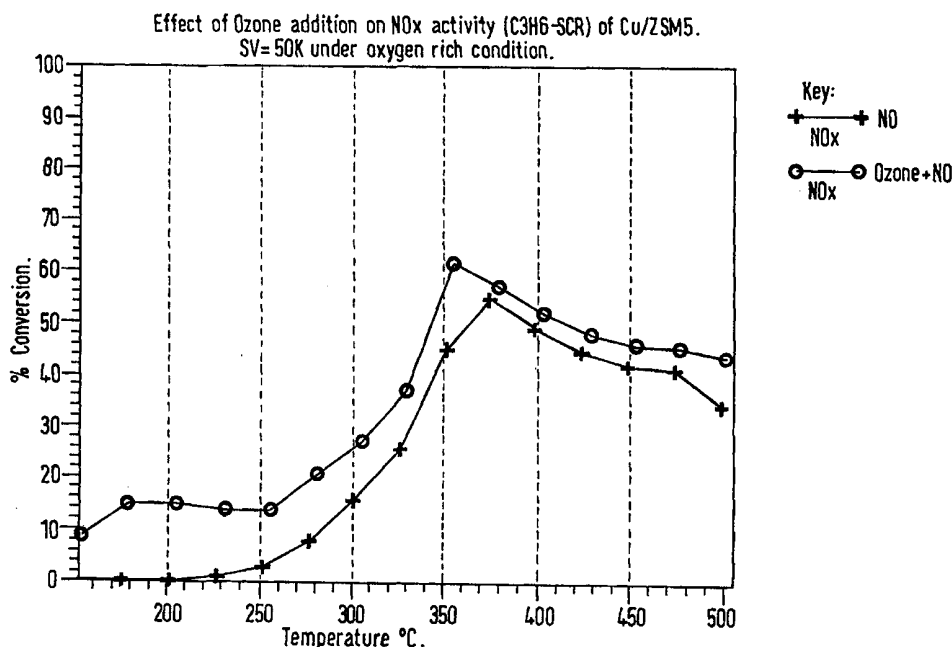




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01D 53/56, F01N 3/20, 3/08, 3/02		A1	(11) International Publication Number: WO 99/36162
			(43) International Publication Date: 22 July 1999 (22.07.99)
(21) International Application Number: PCT/GB99/00090 (22) International Filing Date: 12 January 1999 (12.01.99) (30) Priority Data: 9801023.4 19 January 1998 (19.01.98) GB (71) Applicant (for all designated States except US): JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): CHANDLER, Guy, Richard [GB/GB]; 30 Harlton Road, Little Eversden, Cambridge CB3 7HB (GB). DIWELL, Alan, Francis [GB/GB]; Newhaven, Blounts Court Road, Sonning Common RG4 9RS (GB). RAJARAM, Raj, Rao [MU/GB]; 34 Buckland Avenue, Slough SL3 7PH (GB). (74) Agent: WISHART, Ian, Carmichael; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report.	

(54) Title: COMBATTING AIR POLLUTION



(57) Abstract

In the control of pollutants such as NO_x in the exhaust gases from internal combustion engines, ozone is reacted with NO to form NO₂, which is then reduced catalytically to N₂, by reacting NO₂ with ammonia. The NO₂ produced can react with the particulates of Diesel engine to exhaust gas to regenerate a particulate filter.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

COMBATTING AIR POLLUTION

This invention relates to a method of combatting air pollution from the exhaust gas of an internal combustion engine, and to an internal combustion engine whose exhaust
5 apparatus contains means therefor.

One of the pollutants in the exhaust gas of an internal combustion engine is NO_x (oxides of nitrogen). NO_x is produced by the thermal fixation of nitrogen in the combustion air, leading to thermal NO_x, or by the conversion of chemically bound nitrogen in the fuel,
10 leading to fuel NO_x. The most abundant nitrogen species in an engine exhaust stream is NO, with low amounts of NO₂ and N₂O. For example, the nitrogen oxide species in the exhaust stream of a typical diesel passenger car are about 95% NO, 4% NO₂ and a little N₂O.

15 Although nitrogen monoxide (NO) is the most abundant nitrogen species in an engine exhaust stream, various processes for the treatment of the exhaust gas proceed more rapidly when the NO_x species is NO₂ rather than NO. For example, European patent specification 341832A discloses that in the regeneration of a diesel particulate trap at low temperature, NO₂ is a more effective oxidant than NO or O₂. Again, to combat NO_x
20 emissions from lean-burn engines, it has been proposed to adsorb NO_x by an adsorbent when the exhaust gas is lean (*ie* when there is a stoichiometric excess of oxygen) and release the adsorbed NO₂ when the exhaust gas is rich, the exhaust gas being periodically made rich to release the adsorbed NO_x; during the lean operation, NO is oxidised to NO₂ which can then readily react with adsorbent surface to form nitrate - see for instance European patent
25 specification 560991A. Yet again, in other strategies to combat NO_x emissions from lean-burn engines, such as selective catalytic reduction (SCR), there are indications that the presence of NO₂ may be beneficial, see for instance Applied Catalysis B: Environmental, 2 (1993) 81-100, Elsevier Science Publishers BV and Journal of Catalysis 171, 27-44 (1997), Academic Press.

30

It would be desirable to be able to oxidise NO to NO₂ in engine exhaust gas at a lower temperature, for instance because the engine is operating at a lower temperature or

while the exhaust apparatus is warming up after the engine has been started at ambient temperature.

In addition, it would be desirable to oxidise NO to NO₂ in engine exhaust gas while not oxidising SO₂ to SO₃. Fuels such as petrol (gasoline) or diesel contain small quantities of organo-sulphur compounds, *eg* thiophene. In the engine operation, these compounds are oxidised to SO₂. If the SO₂ is oxidised to SO₃, the SO₃ can readily react to form sulphuric acid or sulphate, which is undesirable. For instance, in diesel engines a small fraction of the SO₂, typically about 2%, is further oxidised to SO₃, which condenses with water in the exhaust gas as sulphuric acid, which is then adsorbed on carbonaceous particulates, hence increasing the mass of particulates. Increasing the amount of SO₃ is thus undesirable. Again, in the technique of NO_x adsorption discussed above, SO₃ readily adsorbs on the NO_x adsorbent to form base metal sulphate, which, since metal sulphates are generally much more stable than nitrates, deactivates the adsorbent and requires high temperature regeneration of it. Yet again, in the SCR technique discussed above, SO₃ can react with reductant ammonia to form ammonium sulphate, which can poison the catalyst.

Catalysts which are active in the oxidation of NO to NO₂ are also very active in the oxidation of SO₂ to SO₃. The most effective, and most commonly used, catalyst for oxidising NO to NO₂ is based on Pt, see for instance European specifications 560991A and 341832A cited above. Pt, however, is very active in the oxidation of SO₂ to SO₃, as shown in the accompanying Figure 1, which is a graph showing % conversion of NO or SO₂ by oxygen on a 2% by weight platinum on alumina catalyst plotted against temperature. The graph shows also that the conversion of NO to NO₂ at low temperature (*eg* below 250°C) is very low.

Furthermore, the oxidation of NO to NO₂ must be practicable in the environment of an engine exhaust gas. Although many catalysts, *eg* Cu, Co or Mn, oxidise NO to NO₂, many are not sufficiently active in an engine exhaust gas or are readily deactivated in this environment. Even Pt catalyst is inhibited by hydrocarbon and SO₂ in this reaction.

The present invention provides a method of combatting air pollution from an internal combustion engine whose exhaust gas contains NO, which method comprises contacting the exhaust gas containing NO with ozone to react the NO with the ozone to produce NO₂ and reducing the NO₂ to nitrogen.

5

The invention provides also an internal combustion engine whose exhaust apparatus contains means to contact exhaust gas containing NO with ozone to react the NO with the ozone to produce NO₂ and means to reduce the NO₂ to nitrogen.

10 International patent application publication WO 97/22794 refers to an apparatus for reducing pollutants from the combustion of a fuel, the apparatus comprising:

a combustion chamber having a pre-combustion gas stream to the combustion chamber and a post-combustion gas stream of exhaust from the combustion chamber;

15 a catalytic converter for treating the exhaust to reduce the amount of at least one pollutant from at least one of incomplete combustion of the fuel and oxides of nitrogen; and

a device for adding ozone to at least one of the pre-combustion gas stream and the post-combustion gas stream to thereby further reduce the amount of at least one pollutant in the exhaust treated by the catalytic converter.

20 There is no mention of reacting ozone with NO in the exhaust gas to produce NO₂. Indeed, while one can see that enhancing the oxidation of hydrocarbon or carbon monoxide in the exhaust gas might be beneficial, it is not apparent why one would wish to choose conditions so that NO in the exhaust gas is oxidised to NO₂ for treatment with a catalytic converter.

25 It can be seen that the present invention does not rely on the use of a catalyst to oxidise the NO. Instead, the oxidation is achieved by use of a particular oxidant, ozone. We have demonstrated that ozone reacts with the NO to produce NO₂ even at low temperature. In addition, we have shown that at low temperature ozone is an excellent selective oxidant, *ie* it converts all or much NO to NO₂ while converting no or little SO₂ to SO₃.

30 The internal combustion engine is usually in a vehicle. The engine is especially a lean-burn engine. The engine can be a diesel or petrol engine.

In the present invention, the ozone is usually injected into the exhaust gas containing NO. Accordingly, the engine usually includes injection means to inject the ozone into the exhaust gas containing NO.

5 The engine usually includes an ozone generator to generate the ozone. The ozone can be generated in ways known in themselves. For instance, the ozone generator can be a corona discharge tube through which passes air between two electrodes which are kept at a large potential difference. Alternatively, the ozone generator can be a high energy lamp to ionise oxygen in air to ozone.

10

Generally, at least 80% and preferably 100%, of the NO in the exhaust gas contacting the ozone is reacted with the ozone to produce NO₂. Sufficient ozone must be employed to carry out the required degree of conversion of the NO. The conversion is $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$. Generally, the exhaust gas containing NO is contacted with at least 80%, preferably
15 at least 100%, of the amount of ozone required to react stoichiometrically with the NO to produce NO₂. The amount of ozone is usually 0.04 - 0.16% by volume of the exhaust gas with which it is contacted. The ozone generator is chosen accordingly. As an example, it has been found that for an exhaust gas flow rate of 7,500 litres per hour, containing 400ppm NO, complete conversion to NO₂ can be achieved if 1 litre of air per minute is fed to an
20 ozone generator (Thermo Electron) operating at 60% capacity; if the operation is reduced to below 40% of capacity or the air flow is reduced below 250ml per minute, the conversion efficiency decreases significantly.

Any ozone in excess over that used in forming the NO₂ can be destroyed over a
25 catalyst. However, excess ozone can be employed advantageously to promote the oxidation of hydrocarbon in the exhaust gas, especially at lower temperature.

The NO₂ produced in the present invention can be employed in the exhaust gas in ways known in themselves, in particular in the control of particulate emissions from a diesel
30 engine or NO_x emission in oxygen-rich conditions.

In a preferred embodiment, the engine is a lean-burn, *eg* diesel, engine and NO₂ produced is adsorbed by an adsorbent which adsorbs the NO₂ when the exhaust gas is lean and releases the adsorbed NO₂ when the exhaust gas is rich, and the exhaust gas is periodically made rich to release the adsorbed NO₂. Accordingly, the engine can be a lean-burn engine and include means to adsorb NO₂ produced when the exhaust gas is lean and release the adsorbed NO₂ when the exhaust gas is rich and means to make the exhaust gas rich periodically to release the adsorbed NO₂. This use of the NO₂ produced can be as known in itself, see for instance the European specification 560991A cited above, whose contents are incorporated herein by reference. The adsorbent usually comprises at least one oxide selected from those of alkali metals (*eg* potassium, sodium, lithium and cesium), alkaline earth metals (*eg* barium, calcium, strontium and magnesium) and rare earth metals (*eg* lanthanum, yttrium and cerium). These oxides are capable of reacting with NO₂ or SO₃ to form the corresponding nitrate or sulphate respectively, but their reaction with NO or SO₂ is very low. The advantage of the present invention in its ability to selectively oxidise the NO is clear. This advantage is apparent compared to the known use of Pt with such adsorbent to oxidise NO to NO₂. In the present invention, such adsorbent can be used advantageously with a catalyst, such as Pd or Rh, which does not oxidise NO or SO₂ but which catalyses other reactions desired in such adsorbent technique. Such other reactions are the reductive release of the NO₂ or reactions to oxidise CO and hydrocarbon contained in the exhaust gas. In a preferred embodiment, the adsorbent includes such catalyst, for instance the adsorbent can be Pd-Ba-Al₂O₃.

In a preferred embodiment, the NO₂ produced is reduced to nitrogen by reaction with gaseous reductant, usually over a catalyst.

In a preferred embodiment, the engine is a lean-burn, *eg* diesel, engine and NO₂ produced is selectively catalytically reduced to nitrogen. Accordingly, the engine can be a lean-burn engine and the means to reduce the NO₂ to nitrogen comprise a SCR catalyst. This use of the NO₂ produced can be as known in itself, see for instance the Applied Catalysis and Journal of Catalysis papers cited above, whose contents are incorporated herein by reference. A preferred SCR catalyst comprises a zeolite, especially ZSM5,

carrying metal, particularly copper. A high conversion efficiency of NO_x to nitrogen can be achieved when the exhaust gas contains a specific NO:NO₂ ratio. Such ratio can be achieved, for instance over a Cu/ZSM5 catalyst, by means of the present invention, *eg* by injecting ozone into the exhaust stream to increase the NO₂ concentration. In this way, significant improvement in the low temperature removal of NO_x can be obtained. Thus, the engine can include means to introduce reductant into the exhaust gas to selectively reduce NO₂ to nitrogen. Advantageously, the NO₂ is reacted with ammonia to selectively catalytically reduce the NO₂ to nitrogen. The engine can include a source of the reductant ammonia. Alternatively, the reductant can be hydrocarbon, *eg* propene. It has been found that while the presence of ozone improves the SCR of NO_x by ammonia at low temperature (for instance below 250°C), it can mar the conversion at higher temperatures, most probably because the stoichiometry required to achieve 100% conversion for the NO₂:NH₃ reaction is higher than that for the NO:NH₃ reaction. In such circumstance, it is advantageous to stop the reaction with ozone when the higher temperatures are reached. It has been found, however, that when the reductant is hydrocarbon, the presence of ozone can enhance the conversion of the NO_x over the entire temperature window.

In a further preferred embodiment, the engine is a diesel engine, and NO₂ produced reacts with particulates from the exhaust gas which have been deposited on a filter, to oxidise and hence remove them. Accordingly, the engine can be a diesel engine and the means to reduce the NO₂ to nitrogen comprise a particulate filter on which particulates from the exhaust gas are deposited, which particulates are reacted with NO₂ to oxidise and hence remove them. This use of the NO₂ produced can be as known in itself, see for instance the European specification 341832A cited above, whose contents are incorporated herein by reference. That European specification describes the use of NO₂ as an oxidant to combust diesel particulate deposited on a filter disposed in a diesel exhaust system. The filter can contain a catalyst which facilitates particulate combustion; the filter catalyst can comprise a base metal, for instance a combination of lanthanum, cesium and vanadium pentoxide. Soot or like carbonaceous particulate is combusted at a temperature usually less than 400°C, generally at a temperature of the order of 250-400°C. The most active catalysts for low temperature NO oxidation and therefore for combusting the diesel particulate, however, are

also high sulphate producers. In such a system, generating the NO_2 instead by means of the present invention is clearly advantageous. It has been found that when ozone is pre-mixed with NO to generate the NO_2 , the oxidation of diesel soot is initiated at much lower temperature than when oxygen is pre-mixed with NO. Ozone itself can be used to oxidise particulates from diesel exhaust gas which have been deposited on a filter, and hence remove them. However, ozone is highly unstable; it readily decomposes on contact with various surfaces, for instance stainless steel pipe. Reacting the ozone with NO to produce NO_2 in the present invention is advantageous for stability. Any ozone in excess over that used in forming the NO_2 , though, can be used to promote particulate oxidation.

In the present invention, the NO is advantageously reacted with the ozone at a temperature from ambient temperature to 250°C , for instance from ambient temperature to 200°C . The engine can be adapted accordingly.

Advantage is also apparent when the exhaust gas contains SO_2 , for instance 2-200 parts per million (ppm) by volume of SO_2 . In a preferred embodiment, the exhaust gas contacting the ozone contains this amount of SO_2 .

The NO is advantageously reacted with ozone in the absence of platinum. Hence, means in the engine to react the NO with the ozone advantageously does not contain platinum.

The present invention is advantageous even when the exhaust gas contacting the ozone has a relatively large gas hourly space velocity such as is employed in vehicles. The exhaust gas contacting the oxone preferably has a gas hourly space velocity of 30,000 to 50,000.

The present invention is advantageous even when the exhaust gas contacting the ozone contains water vapour. The exhaust gas contacting the oxone preferably contains 4-10% by volume water vapour.

The invention is illustrated by the accompanying drawings, which are graphs and in which:

Figure 1 shows % conversion of NO and SO₂ by oxygen on a Pt catalyst against temperature;

5 Figure 2 shows % conversion of NO and SO₂ by ozone without a catalyst against temperature;

Figure 3 shows CO₂ evolved from soot by NO-O₂ or NO-O₃ against temperature;

Figure 4 shows % soot burnt off at 300°C by NO-O₂ or NO-O₃ against time (minutes);

10 Figure 5 shows the ppm of NO_x left in gas on contact with Ba-Al₂O₃ or Pt/Ba-Al₂O₃ catalyst at 150°C against time (minutes);

Figure 6 shows in arbitrary units the SO₂ concentration left in the gas phase on contact with the same catalyst at 650°C against time (minutes);

15 Figure 7 shows the ppm of NO_x left in gas on contact with Ba-Al₂O₃ catalyst at 150°C when ozone is injected into the gas against time (minutes);

Figure 8 shows the % conversion of NO_x by SCR by ammonia at a space velocity of 50,000 per hour with and without ozone addition against temperature;

Figure 9 shows the corresponding conversion with ozone addition which is stopped after the peak at 200°C;

20 Figure 10 shows the % conversion of NO_x by SCR by C₃H₆ at a space velocity of 50,000 per hour with and without ozone addition against temperature; and

Figure 11 shows the % conversion of C₃H₆ in SCR at a space velocity of 50,000 per hour with and without ozone addition against temperature.

25 Figure 1 is discussed further above. The other Figures are discussed further below.

The invention is illustrated also by the following Examples, in which the ozone generator was a Thermo Electron ozone generator.

EXAMPLE 1**Selective Oxidation of NO to NO₂**

The effect of ozone on the oxidation of NO and SO₂ was studied by injecting ozone,
5 produced by passing air at a flow rate of 40ml per minute through an ozone generator, into
a mixture containing 400ppm NO, 50ppm SO₂, 4.5% H₂O, 4.5% CO₂, 0.5% CO and
400ppm C₃H₆, the balance being nitrogen at a flow rate of 5 litres per minute. The NO and
SO₂ conversion is shown in Figure 2. The complete oxidation of NO to NO₂ is apparent at
10 temperatures of 50°C to 200°C. Above that temperature, the conversion decreases, mostly
due to the decomposition of the ozone, and at high temperature to the thermodynamic
instability of NO₂. The oxidation of SO₂ to SO₃ began at 250°C and was then low,
indicating the selectivity of ozone in oxidising NO and not SO₂.

EXAMPLE 2**15 Effect of O₃-NO Mixture on Diesel Particulate Oxidation**

This Example shows that when ozone is pre-mixed with NO to generate NO₂, the
oxidation of diesel soot is initiated at much lower temperature than when NO is pre-mixed
with O₂. The effect was demonstrated in a temperature programmed oxidation experiment
20 in which a gas containing NO (400ppm), SO₂ (50ppm), O₂ (5%) and H₂O (4.5%) with the
balance nitrogen at a flow rate of 5 litres per minute was mixed with O₃ produced by passing
air at a flow rate of 40ml per minute through an ozone generator and the mixture passed over
1g of diesel soot particulate, collected on a filter from a diesel engine exhaust, contained in
a reactor in a furnace which was ramped at 10°C per minute. Figure 3 shows the rate of
25 CO₂ production formed by the particulate oxidation as a function of temperature. Figure 4
shows the fraction of soot burned as a function of time at 300°C when either NO and O₂ or
NO and ozone are used as the oxidant. It can be seen that the mixture of NO and O₃ is
active at lower temperature, and can achieve complete soot oxidation.

EXAMPLE 3**Effect of O₃-NO Mixture on NO_x Storage**

A proposal being considered to decrease NO_x emission in high oxygen-containing exhaust gas is to incorporate an adsorbent material into the catalyst system, together with a catalytic element capable of oxidising nitric oxide to NO₂. The NO₂ is then taken up by the adsorbent to form a nitrate. If the exhaust gas is then switched to reducing condition for a very short period, the surface complex nitrate becomes unstable and releases oxygen and NO₂ which can be reduced. The first step is the oxidation of NO to NO₂ and platinum is an important component of that system. However, Pt also catalyses the oxidation of SO₂ to SO₃ which can interact with the adsorbent.

Figure 5 shows the NO_x adsorption on Ba-Al₂O₃ and Pt/Ba-Al₂O₃ from a gas mixture containing 250ppm NO, 8% O₂ with the balance nitrogen by flowing 2 litres per minute of gas over 0.4g of catalyst at 150°C. It is clear that in the presence of Pt, significant amounts of the NO_x are being stored on the catalyst.

Figure 6 shows the SO₂ breakthrough from a mixture of 50ppm and 8% O₂ with the balance nitrogen on the same catalysts at similar mass hourly space velocity at 650°C. Similar to the NO_x adsorption, in the absence of Pt the SO₂ is not converted or adsorbed over the catalyst. The presence of Pt enhances these processes. In these adsorbent systems, the ability to selectively generate NO₂ instead of SO₃ would be important to decrease catalyst deactivation. Example 1 above demonstrates that ozone can selectively oxidise NO to NO₂ and is not reactive to SO₂.

Figure 7 demonstrates that the NO₂ generated by the interaction of NO with ozone can readily be adsorbed on the storage material at low temperature (150°C). The Figure shows the effect of injecting ozone produced from an ozoniser to a mixture of 250ppm NO, 8% O₂ with the balance nitrogen at 150°C on the storage activity of Ba-Al₂O₃. The NO_x absorption is significantly enhanced with the injection of ozone.

EXAMPLE 4**Promotion of the Selective Catalytic Reduction of NO_x by NH₃**

The effect of injecting ozone to a reactive mixture (200ppm NO, 200ppm NH₃,
5 12% O₂, 4.5% CO₂, 200ppm CO, 4.5% H₂O, 20ppm SO₂ with the balance nitrogen on the
NO_x reduction activity of Cu/ZSM5 is shown in Figure 8. The addition of ozone
significantly improves the reduction of the NO_x by NH₃ at temperatures below 200°C,
through the formation of the more active NO₂ species. However, in the presence of ozone,
the NO_x conversion decreases at higher temperature, because most probably the
10 stoichiometry required to achieve 100% conversion for the NO₂:NH₃ reaction is higher than
that for NO:NH₃ reaction. However, if the ozoniser is switched off after the first peak
conversion at 200°C, the high temperature conversion profile improves - Figure 9. This
ability to generate NO₂ when required is highly desirable for SCR utility.

15

EXAMPLE 5**Promotion of the Selective Catalytic Reduction of NO_x by C₃H₆**

The selective reduction of NO_x by hydrocarbon in an oxidising environment on
Cu/ZSM5 catalyst is believed to occur by a dual function mechanism, with the acid sites
20 promoting coke formation and the Cu sites catalysing NO₂ formation. The reaction of the
NO₂ with the carbonaceous species is believed to lead to the reduction of NO_x to nitrogen.
It has been shown that if NO₂ is present, the reactivity of the Cu/ZSM5 catalyst for the
selective reduction of NO_x by C₃H₆ can be improved at low temperature. The effect of
injecting ozone to a reactive mixture (200ppm NO, 400ppm C₃H₆, 12% O₂, 4.5% CO₂,
25 200ppm CO, 4.5% H₂O, 20ppm SO₂ with the balance nitrogen) on the reduction activity
over Cu/ZSM5 is shown in Figure 10. Figure 11 shows that the addition of ozone catalyses
the hydrocarbon oxidation at a lower temperature.

CLAIMS

1. A method of combatting air pollution from an internal combustion engine whose exhaust gas contains NO, which method comprises contacting the exhaust gas containing
5 NO with ozone to react the NO with the ozone to produce NO₂ and reducing the NO₂ to nitrogen.
2. A method according to claim 1 wherein the ozone is injected into the exhaust gas containing NO.
10
3. A method according to claim 1 or 2 wherein at least 80% of the NO in the exhaust gas contacting the ozone is reacted with the ozone to produce NO₂.
4. A method according to any one of claims 1-3 wherein the engine is a lean-burn
15 engine, and NO₂ produced is adsorbed by an adsorbent which adsorbs the NO₂ when the exhaust gas is lean and releases the adsorbed NO₂ when the exhaust gas is rich, and the exhaust gas is periodically made rich to release the adsorbed NO₂.
5. A method according to any one of the preceding claims wherein the engine is a lean-
20 burn engine, and NO₂ produced is selectively catalytically reduced to nitrogen.
6. A method according to claim 5 wherein the NO₂ is reacted with ammonia to selectively catalytically reduce the NO₂ to nitrogen.
- 25 7. A method according to any one of claims 1-3 wherein the engine is a diesel engine, and NO₂ produced reacts with particulates from the exhaust gas which have been deposited on a filter, to oxidise and hence remove them.
8. A method according to any one of the preceding claims wherein the NO is reacted
30 with the ozone at a temperature of from ambient temperature to 200°C.

9. A method according to any one of the preceding claims wherein the exhaust gas contacting the ozone contains 2-200 parts per million by volume of SO₂.
10. A method according to any one of the preceding claims wherein the NO is reacted with the ozone in the absence of platinum.
11. An internal combustion engine whose exhaust apparatus contains means to contact exhaust gas containing NO with ozone to react the NO with the ozone to produce NO₂ and means to reduce the NO₂ to nitrogen.
12. An engine according to claim 11 which includes injection means to inject the ozone into the exhaust gas containing NO.
13. An engine according to claim 11 or 12 which includes an ozone generator to generate the ozone.
14. An engine according to any one of claims 11-13 which is a lean-burn engine and includes means to adsorb NO₂ produced when the exhaust gas is lean and release the adsorbed NO₂ when the exhaust gas is rich and means to make the exhaust gas rich periodically to release the adsorbed NO₂.
15. An engine according to any one of claims 11-14 which is a lean-burn engine and the means to reduce the NO₂ to nitrogen comprises a selective catalytic reduction catalyst.
16. An engine according to claim 15 which includes means to introduce reductant into the exhaust gas to selectively reduce NO₂ to nitrogen.
17. An engine according to claim 16 which includes a source of the reductant and the reductant is ammonia.

18. An engine according to any one of claims 11-14 which is a diesel engine and the means to reduce the NO₂ to nitrogen comprises a particulate filter on which particulates from the exhaust gas are deposited, which particulates are reacted with NO₂ to oxidise and hence remove them.

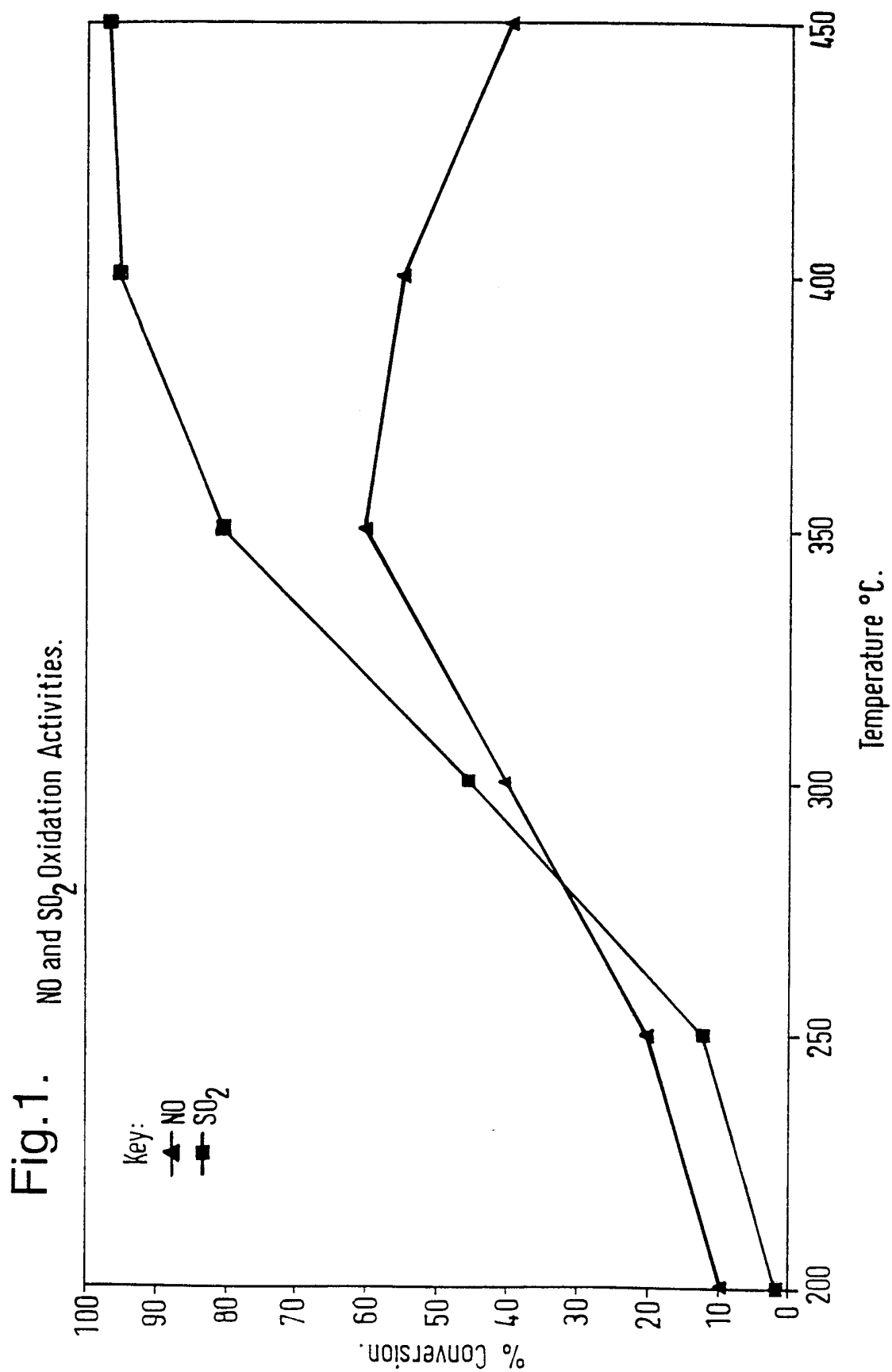
5

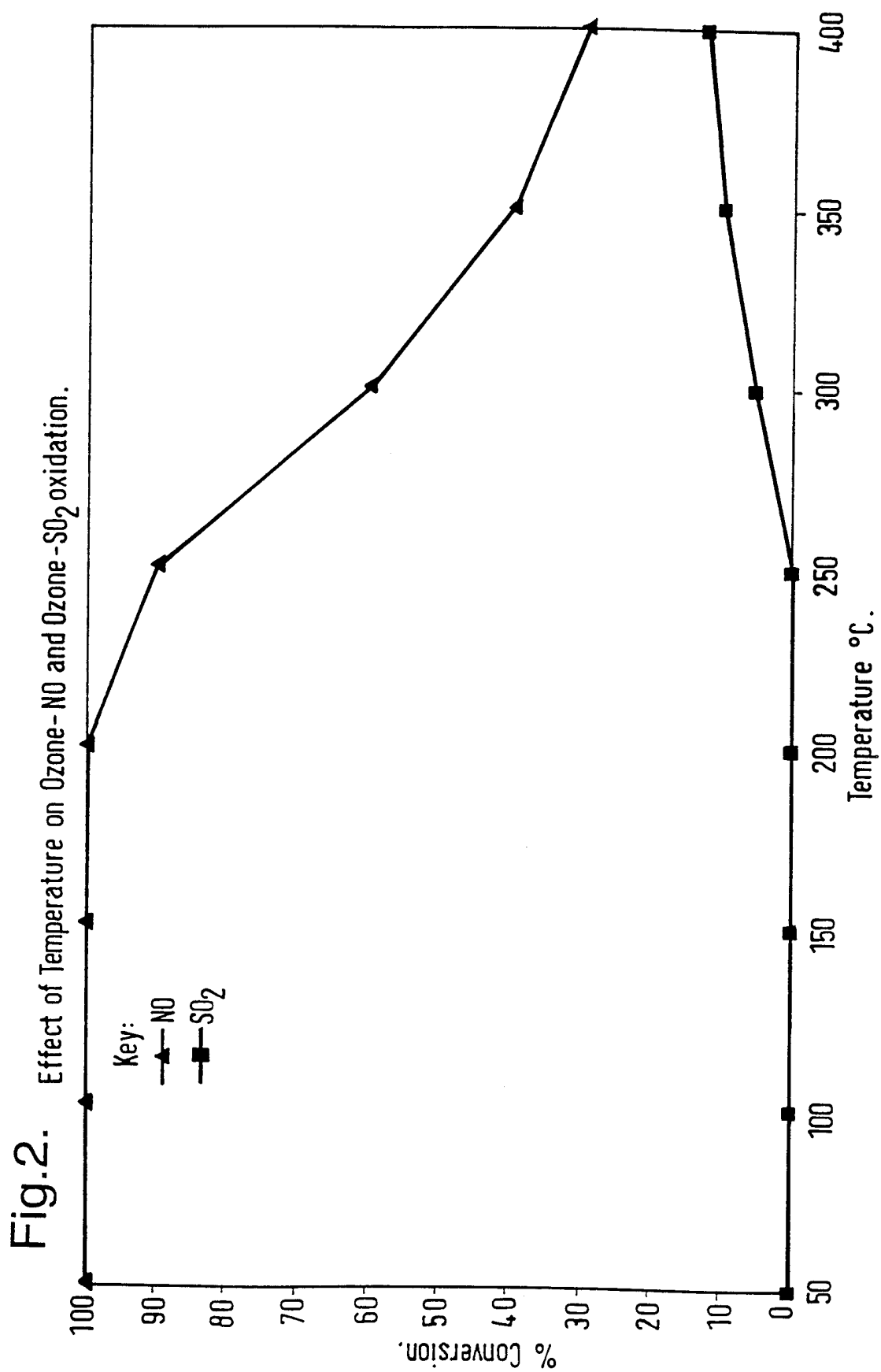
19. An engine according to any one of claims 11-18 adapted so that the NO is reacted with the ozone at a temperature of from ambient temperature to 200°C.

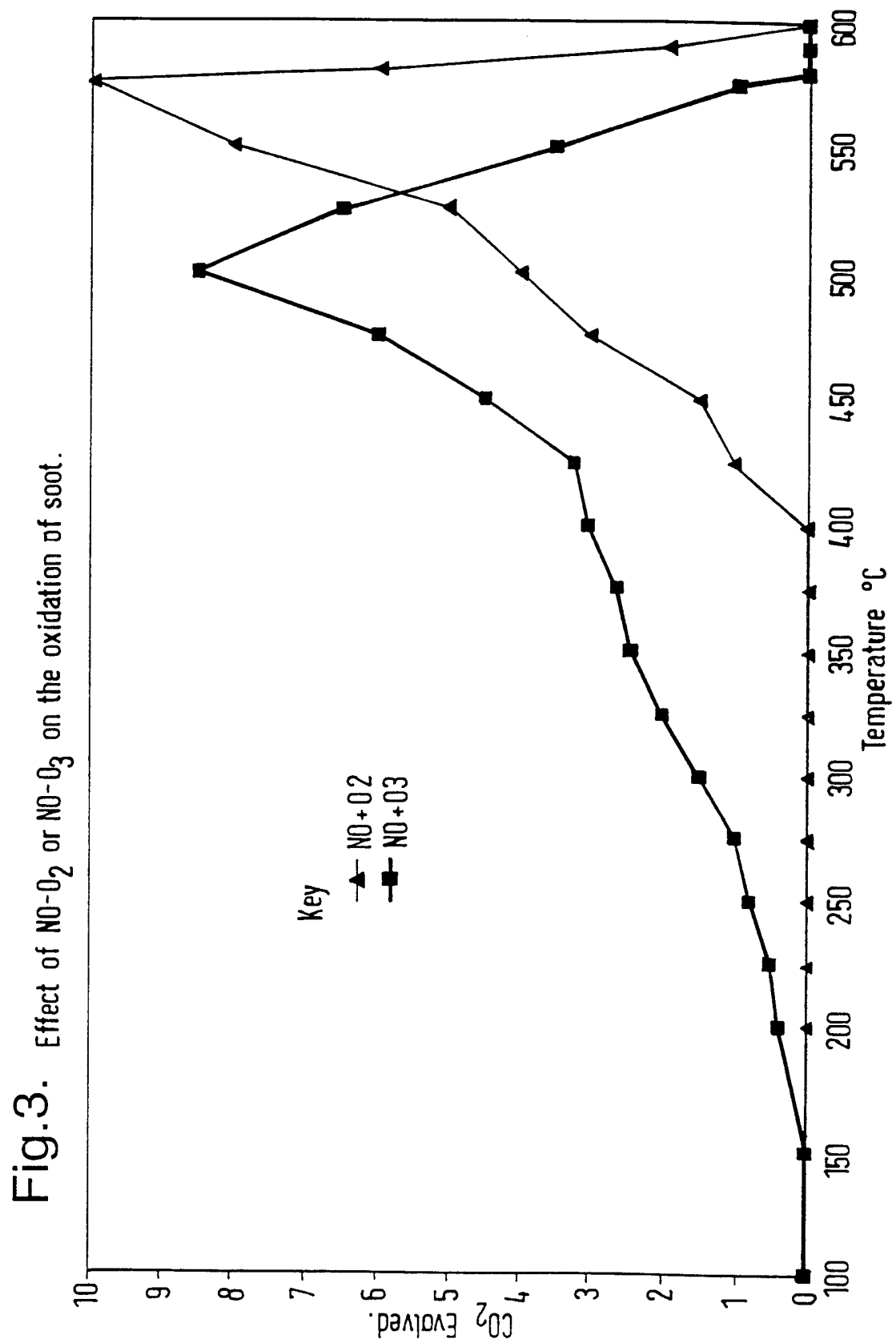
20. An engine according to any one of claims 11-19 adapted so that the exhaust gas
10 contacting the ozone contains 2-200 parts per million by volume of SO₂.

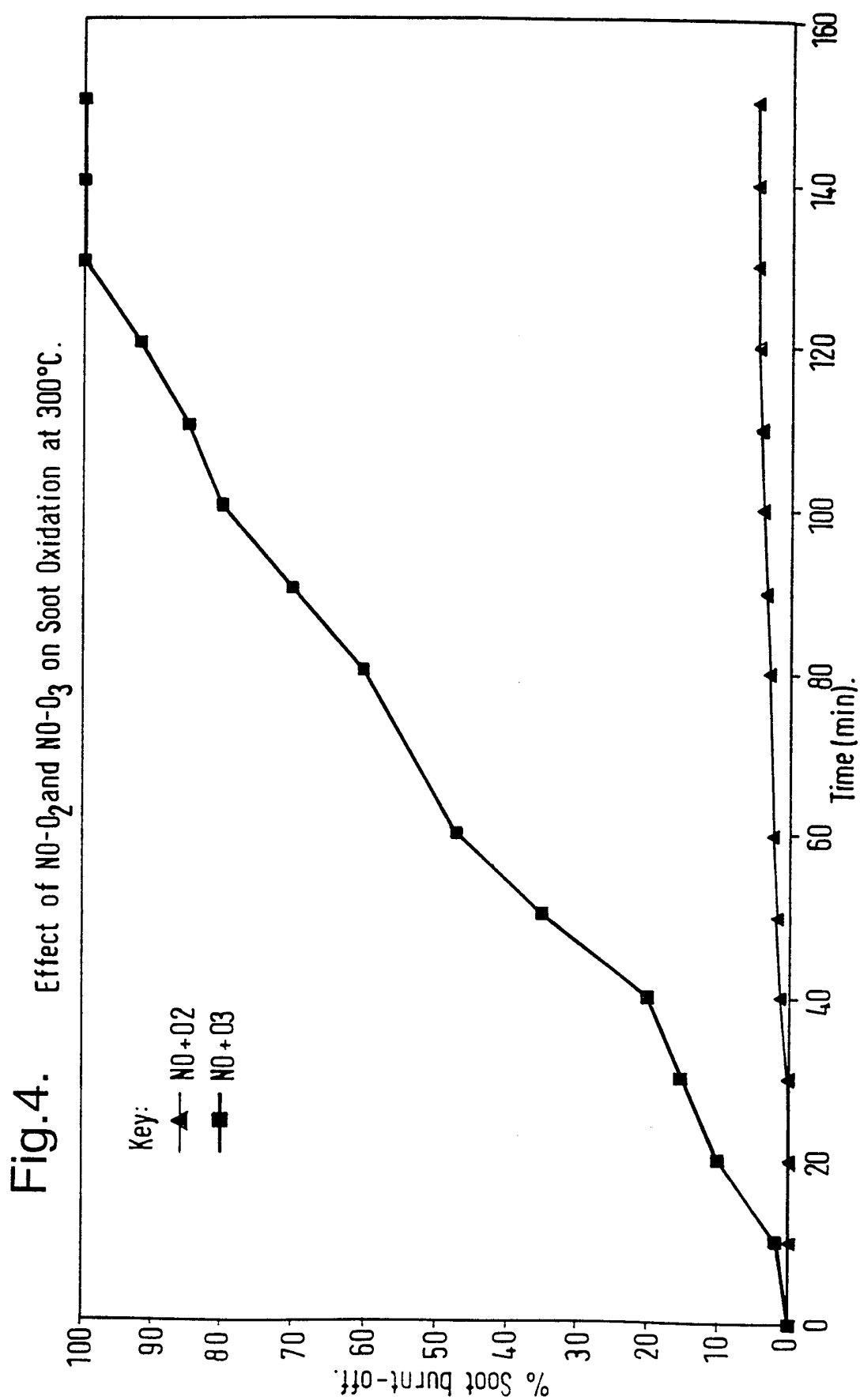
21. An engine according to any one of claims 11-19 wherein the means to react the NO with the ozone does not contain platinum.

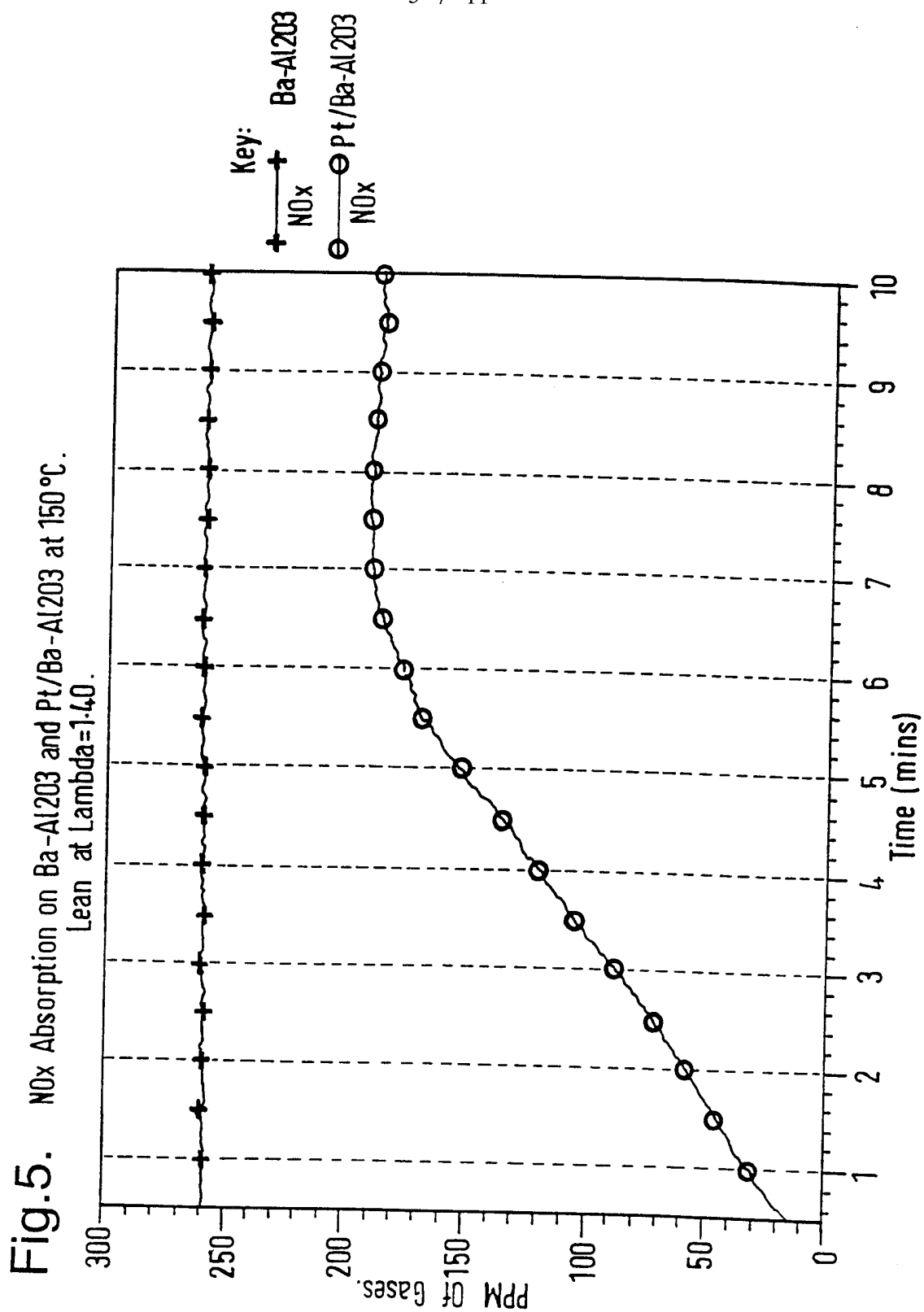
15

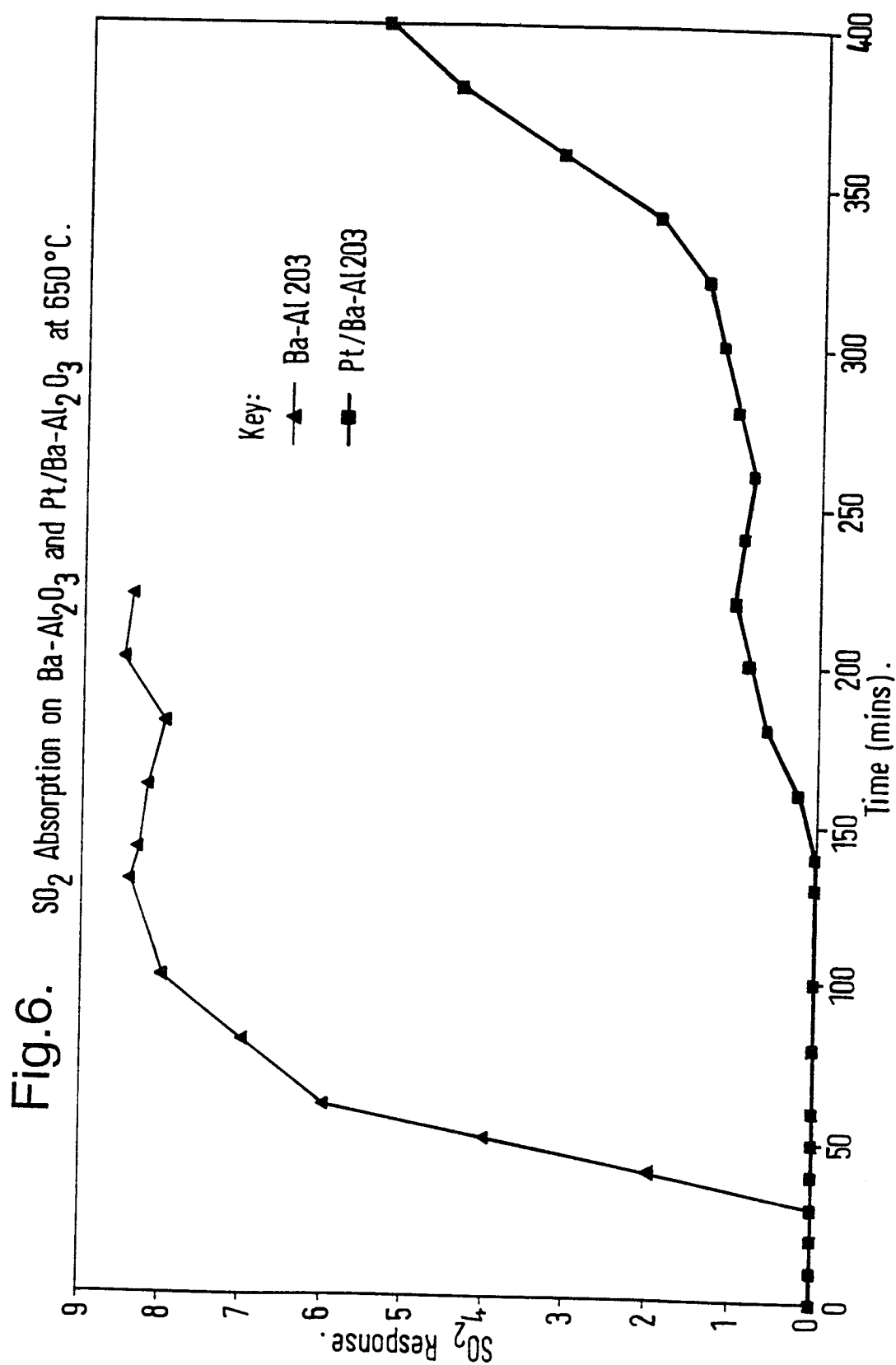


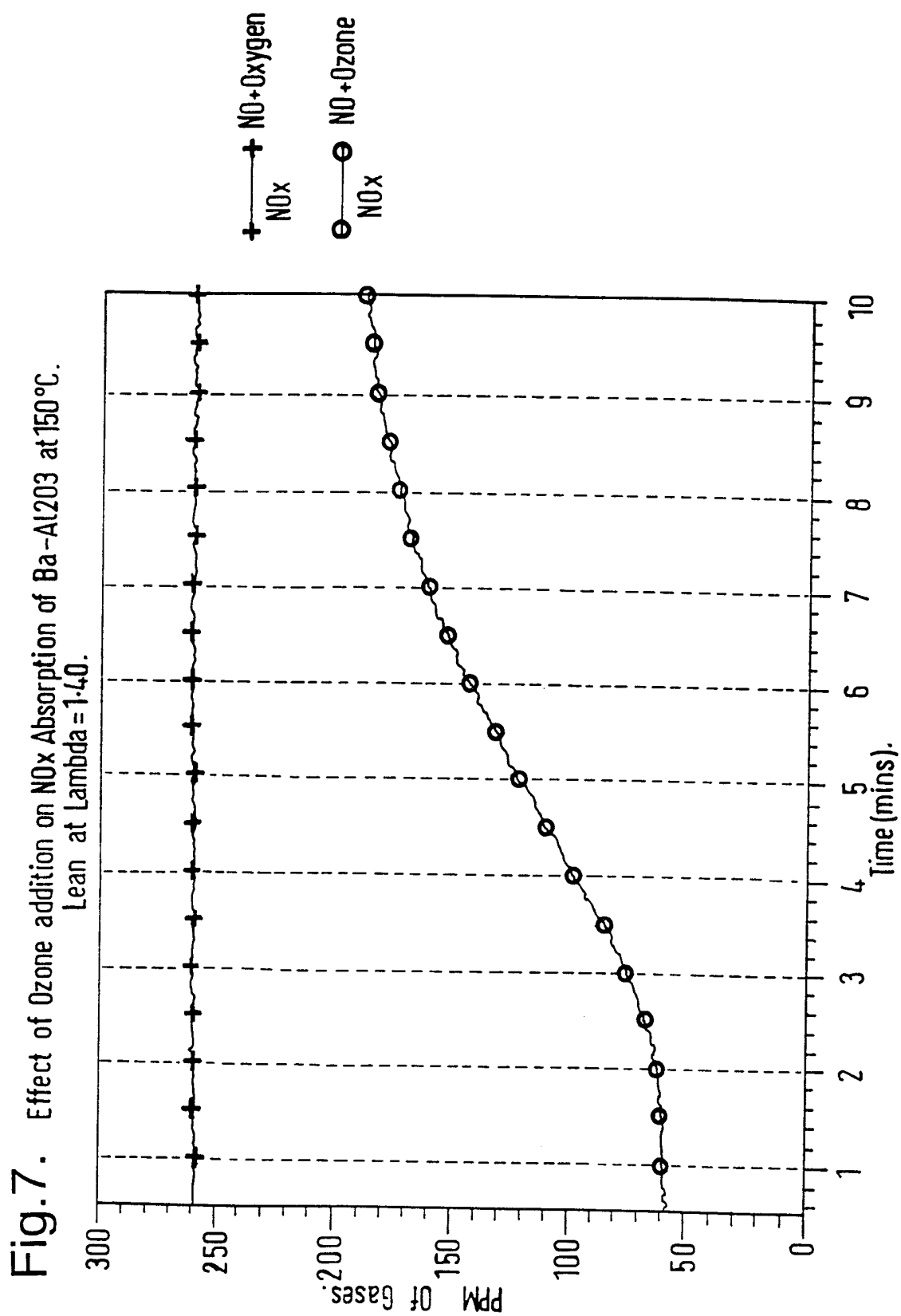


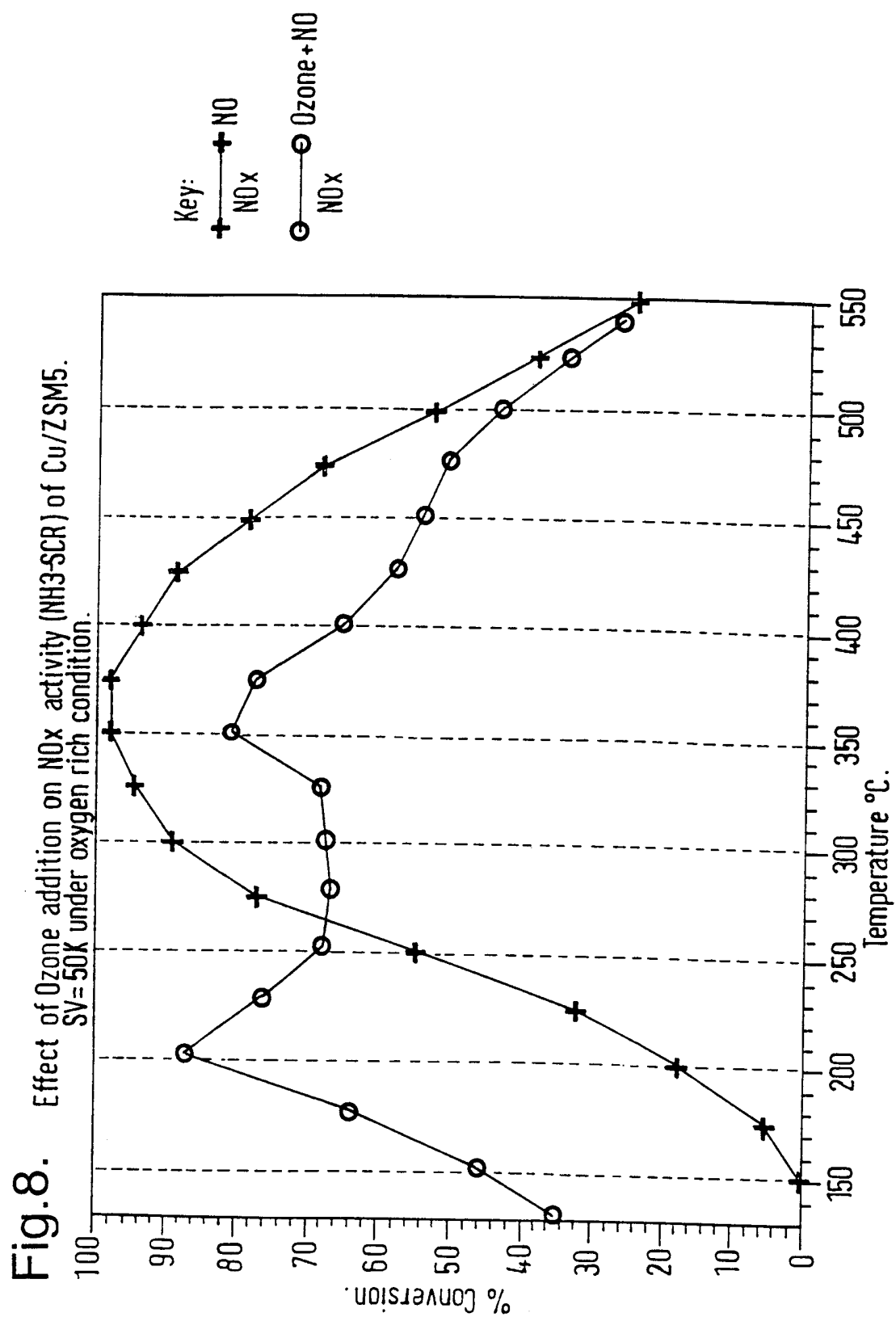


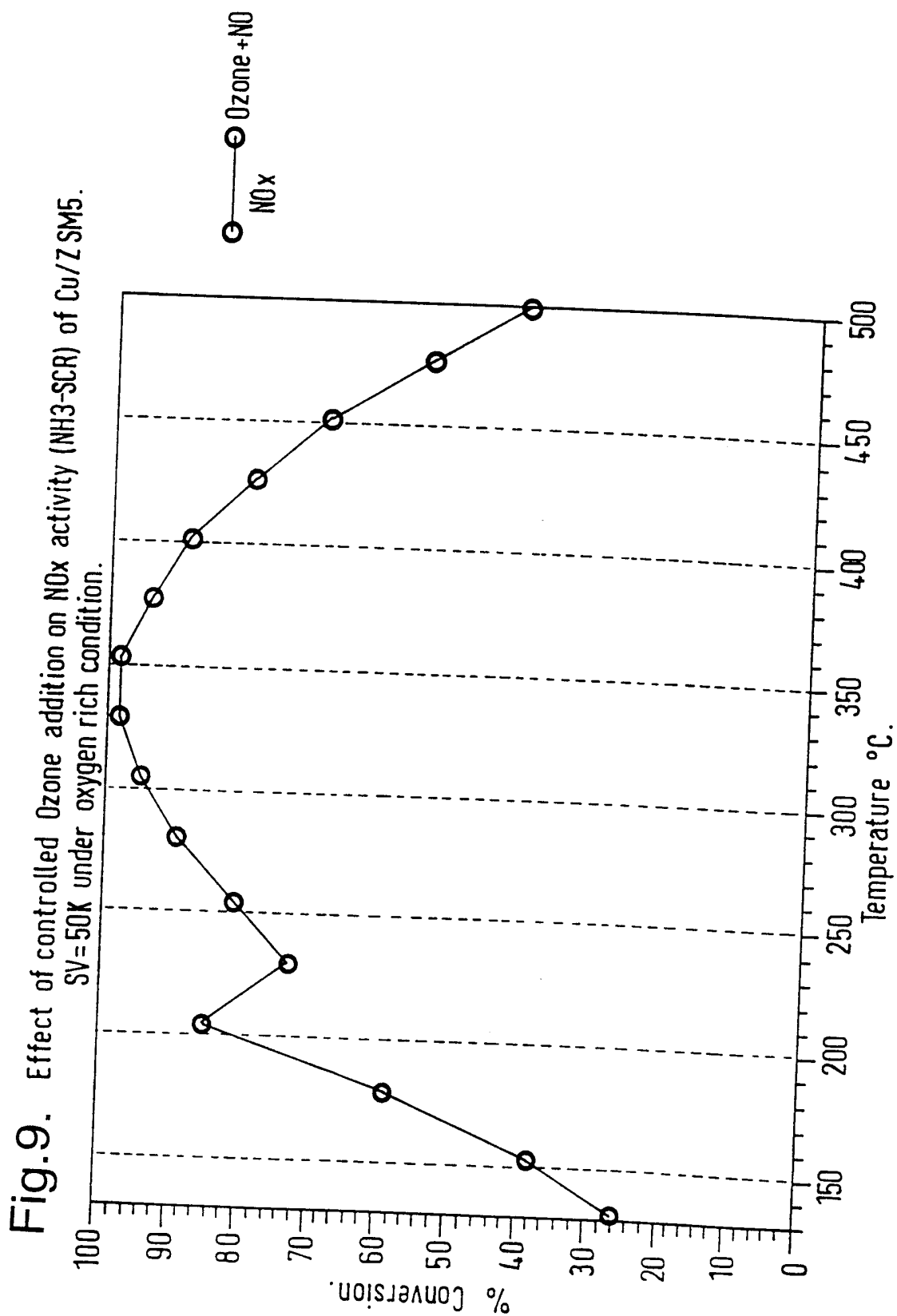


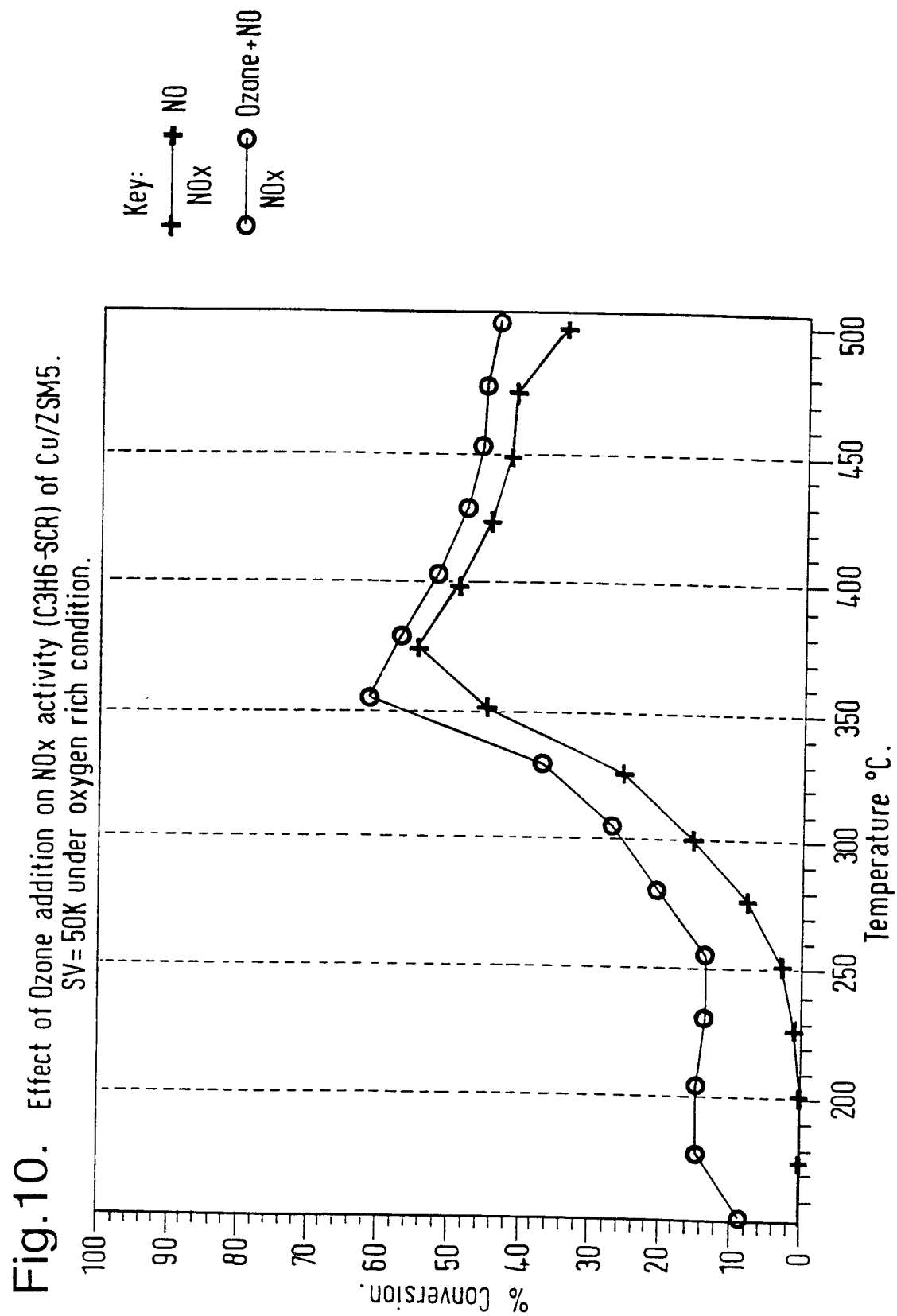


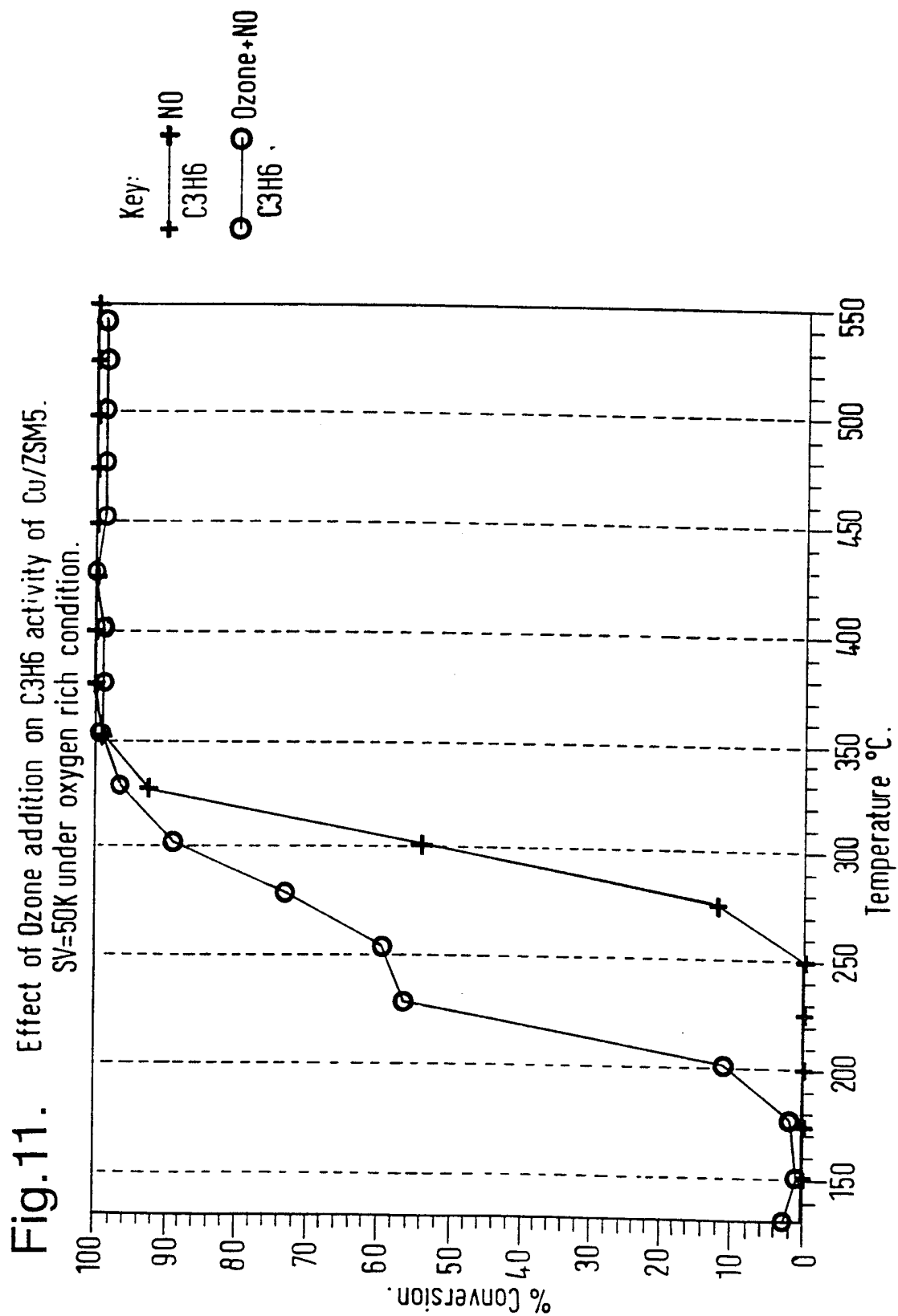












INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/00090

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01D53/56 F01N3/20 F01N3/08 F01N3/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 002, 28 February 1997 & JP 08 281061 A (BABCOCK HITACHI KK), 29 October 1996	1,2,5,6, 11-13, 15-17
Y	see abstract	4,7,8, 14,18,19
Y	EP 0 758 713 A (TOYOTA MOTOR CO LTD) 19 February 1997 see abstract see column 17, line 7 - line 55; figures	4,7,14, 18
Y	EP 0 716 875 A (KANSAI ELECTRIC POWER CO ;MITSUBISHI HEAVY IND LTD (JP)) 19 June 1996 see abstract; figure 1	8,19
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

23 April 1999

Date of mailing of the international search report

07/05/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Sideris, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/00090

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 22794 A (LITEX INC ; LOCKHEED CORP (US)) 26 June 1997 cited in the application see abstract; figures 6-8 ---	1,11,13
A	ENG ET AL: "Kinetic and Mechanistic Study of NOx Reduction by NH3 over H-Form Zeolites" JOURNAL OF CATALYSIS, ACADEMIC PRESS, no. 171, 1997, pages 27-44, XP002100967 cited in the application ---	
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 659 (C-1137), 7 December 1993 & JP 05 212244 A (KUBOTA CORP), 24 August 1993 see abstract -----	

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/GB 99/00090

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0758713 A	19-02-1997	JP 9053442 A	25-02-1997
		US 5746989 A	05-05-1998
EP 0716875 A	19-06-1996	JP 8168638 A	02-07-1996
		CN 1132659 A	09-10-1996
		NO 955026 A	17-06-1996
		US 5648053 A	15-07-1997
WO 9722794 A	26-06-1997	US 5692481 A	02-12-1997
		US 5806305 A	15-09-1998
		AU 1347997 A	14-07-1997
		CA 2241110 A	26-06-1997
		EP 0868605 A	07-10-1998
		US 5863413 A	26-01-1999