(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 487 255 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number : **91310512.8**

(22) Date of filing : **14.11.91**

(51) Int. Cl.[5] : **C10L 10/06,** C10L 1/22, C10L 1/14

(30) Priority : **22.11.90 GB 9025387**

(43) Date of publication of application : **27.05.92 Bulletin 92/22**

(84) Designated Contracting States : **AT BE CH DE DK ES FR GB GR IT LI LU NL SE**

(71) Applicant : **THE BRITISH PETROLEUM COMPANY P.L.C.**
Britannic House, 1 Finsbury Circus
London EC2M 7BA (GB)

(71) Applicant : **BP Chemicals Limited**
Belgrave House 76 Buckingham Palace Road
London, SW1W 0SU (GB)

(72) Inventor : **Clark, Sian Catrin**
The British Petroleum Co. p.l.c, Chertsey Road
Sunbury-on-Thames, Middlesex TW16 7LN
(GB)

Inventor : **Greener, Neil Angus**
BP Chemicals Limited
Salt End, Hull HU12 8DS (GB)

Inventor : **Jeffrey, Gareth Charles**
The British Petroleum Co. p.l.c, Chertsey Road
Sunbury-on-Thames, Middlesex TW16 7LN
(GB)

Inventor : **Ostovar, Peyman**
The British Petroleum Co. p.l.c, Chertsey Road
Sunbury-on-Thames, Middlesex TW16 7LN
(GB)

Inventor : **Reid, Angus Joseph Dickson**
The British Petroleum Co. p.l.c, Chertsey Road
Sunbury-on-Thames, Middlesex TW16 7LN
(GB)

(74) Representative : **Crack, Richard David et al**
BP INTERNATIONAL LIMITED Patents
Division Chertsey Road
Sunbury-on-Thames Middlesex TW16 7LN
(GB)

(54) **Composition and process for inhibiting and removing carbonaceous deposits.**

(57) A hydrocarbon fuel composition suitable for an internal combustion engine comprises a hydrocarbon fuel and as a cleaning agent for carbonaceous deposits a compound selected from 1-(3-aminopropyl)-2-pyrrolidinone, 1-(3 aminopropyl) imidazole, N-hydroxyethyl imidazolidinone, N-aminoethyl-imidazolidinone and 2-(2-aminoethylamino) ethanol. The fuel can be a gasoline and include a carrier in which the cleaning agent is first dispersed before blending with the fuel. The carrier can be a lubricating oil, a polyether or a polymer of a C_2 to C_6 monoolefin.

EP 0 487 255 A1

The present invention relates to the inhibition of formation of carbonaceous deposits and also to their removal from surfaces by the use of a cleaning agent.

US 2 956 910 discloses a method for removing combustion deposits from the combustion chamber of an internal combustion engine by contacting the deposits with N-methyl-2-pyrrolidone and then removing the loosened deposits.

US 3 144 311 discloses the use of an alkyl substituted 2-pyrrolidone in fuel compositions for internal combustion engines to reduce deposition. In particular the addition of the pyrrolidone derivatives to gasoline to reduce the increase in octane number requirement of the engine with use is disclosed. Among pyrrolidone derivatives disclosed are N-methyl-2-pyrrolidone and N-beta-ethylene acetate-2-pyrrolidone. The latter compound gave no reduction in octane number requirement.

US 3 301 784 discloses certain N-hydrocarbyl C-alkyl substituted 2-pyrrolidones (described in the specification as pyrrolidinones). The substituents on the N atom disclosed include methyl, decyl, cyclohexyl and phenyl. No substituted hydrocarbyl substituents are disclosed. The compounds are used in gasolines to reduce deposit formation in the engine combustion chamber.

It is an object of the present invention to provide alternative cleaning agents for the inhibition of formation and the removal of carbonaceous deposits from surfaces.

According to one aspect of present invention a process for removing a carbonaceous deposit from a surface comprises contacting the deposit with a cleaning agent selected from 1-(3-aminopropyl)-2-pyrrolidinone, 1-(3-aminopropyl) imidazole, N-hydroxyethyl imidazolidinone, N-aminoethyl-imidazolidinone and 2-(2-aminoethylamino) ethanol.

The process of the present invention may be applied to carbonaceous deposits resulting from the thermal decomposition of carbon-containing compounds, for example, as a separate cleaning step after a process which produces carbonaceous deposits. Alternatively the cleaning agent may be included in a feed to a process giving rise the carbonaceous deposits to act as a deposit inhibitor. Thus the cleaning agent can be included as a deposit inhibitor in a fuel to an internal combustion engine, in particular in a gasoline fuel.

Thus according to the present invention a hydrocarbon fuel composition suitable for an internal combustion engine comprises a hydrocarbon fuel and, as a cleaning agent for carbonaceous deposits a compound selected from 1-(3-aminopropyl)-2-pyrrolidinone, 1-(3-aminopropyl) imidazole, N-hydroxyethyl imidazolidinone, N-aminoethyl-imidazolidinone and 2-(2-aminoethylamino) ethanol.

Suitable amounts of the cleaning agent are from 10 to 5000 ppm by weight, preferably from 50 to 2000 ppm based on the weight of the composition. The abbreviation ppm means parts per million.

The present invention also provides a process for the operation of an internal combustion engine comprising supplying a hydrocarbon fuel to the engine and to reduce carbonaceous deposits in the engine and/or the inlet system thereof the hydrocarbon fuel supplied to the engine contains a cleaning agent selected from 1-(3-aminopropyl)-2-pyrrolidinone, 1-(3-aminopropyl) imidazole, N-hydroxyethyl imidazolidinone, N-aminoethyl-imidazolidinone and 2-(2-aminoethylamino) ethanol.

1-(3-aminopropyl)-2-pyrrolidinone hereafter referred to as APP is a commercially available compound, obtainable from Aldrich Chemical Company Limited and is liquid at normal ambient temperatures and can thus be used undiluted. In general it will be preferred to use APP in admixture with a liquid diluent, preferably a diluent which is miscible with APP at the treatment temperature.

Mixtures of APP and diluent containing for example 5% to 40% by weight based on total weight of diluent and APP may be used for removal of deposits which have already formed.

The deposit is preferably treated with the cleaning liquid at moderately elevated temperatures. Examples of suitable temperatures are those in the range 100 °C to 200 °C or preferably 150 °C to 170 °C.

The duration of the treatment will depend on the amount of deposit but may for example range from 1 to 30 hours, preferably 10 to 25 hours. In the case of a fuel additive the treatment would be continuous.

For use in fuels the cleaning agent can conveniently be dissolved or dispersed in a carrier such as a lubricating oil, a hydrocarbon polymer or a polyether. Suitable carriers are disclosed, for example, in UK Patent No. 1346765, US Patent No. 4877416 and European Patent No. 62940. The carrier and the cleaning agent can be mixed to form a concentrate and the latter can then be added to the hydrocarbon fuel.

Conveniently the carrier will have a viscosity of between 20 and 2500 centistokes at 20°C and can be a polymer of molecular weight from 300 to 5000. Particularly suitable polymers are polyalkylene glycols such as those of polyoxyethylene and polyoxypropylene and their copolymers. Other polymers that can be used are polymers and copolymers of a C_2 to C_6 monolefin, preferably having a molecular weight from 300 to 5000, more preferably 500 to 2000.

The carrier can be present in the amount from 50 to 20,000 ppm, preferably 200 to 10,000 ppm based on the weight of the fuel composition.

According to another aspect of the invention a concentrate suitable for use in a hydrocarbon fuel in the

gasoline boiling range comprises 1 to 40% of a cleaning agent as specified above and up to 95% of a carrier selected from hydrocarbon polymers, polyethers, and lubricating oils, the % being by weight based on the total composition of the concentrate.

The concentrate can contain up to 75% of a fuel compatible diluent the % being by weight of the total composition of concentrate. The diluent can be one boiling in the range 50 to about 232°C. Suitable diluents are methanol, ethanol, propanol, methyl tertiary butyl ether and ethylene glycol monobutyl ether. Alternatively alkanes can be used such as heptane but preferably an aromatic hydrocarbon such as toluene or xylene can be used.

The invention will now be described by reference to the following examples and comparative tests.

Example 1

A deposit was generated by thermally decomposing a fully-formulated lubricant oil on a stainless steel plate maintained at 270°C. The lubricant oil was a commercially available product sold by BP as Visco 2000. The deposit was generated as follows:

The plate 25 mm × 75 mm was coated with the oil and heated at 270°C in air for 2 hours. Then the metal plate carrying the deposit was immersed in 80 g of a mixture in the weight ratio of 1:1 of (a) the lubricant used in generating the deposit and (b) a 1200 N base oil, the mixture containing 30 % weight/weight APP. The liquid mixture in which the surface carrying the deposit was immersed was heated to 160°C and allowed to remain at that temperature for 18 hours.

The amount of any removal of deposit from a metal surface was assessed by visual inspection. It was rated at 5 on a scale from 0 to 5. A rating of 5 corresponded to about 90% removal.

Example 2

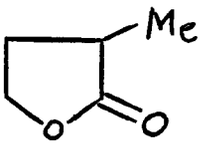
An experiment was carried out as in Example 1 except that the amount of APP used was 6% by weight.

The amount of deposit removed was rated at about 2.5 corresponding to about 40% removal of deposit.

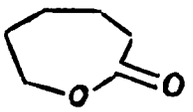
Comparative Test and Example 3

Experiments were carried out as in Example 1 using a variety of heterocyclic or nitrogen containing compound:: in place of APP. In some cases the additive was not soluble but melted at the temperature used and could therefore be used as a dispersion. The amount used was the maximum that could be either dissolved or dispersed in the lubricant/base oil medium. In general the amount of additive introduced was between 6% and 30% by weight. The cleaning ability of the compounds was assessed visually on a scale from 0 to 5 as in Example 1 above.

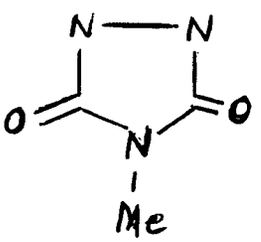
The following compounds were found to give no cleaning, namely



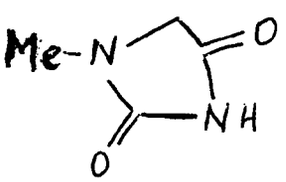
alpha methyl gamma butyrolactone



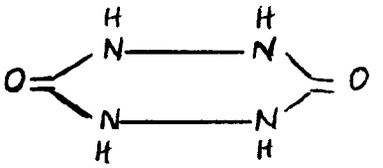
epsilon caprolactone



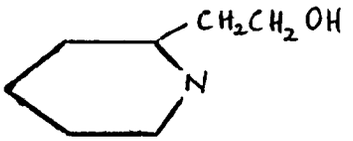
4-methylurazole



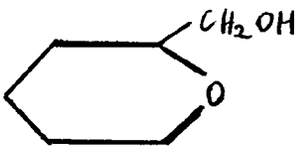
1 methylhydantoin



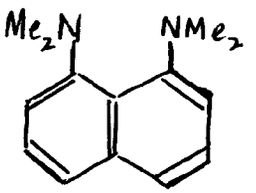
glycoluril



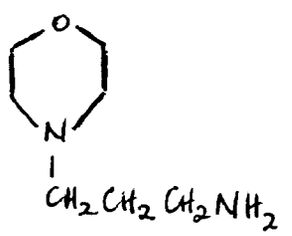
2-(2 hydroxyethyl)piperidine



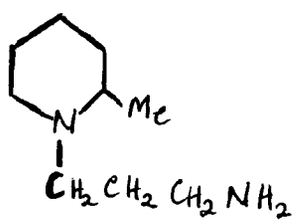
tetrahydropyran-2-methanol



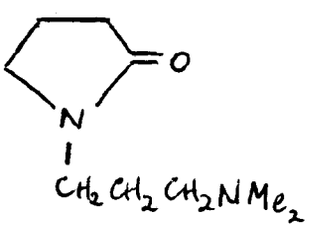
1,8 bis(dimethylamino)naphthalene



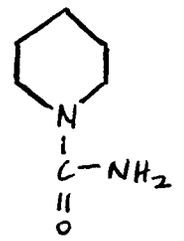
4-(3 aminopropyl)morpholine



1-(3 aminopropyl)-2-pipecoline

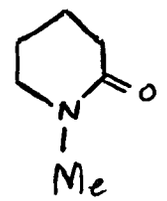


1-(3 dimethylaminopropyl)-2-pyrrolidinone

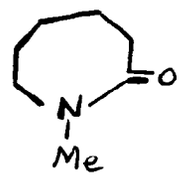


1 piperidinecarboxamide

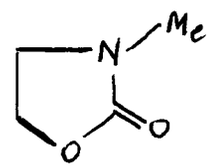
The following compounds were assessed at a cleaning value of 1, namely



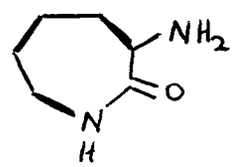
1-methyl-2-piperidone



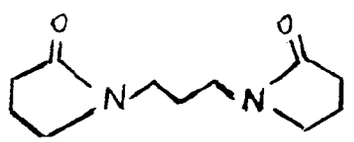
N-methylcaprolactam



3 methyl-2-oxazolidinone

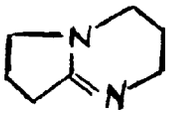


D-3 amino epsilon caprolactam

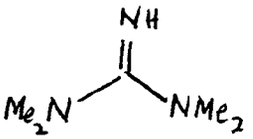


1,1'-(1,3-propanediyl)bis-2 pyrrolidinone

The following compounds were assessed as being a cleaning value of 2, namely

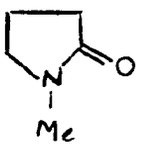


1,5 diaza bicyclo[4.3.0] non-5-ene



1,1,3,3-tetramethylguanidine

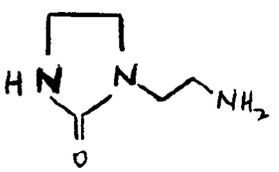
The following compounds were assessed as having a cleaning value of 3, namely



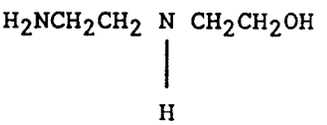
1-methyl-2-pyrrolidinone

Example 3

The following compounds were assessed as having a cleaning value of 4, namely



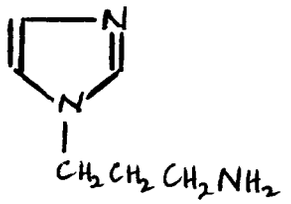
N-aminoethyl-imidazolidinone



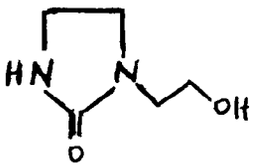
2-(2-aminoethylamino)ethanol

Example 4

and the following were assessed at between 4 and 5, namely,



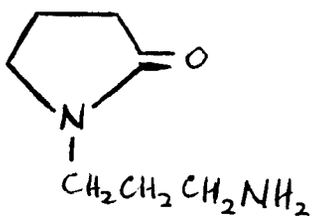
1-(3 aminopropyl)imidazole



N-hydroxyethyl imidazolidinone

Example 5

and assessed at 5 was



1-(3-aminopropyl)-2 pyrrolidinone

These results demonstrate the superior cleaning ability of the compounds according to the invention, namely
1-(3-aminopropyl)-2-pyrrolidinone, 1-(3 aminopropyl) imidazole, N-hydroxyethyl imidazolidinone, N-aminoethyl-imidazolidinone and 2-(2-aminoethylamino) ethanol.

Example 6

The cleaning agents having a cleaning value of 4 and 5 identified above are individually dispersed in a polyethylene glycol carrier of molecular weight 2000 to provide five dispersions containing 20% by weight of cleaning agent based on the total weight of the dispersion.

The dispersion is then added to an unleaded motor gasoline of octane number 97 to give a gasoline containing 500 ppm of cleaning agent. A series of tests are carried out on a Mercedes 102E engine. Firstly the engine is run for 60 hours using the base fuel, ie, the gasoline with no cleaning agent added and the inlet valves examined visually. Carbonaceous deposits are identified.

The engine is then run for a further 60 hours with the same gasoline but containing 500 ppm of the cleaning agent prepared as described above and the inlet valves examined visually. A reduction in the carbonaceous deposits is observed.

The operation of the engine over the 60 hour cycle is as follows: the engine is run for 4 minutes at 1500 RPM and then 6 minutes at 4500 RPM and this procedure repeated over the entire 60 hour cycle.

Claims

1. A hydrocarbon fuel composition suitable for an internal combustion engine comprising a hydrocarbon fuel and, as a cleaning agent for carbonaceous deposits, a compound selected from 1-(3-aminopropyl)-2-pyrrolidinone, 1-(3 aminopropyl) imidazole, N-hydroxyethyl imidazolidinone, N-aminoethyl-imidazolidinone and 2-(2-aminoethylamino) ethanol.

2. A hydrocarbon fuel composition as claimed in Claim 1 wherein the hydrocarbon fuel is a gasoline and the amount of the cleaning agent is from 10 to 5000 ppm by weight based on the weight of the composition.

3. A hydrocarbon fuel composition as claimed in Claim 2 which composition further comprises a carrier for the cleaning agent, the carrier being selected from hydrocarbon polymers, polyethers and lubricating oils.

4. A hydrocarbon fuel composition as claimed in Claim 3 wherein the carrier is present in an amount from 50 to 20,000 ppm by weight based on the weight of the composition.

5. A concentrate suitable for use in a hydrocarbon fuel in the gasoline boiling range comprising 1 to 40% by weight of a cleaning agent specified in Claim 1 and up to 95% of a carrier selected from hydrocarbon polymers, polyethers and lubricating oils, the % being by weight based on the total composition of the concentrate.

6. A concentrate as claimed in Claim 5 which further contains up to 75% of a fuel compatible diluent.

7. A process for removing a carbonaceous deposit from a surface which comprises by contacting the deposit with a cleaning agent selected from 1-(3-aminopropyl)-2-pyrrolidinone, 1-(3 aminopropyl) imidazole, N-hydroxyethyl imidazolidinone,
N-aminoethyl-imidazolidinone and 2-(2-aminoethylamino) ethanol.

8. A process for the operation of an internal combustion engine which process comprises supplying a hydrocarbon fuel to the engine and wherein to reduce carbonaceous deposits in the engine and/or the inlet system thereof the hydrocarbon fuel supplied to the engine contains a cleaning agent selected from 1-(3-aminopropyl)-2-pyrrolidinone, 1-(3 aminopropyl) imidazole, N-hydroxyethyl imidazolidinone, N-aminoethyl-imidazolidinone and 2-(2-aminoethylamino) ethanol.

9. A process as claimed in Claim 8 whereas the hydrocarbon fuel is a gasoline.

10. A process as claimed in Claim 8 wherein the hydrocarbon fuel is a diesel fuel.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 31 0512

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-3 734 865 (HEIBA ET AL.) * the whole document *	1-10	C10L10/06 C10L1/22 C10L1/14
D,A	US-A-2 956 910 (GIAMMARIA) * the whole document *	1-10	
D,A	US-A-3 144 311 (ARMSTRONG ET AL.) * the whole document *	1-10	
A	US-A-3 139 330 (MALEC) * the whole document *	1-10	
A	US-A-3 655 351 (JAMIESON) * the whole document *	1-10	
A	DE-B-1 115 519 (BASF) * the whole document *	1-10	
A	US-A-2 839 371 (SIGWORTH ET AL.) * the whole document *	1-10	
A	US-A-4 224 180 (SUJDAK) * the whole document *	1-10	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C10L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 DECEMBER 1991	DE LA MORINERIE

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)