

Ammonia Oxidation Catalysts

DEPOSITS ON SOME RHODIUM-PLATINUM GAUZES

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Rhodium-platinum gauzes used as catalysts in nitric acid plants operating at various pressures have been examined by microscopy and by X-ray diffraction. Some gauzes possess low conversion efficiency and these are usually covered with deposits that can frequently be traced to sources of contamination. Gauzes operated at pressures of four or more atmospheres also possess coatings of rhodium oxide that are difficult to remove by fusion or pickling. The suggested cause of formation of this oxide shows that it cannot be avoided but that methods exist for cleaning gauzes from higher pressure plants.

Over the past few years we have examined a number of unsatisfactory used rhodium-platinum alloy gauzes from catalytic ammonia burners of several nitric acid plants, both British and foreign. The complaints were that the gauzes had low or suspected low efficiencies, although a few gauzes from plants operated at one atmosphere pressure were satisfactory and of long life. The gauzes were taken, as shown in the table, from plants of various designs. Burner operating pressures were one, four or eight atmospheres, and most of the gauzes were of 10 per cent rhodium-platinum alloy; a few were of 5 per cent rhodium-platinum or of platinum only.

Examination of Gauzes

On receipt of the gauzes, loose dust was removed by gentle tapping. In most cases, pieces of gauze were mounted in a cold

setting resin and the resultant blocks were then ground and diamond polished to a $\frac{1}{4}$ μm finish. These polished mounts were then examined by reflected light microscopy and by electron microprobe analysis. In some instances, selected pieces of the gauzes were examined in the as-received state by scanning electron microscopy.

New gauzes are composed essentially of smooth wires which become roughened during use and which, after a few days' operation, are found to be covered by alloy excrescences, which with time almost invariably show some well-developed crystal faces. The fully activated gauzes thus have increased surface area. It appeared possible that the active gauze surfaces might in some way be different from the initial gauze in composition as well as form.

In some cases, therefore, strands of wire were extracted carefully and were subjected to X-ray diffraction before and after scraping off the excrescences and also after scraping off the compact surface of wire below the excrescences.

The gauzes examined are listed in the table with brief details of origin, composition, use, and findings of the physical examinations.

Plants Operating at One Atmosphere

Ten gauzes were examined, representing five different sites, six different plants and three types of plant design. Certain samples of good efficiency were fairly clean. Others described as dirty were badly contaminated by iron oxide, principally $\alpha\text{-Fe}_2\text{O}_3$, which in some cases (samples 4, 5 and 6) was in the form of fine particles that could be traced to poor air filtration and to sources of iron-

Results of Physical Examination Tests on Rhodium-Platinum Gauzes

Sample No.	Plant Identity	Plant Type	Pressure, atm	Time in Use, months or days	Wire Composition, per cent Rh	Microscopy Test after Use			X-ray Diffraction after Use			Efficiency, Appearance and Treatment
						Rh/Rh ₂ O ₃	Fe ₂ O ₃	Other	Rh/Rh ₂ O ₃	Wire Comp. Rh%	Exces. Comp. Rh%	
1	A1	?	1	5m	10	nd	nd	nd	nil	11.5	nd	good, clean
2	A1	?	1	11m	10	nd	nd	nd	nil	11	11.5	good, clean
3	A2	U	1	6m	10	nil	nil	nil	nd	nd	nd	good, clean
4	B	K	1	5½m	5	nil	heavy	nil	nd	nd	nd	dirty
5	B	K	1	?	5	nil	v. heavy	nil	nd	nd	nd	very dirty
6	B	K	1	?	10	nil	much	nil	nd	nd	nd	dirty
7	C1	K	1	?	5	nil	little	trace SiO ₂	nd	nd	nd	good, clean
8	C1	K	1	?	5	nil	little	little MoS ₂	nd	nd	nd	good, clean, corroded in places
9	D1	D	1	9m	10	nil	little	nil	nd	nd	nd	fairly clean
10	E	?	1	?	10	nil	much	nil	nil	10	11	dirty, corroded
11	C2	?	4	?	10	Rh ₂ O ₃	little	nil	nd	nd	nd	fairly clean
12A	D2	S	4	13m	10	Rh ₂ O ₃	v. lit.	nil	nd	nd	nd	clean
B						?Rh	little	nil	nd	10-11	nd	after placing in 1 atm plant
13	D2	S	4	13m	10	Rh ₂ O ₃	fair	nil	Rh ₂ O ₃	nd	8.5	dirty
14A	D2	S	4	8m	10	Rh ₂ O ₃	fair	nil	Rh ₂ O ₃	8.5	variable	
B						Rh ₂ O ₃	nil	nil	nd	nd	nd	after treatment with fusion mixture
15	D2	S	4	?	10	Rh ₂ O ₃	fair	nil	nd	nd	nd	dirty gauze
16	D2	S	4	?	10	Rh ₂ O ₃ or Rh	fair	nil	nil	10	nd	after 2-3 weeks in D1 at 1 atm
17	D2	S	4	?	10	nil	heavy	nil	nil	10-11	nd	after 8 weeks in E at 1 atm
18A	D3	S	4	7m	10	Rh ₂ O ₃	fair	nil	Rh ₂ O ₃	6	6	
B						Rh ₂ O ₃	fair	nil	nd	nd	nd	heated 11 per cent NH ₃ /air, 25h, 850-900°C, 1 atm
C						Rh ₂ O ₃	fair	nil	nd	nd	nd	heated 100 per cent NH ₃ , 50h, 850°C, 1 atm

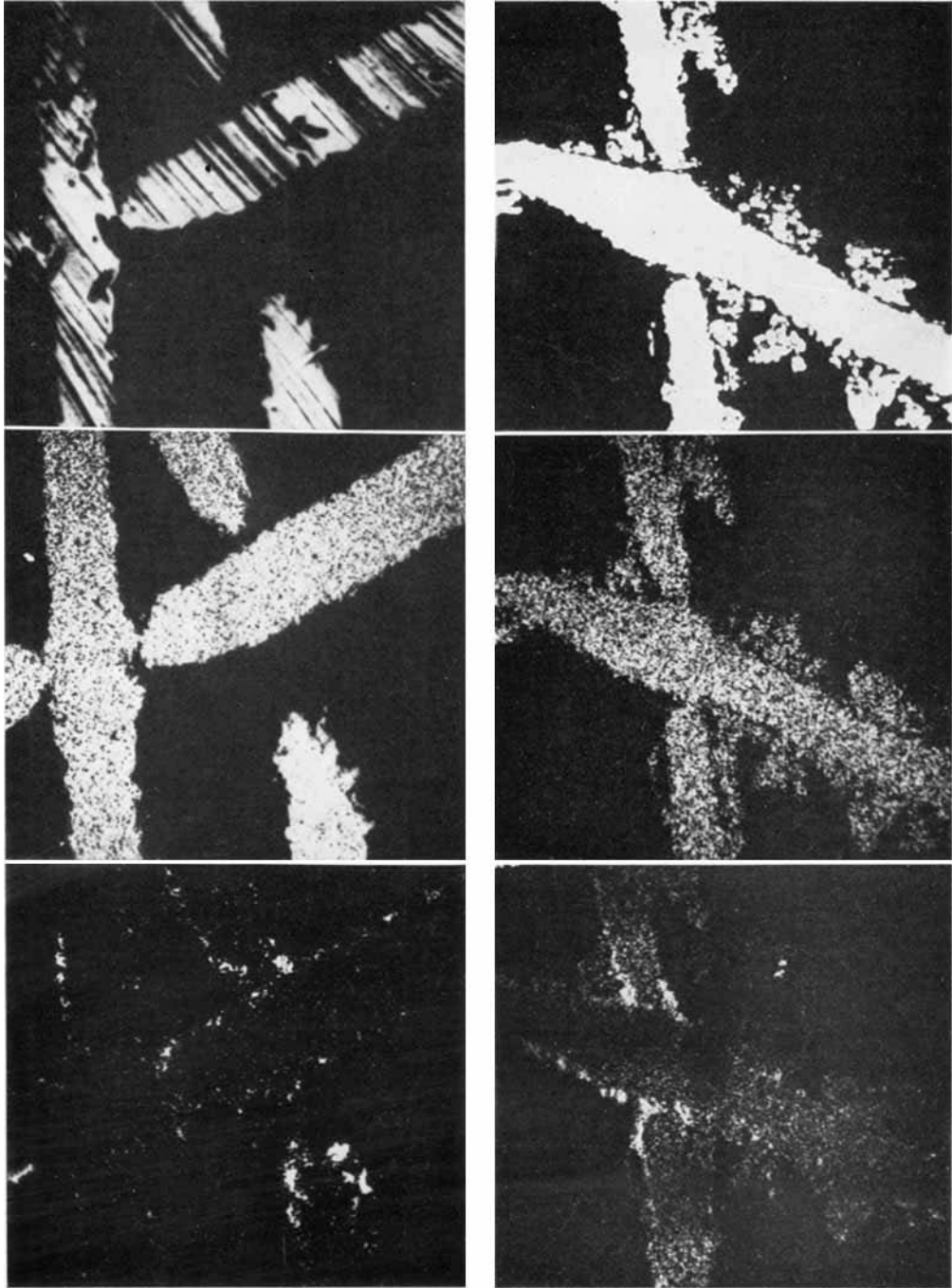
bearing dust in close proximity to the plant, while in other cases (e.g. sample 10, see Fig. 1a, b, c) the texture and microstructure of the iron oxide indicated an origin from plant scale.

Quartz sand grains in sample 7 were due to plant siting and to poor air filtration, while in sample 8 the source of MoS₂ was traced to liberal use of a lubricant.

Sample No.	Plant Identity	Plant Type	Pressure, atm	Time in Use, months or days	Wire Composition, per cent Rh	Microscopy Test after Use			X-ray Diffraction after Use			Efficiency, Appearance and Treatment
						Rh/Rh ₂ O ₃	Fe ₂ O ₃	Other	Rh/Rh ₂ O ₃	Wire Comp. Rh%	Exces. Comp. Rh%	
D						Rh	fair	nil	Rh	6-7	nd	heated 100 per cent N ₂ , 4h, 850°C, 1 atm
E						Rh	fair (Fe?)	nil	Rh	6-9	nd	heated 100 per cent H ₂ , 4h, 850°C, 1 atm
19	D3	S	4	3m	10	Rh ₂ O ₃	trace	nil	nd	nd	nd	good efficiency
20A	D4	S	4	10m	10	Rh ₂ O ₃	some	nil	Rh ₂ O ₃	6-5	variable	
B						Rh ₂ O ₃	nil	nil	nd	nd	nd	after treatment with fusion mixture
21	D4	S	4	3½m	10	Rh ₂ O ₃	some	nil	nd	nd	nd	
22	D4	S	4	3½m	5	Rh ₂ O ₃	trace	nil	nd	nd	nd	
23	D4	S	4	3½m	0	nil	much	nil	nd	nd	nd	
24	D4	S	4	2½m	10	Rh ₂ O ₃	nil	nil	nd	nd	nd	
25	D4	S	4	2½m	5	Rh ₂ O ₃	nil	nil	nd	nd	nd	
26	D4	S	4	1m	10	Rh ₂ O ₃	nil	nil	nd	nd	nd	
27	D4	S	4	1m	5	trace Rh ₂ O ₃	nil	nil	nd	nd	nd	
28	D4	S	4	2d	10	trace Rh ₂ O ₃	nil	nil	nd	nd	nd	
29	D4	S	4	2d	5	nil	nil	nil	nd	nd	nd	
30	D5	S	4	7m	10	Rh ₂ O ₃	trace	nil	nd	nd	nd	good efficiency
31	F	U	4	?	10	trace Rh ₂ O ₃	heavy	Zn, S	nd	nd	nd	badly corroded
32	G	C	8	3m	10	Rh ₂ O ₃	some	nil	nd	nd	nd	unlit portion
33A	H	C	8	1m	10	little Rh ₂ O ₃	trace	nil	nd	nd	nd	pickled in HCl
B						Rh ₂ O ₃	little	nil	nd	nd	nd	lit portion
34	H	C	8	1+m	10	Rh ₂ O ₃	yes	nil	nd	nd	nd	
35	J	C	8	?	10	Rh ₂ O ₃	yes	nil	nd	nd	nd	
36	K	C	8	?	10	Rh ₂ O ₃	yes	nil	nd	nd	nd	

Plant types: U=Uhde, K=Kuhlmann, D=Dutch State Mines, S=Stamicarbon, C=Chemico
nd=not determined

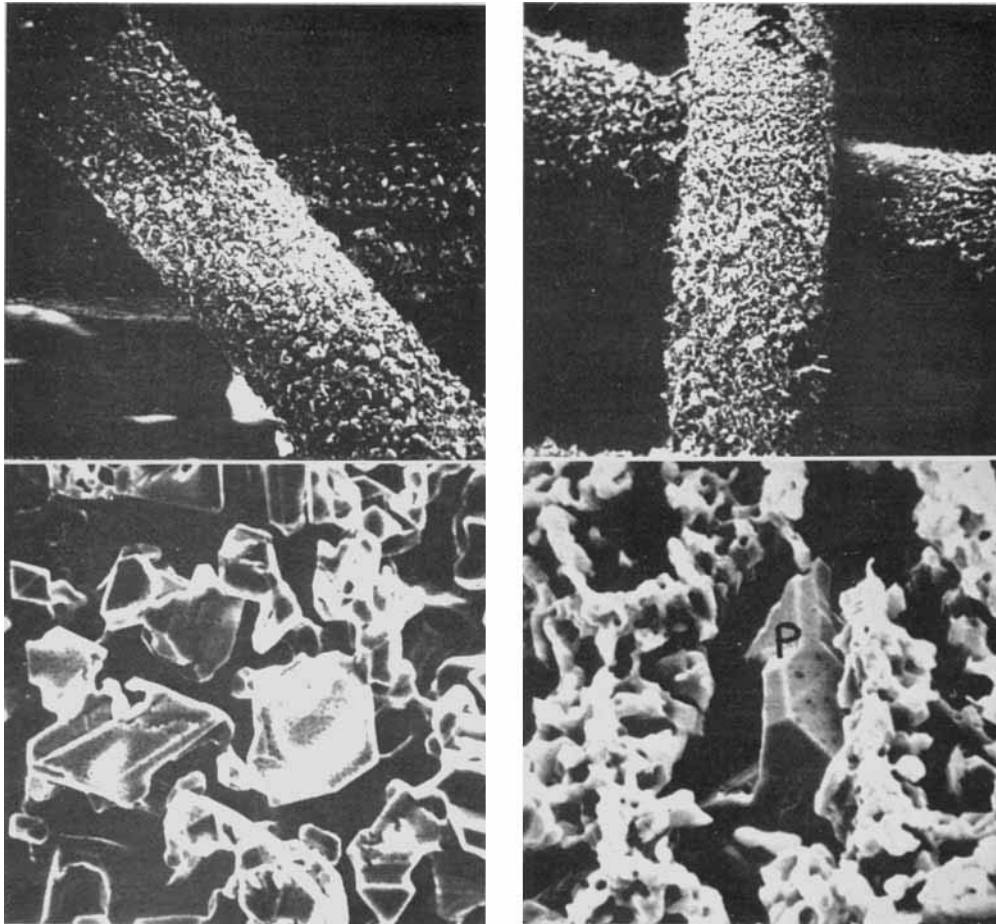
Three samples were examined by X-ray diffraction, which showed that excrescence formation was accompanied by preferential platinum loss, with consequent slight enrichment in rhodium over the original 10 per cent in the excrescences and in the compact surface of the wire immediately below the excrescences.



1a top, 1b middle, 1c bottom

1d top, 1e middle, 1f bottom

Fig. 1 Electron and X-ray images of gauzes from one and four atmosphere nitric acid plants. (a) Electron image, Fe-contaminated gauze, 1 atm plant; (b) platinum X-ray image of gauze in (a); (c) iron X-ray image of gauze in (a). (d) Electron image of gauze from 4 atm plant; (e) platinum X-ray image of gauze in (d); (f) rhodium X-ray image of gauze in (d)



2a above, 2b below

2c above, 2d below

Fig. 2 Scanning electron microscope photomicrographs of two gauzes from a 4 atm plant. (a) Gauze with freshly activated platinum alloy surface $\times 500$; (b) detail of (a) $\times 4000$; (c) low efficiency gauze after use $\times 500$; (d) detail of (c) showing alloy crystal P poking through blanket of porous Rh_2O_3 $\times 4000$

Plants Operating at Four Atmospheres

Twenty-one gauzes were examined, representing three sites, four different plants and two types of plant design. As in the case of plants operating at one atmosphere burner pressure, some gauzes were contaminated by iron oxide (particularly samples 17, 23 and 31), which in most cases could be traced to plant scale and general corrosion. In sample 31 both zinc and sulphur were detected by microprobe analysis. The source of this contamination was found to be zinc-coated wire filters in the air intake that were badly corroded and had disintegrated under attack from

sulphurous effluent from a neighbouring plant.

In addition to the contamination of the gauzes by material from external sources, all of the four atmosphere gauzes (with the exception of sample 17—unknown time on line, sample 23—a platinum gauze, and sample 29—a 5 per cent rhodium-platinum gauze of only two days usage) had further physical contamination as shown in Fig. 1d, e, f and in Fig. 2. The platinum excrescences of the active gauze surfaces were masked by blankets of Rh_2O_3 . As shown by results of X-ray diffraction studies, the formation of

Rh_2O_3 leads to depletion of rhodium from the gauze, giving rise to compositions as low as 6 per cent rhodium from an original 10 per cent rhodium-platinum gauze (sample 18A), whereas in plants operating at one atmosphere burner pressure the rhodium content tends to increase in the alloy with time.

Plants Operating at Eight Atmospheres

Six gauzes were examined from four different plants, all of the same type of plant design. Again the amount of iron contamination was variable and in some cases attributable to plant scale. All gauzes showed evidence of blanketing of the active alloy surface by a surface covering of Rh_2O_3 and are thus similar to gauzes operating at four atmospheres burner pressure.

Gauze Cleaning

Examination of used and Rh_2O_3 -contaminated gauzes after plant cleaning procedures showed that the fusion mixture normally used (see samples 14B and 20B) removes iron oxide but has little effect on rhodium oxide. Similarly, pickling in HCl acid (see sample 33) is not very efficient for Rh_2O_3 removal.

However, since the Rh_2O_3 coating arises by oxidation of rhodium in the alloy, the process should be easily reversible. Indeed, it is easily accomplished by heating the gauzes in hydrogen (see sample 18E), when the oxide is reduced to metal, or in nitrogen (see sample 18D), when it dissociates to metal and oxygen. A like effect is obtained by placing the gauzes in a one atmosphere plant for several weeks (samples 12B, 16 and 17), when they reach equilibrium with the gas compositions and the alloy becomes rhodium-rich and returns to a composition close to the original alloy.

Corrosion of the gauzes used in ammonia burners of nitric acid plants has been shown to occur and has been caused by those contaminants which are expected to attack rhodium-platinum alloys, e.g. zinc, sulphur, molybdenum disulphide, and iron compounds. Contaminants also cause blanketing of the

active gauze surface. In the samples examined the principal extraneous contaminant is iron oxide from plant scale or elsewhere.

In plants operating at one atmosphere burner pressure the alloy at the surface of the wire and in the active excrescences tends to become enriched in rhodium by preferential loss of platinum. Although the vapour pressures of platinum and rhodium are very close, Alcock and Hooper (1) have shown that, in a flowing gas stream containing oxygen, metal loss from platinum and from rhodium is via two volatile oxide species, PtO_2 and RhO_2 , and that PtO_2 is more volatile than RhO_2 . Therefore, preferential platinum loss probably is due to formation of the more volatile PtO_2 .

In plants operating with burner pressures of four atmospheres and above there is preferential oxidation of rhodium to a more stable solid oxide, Rh_2O_3 , under these conditions of increased partial pressure of oxygen. This leads to surface blanketing of the wires by solid Rh_2O_3 and, in contrast to gauzes used at one atmosphere burner pressure, also leads to depletion of rhodium in the alloy of the excrescences and of the wire surface.

The prevention of the oxidation of rhodium at higher pressures is not possible while rhodium-platinum gauzes are used. Traditional cleaning methods, while dealing adequately with iron oxides, do not appear to be particularly efficient in the removal of Rh_2O_3 . However, as shown by our own thermogravimetric analyses, since the dissociation temperature of Rh_2O_3 of about 1050°C in air at 1 atm is lowered in nitrogen to about 790°C , heating Rh_2O_3 -contaminated gauzes in nitrogen at high temperature will convert Rh_2O_3 into rhodium, which can then slowly diffuse back into the alloy surface. Reduction to metal may also be done with hydrogen. Insertion of the Rh_2O_3 -covered gauzes into a one atmosphere plant has a similar effect, with slow disappearance of Rh_2O_3 and diffusion of rhodium back into the alloy.

1 C. B. Alcock and G. W. Hooper, *Proc. Roy. Soc. A*, 1960, **254**, 551