

Platinum Catalysts for the Control of Air Pollution

THE ELIMINATION OF ORGANIC FUME BY CATALYTIC COMBUSTION

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A new platinised ceramic honeycomb catalyst has been developed by Matthey Bishop Inc. for the combustion of organic fume. The low pressure drop, attrition resistance and high activity of this catalyst make it especially suitable for a wide range of processes requiring air pollution control. The operating conditions for this catalyst are described and details of a number of applications are given.

An increasing scientific awareness of the long-term effects of air pollution on all forms of life, together with public demands for clean air, have led many industrialised countries to reassess their controls on the emission of both solid and gaseous effluents into the atmosphere.

The United Kingdom was one of the first countries to introduce legislation for the control of emissions from specified industrial processes and the Alkali Act, which was passed over 100 years ago, still exists in a revised form to combat air pollution (1). This legislation, together with the recent Clean Air Act, is mainly concerned with gaseous effluents of a poisonous or corrosive nature and the emission of smoke, grit and dust. For these problems effective control methods now exist.

As a result of detailed investigations of the recurrent Los Angeles smog problem, another group of potentially hazardous air pollutants has been identified. These include nitric oxide, carbon monoxide and a wide range of organic compounds, some of which only become hazardous after undergoing partial oxidation in the atmosphere.

Other organic materials which are emitted into the atmosphere, either directly from

industrial processes or as a result of waste disposal, may create a public nuisance without being a hazard to health. Their unpleasant odour or the irritation they cause to the nose, throat and eyes, even when highly diluted, may give rise to complaints if they are emitted in areas of dense population.

Although the air pollution problems in California are not likely to be repeated in the United Kingdom or Europe there is still a growing need for low cost methods of destroying gaseous organic pollutants.

Control by Direct Combustion

The majority of the pollutants creating the new air pollution problems are combustible. The main products of combustion are carbon dioxide, nitrogen and water.

There are also organic pollutant molecules such as mercaptans and chlorinated hydrocarbons which may be combusted but which then may give rise to an acid fume problem. If they are present in significant concentrations, the exhaust gases from the combustion unit may require further treatment before being released into the atmosphere.

For safety reasons, the concentration of combustible fume in plant air streams does not exceed 25 per cent of the lower explosion



Fig. 1 The successful use of THT platinum catalyst is seen here in a nitric acid plant. The centre stack, fitted with the catalyst system, is free from fume while the other three stacks are emitting nitrogen oxides. These three stacks have since been equipped with THT catalyst units and all are now completely clear

limit and therefore cannot be ignited. The fume concentrations encountered in air pollution problems may range from 1 to 1000 p.p.m. and for combustion to take place, the fume laden air must be raised to the autogenous ignition temperature. This temperature will depend upon the chemical composition of the fume. It is rarely below 500°C and may be as high as 1000°C for complete combustion.

The cost of the fuel required to achieve these temperatures is more often than not prohibitive and in some cases may be higher than the operating cost of the process generating the fume. Therefore, although combustion is an attractive method of destroying organic pollutants because it is continuous and produces no effluent, a means of reducing the reaction temperature is required to make the process more economic.

Control by Catalytic Combustion

The platinum metals, preferably in a finely divided form on a carrier, have for many years been used as catalysts for the

oxidation of carbon monoxide and a wide range of organic molecules in the presence of air or oxygen. Generally the reaction takes place at a much lower temperature than that required by the direct combustion technique and, because it is surface reaction, is less influenced by the concentration of the reactants. For example, a good platinum oxidation catalyst will completely remove most hydrocarbon vapours from an air stream at 225°C whereas the corresponding direct flame combustion temperature would be 450°C , Fig. 2. Thus fuel costs for catalytic combustion are substantially lower than those for direct flame combustion.

Air pollution control by catalytic combustion imposes a number of restrictions on the type of catalyst which may be used. In addition to it being active at low temperatures it must also be stable under both oxidising and reducing conditions. The catalyst when packed into a reactor should have a very low pressure drop across the bed and it should be resistant to attrition, thermal shock and clogging by dust particles.

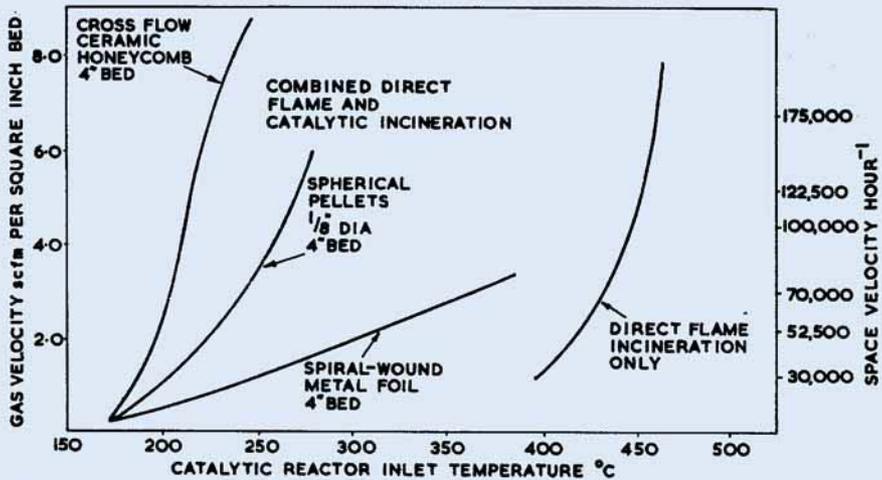


Fig. 2 Curves showing the effect of inlet temperature and gas velocity on the 90 per cent oxidation level of *n*-heptane in air by direct flame and catalytic incineration. Horizontal distances between the curves are temperature differences realisable as fuel savings

Platinum, either alone or in combination with other noble metals, is the preferred catalyst for air pollution control. In the supported form it is more active than the best of the base metal catalysts, it is stable up to at least 750°C and is resistant to poisoning by most elements except lead and phosphorus.

Supported platinum has been used, as have base metal catalysts, in pelleted form but pressure drop problems through the catalyst bed and attrition between the individual

catalyst pellets impose severe limitations on the design of the catalyst reactor.

A number of unique catalyst systems for air pollution control have been designed to overcome these problems and have been widely used in recent years.

Shallow beds or cylindrical cartridges of platinum coated nickel-chromium alloy ribbon were developed largely to overcome the problems of attrition and pressure drop (2). However, the activity of this catalyst is lower than that of platinum supported on

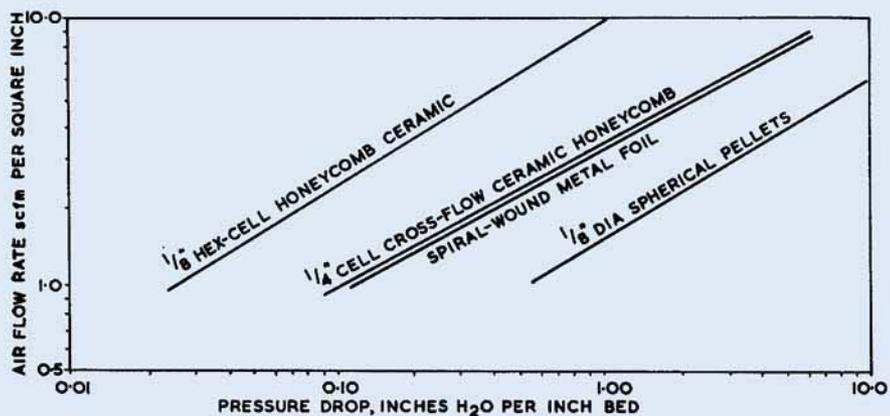
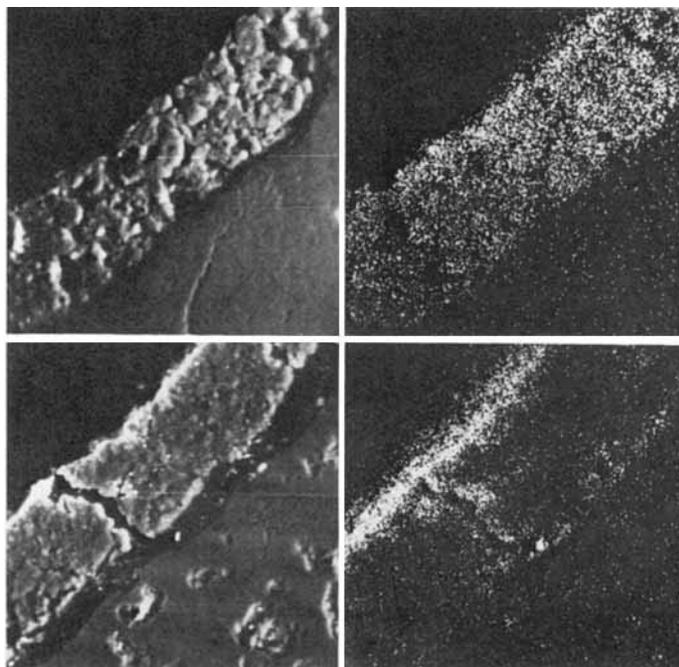


Fig. 3 Logarithmic plots of air flow rate versus pressure drop for catalyst beds of ceramic honeycomb, spiral metal foil and spherical pellets

Fig. 4 Electron image (left) and electron probe pictures (right) of platinum impregnated honeycomb catalysts. The top pictures show the homogeneous distribution of platinum produced by impregnating the support by a conventional technique such as aqueous chloroplatinic acid followed by gas phase reduction in hydrogen. The bottom pictures show the surface distribution of platinum on THT catalyst



alumina pellets probably because the surface area per unit weight of platinum is lower. Figure 2 illustrates these comparisons.

To some extent, the platinum impregnated ceramic rod units developed by Houdry and Cleaver (3) overcame some of the limitations of the ribbon. However, the effective catalytic area per unit volume is lower than the supported pelleted catalyst and the activity at high space velocity is impaired.

Ceramic Honeycomb Supported Platinum Catalysts

The development of ceramic honeycomb materials such as TORVEX*, and improved methods for impregnating them with platinum metals represent a major advance in the use of catalysts for air pollution control. These new catalysts which are more active than previous catalysts also overcome the limitations of the earlier systems and thus make catalytic combustion an attractive means of pollution control, as shown again in Fig. 2.

The thin wall honeycomb structures have a high surface-to-volume ratio and therefore

*Du Pont registered trade name.

make catalysts which are as good or better than pelleted catalysts. However, because of their open structure the pressure drop across a bed is only 1/20 of that across a pellet bed of similar dimensions as shown in Fig. 3. Honeycomb supports also have high thermal shock resistance and structural strength and above all are attrition resistant.

Platinum supported on Torvex has been evaluated for the oxidation of a wide range of organic fumes (4). In this work the activity of the catalyst was compared with platinum on alumina pellets and platinum on nickel-chromium ribbon. Some of these results are shown in Figs. 2 and 3, which are reproduced by permission of Du Pont.

In our development of these new supports into catalysts for air pollution control, a number of important considerations were taken into account. One of these was the need for a single catalyst which would have a high activity for the oxidation of a wide range of organic molecules. It must also be stable in either oxidising or reducing conditions at temperatures up to 750°C. Platinum was therefore chosen as the active metal.



Fig. 5 A NO_x abatement reactor loaded with twelve inch square and triangular THT catalyst modules, which are easily installed or removed for regeneration. A similar system may be used for large fume abatement installations

Catalytic oxidation reactions are usually fast and diffusion-limited and a surface impregnated platinum catalyst is required to give high activity and at the same time minimise the platinum content of the catalyst. To achieve this, a new technique was developed for impregnating the ceramic honeycomb with platinum metals. The effectiveness of the method is shown by the electron probe pictures in Fig. 4.

The resulting catalyst which is designated THT* was developed by Matthey Bishop Inc., and has been sold in America for three years, where it has been used in a wide range of air pollution problems. It is now available in the United Kingdom from Johnson Matthey.

THT catalyst can be made up in modules for easy installation into large plants, as shown for example in Fig. 5. A wide range of shapes and sizes including cylindrical units can also be made to suit the smaller applications where it is necessary to engineer the catalyst into an existing installation.

*A Matthey Bishop registered trade name.

Unlike a pellet catalyst bed which must be vertical with downward gas flow, there is no restriction on either the position of THT catalyst or the direction of the gas flow through the reactor.

Operating Conditions for THT Catalyst

The applications for THT catalyst are wide and varied and it is therefore not practical to lay down fixed operating conditions. Three critical parameters determine the amount of catalyst and the type of plant required for fume abatement.

The Volume of Gas to be Treated

In a catalytic abatement system, the oxidation reaction takes place on the surface of the catalyst. The adsorption of the reactants, their reaction on the surface and the desorption of the products takes a finite time. To achieve the required degree of conversion, the polluted gas stream must be in contact with the catalyst long enough for these reactions to occur. For most applica-

tions, a space velocity of 100,000 hr⁻¹ is used and this determines the volume of catalyst required.

After fixing the volume of catalyst required by considering the volume of gas to be treated, the dimensions of the catalyst bed are determined by the maximum pressure drop permitted in the installation. The pressure drop is proportional to bed depth and is related to the gas flow per unit area of the catalyst bed as shown in Fig. 3.

The Composition of the Gas Stream

Most catalytic oxidation reactions require a minimum temperature for any significant reaction to occur. This is generally expressed as the ignition temperature. This is set by the chemical composition of the combustibles present in the polluted air and also by the activity of the catalyst. The ignition temperatures on THT catalyst for a wide range of molecules often encountered in polluted air are given in Table 1. Fume with components similar in chemical composition to those in the table will have similar ignition temperatures, although an increase in molecular weight will result in a decrease in the temperature.

The temperature required for high conversion of a fume depends on the ignition temperature, the space velocity and the type of catalyst. On THT catalyst, the temperature required for conversions higher than 90 per cent is usually 50 to 100°C higher than the ignition temperature. Typical results are given in Table 1.

A knowledge of the composition of a fume can therefore be used to determine the inlet temperature required to THT catalyst to give the required conversion. When the fume is complex, it is usual for this temperature to be determined in the laboratory or with an "on site" pilot plant.

The concentration of organic compounds in the fume is also important. In most cases, the concentration does not significantly affect the ignition temperature. A notable exception, however, is methane. The concentration of the fume and its composition

Table 1
Ignition Temperatures on THT Catalyst for Molecules Encountered in Polluted Air

	Ignition temperature °C	Inlet temperature for 90% conversion °C
Hydrogen	20	20
Carbon monoxide	150	150-200
Benzene	180	250-300
Toluene	170	250-300
Xylene	200	250-300
Alpha pinene	190	250-300
Mesityl oxide	180	250-300
Ethanol	160	250-300
n heptane	160	250-300
Methyl isobutyl ketone	175	300-350
Methyl ethyl ketone	175	300-350
Dimethylformamide	200	350-400
Ethyl acetate	275	400-450
Methane (air)	300	400-450
Methane (3% O ₂ /N ₂)	400	450-500
Thiophen	335	400-450
Pyridine	407	400-450
Chlorobutane	425	450-500
Hydrogen sulphide	400	400-425
Carbon disulphide	350	375-400

does, however, determine the amount of oxygen that will be consumed and the temperature rise that will occur on the catalyst. This may be calculated and used in the design of the abatement plant. Where it is significant, the heat generated may be used to sustain the oxidation or recycled to maintain the temperature of the process gas.

The Temperature of the Gas Stream

The temperature of the gas stream containing the fume to a large extent determines the design of the plant required for pollution control. When the temperature is above that required for ignition, the catalyst may be placed directly in the gas stream. Examples of this use are wire-enamelling ovens, some paint-drying ovens, self-cleaning cookers and diesel or internal combustion engine exhaust systems.

More often than not, the temperature of the polluted air is lower than the ignition temperature and an additional heater or a separate fume abatement plant is required. This usually consists of a preheat burner, a catalyst chamber and a heat exchanger. The burner may be gas or liquid fuel fired or a primary heat exchanger with high pressure steam may be used. The efficiency of the secondary heat exchanger used to recoup the heat from the clean exhaust gases will depend upon economic considerations and the inlet and exhaust temperatures of the gas stream. Up to 50 per cent efficiency is usually possible on a catalytic combustion system.

Some Applications of THT Catalyst for Air Pollution Control

Air pollution problems in industry arise from a wide variety of processes and require the treatment of polluted air ranging from 100,000 up to 4,000,000 SCFH. With THT catalyst modules there is no real limit either high or low on the size of an installation. A list of processes for which THT catalyst might be used for air pollution control is given in Table 2.

NOX Abatement

A major source of air pollution is the nitrogen oxide mixture (NOX) which is discharged into the atmosphere as a tail gas from nitric acid plants. This tail gas, which on a large modern installation may be 2,000,000 SCFH is mainly nitrogen with about 3 per cent oxygen and between 0.1 and 0.3 per cent NOX by volume.

Without some form of abatement system the tail gas plume is an intense reddish brown due to the nitrogen dioxide content of the gas. This in itself may be a public nuisance, but in addition the fume is acidic and it may also be a danger to life.

The nitrogen oxides cannot be oxidised but they can be reduced catalytically to nitrogen and water by adding a reducing agent to the tail gas. The reducing agents which are normally used are hydrogen (as

purge gas), light naphtha and methane (as natural gas). The use of THT catalyst for this reaction was described in an earlier article in this journal (5).

In the United Kingdom and Europe natural gas, when it is available, is the cheapest of the three reducing agents and is therefore preferred. Unfortunately, some or all of the oxygen must be removed from the tail gas depending upon the degree of abatement required and the ignition temperature for the reaction between methane and oxygen is much higher than that of the other reducing agents.

With THT catalyst, the minimum inlet temperature required to the catalyst for total abatement using the three most readily available fuels are:

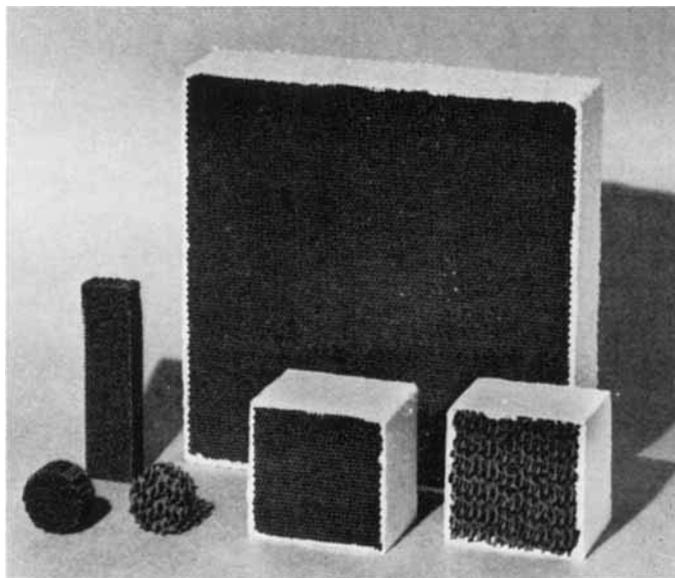
Purge gas (hydrogen)	100°C
Light naphtha (C ₆ -C ₈ hydrocarbons)	250°C
Natural gas (methane)	475°C

THT catalyst has now been in successful operation in eight plants for periods ranging

Table II
Processes for which THT Catalyst may be used for Air Pollution Control

Wire and strip enamelling
Paint baking ovens
Processing, drying and curing of phenol
Formaldehyde and cellulose varnishes
Manufacture of liquid golds
Production of paper pulp
Manufacture of fibre glass
Manufacture of phthalic and maleic anhydride, ethylene oxide
Paper coating
Printing including transfer manufacture
Solvent cleaning and storage
Carbon and graphite baking ovens
Production of man-made fibres
Manufacture of tungsten filaments
Core baking in foundry work
Nitric acid
Oil refining and petrochemicals
Processing of animal carcasses
Fish meal processing
Fat rendering
Processing of cereals, potato crisps and fish frying
Feather burning
Tobacco drying

Fig. 6 Some THT catalyst modules which have been used for air pollution control. The applications include NOX abatement, diesel exhaust purification, electric incinerators and self-cleaning cookers



from 8 months to 2½ years. Some are being used for decolourisation and others for total abatement. In all of these plants, including those using natural gas, the drop in catalyst activity with operating time has not been significant.

As most systems in the United Kingdom and Europe will be total abatement units using natural gas, an improved THT catalyst is under development for this application. It will require a much lower inlet temperature than that required on existing catalysts and this will enable a single bed of catalyst to be used, thus reducing the catalyst cost and also increasing the fuel efficiency.

Fume Elimination from Paint Baking Ovens

Car bodies and also many other industrial and domestic items which have a paint spray finish are dried in continuous baking ovens. To maintain the solvent vapour concentration in the oven at not more than 25 per cent of the lower explosion limit some of the contaminated air is exhausted into the atmosphere. Fresh make-up air, after preheat is added to the oven to maintain the flow. On large ovens, such as those used in the motor industry, 2,000,000 SCFH of air containing up to 0.1 per cent by volume of hydro-

carbons may be exhausted into the atmosphere.

THT crossflow catalyst has been used to control this problem and may be placed directly into the oven system when the oven temperature is above the ignition temperature which in this case is 350°C. The catalyst may also be used in a fume abatement system attached to the exhaust stacks when the oven temperature is lower than the ignition temperature. In both cases, the use of the catalyst for pollution control also gives a net saving in the amount of fuel required to maintain the oven temperature.

Fume Elimination from Enamel and Varnish Manufacture

Many enamels and varnishes are prepared by heating a mixture of natural resins. During the reaction, which is usually carried out in an open boiler, unpleasant odours are given off. THT catalyst has been evaluated for the removal of these odours and has been found satisfactory with inlet temperatures of 250°C. A conventional catalytic fume abatement unit with a gas fired burner would be used.

Fume Elimination from Polyurethane Cutting

Many synthetic polymeric materials when heated to their decomposition temperature

either for cutting and forming or for disposal emit unpleasant odours. THT catalyst has been evaluated for the removal of the fume produced by the hot wire forming of polyurethane foam. The inlet temperature to the catalyst for complete odour removal is 350°C.

Smoke and Odour Removal from the Exhaust of Self-cleaning Cookers

By incorporating additional heating elements into the oven of a domestic cooker, the temperature of the oven walls may be raised above that required to burn off the cooking residues. The carbon monoxide and partially oxidised hydrocarbon residues if emitted into the kitchen without treatment would be unpleasant. THT catalyst placed in the oven exhaust duct will remove the carbon monoxide at 150°C but the temperature must be increased to 300 to 350°C to eliminate the odour.

Internal Combustion and Diesel Engine Exhaust Purification

One of the most widespread and potentially one of the most serious air pollution problems is that occurring in areas of high traffic density. The fume emitted by both diesel and

internal combustion engines contains carbon monoxide, nitrogen oxides and unburnt hydrocarbons.

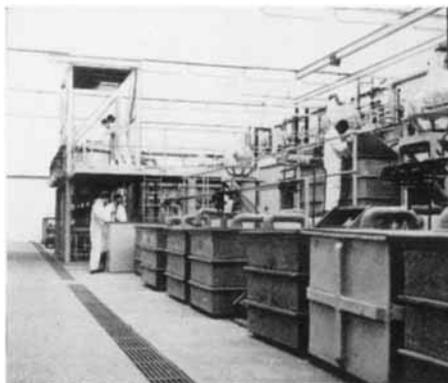
Already, exhaust units using THT catalyst are installed on diesel engines operating in mines and enclosed areas. The catalyst may also be used on internal combustion engines using non leaded fuel. At exhaust temperatures above 150°C, that is at all engine conditions except slow idling, the catalyst will remove between 80 and 90 per cent of carbon monoxide and unburnt hydrocarbons from the exhaust gases without increasing the concentration of the nitrogen oxides when excess oxygen is present. Under reducing conditions, i.e., when there is an excess of CO and hydrocarbons over oxygen in the exhaust gas the catalyst will reduce the concentration of nitrogen oxides.

References

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- 2 D. P. Thornton, *Platinum Metals Rev.*, 1963, 7, 82
- 3 British Patent No. 954,504
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New Platinum Refinery in South Africa

The new Johnson Matthey platinum refinery at Wadeville was opened officially in October 1969. Previously the entire output of partially refined material treated by Matte Smelters (Pty) Ltd at Rustenburg had been sent to England for final refining. A proportion of this material will now be processed at Wadeville to produce pure platinum group metals and compounds ready for marketing. The new refinery, in which Rustenburg Platinum Mines is a partner, is part of the implementation of the joint policy of Rustenburg and Johnson Matthey to assure industry throughout the world of adequate and continuing supplies of platinum metals. Rustenburg Platinum



Mines, the world's largest producer, currently produces 850,000 ounces troy of platinum per year and has an expansion programme to provide 1,000,000 ounces per year in 1970 and to increase capacity to 1,200,000 ounces per year by 1973.