A sensor system is disclosed for detecting nitrogen oxides in a flowing gas stream, having a sensor oxidation catalyst capable of both oxidizing CO and NO in the gas sample to CO₂ and NO₂, respectively, which is incorporated into the system so as to oxidise the CO and NO in the flowing gas stream prior to the gas stream contacting a metal oxide semiconducting sensor; an n-type semiconducting metal oxide sensor, whose electrical resistance varies in relation to the concentration of nitrogen oxides in the flowing gas stream.
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METAL OXIDE SENSOR FOR DETECTING NITROGEN OXIDES

This application claims the benefit of U.S. Provisional Application No. 60/070,272, filed December 31, 1997 entitled METAL OXIDE SENSOR FOR DETECTING NITROGEN OXIDES by Margaret K. Faber and Yuming Xie.

The invention relates to a gas sensor system for detecting low concentrations of NOx in a flowing gas stream and more particularly to a gas sensor system having increased sensitivity for NOx, comprising a sensor oxidation catalyst and a n-type metal oxide semiconductor sensor.

BACKGROUND OF THE INVENTION

Catalytic converters have been used on gasoline-fueled automobiles produced in the United States since the mid-1970's for the purpose of promoting the oxidation of unburned hydrocarbons (HCs) and of carbon monoxide (CO). Soon after their introduction, the converters were adapted to promote the chemical reduction of oxides of nitrogen (NOx). At the present time these converters typically employ small amounts of platinum, palladium and rhodium dispersed over a high surface area particulate carrier vehicle which, in turn, is distributed as a thin, porous coating (sometimes called a washcoat) on the wall of a ceramic monolith substrate. These flow-through catalytic devices are housed in a suitable stainless steel container and placed in the exhaust stream under the vehicle downstream from the engine's exhaust manifold.

These conventional catalytic converters effectively and efficiently remove most of the automotive emissions, however, the catalyst system may become malfunctioning
after experiencing thermal aging at an unusually high temperature and after high temperature exposure to poisoning gases like SO₂ and Pb. Furthermore, as a means to ensure that vehicles meet the certified emission standards throughout the vehicle's operation life, On-Board Diagnostics-II (OBD-II) regulation, as passed by the California Air Resource Board (CARB) and currently being gradually implemented in cars from model years 1994 to 2001, calls for continuous monitoring of the efficiency of catalytic converters.

Specifically, this legislation requires that the exhaust from the catalytic converter be monitored, to determine when the steady-state conversion of regulated gases, such as the non-methane hydrocarbons, NOₓ, and CO, falls below about 60-80%. This OBD-II legislation requires that for low emission vehicles the catalyst is considered to be malfunctioning when the HC, NOₓ, or CO emissions exceed 1.75 times the Federal Test Procedure (FTP) standard. Given these conditions, there is a strong interest in incorporating additional sensors to the vehicle; e.g., specifically NOₓ sensors.

For a NOₓ sensor to be effective and useful there are certain requirements which the they must exhibit, including the ability to operate at temperatures from 200-800°C, as well as the ability to sense NOₓ concentrations as low as 25 ppm to those as high as 2,000 ppm. Furthermore, the sensor response time required for OBD-II monitoring must be on the order of 10 seconds or less, preferably as low as 1 second, while response time for engine feedback, generally needs to be on the order of 1 second, with times as quick as 100 milliseconds being preferred. Finally, the temperature of operation must be high, usually from 300°C to 700°C; an advantage for high temperature sensor applications.

It is generally known that metal oxide semiconductor materials can be used as chemical sensors for detecting specific components of test gases, e.g., NOₓ in internal combustion engine exhaust gas. Ceramics which have been utilized include, SnO₂, doped SnO₂ (Ti, In), TiO₂, WO₃, Fe₂O₃, ZnO, LaFeO₃, NiO-ZnO, Cr₂O₃-Nb₂O₅ and YBa₂Cu₃Oₓ, among many others. The advantages of these materials for gas sensor applications are several. For example, the samples can readily be prepared as thin or thick films by methods including ion-beam sputtering, magnetron sputtering, screen printing, and sol-gel processing. Depending on the test conditions and the nature of the
sample, these sensors can detect gases in concentrations ranging from 10 ppm to \(\geq\) 1,000 ppm. Response times as low as 1 second or less have been reported.

Tin oxide (SnO_2) is a preferred metal oxide semiconducting material, and thus is widely used as the basis of solid state sensors. Tin (IV) oxide is an n-type semiconductor in which electrical conductivity occurs through negative charge carriers. The mechanism by which semiconducting ceramics such as SnO_2 respond to gases is by a change in the surface resistance of the materials upon the adsorption of a gas. The adsorbing gases react with the surface oxides on the SnO_2. For an n-type semiconducting material such as SnO_2, the resistance increases upon the absorption of an oxidizing gas such as NO_x (NO or NO_2), and decreases upon the adsorption of a reducing gas such as CO. This can described via the following reactions.

\[
\begin{align*}
(1) \quad \text{NO (g)} + \text{O}_2-(s) + e^- &\rightarrow \text{NO}_2^- + \text{O}^- \\
(2) \quad \text{NO}_2^- (g) + e^- &\rightarrow \text{NO}_2^- \\
(3) \quad \text{NO}_2^- (g) + \text{O}_2-(s) + 2e^- &\rightarrow \text{NO}_2^- + 2\text{O}^- \\
(4) \quad \text{NO}_2^- (g) + \text{O}_2-(s) &\rightarrow 2 \text{CO}_2 + e^- 
\end{align*}
\]

Although tin oxide is widely used, they do suffer a major drawback in that they are sensitive to many gases and worse they also exhibit some cross-sensitivities; i.e. the presence of one gas alters the sensitivity of the sensor to the presence of a second gas. Given the fact that SnO_2 has been found to exhibit a good response to many gases, including NO, NO_2, CH_4, C_6H_8, C_6H_14, CO, H_2O, SO_2, H_2, and O_2 itself, this shortcoming is especially prevalent. As such, tin oxide sensors are not satisfactory in terms of their response to low concentrations of NO_x.

U.S. Pat. No. 5,624,640 (Potthast et al.) discloses a sensor having increased sensitivity for detecting nitrogen oxides in a test gas. This sensor comprises a semiconducting metal oxide layer which is deposited on a ceramic substrate and whose electrical resistance provides information about the concentration of nitrogen oxides. The main components of the sensor comprise a converter layer which is deposited on the metal oxide layer and is made of a material which cause the oxidation of the combustible components of the test gas and converts the NO in the test gas into NO_2 or N_2O_4. The converter layer comprises TiO_2 and/or ZrO_2 and/or SiO_2 and/or Al_2O_3 and has a platinum content. Although this sensor provides improved NO_x sensitivity over the prior
art sensors to date, there still remains a need for NO\textsubscript{x} sensors having improved sensitivity.

**SUMMARY OF THE INVENTION**

In view of the drawbacks in the known technology, the invention is directed, in its broadest sense, at a system and a method exhibiting an increased sensitivity for measuring the NO\textsubscript{x} concentration in a gas sample.

The invention is based on the principle that tin oxide has been found to have no response to CO\textsubscript{2}, and only a slight response to H\textsubscript{2}O. In addition, it has been found that SnO\textsubscript{2} is more responsive to NO\textsubscript{2} than to NO, and the presence of NO actually reduces the sensitivity of the response to NO\textsubscript{2}.

In general, this invention is directed at a sensor system which takes advantage of the aforementioned principle and comprises a metal oxide semiconductor with improved response to NO\textsubscript{x} emissions due to the incorporation of suitable oxidation catalysts within the sensor system. Specifically, the sensor system for measuring the NO\textsubscript{x} concentration of a flowing gas stream according to the present invention comprises a sensor oxidation catalyst capable of both oxidizing CO and NO in the gas sample to CO\textsubscript{2} and NO\textsubscript{2}, respectively. The catalyst is incorporated into the system so as to oxidize the CO and NO in the flowing gas stream prior to the gas stream contacting a metal oxide semiconducting sensor. As such, downstream of the sensor catalyst is positioned an n-type semiconducting metal oxide sensor, preferably tin oxide, whose electrical resistance varies in relation to the concentration of nitrogen oxides in the flowing gas stream.

Preferably, the semiconductor metal oxide sensor comprises tin oxide (SnO\textsubscript{2}) and the oxidation catalyst incorporated within the system is capable of oxidizing NO and/or CO in the temperature range of between about 200-500°C; more preferably in the temperature range of between about 250-400°C.

**BRIEF DESCRIPTION OF THE FIGURES**

FIG. 1 is a block/flow diagram of the inventive sensor system;
FIG. 2 is a schematic diagram of an exhaust system incorporating one embodiment of an inventive sensor system for measuring the NO\textsubscript{x} concentration of an exhaust gas stream;

FIG. 3 is a schematic diagram of an exhaust system incorporating another embodiment of an inventive sensor system for measuring the NO\textsubscript{x} concentration of an exhaust gas stream;

FIGS. 4-8 illustrates three top views, a lateral view and a bottom view, respectively, of another embodiment of a sensor system for measuring the NO\textsubscript{x} concentration of an exhaust gas stream.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed at a system for measuring the NO\textsubscript{x} concentration of a gas sample. In its simplest embodiment as depicted in FIG. 1, the system comprises a sensor oxidation catalyst and a downstream-positioned metal oxide semiconductor sensor, the sensor having an electrical resistance which varies in relation to the concentration of nitrogen oxides (NO\textsubscript{x}) in the flowing gas stream. The sensor catalyst is capable of both oxidizing CO and NO in the gas sample to CO\textsubscript{2} and NO\textsubscript{2} respectively, the catalyst being positioned upstream of the metal oxide semiconducting to oxidize the CO and NO in the flowing gas stream prior to the gas stream contacting the metal oxide semiconducting sensor.

Referring to FIG. 2, illustrated therein is a schematic representation of the system 10 for measuring the NO\textsubscript{x} concentration of exhaust gases in a flowing exhaust stream, according to one embodiment of the present invention. A main catalytic converter 12 is located in the exhaust gas downstream of an internal combustion engine. This main catalytic converter 12 is capable of catalyzing the exhaust gas so as to reduce the pollutants present in the exhaust gas. Preferably, the catalyst is a three-way catalyst which functions to oxidize both HCs and CO, as well as to reduce NO\textsubscript{x}, in the exhaust gas. The sensor system 10 generally comprises a sensor oxidation catalyst 14 and a n-type metal oxide semiconductor sensor 16 for directly measuring the NO\textsubscript{x} concentration in the exhaust gas.
Referring still to FIG. 2, the sensor system 10 includes a housing 18, located downstream of the catalytic converter 12, within which are disposed both the sensor oxidation catalyst 14 and the metal oxide semiconductor sensor 16; supports 16A and 16B are used to support the sensor 16. Furthermore, the sensor communicates with a resistance measuring device which measures the increase of the electrical resistance of the metal oxide semiconducting sensor 16 in a known manner.

In a separate embodiment, the housing, sensor catalyst and the sensor could be located upstream of the main converter, thereby functioning to measure the concentration of an upstream portion of exhaust gas.

Referring now to FIG. 3, illustrated therein is another embodiment of the sensor system, wherein the tubular housing 26, is not only located downstream of the main catalytic converter 12, but is remote or off-line from the main flow of the exhaust gas. In this embodiment the sensor oxidation catalyst 28 comprises a tubular body comprised of a catalyst-support material and upon which a catalytically active metal material is deposited; one benefit of this embodiment is that the tubular sensor oxidation catalyst 28 can be uniformly heated by a heater 30 which surrounds the sensor oxidation catalyst thereby ensuring and accelerating the oxidation of the CO and NO in the flowing exhaust gas stream. The metal oxide semiconductor sensor 16 is located within a separate downstream housing portion 32.

The metal oxide sensor utilized in the aforementioned two embodiments comprises any conventional metal oxide sensor, including, for example, SnO2, In2O3, Fe2O3, ZnO, TiO2, WO3, Nb2O5 and the like. Three examples of tin oxide sensors, the preferred metal oxide sensor, suitable for use in the instant invention, are disclosed in the following U.S. Patents., Pat. Nos. 4,592,967 (Komatsu et al.), 4,535,351 (Sakai) and 5,427740 (Coles et al.). Optionally, the metal oxide sensor may include a heater which increases the conductivity of the metal oxide.

As described above, in the first embodiment, the sensor oxidation catalyst comprises a honeycomb body comprised of a catalyst-support material, upon which an appropriate catalytically active metal is deposited. In the second embodiment the sensor oxidation catalyst comprises a tubular body comprised of a catalyst-support material and upon which an appropriately catalytically active metal catalyst is deposited. In either
embodiment, suitable catalytic-support materials include any high surface area material, preferably a ceramic material, including for example, silica, alumina, zirconia, ceria, titania and mixtures thereof. A preferred catalyst material comprises γ-alumina.

Alternatively, the suitable catalyst support material comprises an oxygen storage support material such as ceria-alumina, or preferentially, ceria-stabilized zirconia. Both oxygen storage support materials may result in improved activity of the catalyst for low temperature NO oxidation, as well as low temperature CO oxidation. Since normal engines typically operate at a slightly rich A/F ratio, i.e., an A/F ratio around 14.6, more oxygen is required during these rich conditions so as to ensure that this second catalytic reaction occurs and thus this downstream sensor functions properly. Although excess oxygen can be supplied by providing an air supply line, or the like, to the exhaust gas, it is preferred that the excess oxygen be supplied through the use of these catalyst-support materials comprised of an oxygen storage material. In this case, the catalyst-support materials are capable of storing and releasing oxygen depending upon the widely and rapidly varying oxygen concentration in the exhaust stream.

As described above, it is desirable that the oxidation catalyst improves the selectivity and response of n-type metal oxide to NO\textsubscript{x} gases, by combining the metal oxide with suitable catalysts. Suitable catalytically active materials improve the responses of the metal oxide, e.g., tin oxide, both by (1) oxidizing CO (to which tin oxide responds) to CO\textsubscript{2} (to which tin oxide does not respond), thus removing the interfering signal of CO, and (2) more especially, by oxidizing NO to NO\textsubscript{2}. The ability to oxidize NO to NO\textsubscript{2} improves the response of the sensors to the NO\textsubscript{x} emissions from auto exhaust, since the NO\textsubscript{x} portion of the exhaust consists of approximately 90% NO and 10% NO\textsubscript{2}. In the case of the SnO\textsubscript{2} metal oxide sensor, SnO\textsubscript{2} it is more responsive to NO\textsubscript{2} than to NO, and the presence of NO tends to decrease the response to NO\textsubscript{2}. The catalyst serves to either fully oxidize the NO to NO\textsubscript{2}, and/or to maintain the molar ratio of NO to NO\textsubscript{2} at the equilibrium value for a given temperature. The advantage is that the sensor response no longer varies as the NO/NO\textsubscript{2} ratio varies, but gives a constant output that is dependent only on the total [NO+ NO\textsubscript{2}] concentration.

It is also desirable to have the catalyst sufficiently active for NO oxidation and/or CO oxidation, low temperatures, that is, from 200 to 500°C, and preferably from 250 to
400°C. It has been found that when the sensor system is operated temperatures of 500°C or higher, the sensor is only sensitive to lower concentrations of NOx, from 0 ppm to 20 ppm, for example. Thus, it is necessary to operate the metal oxide sensor at temperatures less than 500°C in order to maintain a sensitivity to NOx up to 1000 ppm, or greater, as is required for the automotive exhaust gas sensing application. In addition, it is advantageous to use a catalyst that is active at lower temperatures for NO oxidation because the reaction of NO with O2 to form NO2 is thermodynamically favored at lower temperatures.

Given the aforementioned parameters for use, several suitable catalytically active materials have been found to be effective for use in conjunction with the metal oxide sensor in the instant invention. Specific catalytically active materials include, for example, Pt, CuO-Pt, Fe2-CuO-Pt. Alternatively, the catalytically active material may be comprised of Rh. In those embodiments where Pt and Rh are utilized as the catalyst, it is preferred that the catalyst support material comprise the aforementioned oxygen storage support material; i.e., either ceria-alumina or ceria-stabilized zirconia. It should be noted that Rh catalyst supported on ceria-stabilized zirconia is most suitable for applications where the NOx sensors would be primarily used for NOx detection for engine management in lean burn gasoline engines or diesel engines. In these highly oxidizing environments (6% O2), the Rh catalyst may no longer be active for NOx reduction, but may be very suitable for relatively low temperature NOx oxidation.

Alternatively, other novel low temperature CO oxidation catalytically active material/support material combinations which may be used in the invention described herein include Au supported on MnO2, TiO2, Fe2O3 or other oxides, as well as perovskite catalysts (e.g., LaCoO3) alone or supported on γ-alumina.

The amount of the catalytically active metal material present in the sensor oxidation catalyst will be at least an effective amount and will depend, for example, on required catalyst activity, ease of uniform dispersion, and the type of substrate utilized. Generally, however, the level of catalytically active metal present will range from about 0.01% to 5.0%, and more preferably, 0.01% to 3.5%.

The catalytically active material can be applied onto the catalyst-support material by any known method such as for example, by conventional washcoat or spraying
techniques. In the washcoat technique, the substrate is contacted with a slurry containing the catalytically active material and other components such as temporary binders, permanent binders or precursors, dispersants and other additives as needed. Such methods are well known in the art. The slurry is then applied (for example, by repeated spraying, dipping or vacuum suction) to the substrate until the desired amount of catalytically active material has been applied.

Referring now to FIGS. 4-8 illustrated therein is another embodiment of the sensor system 10 which is embodied in the shape of a rod, which could be incorporated into the exhaust system of either FIG. 2 or 3 in place of the sensor embodiments described therein. Substrate 34 is comprised of a catalytic support material which is electrically insulating and heat resistant; suitable materials for the catalytic support material are described above. Two strip conductors 36 are mounted on the surface of the substrate 34 which interlock in a comb-like fashion. A semiconducting metal oxide layer 38 of a thickness of 10-500 μm is suitably deposited over the strip conductors in the area of the interlocking ends; these strips communicate with a resistance measuring device which, as before, detects and measures any increase in electrical resistance of the semiconducting metal oxide layer 38. As before, the metal oxide semiconductor comprises an n-type semiconductive metal oxide, preferably tin oxide (SnO₂). A sensor oxidation catalyst layer 40 is deposited at a suitable thickness of 10-100 μm over the metal oxide semiconducting layer; it is preferably comprised of the catalytically active metal material described above. Lastly, the underside of the substrate is provided with a heater 42 which, as described before, is capable of both increasing the conductivity of the metal oxide and of ensuring and accelerating the oxidation of the NO and CO. Each of the aforementioned components which make up this sensor embodiment are deposited using thick film technology as known to those skilled in the art.

This invention has been disclosed by description and examples and should not be used to limit the scope of the invention here claimed in any way. Additionally, it will be apparent to a reader having ordinary skill in this art that certain variations and equivalents will operate in the same way in measuring NOx and yet be within the spirit of these claims.
We claim:

1. A sensor system for measuring the NO\textsubscript{x} concentration of a flowing gas stream, comprising:
   a sensor oxidation catalyst capable of both oxidizing CO and NO in the gas sample to CO\textsubscript{2} and NO\textsubscript{2} respectively, the catalyst being positioned to oxidize the CO and NO in the flowing gas stream prior to the gas stream contacting a metal oxide semiconducting sensor;
   an n-type semiconducting metal oxide sensor, whose electrical resistance varies in relation to the concentration of nitrogen oxides in the flowing gas stream.

2. The sensor system of claim 1 wherein the semiconductor metal oxide sensor is selected from the group consisting of SnO\textsubscript{2}, In\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}, ZnO, TiO\textsubscript{2}, WO\textsubscript{3}, Nb\textsubscript{2}O\textsubscript{5} and mixtures thereof.

3. The sensor system of claim 1 wherein the semiconductor metal oxide sensor is SnO\textsubscript{2}.

4. The sensor system of claim 1 wherein the oxidation catalyst is capable of oxidizing NO and/or CO in the temperature range of between about 200-500\textdegree}C.

5. The sensor system of claim 1 wherein the oxidation catalyst is capable of oxidizing NO and/or CO in the temperature range of between about 250-400\textdegree}C.

6. The sensor system of claim 1 wherein the sensor oxidation catalyst is comprised of a high surface area catalyst-support material and a catalytically active metal material.

7. The sensor system of claim 6 wherein the sensor oxidation catalyst comprises either a tubular body or a monolithic honeycomb body and comprises the high surface area catalyst-support material upon which the catalytically active metal is deposited.
8. The sensor system of claim 1 wherein the system further includes a heater for maintaining each of the sensor oxidation catalyst and the metal oxide semiconductor catalyst at a temperature sufficient to effect substantially complete oxidation of the CO and the NO in the flowing exhaust gas stream.

9. The system of claim 6 wherein the catalyst-support material is comprises high surface area γ-alumina.

10. The system of claim 6 wherein the catalytically active metal material is selected from the group consisting of Pt, CuO-Pt, and Fe₂O₃-CuO-Pt.

11. The sensor system of claim 6 wherein the catalyst support material comprises either a ceria/alumina material or a ceria-stabilized zirconia.

12. The sensor system of claim 6 wherein the catalytically active metal material comprises either Pt or Rh.

13. The system of claim 1 wherein the sensor system is located within a tubular housing which is located in an internal combustion engine exhaust stream downstream of a main catalytic converter.

14. The system of claim 1 wherein the sensor system comprises a unitary rod-shaped device comprising a catalytic support material substrate upon which the semiconducting metal oxide sensor is deposited as a layer on the substrate and the sensor oxidation catalyst is deposited as a layer over the semiconducting metal oxide layer.

15. A method of measuring the hydrocarbon concentration of an exhaust gas comprising the steps of:
   contacting a portion of the exhaust gas with a sensor catalyst which oxidizes both the CO and NO₂ in the exhaust gas; and thereafter
contacting the oxidized portion of the exhaust gas with a sensor whose electrical resistance varies in relation to the concentration of nitrogen oxides in the exhaust gas;
analyzing the electrical resistance change thereby determining the NOx concentration in the exhaust gas.

16. The method of claim of claim 15 wherein the exhaust gas is part of an exhaust stream produced by an internal combustion engine and the contacting steps are performed downstream of a catalytic converter.
FIG. 1

INCOMING GAS
(NO, CO, H₂)

SENSOR OXIDATION CATALYST
(NO₂, CO₂, H₂O)

NOₓ SENSOR

NOₓ SENSOR MEASUREMENT

TO DISPOSAL
FIG. 3
**INTERNATIONAL SEARCH REPORT**

**International application No.**

PCT/US98/25118

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**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : G01N 27/12

US CL. : 73/23.31, 31.06; 422/94; 436/116, 118

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

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**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 73/23.2, 23.31, 31.06; 422/94; 436/116, 117, 118

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

NONE

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

NONE

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**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>JP 03-59450 A (KURABE KK) 14 March 1991 (14.03.91), abstract and Figure 1.</td>
<td>1-3, 6, 8, 10, 12, and 15</td>
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<tr>
<td>X</td>
<td>US 4,592,967 A (KOMATSU et al.) 03 June 1986 (03.06.86), col. 1, lines 11-32.</td>
<td>1-6, 8, 10, 12, and 15</td>
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<td>X, P</td>
<td>US 5,810,984 A (KUDO et al.) 22 September 1998 (22.09.98), Figures 9 and 10, col. 5, lines 61-67 through col. 6, lines 1-17, and col. 7, lines 41-50.</td>
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<td>A</td>
<td>RU 2011985 A (KONOVALOV) 30 April 1994 (30.04.94), abstract and figure.</td>
<td>1-3, 6, 8, 10, 12, and 15</td>
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[X] Further documents are listed in the continuation of Box C.  See patent family annex.

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**Date of the actual completion of the international search**

07 JANUARY 1999

**Date of mailing of the international search report**

03 FEB 1999

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**Name and mailing address of the ISA/US Commissioner of Patents and Trademarks**

Box PCT

Washington, D.C. 20231

**Authorized officer**

[DANIEL S. LARKIN](#)

**Telephone No.**

(703) 308-6724

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### INTERNATIONAL SEARCH REPORT

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**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

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<tr>
<td>X</td>
<td>US 4,457,161 A (IWANAGA et al.) 03 July 1984 (03.07.94), Figures 4a, 4b, and 6, col. 4, lines 36-37 and 65-68 through col. 5, lines 12-30, and col. 8, lines 4-6.</td>
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<td>X, P</td>
<td>US 5,705,129 A (TAKAHASHI et al.) 06 January 1998 (06.01.98), Figure 1 and col.2, lines 36-67 through col. 4, lines 1-34.</td>
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<td>X</td>
<td>US 5,389,340 A (SATAKE) 14 February 1995 (14.02.95), whole document.</td>
<td>1-1-8, 10, 12, and 13-16</td>
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<td>X</td>
<td>US 5,624,640 A (POTTHAST et al.) 29 April 1997 (29.04.97), whole document.</td>
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