

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
24 February 2005 (24.02.2005)

PCT

(10) International Publication Number
WO 2005/016480 A2

- (51) International Patent Classification⁷: **B01D**
- (21) International Application Number:
PCT/US2004/020404
- (22) International Filing Date: 24 June 2004 (24.06.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
10/636,676 7 August 2003 (07.08.2003) US
- (71) Applicant (for all designated States except US): **GENERAL MOTORS CORPORATION** [US/US]; Legal Staff - Mail Code 482-C23-B21, P.O. Box 300, Detroit, MI 48265-3000 (US).
- (72) Inventors: **LI, Wei**; 6623 Emerald Lake Drive, Troy, MI 48085 (US). **MONROE, David, R.**; 1065 Timber Lake Drive, Bloomfield Hills, MI 48302 (US).
- (74) Agent: **MARRA, Kathryn, A.**; General Motors Corporation, Legal Staff - Mail Code 482-C23-B21, P.O. Box 300, Detroit, MI 48265-3000 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

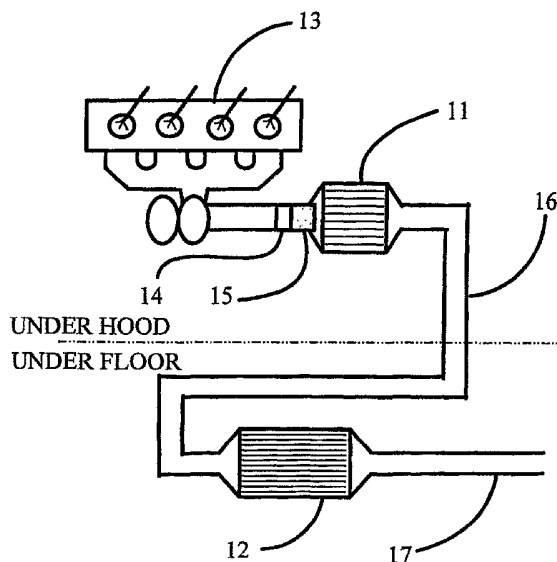
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

[Continued on next page]

(54) Title: REMOVING NITROGEN OXIDES DURING A LEAN-BURN ENGINE COLD START



(57) Abstract: An apparatus and method for removing NO_x from an exhaust stream of a lean-burn engine during an engine cold start is provided. The apparatus includes a close-coupled LNT coupled to a main LNT by a hollow conduit. NO_x from the cold exhaust is initially stored on the close-coupled LNT. As the engine exhaust warms up, the close-coupled LNT reaches its operating temperature and reduces the stored NO_x to N₂. When the temperature of the close-coupled LNT reaches approximately 350 °C, NO_x is released from the close-coupled LNT, is absorbed on the main LNT, and is converted to N₂ during fuel-rich conditions. The close-coupled LNT can be regenerated after the engine is turned off by providing heat. The released NO_x during the regeneration of the closed-coupled LNT is absorbed by the main LNT. The stored NO_x on the main LNT can be reduced to N₂ during the next vehicle operation.



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

REMOVING NITROGEN OXIDES DURING A LEAN-BURN ENGINE COLD START

FIELD OF THE INVENTION

[0001] The present invention relates generally to the catalytic reduction of nitrogen oxides in engine exhaust, and more particularly to reducing emissions of NO_x from an exhaust stream during a lean-burn engine cold start.

BACKGROUND OF THE INVENTION

[0002] Certain compounds in the exhaust stream of a combustion process, such as the exhaust stream from an internal combustion engine, are undesirable in that their release into the environment would contribute to lower air quality. As a result, they must be controlled in order to protect the environment and to meet or exceed government emissions regulations. Among such undesirable compounds are nitrogen oxides, which will be referred to as NO_x. There are a wide variety of combustion processes that produce NO_x, such as coal- or oil-fired furnaces, reciprocating internal combustion engines (including gasoline and diesel engines), and gas turbine engines. In each of these combustion processes, control measures to prevent or diminish atmospheric emissions of NO_x are needed in order to improve air quality and comply with governmental regulations.

[0003] In order to remove pollutants (*e.g.*, NO_x, CO, and hydrocarbons) from an exhaust stream of an engine, catalytic converters containing three-way catalysts have been installed in automobiles. For most of the light-duty vehicles in US, the vehicle engines operate in a stoichiometric mode; *i.e.* stoichiometric amounts of fuel and air are

fed into the engine and after combustion the exhaust stream contains roughly equal amount of residual oxygen and reductants (e.g., hydrocarbons, CO, and H₂). In these exhaust stream, the three-way catalysts are able to reduce NO_x to N₂, and oxidize CO, H₂, and hydrocarbons to CO₂ and H₂O. However, in a fuel-rich exhaust, CO and hydrocarbons cannot be completely oxidized to CO₂ and H₂O due to an insufficient amount of oxygen present in the exhaust. On the other hand, in a fuel-lean exhaust, NO_x cannot completely reduced to N₂ due to an insufficient amount of reductants and an excess of oxygen in the exhaust.

[0004] Lean-burn engines typically operate in a fuel-lean mode; *i.e.* a more than stoichiometric amount of air is fed with fuel into the engine cylinders. Compared with stoichiometric engines, lean-burn engines offer superior fuel economy. One typical example of a lean-burn engine is a diesel engine. However, the fuel-lean exhaust stream from the lean-burn engines render the three-way catalytic converters inadequate in converting NO_x to N₂ and reducing tailpipe NO_x emissions due to the reason mentioned above. Lean NO_x traps, sometimes called LNT's, are considered to be one of the leading technologies for removing NO_x from the exhaust stream of lean-burn engines. They contain catalysts that reduce NO_x to N₂ and compounds (such as metal nitrates) that can store NO_x as nitrates. However, LNT's operate most effectively within a temperature range of approximately 250 - 550 °C, and undesirable emissions of NO_x into the atmosphere are more likely to occur at temperatures outside that range. At temperatures below about 250 °C, such as in an engine cold start, the LNT does not effectively convert NO_x to nitrates (for storage) in a fuel-lean mode or convert released NO_x to N₂ in a fuel-

rich mode. When the LNT temperature is above approximately 550 °C, the metal nitrates are not stable enough to store the NO_x.

[0005] Therefore, despite efforts to develop a device or system effective for reducing NO_x to nitrogen in a lean-burn engine (such as a diesel engine), the need for adequate conversion effectiveness has remained unsatisfied. Moreover, there is a continuing need for improved effectiveness in treating NO_x emissions from any combustion process, but especially during an engine cold start.

SUMMARY OF THE INVENTION

[0006] An apparatus for selectively removing NO_x from the exhaust stream of a lean-burn engine during an engine cold start is provided. The device includes a close-coupled LNT connected to a main LNT. The close-coupled LNT may be smaller in size than the main LNT. In addition, the close-coupled LNT may be positioned under the hood of the automobile and the main LNT may be positioned in an under-floor location (*e.g.*, under the floor of the passenger compartment). The apparatus may further include an electrical heater to heat the close-coupled LNT to a temperature at which the close-coupled LNT will release any stored NO_x, *e.g.*, approximately 600 °C. An air pump may also be provided to pump air to the close-coupled LNT.

[0007] A method for selectively removing NO_x from the exhaust stream of a lean-burn engine during an engine cold start comprising passing the exhaust sequentially through a first (close-coupled) LNT and a second (main) LNT. The close-coupled LNT and the main LNT contain catalysts that catalyze reduction of NO_x to N₂, and compounds that can store NO_x as nitrates. During a cold start, NO_x contained in the

exhaust exiting the engine is initially stored on the close-coupled LNT. As the engine exhaust warms up, it heats the close-coupled and the main LNT. As the close-coupled LNT is heated above ambient by the hot exhaust gas, it reaches its catalytic temperature (typically 250°) and becomes catalytically active to convert NO_x to N₂ when excess reductants (*e.g.*, hydrocarbons, CO, or H₂) are available.

[0008] When the temperature of the close-coupled LNT is higher than about 350 °C, the stored NO_x can be released under both rich and lean modes. Under a fuel-rich mode, the released NO_x is converted to N₂ by the catalysts on the close-coupled LNT. Under a fuel-lean mode, the close-coupled LNT will also release the stored NO_x. However, the released NO_x may not be converted to N₂ on the close-coupled LNT due to the lack of available reductants. Because the main LNT is located farther from the exhaust manifold of the engine than the close-coupled LNT, the temperature of the main LNT is generally lower than that of the close-coupled LNT. NO_x released from the close-coupled LNT will be stored on the main LNT, where it can be reduced to N₂ during fuel-rich modes.

[0009] A method is also provided for reducing the total NO_x released into the environment during operation of a vehicle containing a lean-burn engine. Cold start and engine operation are carried out as above. After the engine is turned off, the close-coupled LNT can be regenerated, such as by heating and by air provided by a heater and an air flow member, respectively. The heater on the close-coupled LNT and an air flow member, *e.g.*, air pump, may be turned on for a brief period (*e.g.*, 30 seconds) to heat the close-coupled LNT to a temperature where the closed-coupled LNT will release its absorbed NO_x (*e.g.*, approximately 600 °C). The NO_x released during this regeneration

of the closed-coupled LNT may be absorbed by the main LNT, thereby releasing little or no NO_x into the atmosphere. The close-coupled LNT may then be permitted cool down in the air.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The advantages of this invention will be apparent upon consideration of the following detailed disclosure of the invention, especially when taken in conjunction with the accompanying drawings wherein:

[0011] FIG. 1 is a schematic illustration of an apparatus for the removal of NO_x according to one exemplary embodiment of the present invention;

[0012] FIG. 2 is a graphical illustration of the NO_x concentration at the exit of a main lean NO_x trap (main LNT) with a lean exhaust feed that contains 250 ppm of NO during a NO_x storage capacity measurement at 150 °C;

[0013] FIG. 3 is a graphical illustration of an engine out emission and temperature data during cycle 1 of a cold start FTP (U.S. Federal Test Procedure); and

[0014] FIG. 4 is a graphical illustration of the NO_x concentration at the exit of a main lean NO_x trap (main LNT) with a lean exhaust feed that contains 250 ppm of NO during a NO_x storage capacity measurement at 150 °C, a temperature ramp up to approximately 600 °C, and subsequent cool down to 150 °C.

DETAILED DESCRIPTION OF THE INVENTION

[0015] It is known that internal combustion engines can operate in fuel-rich, stoichiometric, or fuel-lean modes in terms of a fuel-to-oxygen ratio. For example, when an engine operates in a fuel-rich mode, the exhaust stream contains excess reductants (e.g., fuel, CO, and H₂) and little oxygen after combustion in the engine cylinders. On the other hand, when the engine operates in a fuel-lean mode, the exhaust stream contains excess oxygen and few reductants. When the engine operates in a stoichiometric mode, which is the conventional operating mode for gasoline engines, the

exhaust stream contains an approximately equal amount of residual oxygen and reductants. For lean-burn engines, three-way catalytic converters cannot effectively remove NO_x emissions from the fuel-lean exhaust. Therefore novel catalyst technologies such as the lean NO_x traps are being developed to address this issue. For the LNTs to effectively remove NO_x emissions, the engines operate mostly in a fuel-lean mode with excursions of operating in a fuel-rich mode. During the fuel-lean mode, NO_x in the exhaust stream is absorbed by the LNTs to form metal nitrates. During the fuel-rich mode, the nitrates decompose and release NO_x. The released NO_x is reduced to N₂ in the rich exhaust by the excess reductants. Thus during both fuel-lean and fuel-rich modes, very little NO_x passes through the LNT and into the tailpipe emissions. The operating temperature window for LNTs are typically between 250-550 °C.

[0016] Before an engine is started, the LNT catalyst is at an ambient temperature. Once the engine is started, the catalyst is slowly heated by the hot exhaust gas from the engine. In the first several minutes, the catalyst temperature is substantially below 250 °C, *e.g.*, 50 – 150 °C. This period, when an engine is started yet the catalyst is at a temperature below its operating temperature, is termed “cold start”.

[0017] Referring to FIG. 1, a schematic illustration of a device for removing NO_x during such an engine cold start according to the present invention can be seen. In particular, the apparatus combines a close-coupled cold start LNT (lean NO_x trap) 11 with a main LNT (lean NO_x trap) 12. The close-coupled LNT 11 may be smaller in size than the main LNT 12. As shown in FIG. 1, the close-coupled LNT 11 may be positioned under the hood of an automobile and the main LNT 12 may be positioned under a floor of the automobile, *e.g.*, under the floor of the passenger compartment.

Thus, the main LNT 12 may be positioned at a location that is farther from the exhaust manifold of the engine than the close-coupled LNT 11. The close-coupled LNT 11 may be connected to the main LNT 12 by a hollow conduit 16 that permits the passage of an exhaust stream. During an engine cold start, e.g., when the catalyst temperature is below 250 °C, exhaust from the engine 13 is directed to the cold start LNT 11. The NO_x from the cold exhaust is stored in the close-coupled LNT 11 before the close-coupled LNT 11 and the main LNT 12 reach their respective operating temperatures, approximately 250 - 450 °C and approximately 250 - 500 °C respectively. The stored NO_x will not be released from the close-coupled LNT 11 under a fuel-lean mode until the close-coupled LNT 11 reaches approximately 350 °C. Therefore, when the temperature of the close-coupled LNT 11 is between 250 and 350 °C, the stored NO_x will only be released under a fuel-rich mode where excess reductants (e.g., hydrocarbons, CO, or H₂) are available. Because the close-coupled LNT 11 is catalytically active at these temperatures, close-coupled LNT 11 reduces the released NO_x to N₂.

[0018] When the temperature of the close-coupled LNT is higher than 350°C, the stored NO_x can be released under both fuel-rich and fuel-lean modes. Under a fuel-rich mode, the released NO_x is converted to N₂ by the catalysts on the close-coupled LNT. Under a fuel-lean mode, the close-coupled LNT will also release the stored NO_x. However, the released NO_x will not be converted to N₂ on the close-coupled LNT due to the lack of available reductants. Because the main LNT is located farther from the exhaust manifold of the engine than the close-coupled LNT, the temperature of the main LNT is lower than the close-coupled LNT and, as a result, the released NO_x will be stored on the main LNT and will be reduced to N₂ during fuel-rich modes.

[0019] Once the close-coupled LNT 11 reaches an operating temperature corresponding to an effective catalytic temperature (e.g., approximately 250 – 450 °C), the engine 13 may operate in a fuel-lean mode with periodic operation in a fuel-rich mode to convert the NO_x stored on the close-coupled LNT 11 to N₂. For example, the engine 13 may operate in a lean-rich cyclic operation mode such as, but not limited to 30 seconds lean/2 seconds rich. During the fuel-rich mode, the exhaust from engine 13 has a low oxygen content and a high content of reductants such as CO and H₂. These reductants can reduce the NO_x stored on the close-coupled LNT 11 to nitrogen (N₂). Under fuel-rich conditions, any NO_x released from the close-coupled LNT 11 that has not been converted by the reductants is absorbed on the main LNT 12 since the main LNT 12 is at a lower temperature than the close-coupled LNT 11. As a result, there is very little, if any, NO_x released from the main LNT 12 through the tailpipe 17 and into the environment.

[0020] Before an engine cold start, the close-coupled LNT 11 has a high NO_x storage capacity. However, after the engine 13 has been turned on and the close-coupled LNT 11 has been used to store NO_x and convert the stored NO_x to N₂, the close-coupled LNT 11 has a reduced storage capacity for NO_x. Therefore, the close-coupled LNT 11 may be regenerated after each use. In one embodiment, the close-coupled LNT such as illustrated in Figure 1 may be regenerated by heating above a temperature at which the compounds in the LNT release NO_x. In Figure 1 for example, to regenerate the close-coupled LNT 11, the engine 13 is turned off, and a heater 15 (e.g., electrical heater) on the close-coupled LNT 11 and an air flow member 14 (e.g., air pump) is turned on for a brief period, e.g. 30 seconds. Because the NO_x are stored on the LNTs 11 and 12 as

nitrate, they decompose at elevated temperatures and release NO_x. Thus, when the close-coupled LNT 11 is heated by the heater 15, the close-coupled LNT 11 releases its stored NO_x. The released NO_x is then absorbed by the main LNT 12. The absorbed NO_x is subsequently reduced to N₂ during the next vehicle operation. Because the NO_x released from the close-coupled LNT 11 is absorbed by the main LNT 12, there is a minimal, if any, release of NO_x through main LNT 12 during this regeneration of the NO_x storage capacity for the close-coupled LNT 11. In addition, the close-coupled LNT 11 will have sufficient storage capacity for the next engine cold start.

[0021] Each LNT catalyst has a fixed capacity for NO_x storage, which corresponds to the amount of NO_x storage components (e.g., alkali metal, alkaline earth metals, and/or rare earth metals) in the catalyst. When the catalyst is saturated, e.g., when all the NO_x storage components have been converted to nitrates by NO_x, the LNT can no longer store NO_x. Ideally, before this full storage capacity is reached, the exhaust exiting the LNT should contain no NO_x, i.e., zero NO_x breakthrough. However, as shown in FIG. 2, even when the close-coupled LNT catalyst has a 50% storage capacity, the exit NO_x concentration, i.e., the NO_x breakthrough, approaches 60% of the inlet NO_x concentration at 150 °C. This NO_x breakthrough indicates that the LNT can only store approximately 40% of the incoming NO_x even when it still has about 50% NO_x storage capacity.

[0022] Consequently, in order for a close-coupled LNT to have a low NO_x breakthrough and to efficiently reduce NO_x emissions during engine cold starts, the close-coupled LNT should retain most of its NO_x storage capacity. As a result, in a preferred embodiment of the present invention, the close-coupled LNT 11 is regenerated

before each engine cold start. The regeneration process converts the stored metal nitrates to metal oxides, carbonates, or hydroxides, and can be conducted in both fuel-rich and fuel-lean exhausts. The regeneration in a fuel-rich exhaust can be carried out at lower temperatures. However, at 150 °C, the close-coupled LNT 11 recovered only about 50% of its capacity after regenerating for 1 minute in a fuel-rich exhaust (see FIG. 4). In a fuel-lean exhaust, the close-coupled LNT recovered its full storage capacity after a 30-second regeneration at 600 °C (see FIG. 4). To ensure that the regenerated close-coupled LNT retains its full storage capacity, it should be cooled down in a NO_x-free exhaust.

[0023] Both the close-coupled LNT 11 and main LNT 12 can be made of a honeycomb-like substrate with the inner walls coated with at least one catalyst. The catalysts typically contain noble metals (e.g., Pt, Pd, and/or Rh), and NO_x storage materials including, but not limited to, oxides, hydroxide, and/or carbonates of alkali metals (e.g., Li, Na, or K), alkali earth metals (e.g., Ca, Sr, or Ba), or lanthanum group metals (e.g., La, Ce, etc.), compounds containing elements that form stable nitrates (e.g., alkali metal, alkaline earth metals, and/or rare earth metals), or a combination of such elements.

[0024] In a fuel-lean mode, NO_x in the exhaust is oxidized and stored as nitrates on the LNT catalyst. The stored NO_x can be released under both fuel-rich and fuel-lean conditions depending on the catalyst temperature and the catalyst formulation. For example, barium is a commonly used component in NO_x storage catalysts. Barium nitrate is stable in a fuel-lean exhaust at temperatures up to approximately 600 °C. However, barium nitrate will decompose and release NO_x at temperatures as low as 250 °C in a fuel-rich exhaust. Therefore, under normal operating conditions for lean burn

engines, an LNT will not release NO_x during a lean mode because the exhaust temperature is typically below 600 °C. The released NO_x will remain NO_x in a fuel-lean exhaust or in a fuel-rich exhaust before the LNT reaches its operating temperature range, e.g., 250 - 550 °C. Further, the released NO_x will be converted to N₂ by the LNT in a rich exhaust when the LNT reaches its operating temperature.

[0025] Having generally described this invention, a further understanding can be obtained by reference to certain specific examples illustrated below which are provided for purposes of illustration only and are not intended to be all inclusive or limiting unless otherwise specified.

[0026] Table 1 set forth below shows the experimental conditions for the following examples. The total flow rate was 6 liters per minute.

Table 1

Feed Composition		
	Lean	Rich
O ₂	10%	0
CO	0	3.6%
NO	250 ppm	0 or 60 ppm
H ₂	0	1.2%
HC	0	200 ppm
H ₂ O	5%	5%
CO ₂	5%	5%

[0027] Example 1

[0028] Referring to FIG. 2, the NO_x concentration profile at the exit of a main LNT with a fuel-lean air feed that contains 250 ppm of NO during a storage capacity measurement at 150 °C can be seen. At time 0, a gas stream was switched from a fuel-rich feed containing no NO to a fuel-lean air feed containing approximately 250 ppm of NO. The difference between the exit NO_x concentration and the inlet NO_x concentration (250 ppm), which was measured with a chemiluminescence NO_x analyzer, corresponds to the amount of NO_x absorbed by the catalyst. A blank cordierite sample was used to correct for the flow dynamics. Integrating the difference between the outlet NO_x concentrations after the blank cordierite and the catalyst with time yields the total amount of NO absorbed by the catalyst, i.e. yields the storage capacity.

[0029] After about 200 seconds, the outlet NO_x concentration approached, but did not reach the inlet NO_x concentration, e.g., the outlet NO_x almost reached 250 ppm. This result suggests that although the majority of the storage of NO_x was completed in the first 200 seconds of the measurement, there was an additional, although much slower storage process of NO_x that continued to occur after the first 200 seconds had passed. Although not wishing to be bound by theory, this additional storage process may be due to NO_x absorption on the alumina support. However, because this is a much slower process, it plays a relatively insignificant role in the ability of the LNTs to remove NO_x from an engine exhaust stream during an engine cold start.

[0030] Using an estimate of the amount of NO_x absorbed, excluding the contribution from the slower NO_x absorption, the storage capacity was calculated to be approximately 0.6 gram NO/L catalyst. On the other hand, during an FTP (U.S. Federal Test Procedure) driving cycle, the cumulative NO_x engine-out emission during a cold

start (e.g., less than approximately 200 °C) for a 4.9 L engine was determined to be approximately 0.1 - 0.2 grams (see FIG. 3). As shown in FIG. 3, a significant NO_x breakthrough started to occur only after the first 50 seconds of the measurement when about 50% of the storage capacity of the LNT had been consumed. This indicates that a reasonably sized LNT (e.g., greater than 1 liter) may have enough storage capacity to remove NO_x emissions from an engine exhaust during a cold start. However, it is preferable that the LNT maintain greater than 50% of the original storage capacity in order to avoid significant NO_x breakthrough.

[0031] Example 2

[0032] Referring now to FIG. 4, the exit NO_x concentration during a storage capacity measurement at 150 °C and a subsequent temperature ramp to 600 °C in the fuel-lean feed can be seen. The composition of the fuel-lean exhaust feed is set forth in Table 1 above. After the close-coupled LNT was saturated with NO_x at 150 °C, the temperature was gradually increased to 600 °C. During the heating, additional NO_x storage occurred with a small absorption peak at approximately 250 °C, followed by a much larger absorption peak at approximately 330 °C. Although not wishing to be bound by theory, the small absorption peak at 250 °C may be due to a minor storage component in the catalyst, and the larger absorption peak at 330 °C may be due to the formation of barium nitrate. At 350 °C, the LNT began to release the stored NO_x. As shown in FIG. 4, a peak release of NO_x occurred at approximately 420 °C. At approximately 600 °C, the exit NO_x concentration returned to the level of the inlet NO_x concentration, indicating that the LNT no longer stores or releases NO_x at 600 °C. The equal

inlet/outlet concentration of NO_x at 600 °C indicates that the NO_x storage capacity of the LNT can be thermally regenerated in fuel-lean exhaust feeds.

[0033] To verify that LNTs restore their storage capacity after a high temperature regeneration, the LNT was cooled to 150 °C in a fuel-lean exhaust feed containing approximately 250 ppm NO following a regeneration at 600 °C (see FIG. 4). It was determined that although the LNT was fully regenerated, its storage capacity was completely consumed during the cooling process in the temperature range of approximately 350 - 500 °C. Therefore, very little, if any, storage capacity remained at 150 °C. In order to maintain the NO_x storage capacity of the LNT, the LNTs are preferably cooled down in a NO_x-free gas stream after a high-temperature thermal regeneration in a fuel-lean gas stream.

[0034] The invention of this application has been described above both generically and with regard to specific embodiments. Although the invention has been set forth in what is believed to be the preferred embodiments, a wide variety of alternatives known to those of skill in the art can be selected within the generic disclosure. The invention is not otherwise limited, except for the recitation of the claims set forth below.

We claim:

1. An apparatus for the selective removal of NO_x from a gaseous stream comprising:
 - a first lean NO_x trap;
 - a second lean NO_x trap operatively connected to the first lean NO_x trap by a hollow conduit; and
 - a heater connected to the first lean NO_x trap.
2. The apparatus of claim 1, further comprising an air flow member operatively connected to the heater to blow heated air to the first lean NO_x trap.
3. The apparatus of claim 1, wherein the first lean NO_x trap absorbs NO_x when the first lean NO_x trap has a temperature of from 50 - 150 °C.
4. The apparatus of claim 1, wherein the first lean NO_x trap stores NO_x when the first lean NO_x trap has a temperature below approximately 250 °C.
5. The apparatus of claim 3, wherein the first lean NO_x trap releases NO_x when the first lean NO_x trap has reached a maximum storage capacity.

6. The apparatus of claim 4, wherein the second lean NO_x trap stores NO_x released from the first lean NO_x trap when the temperature of the second lean NO_x trap reaches approximately 350 °C.

7. The apparatus of claim 3, wherein the first lean NO_x trap has a smaller size than the second lean NO_x trap.

8. The apparatus of claim 1, wherein the first lean NO_x trap is positioned under a hood of an automobile and the second lean NO_x trap is positioned under a floor of the automobile.

9. An apparatus for the selective removal of NO_x from a gaseous stream comprising:

- a first lean NO_x trap positioned under a hood of an automobile;
- a second lean NO_x trap positioned under a floor of the automobile and operatively connected to the first lean NO_x trap by a hollow conduit;
- a heater connected to the first lean NO_x trap; and
- a air flow member operatively connected to the heater to blow air to the first lean NO_x trap.

10. The apparatus of claim 9, wherein the first lean NO_x trap stores NO_x when the first lean NO_x trap has a temperature below approximately 250 °C.

11. The apparatus of claim 10, wherein the first lean NO_x trap releases NO_x when the first lean NO_x trap has reached a maximum storage capacity.

12. The apparatus of claim 11, wherein the second lean NO_x trap stores NO_x released from the first lean NO_x trap when the temperature of the first lean NO_x trap reaches approximately 350 °C.

13. A method for the selective removal of NO_x from a gaseous stream comprising:

passing the gaseous stream through a first lean NO_x trap, the first lean NO_x trap storing the NO_x when the gaseous stream has a temperature below approximately 250 °C; and

passing the gaseous stream through a second lean NO_x trap, the second lean NO_x trap storing NO_x released from the first lean NO_x trap.

14. The method of claim 13, further comprising blowing heated air to the first lean NO_x trap.

15. The method of claim 13, further comprising heating the close coupled lean NO_x trap to a temperature sufficient to release stored NO_x from the close coupled lean NO_x trap.

16. The method of claim 15, wherein the temperature is approximately 600 °C.
17. The method of claim 15, further comprising cooling the close coupled lean NOx trap in an environment which does not contain NOx.
18. A method of regenerating a close coupled lean NOx trap comprising:
heating the close coupled lean NOx trap to a temperature sufficient to release
stored NOx from the close coupled lean NOx trap; and
cooling the close coupled lean NOx trap in an environment which does not
contain NOx.
19. The method of claim 18, wherein the temperature sufficient to release
stored NOx from the close coupled lean NOx trap is approximately 600 °C.
20. The method of claim 19, wherein the close coupled lean NOx trap is
heated for a period of approximately 30 seconds.
21. A method for selectively removing NOx from the exhaust stream of an
internal combustion engine during engine cold "start up" comprising:
passing the exhausts streams sequentially through a first lean NOx trap (LNT) and
a second lean NOx trap (LNT)
wherein the lean NOx traps comprise a catalyst that can catalyze the reduction of an NOx
to N₂ and a compound that can store NOx as nitrates.

22. A method according to claim 21, comprising storing NO_x as nitrates in the first LNT at a temperature below a catalytic temperature at which the catalyst in the first LNT catalyzes reduction of NO_x to N₂.

23. A method according to claim 22 comprising reducing the stored NO_x to N₂ in the first LNT under stoichiometric or fuel-rich engine operating conditions when the temperature of the first LNT reaches the catalytic temperature.

24. A method according to claim 22 comprising storing NO_x as nitrates in the second LNT under fuel-lean conditions when the first LNT reaches a temperature at which it releases the stored NO_x.

25. A method for reducing the total NO_x released into the environment during operation from cold start to shut down of a vehicle containing an internal combustion engine comprising:

passing an exhaust stream comprising NO_x from the engine sequentially through a first LNT and a second LNT, wherein the LNTs comprise a catalyst that can catalyze the reduction of NO_x to N₂ and compounds that can store NO_x as nitrates; and
regenerating the first LNT to release stored NO_x.

26. A method according to claim 25, further comprising operating the internal combustion engine with alternating cycles of rich and lean fuel.

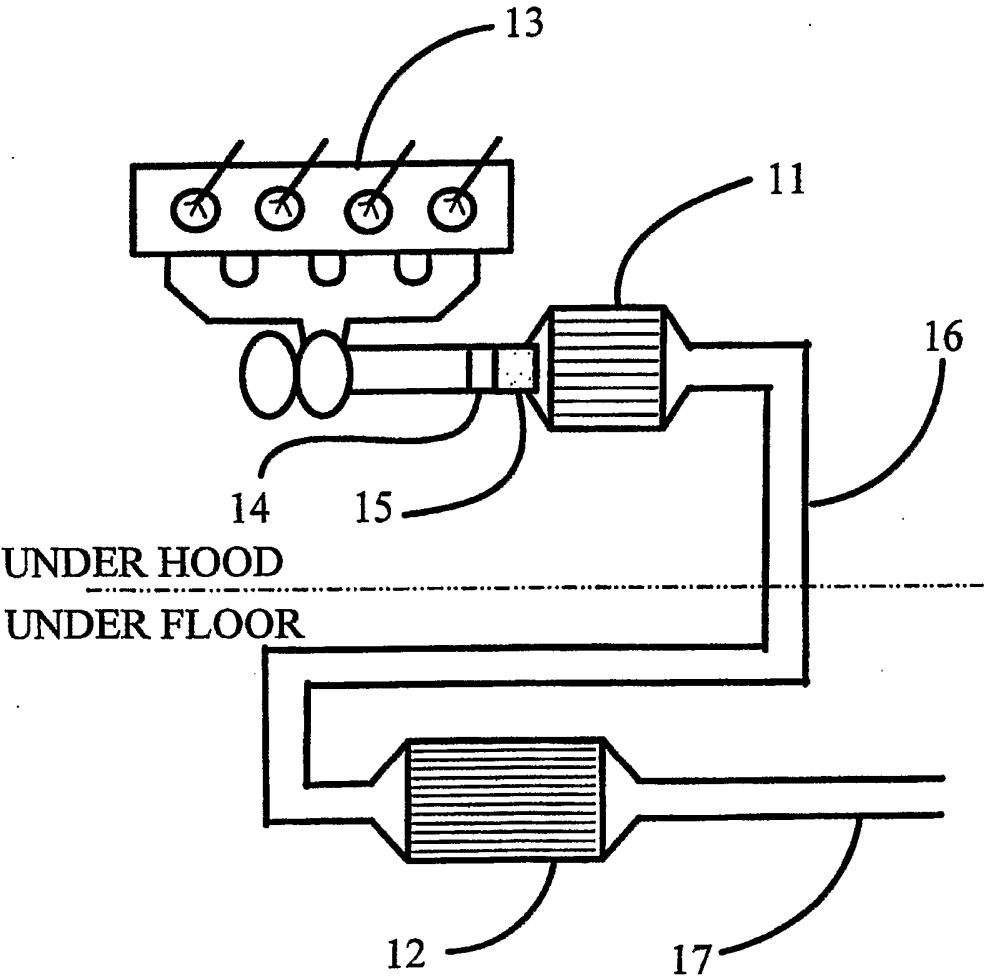
27. A method according to claim 25, wherein regenerating the first LNT comprises heating the compounds above a temperature at which they release NO_x.

28. A method according to claim 27 wherein the heating step is carried out in the presence of a fuel rich exhaust.

29. A method according to claim 27 wherein the heating step is carried out in the presence of a fuel lean exhaust.

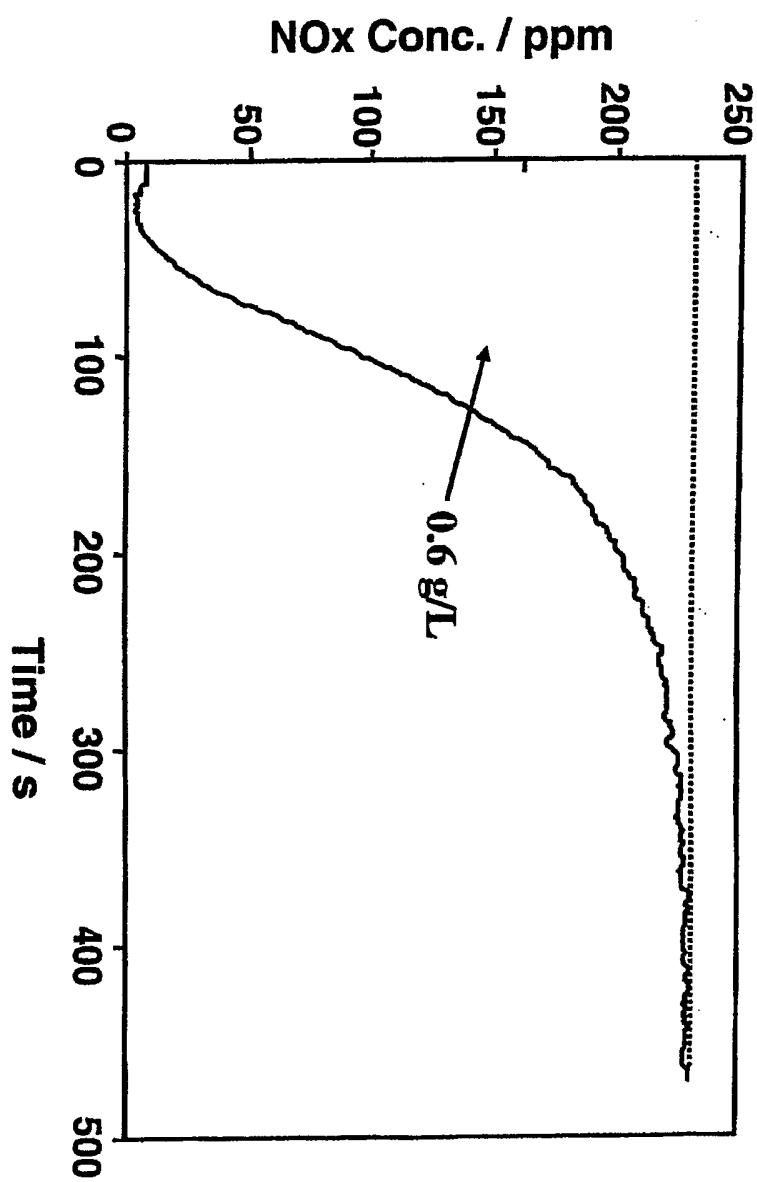
30. A method according to claim 27 wherein the heating step is carried out after the engine is turned off.

FIG. 1



2/4

FIG. 2



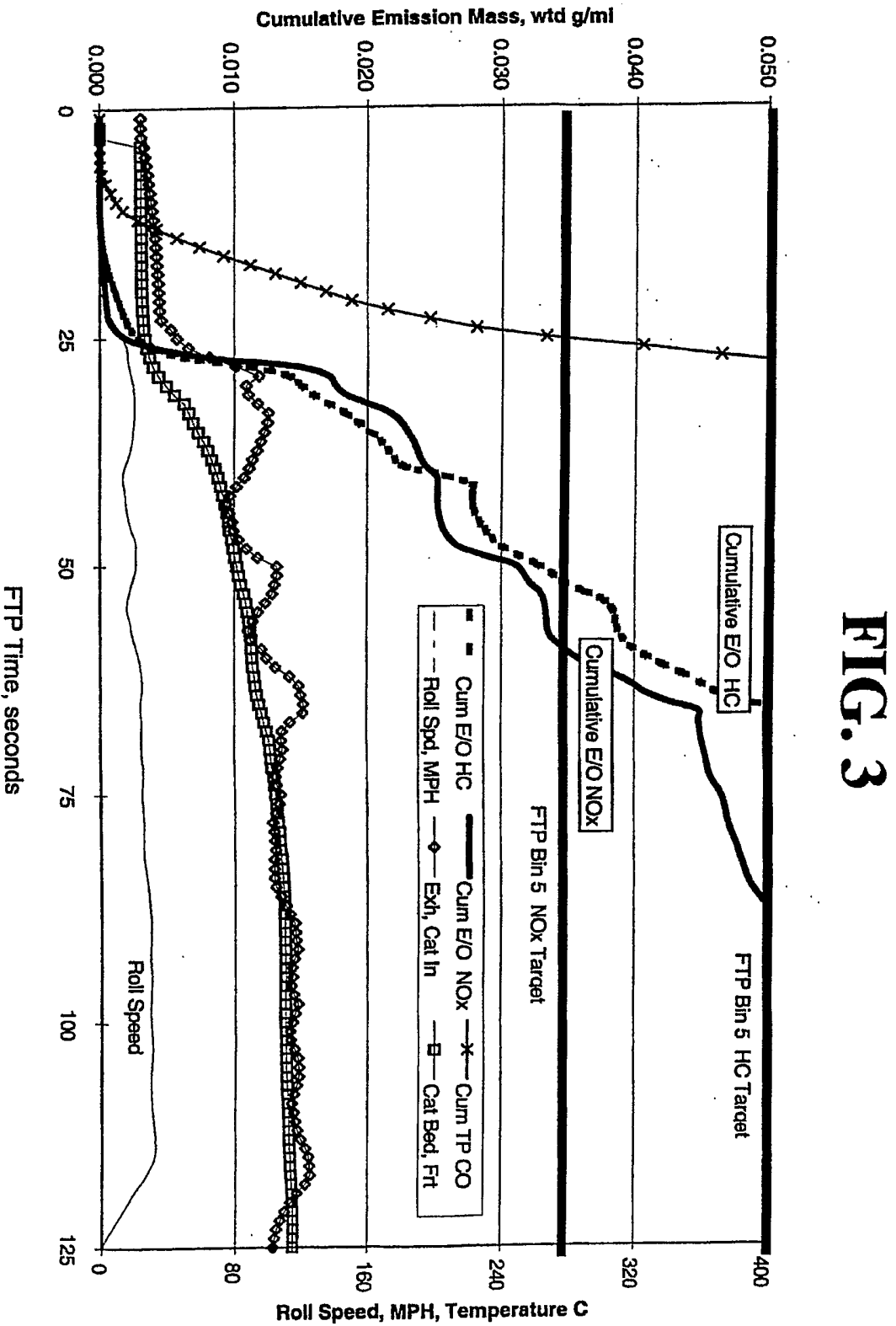


FIG. 4

