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(54) **Use of an additive to reduce valve sticking**

Verwendung von Additiv um das Ventilkleben zu verringern

Utilisation d'un additive pour reduire l'adhésion de soupape

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WO-A-90/10051
US-A- 3 438 757
US-A- 4 039 300
US-A- 4 155 718

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Description

This invention relates to the use of additives in gasoline fuels for internal combustion engines.

The increasing density of traffic in large towns and on the roads is accompanied by pollution of the air by partially burnt or unburnt portions of motor vehicle fuels. One important factor contributing to the incomplete combustion of petroleum hydrocarbons and to the occurrence of residues of lubricating oil mist is the occurrence of unduly rich mixtures caused by impurities and deposits in the intake system of a spark ignition engine such as the carburettor.

The crank chamber of the engine is vented by recycling the blow-by gas to the suction point of the carburettor or to its air filter. Thus a portion of the oil mist formed in the crank chamber passes through the carburettor to the engine, where it is largely destroyed by combustion. However, portions of the oil mists become deposited on the inner surfaces of the carburettor. Modern high efficiency carburettors are complicated structures containing very fine channels and bores and precisely calibrated nozzles for atomizing and metering the petrol. The occurence of even small amounts of residues in these fine control members, nozzles and channels in the carburettor greatly impairs the efficiency of the latter, as a result of which the proportions of the components in the fuel/air mixture are changed undesirably so that the combustion of the fuel in the engine is not as complete as when the carburettor is clean. As mentioned above, the exhaust gases consequently contain unburnt and partially burnt hydrocarbon residues. At the same time, there is an undesirable shift of the ratio of carbon monoxide to carbon dioxide in the exhaust gases, i.e. the proportion of carbon monoxide is raised when the carburettor is fouled.

It has therefore been desirable to find ways of keeping internal combustion engines clean, of preventing the occurrence of deposits on inlet valves and in carburettor parts and, where carburettors are already fouled, of creating a detergent action by including suitable additives in the fuel for washing away the deposits and dirt present in the carburettor.

The art describes many proposals for overcoming the above problems by use of detergent additives in gasoline petroleum fuels. For example, GB-A-1 410 788 describe using various amine derivitives of carboxylic acids and the following patent specifications describe using aminated polyolefins such as aminated polyisobutylene: GB-A-1 346 765; US-A-3 438 757; US-A-3 565 804; US-A-3 574 576; and US-A-4 022 589. Certain of the above-mentioned specifications describe use of aminated polyolefins in admixture with certain hydrocarbon oils. Thus, GB-A-1 346 765 describes use of a polyamine together with a substance which does not consist of mineral oil constituents, but states that mineral oil constituents having a viscosity of from 20 to 2500 cS at 20°C may additionally be present. US-A-4 022 589 describes use of a polybutene amine together with a paraffinic hydrocarbon oil having a viscosity at 38°C (100°F) between 250 and 500 SUS.

US-A-3 438 757 describes the use of version polyamines in combination with a non-volatile lubricating mineral oil. The examples in the Table of this document show that large excesses of such a mineral oil, measured on a weight basis relative to the weight of polyamine, are required to reduce valve sticking in a harm test.

US 4 039 300 describes a gasoline additive comprising a detergent - which may be a long chain polyamine - and a mineral oil of lubricating viscosity and rich in aromatics, which additive is taught to inhibit the formation of hard, tenacious deposits on, inter alia, intake valves of internal combustion engines. Such deposits are different in nature to those deposits giving rise to valve sticking, and are known to form on the tulip sections of intake valves, rather than on the valve stems. SAE Paper No. 881643 indicates that the formation of valve tulip deposits is a different problem to that of the valve stem deposits which gives rise to valve sticking.

The present invention is concerned with the use, in combination, of a polyamine of a specified molecular weight and a hydrocarbon oil of specified viscosity.

The invention is the use of an additive in a gasoline petroleum fuel to reduce valve sticking within a spark ignition internal combustion engine in use of the fuel in said engine, the additive comprising an oil soluble polyolefin polyamine that contains at least one olefinic polymer chain attached to nitrogen atoms or carbon atoms of the alkylene radicals connecting the amine nitrogen atoms or both, the polyolefine having a number average molecular weight of greater than 500, and a hydrocarbon oil in the form of a mineral oil having a viscosity in the range of 200 to 1000 cSt at 40°C, the additive containing from 0.5 to 1.1 parts by weight of the polyolefin polyamine for each part of the hydrocarbon oil, and the weight of the additive, based on the weight of the gasoline petroleum fuel, being in the range of 20-2000 ppm.

As will be demonstrated in the examples of this specification, the invention is surprisingly effective in reducing valve sticking.

The features of the invention will now be discussed in greater detail.

ADDITIVE

(i) Polyolefine Polyamine

As stated above, such materials are known in the art. Preferably the polyolefine polyamine contains at least one

olefinic polymer chain attached to nitrogen or carbon atoms of the alkylene radicals connecting the amine nitrogen atoms or both. For example, the polyamine may have the general structural formula:

$$R^1{}_2N - R^2 - (NR^2)_x - NR^3{}_2$$

where

R^1 is hydrogen or polyolefin provided that at least one R^1 is polyolefin;

R^2 is alkylene having from 1 to 8 carbon atoms;

R^3 is hydrogen or alkyl having from 1 to 6 carbon atoms; and

x is from 0 to 5,

R^1, R^2 and R^3 being each independently branched or straight chained where appropriate.

R^1 may, for example, be polyethylene, polypropylene, polybutylene, polyisobutylene, polyethylene/polypropylene, or polyethylene/poly alpha-methyl styrene. Polyisobutylene is particularly preferred.

The polyolefine polyamine may be made by reacting an olefinic polymer such as exemplified above in respect of R^1 with a polyamine. Such polyamines may have, for example, from 2 to 12 nitrogen atoms and from 2 to 40 carbon atoms. They may be derived, for example, from polyalkylene polyamines including alkylene diamines and substituted polyalkylene polyamines. Preferably, the alkylene has 2 to 6 carbon atoms, more preferably 2 to 3 carbon atoms, between nitrogen atoms. Specific examples of such polyamines are primary and secondary low molecular weight aliphatic polyamines such as ethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, butylene diamine, trimethyl trimethylene diamine, tetramethylene diamine, diaminopentane or pentamethylene diamine, hexamethylene diamine, heptamethylene diamine, diaminooctane, decamethylene diamine, and higher homologues up to 18 carbon atoms. Ethylene diamine is preferred.

The number average molecular weight of the polyolefine of the polyolefine polyamine is as measured by vapour phase osmometry. Preferably it is 900 or greater, more preferably in the range of from 1000 to 5000, and most preferably in the range of from 1200 to 2500.

The polyolefine polyamine may be made by methods described in the art such as halogenating a polyolefine and reacting the resulting halide with a polyamine. See, for example, US-A-3 275 554 and DE-A-2 125 039. Moreover, US-A-4 832 702 describes its preparation by hydroformylating a polybutene or polyisobutene and subjecting the resulting oxo product to a Mannich reaction or amination under hydrogenating conditions.

Mineral Oil

"Mineral Oil" includes all components or mixtures of components which are obtained in refining naturally occuring petroleum oils such as distillates, residues and products obtained in conversion processes. It comprises one or more hydrocarbons. Preferably, the mineral oil is an oil obtained from residues of petroleum distillation such as a lubricating oil of high viscosity. Preferably, the viscosity of the mineral oil is in the range of 400 to 800 centistokes (cSt) at 40°C.

Proportions

The additive contains from 0.5 to 1.1 parts by weight of polyolefine polyamine for each part by weight of the hydrocarbon oil.

In the first, second and fourth aspects of the invention, the weight of additive based on the weight of the gasoline petroleum fuel is preferably in the range of 20 to 2,000 ppm, more preferably in the range from 50 to 500 ppm.

When the invention is a concentrate, the solvent therefor may be, for example, a hydrocarbon or an oxygen-containing hydrocarbon. Examples of hydrocarbons are alkanes or aromatic hydrocarbons such as benzene and xylene. Examples of oxygen-containing hydrocarbons are a butanol, a pentanol, and a hexanol. The concentration of the additive in the concentrate may be varied within wide limits according to needs and restrictions. In general, it may be in the range of 5 to 90% by weight, for example 10 to 70% by weight.

Other Additive Components

Other additives may be used in combination with the additive of this invention in the practice of the invention. Examples are: di (fatty acid amides) of aliphatic polyamines such as the di(oleic acid amide) of diethylene triamine, the di (stearic acid amide) of dipropylene triamine, the di(palmitic acid -amide) of diethylene triamine, the di(palmitic acid amide)

of diethylene diamine and the di(undecanoic acid amide) of triethylene tetramine.

Other examples are carboxylic acid derivatives of polyamines containing 1 to 6 nitrogen atoms per molecule such as palmitic, stearic, isostearic and undecanoic acid esters and tallow oil acid derivatives of polyamines or hydroxy amines, such as ethanolamines, isopropanolamines and polyamines such as tetraethylene pentamine.

Further additives which may be included are co-components such as plasticiser esters, for example adipates and mixtures thereof, antioxidants, scavengers, ignition improvers and metal deactivators. Such other additives may, for example, be present in the fuel in the range of 50 to 500 ppm (weight/weight).

FUEL

The fuels employed are compositions comprising hydrocarbons such as straight chain paraffins, branched chain paraffins, olefins, aromatic hydrocarbons, naphthenic hydrocarbons. Examples are those with initial boiling points of about 21°C (70°F) and final boiling points of about 232°C (450°F) (ASTM D-86). The fuel components can be derived by any of the conventional refining and blending processes. Synthetic fuels are also included.

The additive of the present invention can be added to the fuel as a mixture or separately in any order using conventional fuel additive injection methods. Preferably, the additive is added as a concentrate according to the third aspect of the invention.

EXAMPLES

The invention will now be particularly described in the following examples in which the following additive components were used:

A: a polyisobutylene polyamine prepared by aminating a polyisobutylene of number average molecules weight of 1300 with ethylene diamine.

B: a hydrocarbon oil comprising a mineral oil in the form of a lubricating oil of high viscosity obtained from residues of petroleum distillation and having the properties set out in Table I shown overleaf.

TABLE I

PROPERTY & ASTM TEST METHOD No.	ADDITIVE COMPONENT		
	B	D	E
Kinematic Viscosity (cS)			
- at 100°C	31.46	5.245	12.05
- at 40°C	492.5	29.93	113.1
(D 445)			
Viscosity Index (D 2270)	94	106	95
Ramsbottom Carbon No (D 524)	0.392	0.07	0.136
Pour Point (deg C) (D 97)	-12	-10	-13
Flash Point (deg C) (D 92)	315	229	272

C: a polyisobutylene polyamine prepared by aminating a polyisobutylene of number average molecular weight of 900 with ethylene diamine.

D: a hydrocarbon oil comprising a mineral oil having the properties set out in Table I.

E: another hydrocarbon oil having the properties set out in Table I.

It will be noted that additives including D or E as components do not fall within the definition of additives in the present invention.

General Procedure

A gasoline fuel was treated with an additive composition and a test engine was run on the treated fuel under conditions simulating the driving patterns of the police or sales personnel, ie mixed loads, urban, highway and country road driving, the daily mileage being from 350 to 500 and there being a cool down phase of about one hour between the engine being switched off and restarted at low ambient temperature. At the end of the test, the cylinder head of the engine was removed and inverted. The ease or otherwise with which the valves fell from the cylinder head under their own weight was used as a measure of the valve sticking effect, a PASS being recorded if the valves fell readily with no resistance to movement and a FAIL being recorded if the valves did not fall readily. Specific examples were as follows where all proportions are by weight based on the weight of fuel.

Example 1

A PASS was recorded when the additive composition comprised 228 ppm of A, 200 ppm of B and 152 ppm of diisodecyl adipate. The concentration of B was regarded as representing a minimum for passing the valve sticking test.

Example 2

A borderline PASS was recorded when the additive composition comprised 200 ppm of A and 400 ppm of E.

Example 3

A PASS was recorded when the additive composition comprised 300 ppm of C, 200 ppm of B and 500 ppm of diisodecyl adipate. The concentration of B was regarded as a minimum for passing the valve sticking test.

Example 4

A FAIL was recorded when the additive composition comprised 300 ppm of C and 500 ppm of E.

Example 5

A PASS was recorded when the additive composition comprised 230 ppm of A and 230 ppm of B.

Example 6

A FAIL was recorded when the additive composition comprised 300 ppm of C and 500 ppm of E.

Example 7

A FAIL was recorded when the additive composition comprised 300 ppm of C and 300 ppm of D.

Example 8

A PASS was recorded when the additive composition comprised 300 ppm of C, 300 ppm of B and 200 ppm of diisodecyl adipate.

It can be concluded from the above results that the additive composition of the invention (as in Example 1) requires a lower treat rate of hydrocarbon oil for detergency (cf Example 2), and that the use of additive B has an advantageous effect in comparison with use of additive D or additive E.

It should be noted that, in the examples, the esters were not considered to have any significant effect. In Examples 1 to 6, the test engine was a General Motors 1.6L engine and in Examples 7 and 8, the test was the VW Boxer engine test.

Claims

1. The use of an additive in a gasoline petroleum fuel to reduce valve sticking within a spark ignition internal combustion engine in use of the fuel in said engine, the additive comprising an oil soluble polyolefin polyamine that contains at least one olefinic polymer chain attached to nitrogen atoms or carbon atoms of the alkylene radicals connecting the amine nitrogen atoms or both, the polyolefin having a number average molecular weight of greater than 500, and

a hydrocarbon oil in the form of a mineral oil having a viscosity in the range of 200 to 1000 cSt at 40°C, the additive containing from 0.5 to 1.1 parts by weight of the polyolefin polyamine for each part by weight of the hydrocarbon oil, and the weight of the additive, based on the weight of the gasoline petroleum fuel, being in the range of 20 to 2000ppm.

2. The use of claim 1 wherein the polyolefin polyamine has the general structural formula:

$$R^1{}_2N - R^2 - (NR^2)_x - NR^3{}_2$$

where

R^1 is hydrogen or polyolefin provided that at least one R^1 is polyolefin;

R^2 is alkylene having from 1 to 8 carbon atoms;

R^3 is hydrogen or alkyl having from 1 to 6 carbon atoms; and

x is from 0 to 5,

R^1, R^2 and R^3 being each independently branched or straight chained where appropriate.

3. The use of claims 1 or 2 wherein the polyolefin polyamine is polyisobutylene aminated with ethylene diamine.

4. The use of any of the preceding claims wherein the number average molecular weight of the polyolefin is from 1000 to 5000.

5. The use of any of the preceding claims wherein the number average molecular weight of the polyolefin is from 1200 to 2500.

6. The use of any of the preceding claims wherein the viscosity of the mineral oil is in the range of 400 to 800 cSt at 40°C.

7. The use of any of the preceding claims wherein the range is 50 to 500 ppm.

Patentansprüche

1. Verwendung eines Additivs in einem Benzin-Erdölkraftstoff zur Verringerung des Ventilklebens in einem funkengezündeten Verbrennungsmotor bei Verwendung des Brennstoffs in dem Motor, wobei das Additiv ein öllösliches Polyolefinpolyamin, das mindestens eine olefinische Polymerkette enthält, die an Stickstoffatome oder Kohlenstoffatome der Alkylenreste, die Amin-Stickstoffatome verbinden, oder beide gebunden ist, wobei das Polyolefin ein durchschnittliches Molekulargewicht (Zahlenmittel) von mehr als 500 hat, und ein Kohlenwasserstofföl in Form eines Mineralöls mit einer Viskosität im Bereich von 200 bis 1000 cSt bei 40°C umfaßt, wobei das Additiv 0,5 bis 1,1 Gewichtsteile des Polyolefinpolyamins auf jeden Gewichtsteil des Kohlenwasserstofföls enthält und das Gewicht des Additivs im Bereich von 20 bis 2000 ppm, bezogen auf das Gewicht des Benzin-Erdölkraftstoffs, liegt.

2. Verwendung nach Anspruch 1, bei der das Polyolefinpolyamin die allgemeine Strukturformel

$$R^1{}_2N - R^2 - (NR^2)_x - NR^3{}_2$$

hat, in der R^1 Wasserstoff oder Polyolefin ist mit der Maßgabe, daß mindestens ein R^1 Polyolefin ist,
R^2 Alkylen mit 1 bis 8 Kohlenstoffatomen ist,
R^3 Wasserstoff oder Alkyl mit 1 bis 6 Kohlenstoffatomen ist, und
x 0 bis 5 ist, wobei
R^1, R^2 und R^3 gegebenenfalls jeweils unabhängig verzweigt oder geradkettig sind.

3. Verwendung nach Anspruch 1 oder 2, bei der das Polyolefinpolyamin mit Ethylendiamin aminiertes Polyisobutylen ist.

4. Verwendung nach einem der vorhergehenden Ansprüche, bei der das durchschnittliche Molekulargewicht (Zahlen-

mittel) des Polyolefins 1 000 bis 5 000 beträgt.

5. Verwendung nach einem der vorhergehenden Ansprüche, bei der das durchschnittliche Molekulargewicht (Zahlenmittel) des Polyolefins 1 200 bis 2 500 beträgt.

6. Verwendung nach einem der vorhergehenden Ansprüche, bei der die Viskosität des Mineralöls im Bereich von 400 bis 800 cSt bei 40°C liegt.

7. Verwendung nach einem der vorhergehenden Ansprüche, bei der der Bereich 50 bis 500 ppm beträgt.

Revendications

1. Utilisation d'un additif dans un combustible dérivé du pétrole, consistant en essence, pour réduire le collage des soupapes dans un moteur à combustion interne à allumage par étincelle lors de l'utilisation du carburant dans ledit moteur, l'additif comprenant une polyoléfine-polyamine soluble dans l'huile, qui contient au moins une chaîne polymérique oléfinique fixée à des atomes d'azote ou des atomes de carbone des radicaux alkylène connectant les atomes d'azote de groupes amine, ou bien à la fois à des atomes d'azote et des atomes de carbone, la polyoléfine ayant une moyenne numérique du poids moléculaire supérieure à 500, et une huile hydrocarbonée sous forme d'une huile minérale ayant une viscosité de 200 à 1000 cSt à 40°C, l'additif contenant 0,5 à 1,1 partie en poids de la polyoléfine-polyamine pour chaque partie en poids de l'huile hydrocarbonée, et le poids de l'additif, sur la base du poids du carburant dérivé du pétrole, consistant en essence, étant compris dans l'intervalle de 20 à 2000 ppm.

2. Utilisation suivant la revendication 1, dans laquelle la polyoléfine-polyamine répond à la formule structurale générale :

$$R^1{}_2N - R^2 - (NR^2)_x - NR^3{}_2$$

dans laquelle

R^1 représente l'hydrogène ou une polyoléfine, sous réserve qu'au moins un groupe R^1 représente une polyoléfine ;
R^2 représente un groupe alkylène ayant 1 à 8 atomes de carbone ;
R^3 représente l'hydrogène ou un groupe alkyle ayant 1 à 6 atomes de carbone ; et
x a une valeur de 0 à 5,

R^1, R^2 et R^3 représentant chacun indépendamment un groupe à chaîne ramifiée ou à chaîne droite, suivant les besoins.

3. Utilisation suivant la revendication 1 ou 2, dans laquelle la polyoléfine-polyamine consiste en un polyisobutylène aminé avec l'éthylènediamine.

4. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle la moyenne numérique du poids moléculaire de la polyoléfine va de 1000 à 5000.

5. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle la moyenne numérique du poids moléculaire de la polyoléfine va de 1200 à 2500.

6. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle la viscosité de l'huile minérale a une valeur de 400 à 800 cSt à 40°C.

7. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle l'intervalle va de 50 à 500 ppm.