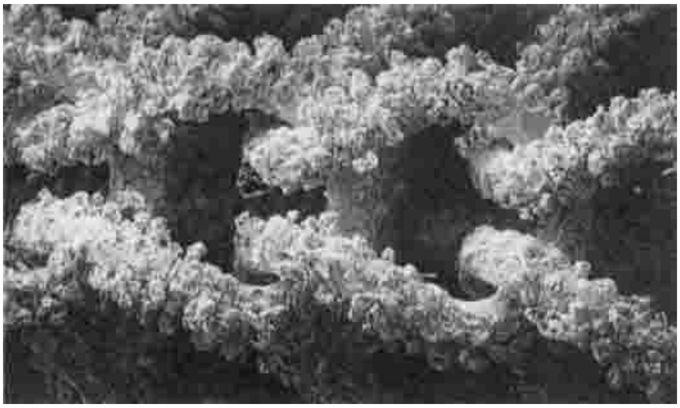

**Fig. 3 After commercial trials under atmospheric conditions, excellent surface development was evident on a knitted gauze, and this extended to areas of potential masking**
**× 100 approx.**

X-ray analysis) of the gauze surface were most informative, and are given in Table III. Only low levels of rhodium were detected on the surface of the knitted samples. These may be explained by a better gas distribution throughout the catalyst pack, which promotes a more consistent temperature profile and thus reduces the redistribution of rhodium, which usually occurs at low operating temperatures. This unexpected finding is still under investigation, and is supported by the results of further trials. Generally a pack becomes uneconomic to use when rhodium levels on the surface reach 50 per cent. Any lowering of this rate of rhodium redistribution would be expected to extend the life of the catalyst. A reduction in the redistribution of rhodium should also reduce rhodium losses which, at the present time, could provide a significant financial saving. Total noble metal loss when using a knitted catalyst was, however, the same as when a woven catalyst gauze was employed.

Several industrial trials are at present being conducted at low, medium and high pressures, and initial results show that knitted catalysts give a performance superior to that of woven gauzes. These trials will be reported in a later issue of *Platinum Metals Review*.

## Summary

The development of knitted gauzes has many potential benefits both for the catalyst supplier and the nitric acid producer, and thus the present project has met most of its initial aims. The

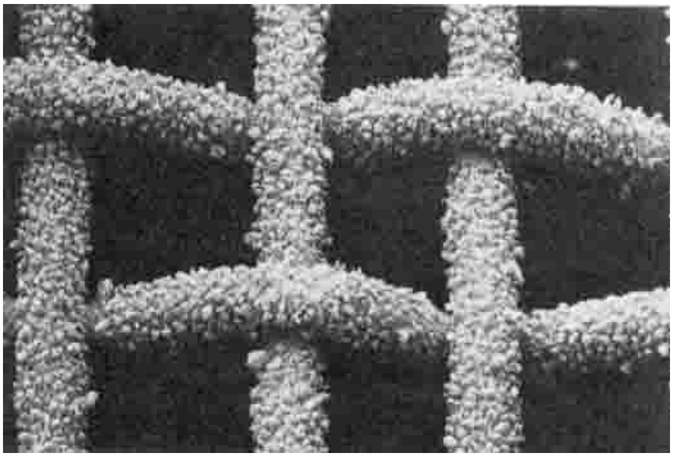

**Fig. 4 Characteristic faceted development on the surface of a conventionally woven rhodium-platinum catalyst gauze, after use for the oxidation of ammonia**
**× 100 approx.**

**Table III**

**Surface Rhodium Concentrations as Determined by EDXA**
per cent

| Knitted pack | | | Conventional woven pack |
|---|---|---|---|
| Gauze 1 | knitted | 8.9 | 12.5 |
| Gauze 2 | knitted | 9.0 | 12.7 |
| Gauze 3 | woven | 11.5 | 11.4 |
| Gauze 4 | woven | 11.9 | 11.5 |
| Gauze 5 | woven | 9.7 | 11.2 |

Starting rhodium content of knitted gauze 10.05 per cent

potential benefits can be summarised as follows:

(a) Increased conversion efficiency

(b) Reduced rhodium oxide formation

(c) Higher surface area available for catalysis

(d) Fabric flexibility providing greater resistance to damage by thermal shock

(e) Stronger material, the ability to resist tearing being superior to that of woven gauze

(f) Choice of alloy: any changes from the standard 10 per cent rhodium-platinum catalyst can be considered; indeed any combination of rhodium, platinum and palladium can be knitted into gauzes, and many have been. If a chosen alloy can be processed to wire of a suitable diameter, then the possibility of knitting it is extremely high

(g) Only minimal stock levels are required; this enables the supplier to respond more quickly to the needs of the consumer.

Johnson Matthey believe that this range of products and the associated technology, will have a major impact on the chemical industry and will encourage platinum metals catalyst development to take place in ways that, previously, have only been considered in theory.

### References

1 K. Kaiser, *German Patent* 271,517, 1909

2 S. L. Handforth and J. N. Tilley, *Ind. Eng. Ind.*, 1934, **26**, (12), 1287

3 K. G. Gough and B. L. Wibberley, *Platinum Metals Rev.*, 1986, **30**, (4), 168

# Platinum and Iridium Silicide Infrared Imagers

## INCREASING OPPORTUNITIES FOR DIVERSE APPLICATIONS

In a recent communication from the David Sarnoff Research Center, Princeton, New Jersey, the background to the continuing development of platinum silicide infrared imaging devices is discussed (J. R. Tower, *Infrared Technol.*, 1991, **25**, (2), 103–106).

When the concept of Schottky-barrier infrared focal plane arrays was first put forward by researchers at the Rome Air Development Center, in 1973, it was proposed that detectors formed by the reaction of platinum, or palladium, with *p*-type silicon would be sensitive in the 1 to 5 μm band. Before the end of the decade the Sarnoff Laboratory had demonstrated a 25 x 50 platinum silicide imager operating in the 3 to 5 μm band, and five years later they had developed a 160 x 244 array with a noise equivalent temperature difference of 0.1 K. Now they are developing cameras around three focal plane arrays, namely 64 x 128 and 320 x 244 infrared charge-coupled devices and a 640 x 480 complementary metal-oxide silicon infrared imager. Applications include thermography, radiometry, industrial process control and scientific imaging.

In the future it is planned to produce iridium silicide complementary metal-oxide silicon infrared imagers with wavelength capability from 1 to 10 μm or 0.2 to 10 μm with back- or front-side illumination, respectively.