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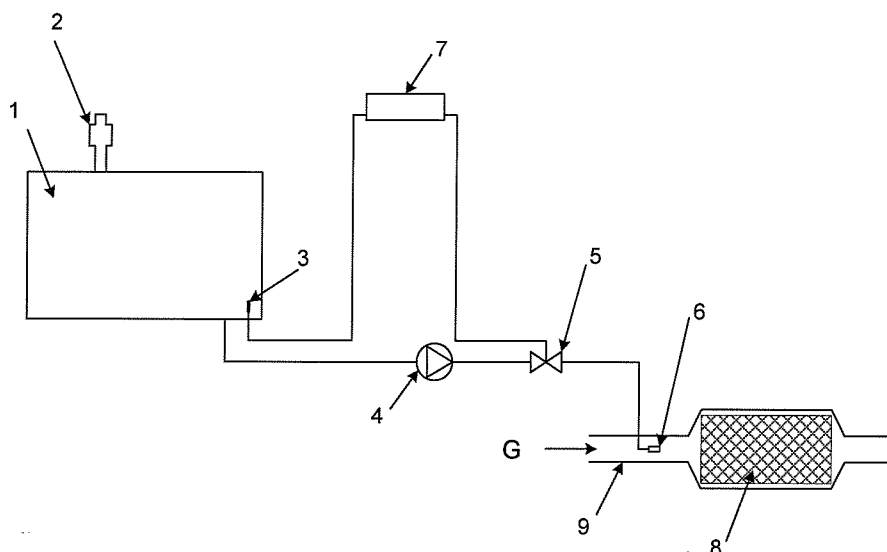
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(54) Title: METHOD AND SYSTEM FOR METERING AN AQUEOUS AMMONIA PRECURSOR SOLUTION INTO THE
EXHAUST GASES OF AN ENGINE



(57) Abstract: Method for metering an aqueous ammonia precursor solution stored in a ventilated and/or pressure-calibrated tank (1) into the exhaust gases (9) of an internal combustion engine, said method consisting in determining the precursor concentration of the solution based on a measurement of the temperature of the solution in the tank and on nomograms obtained by ageing of reference solutions and establishing, for various temperatures, the change in the precursor concentration as a function of the calibration pressure of the tank.

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Method and system for metering an aqueous ammonia precursor solution
into the exhaust gases of an engine

The present invention relates to a method and system for metering an aqueous ammonia precursor solution into the exhaust gases of an engine.

The change in legislation relating to emissions from diesel vehicles especially stipulates a significant reduction in releases of nitrogen oxide in exhaust gases. The SCR (Selective Catalytic Reduction) process in which
5 nitrogen oxides (NO_x) are reduced by ammonia is one of the technologies of choice for achieving this pollution control objective. An aqueous solution of an ammonia precursor (generally of urea or of a mixture of urea and ammonium formate) is then injected into the exhaust line upstream of the SCR catalyst. The
10 operation of this catalyst requires precise metering of the amount of solution sprayed. This is because both overmetering (leading to a release of ammonia into the atmosphere) and undermetering (leading to an expulsion of untreated nitrogen oxides into the atmosphere) are harmful.

However, these solutions are not stable over time, as the urea (and the
15 formate, where appropriate) decompose in water (and even more so when the temperature is high) into ammonia and into carbon dioxide. Therefore, certain systems of the prior art provide a correction of the amount of solution injected as a function of the change in the urea concentration as a function of the time, temperature and pressure. Such a system is, for example, described in Patent US
20 6,408,619 and Application US 2003/0033799 which describe the fact of correcting the volume of solution injected as a function of its effective urea concentration following its ageing. However, the methods described in these documents require specific sensors (of conductivity and of pressure respectively) which affect the cost of the SCR system.

25 The present application aims to solve this problem by providing an accurate and simple metering method that allows the ageing of the solution to be taken into account.

Therefore, the present invention relates to a method for metering an aqueous ammonia precursor solution stored in a ventilated and/or pressure-calibrated tank into the exhaust gases of an internal combustion engine, said
30 method consisting in determining the precursor concentration of the solution based

on a measurement of the temperature of the solution in the tank and on nomograms obtained by ageing of reference solutions and establishing, for various temperatures, the change in the precursor concentration as a function of the calibration pressure of the tank. This method has the advantage of being simple and of not adding a specific sensor to the system, a temperature sensor often being present already (especially for thermal conditioning of the solution).

Any ammonia precursor in aqueous solution may be suitable within the context of the invention. The invention gives good results with eutectic solutions of urea for which there is a standard quality: for example, according to the standard DIN 70070, in the case of the AdBlue[®] solution (commercial solution of urea), the urea content is between 31.8% and 33.2% (by weight) (i.e. 32.5 +/- 0.7% by weight) hence an available amount of ammonia between 18.0% and 18.8%. The invention may also be applied to the urea/ammonium formate mixtures sold under the trade name Denoxium[™] and of which one of the compositions (Denoxium-30) contains an equivalent amount of ammonia to that of the Adblue[®] solution. The latter have the advantage, with respect to urea, of only freezing from -30°C onwards (as opposed to -11°C), but have the disadvantages of corrosion problems linked to the possible release of formic acid.

The present invention may be applied to any internal combustion engine likely to generate NO_x in its exhaust gases. It may be an engine with or without a fuel return line (that is to say, a line returning the surplus fuel not consumed by the engine to the fuel tank). It is advantageously applied to diesel engines, and in particular to vehicle diesel engines and particularly preferably to the diesel engines of heavy goods vehicles.

One advantageous variant of the invention consists in taking into account all the forms of ammonia available directly or indirectly in the solution (in the form of precursor, ammonia and ammonium hydroxide), and not solely that derived from the precursor. It takes into account the fact that:

- urea hydrolyses according to the following overall reaction:



- the ammonia released is found partly in the atmosphere above the solution, partly dissolved in the latter and reacts partly with water to form ammonium hydroxide according to the reaction:



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- the ammonia and the ammonium hydroxide present in the solution are injected with it and participate in the reaction with the NO_x :



the equilibrium reaction (2) being displaced towards the left as the ammonia is consumed.

Similar reactions take place with the ammonium formate which, in solution, may release ammonia and formic acid and which decomposes at high temperature to form ammonia, carbon monoxide and carbon dioxide.

In the method according to the invention, the concentrations of precursor (urea and/or ammonium formate for example), and optionally of ammonia and of ammonium hydroxide, are first determined for reference solutions that have been intentionally left to age at various temperatures, so as to obtain nomograms.

According to one variant, in order to find out these concentrations, the total nitrogen is metered by an analytical chemistry method and the corresponding number of moles of NH_3 per litre of solution are deduced therefrom. Methods which are particularly suitable for this purpose are the Kjeldahl method and a pyrometry/chemiluminescence combination such as applied, for example, by analysers of the ANTEK 9000 NS type.

According to another variant, separate determinations of the precursor content (for example, by a conductivity method such as described in the aforementioned Patent US '619) and the content of ammoniacal nitrogen derived from its decomposition (for example, using an ammonia probe or by a colorimetric method, for example based on indophenol blue) are carried out, and the amounts of NH_3 available via these two sources are added together.

Whichever variant is used, either the calculated value is compared with the theoretical value given before (around 18% for the AdBlue[®] or Denoxium -30TM solutions) and a correction factor is deduced therefrom for the volume of solution to be injected; or the method according to the invention makes use of a computer which directly uses the calculated concentration value to deduce therefrom the volume to be injected.

According to the invention, the precursor solution is stored in a tank that is ventilated and/or of which the pressure is calibrated so that only the temperature, and not the pressure, is to be considered as a parameter for establishing the nomograms.

According to another advantageous variant which will be described in greater detail later on, the method according to the invention uses a computer

designed to be able to combine the conditioning times when the temperature of the solution varies over time (or in other words: that it can jump from one nomogram to another when the temperature varies and this with a view to combining the thermal ageing effects at the various temperatures). Alternatively, the tank could be equipped with a conditioning system that ensures a constant temperature in the tank, but this variant is more difficult and expensive to carry out in practice.

The present invention also relates to a system for metering an aqueous ammonia precursor solution and injecting it into the exhaust gases of an internal combustion engine, said system comprising at least one ventilated and/or pressure-calibrated tank, equipped with a temperature sensor and intended for storing the solution; a line for injecting the solution into the exhaust gases; and a computer that makes it possible to calculate the amount of solution to be injected into said gases as a function of at least one operating parameter of the engine and of the amount of precursor present in the solution obtained based on information from the temperature sensor and on nomograms obtained by ageing of reference solutions and establishing, for various temperatures, the change in the precursor concentration as a function of the calibration pressure of the tank.

The system according to the invention comprises at least one tank intended for storing the additive (precursor solution). This tank may be made from any material, preferably one that is chemically resistant to the additive in question. In general, this is metal or plastic. Polyolefin resins, in particular polyethylene (and more particularly HDPE or high-density polyethylene), constitute preferred materials.

The system according to the invention generally comprises a pump that is used to bring the additive solution to the pressure required for metering and injecting it. Various types of pumps may be suitable for the application: gear pump, piston pump, diaphragm pump, etc. This pump may be located in the additive tank (with the advantage of forming, with it, a compact and integrated module) or, considering the corrosive environment, be located outside of the additive tank. Its constituent materials will preferably be chosen from corrosion-resistant metals (especially certain grades of stainless steel and aluminium). The use of copper, even for connection components, is undesirable.

According to the invention, the tank is ventilated (i.e. vented to the atmosphere) and/or the pressure in the latter is calibrated by means of a suitable device. The latter may consist of a simple calibrated valve. Preferably, this valve

can direct vapours that create an overpressure in the tank towards a canister so that these vapours are not expelled as they are into the atmosphere but are first purified by the ammonia. This variant (with overpressure) also has the advantage that the solubility of the ammonia is increased and that therefore, a large part of the ammonia derived from the degradation of the precursor in the end remains available for the SCR reaction.

In this variant, the overpressure range generally extends from 100 mbar to 1 bar, with a preferred interval between 250 and 500 mbar. At the time of filling, the pressure inside the tank is atmospheric pressure. After closing the tank, the internal pressure results from the autogenous overpressure (resulting from the decomposition of the urea, a function of the temperature) and may not reach the calibration value of the valve.

The system according to the invention also comprises an injection line intended to bring the additive to the exhaust pipe of the engine and in order to do this connecting the tank and an injector generally located at the end of the injection line that opens into or near the exhaust pipe. This injector may be of any known type. It may be a so-called "active" injector, i.e. that includes a metering function, or a so-called "passive" injector then coupled to an additional metering device, such as a metering valve for example. It is advantageously a passive injector, and in particular a nozzle or spray gun making it possible to obtain drops of solution having a diameter between 5 and 100 μm . Such a nozzle is advantageously equipped with an orifice having a diameter of around 150 μm - 250 μm . This orifice is preferably supplied by a system of narrow channels (3-4) producing a "swirl" phenomenon (vortex) of the solution upstream of the nozzle. Clogging could be avoided by the purge which removes the last droplets of urea; there is therefore no crystallization by evaporation.

In this variant according to the invention, the amount of solution is preferably metered by regulating the opening frequency and duration of the metering valve. This valve may be a piezoelectric or solenoid valve, the regulation of which may be electronic.

The system according to the invention comprises a computer connected to the metering device and enabling the amount of additive required, as a function of the state of ageing of the solution and of at least one engine operating parameter which may be chosen from the emission level and degree of conversion of the NO_x ; temperature and/or pressure; engine speed and/or load, etc., to be brought to the injector.

In a preferred variant of the invention, this computer has a memory, in which nomograms are stored that give the change, as a function of time, of the concentration of precursor and of ammonia/ammonium hydroxide of the solution (expressed as they are or in the form of total available ammonia) for which the system is intended and this at various temperatures or even at various pressures corresponding to the different calibration devices (valves) that it is possible to use in this type of system.

The system according to the invention finally comprises a sensor for the temperature in the tank. Advantageously, this temperature sensor may also fulfil another role in the system (for example, for thermal conditioning of the solution).

The present invention is illustrated, in a non-limiting manner, by Figure 1 which illustrates a system according to a preferred variant of the invention. The flow direction of the exhaust gases is indicated therein by an arrow marked "G".

This system comprises a tank (1) containing the ammonia precursor solution. This tank is equipped with a system for maintaining an overpressure (250 – 500 mbar) (2) and a sensor (3) enabling the temperature of the solution to be measured. The overpressure has the advantage of increasing the solubility of the ammonia produced by degradation of the precursor.

The ammonia precursor is conveyed by the action of a pump (4) towards a nozzle (6) located in the line (9) for discharging the exhaust gases of the engine, upstream of an SCR catalyst (8). The amounts injected are controlled by a metering valve (5), the opening of which is operated by an electronic control unit or ECU (7). A temperature sensor (3) supplies data for input into the control unit (7).

The changes in the concentration of urea and of ammonia/ammonium hydroxide of the precursor solution as a function of time, determined in addition (for example by using the analytical methods described previously on solutions intentionally aged in the same system and from which samples are regularly withdrawn for analysis), are introduced into the ECU, considering the temperature as a parameter.

The temperature of the precursor solution is recorded over time. For given temperature levels, the conditioning times are combined. The ECU then refers to the changes in the concentration of urea and of ammonia/ammonium hydroxide and establishes the equivalent amount of ammonia available in the precursor solution at any point in the ageing. This equivalent amount is then compared to the initial amount, for which there is a standard quality: for example, according

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to the standard DIN 70070, in the case of the AdBlue[®] solution, the urea content is between 31.8% and 33.2% (by weight), hence an amount of available ammonia between 18.0% and 18.8%, and the correction factor for the volume to be injected is thus determined.

C L A I M S

- 1 - Method for metering an aqueous ammonia precursor solution stored in a ventilated and/or pressure-calibrated tank into the exhaust gases of an internal combustion engine, said method consisting in determining the precursor concentration of the solution based on a measurement of the temperature of the solution in the tank and on nomograms obtained by ageing of reference solutions and establishing, for various temperatures, the change in the precursor concentration as a function of the calibration pressure of the tank.
- 2 - Method according to the preceding claim, characterized in that the aqueous ammonia precursor solution is a eutectic solution of urea.
- 3 - Method according to either of the preceding claims, characterized in that the nomograms make it possible to deduce the total amount of ammonia available in the solution in the form of precursor, ammonia and ammonium hydroxide.
- 4 - Method according to Claim 3, characterized in that the amount of ammonia available in the reference solutions is determined by analytical metering of the total nitrogen present in the solution.
- 5 - Method according to Claim 3, characterized in that the amount of ammonia available in the reference solutions is determined based on the precursor content and the ammoniacal nitrogen content, determined independently by specific methods.
- 6 - Method according to any one of the preceding claims, characterized in that it uses a computer designed to be able to combine the conditioning times when the temperature of the solution varies over time.
- 7 - System for metering an aqueous ammonia precursor solution and injecting it into the exhaust gases of an internal combustion engine, said system comprising at least one ventilated and/or pressure-calibrated tank, equipped with a temperature sensor and intended for storing the solution; a line for injecting the solution into the exhaust gases; and a computer that makes it possible to calculate the amount of solution to be injected into said gases as a function of at least one operating parameter of the engine and of the amount of precursor

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present in the solution obtained based on information from the temperature sensor and on nomograms obtained by ageing of reference solutions and establishing, for various temperatures, the change in the precursor concentration as a function of the calibration pressure of the tank.

- 5 8 - System according to the preceding claim, characterized in that the tank comprises a calibrated valve capable of directing vapours that create an overpressure in the tank towards a canister.

- 9 - System according to Claim 7 or 8, characterized in that the nomograms make it possible to deduce the total amount of ammonia available in the solution
10 in the form of precursor, ammonia and ammonium hydroxide.

- 10 - System according to the preceding claim, in which the memory of the computer comprises several series of nomograms obtained at different calibration pressures.

- 1 / 1 -

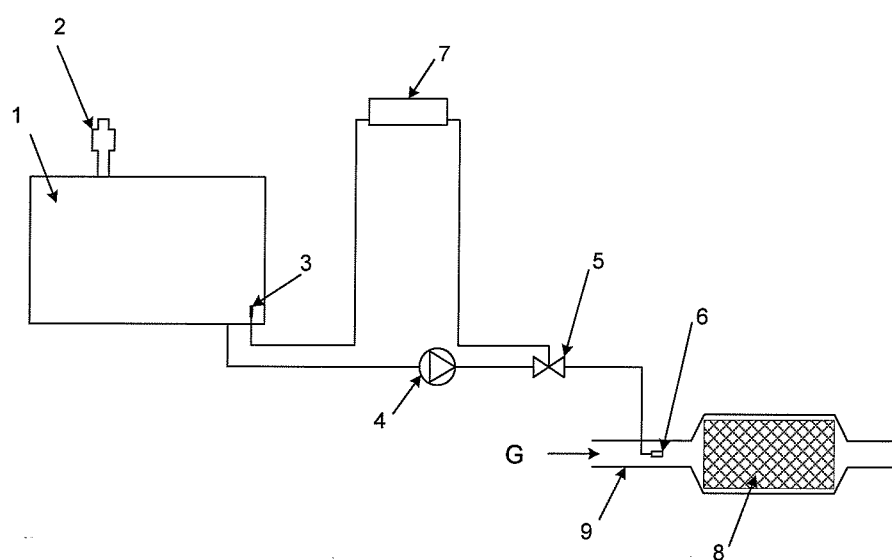


Fig.1

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

INV. B01D53/90 B01D53/94 F01N3/20

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

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Minimum documentation searched (classification system followed by classification symbols)

B01D 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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/033799 A1 (SCHEYING GERD [DE]) 20 February 2003 (2003-02-20) cited in the application figure 1 claims 1,14,20 paragraphs [0002], [0010], [0012], [0013], [0015], [0018], [0021], [0024], [0028], [0030], [0038] - [0056]	1-10
A	US 6 408 619 B1 (WISSLER GERHARD [DE] ET AL) 25 June 2002 (2002-06-25) cited in the application page 2, line 20 - page 3, line 16; claim 1	7-10



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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US 2003033799 A1	20-02-2003	DE 10139142 A1 EP 1283332 A2	20-02-2003 12-02-2003
US 6408619 B1	25-06-2002	AT 214628 T WO 9930810 A1 DE 19756251 C1 DK 1042052 T3 EP 1042052 A1 ES 2174545 T3 JP 2002508466 T	15-04-2002 24-06-1999 22-07-1999 08-07-2002 11-10-2000 01-11-2002 19-03-2002