FUEL FORMULATIONS CONTAINING DIALKYL CARBONATE

Field of the Invention

This invention relates to the use of certain materials in fuel formulations for new purposes.

Background to the Invention

In the interests of the environment, and to comply with increasingly stringent regulatory demands, it is necessary to increase the amount of biofuels used in automotive fuels.

Biofuels are combustible fuels, typically derived from biological sources, which result in a reduction in "well-to-wheels" (i.e. from source to combustion) greenhouse gas emissions. In gasoline fuels for use in spark ignition engines, the most common biofuels are alcohols, in particular ethanol. These are typically blended with more traditional gasoline fuel components. For use in diesel engines, fatty acid methyl esters (FAMEs) such as rapeseed methyl ester and palm oil methyl ester are the biofuels most commonly blended with conventional diesel fuel components.

Dialkyl carbonates, in particular the lower dialkyl carbonates dimethyl carbonate (DMC) and diethyl carbonate (DEC) are also biofuels which have in the past been added to both gasoline and diesel fuels. DMC and DEC have been used for instance as oxygenates, as combustion improvers and to reduce pollution levels. However, there are a number of practical constraints on the concentrations at which DMC and DEC can be included in automotive fuels. In particular, they appear to cause undesirable swelling of elastomeric engine components such as fuel pump seals, an effect which can reach unacceptable levels at as low as

5% v/v for DEC. In gasoline formulations, oxygen content specifications limit DMC and DEC concentrations to around 5% v/v. In diesel fuels, at least for use in the European Union, flash point and density specifications tend to limit DMC concentrations to less than 2% v/v and DEC concentrations to around 3% v/v. As a result, dialkyl carbonates have received little attention as fuel components other than at relatively low levels.

It would be desirable to provide new biofuel-containing fuel formulations which could overcome or at least mitigate the above problems.

Statements of the Invention

According to a first aspect of the present invention there is provided the use of

a dialkyl carbonate (DAC) having 6 or more carbon atoms in a fuel formulation for the purpose of improving the lubricity of the formulation.

It has surprisingly been found that higher molecular weight DACs can cause less elastomer damage than DMC and DEC in blends with both gasoline and diesel fuels. It has also surprisingly been found that these DACs can improve the lubricity of gasoline and diesel fuels. The use of a higher molecular weight DAC as a replacement for either DMC or DEC can therefore provide fuel benefits. Their reduced elastomer damaging effects can also allow the higher molecular weight DACs to be included in fuels at higher concentrations, thus providing increased bioenergy contents.

There can be a number of advantages to the use of DACs in fuel formulations, which advantages can be increased if the DACs can be included at higher concentrations. DACs for instance have low toxicity and are biodegradable. They have good octane blending properties, making them suitable for use in gasoline fuels. Unlike ethanol, which at blend ratios less than

7% v/v typically requires base fuel modification to compensate for undesirable RVP (Reid vapour pressure) boost, DACs do not significantly impact on the RVP of the base fuel blend at any blend ratios, making it easier to control evaporative emissions when they are used as components of gasoline formulations.

The use of DACs in diesel fuels can cause less environmental impact than the more traditional use of FAME biofuel components. DACs also show resistance to phase separation in hydrocarbon-water mixtures, which makes them less likely to migrate into water which may be present in wet storage tanks; they can also therefore help to stabilise ethanol-containing fuels.

DACs can be produced from renewable ingredients (carbon dioxide and bio-alcohols). DEC in particular can be produced from azeotropic ethanol, thus avoiding the energy penalty associated with breaking the azeotropic ethanol/water mix to produce anhydrous ethanol. DACs can thus provide a route to including an alcohol-based (in particular ethanol-based) oxygenate in a fuel, but with less carbon consumption.

A fuel formulation according to the invention may be suitable for use in an internal combustion engine. It may in particular be an automotive fuel formulation. In an embodiment, it is a gasoline fuel formulation which is suitable and/or adapted for use in a spark ignition (petrol) engine. In an alternative embodiment it is a diesel fuel formulation which is suitable and/or adapted for use in a compression ignition (diesel) engine. In further embodiments it may be suitable and/or adapted for use as an industrial gas oil, or as a domestic heating oil.

The DAC used in a fuel formulation according to the invention has 6 or more carbon atoms, including the carbonate (-C(O)O-) carbon. It is referred to herein as a "≥C6 DAC". It may contain 7 or 8 or more carbon atoms. It may contain up to 15 carbon atoms, or up to 14 or 13 or 12 or 11 or 10 or 9 carbon atoms. It may be a symmetric or an asymmetric DAC. In an embodiment, it is a symmetric DAC. Each of its two alkyl groups may independently be either straight chain (n-) or branched (as in for example an isopropyl or tert-butyl group). In an embodiment, at least one of the alkyl groups is a straight chain alkyl group. In an embodiment, both of the alkyl groups are straight chain alkyl groups.

Suitable symmetric ≥C6 DACs for use in the formulation of the invention include di-n-propyl carbonate (DPrC), di-isopropyl carbonate (DiPrC), di-n-butyl carbonate (DBC), and mixtures thereof. Other suitable symmetric ≥C6 DACs include dipentyl carbonate (DPeC), dihexyl carbonate (DHexC), diheptyl carbonate (DHeptC) and mixtures thereof; in each case the two alkyl groups may independently be either straight chain or branched.

Suitable asymmetric ≥C6 DACs include propyl ethyl carbonate (PrEC), butyl ethyl carbonate (BEC), pentyl ethyl carbonate (PeEC), hexyl ethyl carbonate (HexEC), heptyl ethyl carbonate (HeptEC), and mixtures thereof; in each case the alkyl group having three or more carbon atoms may be either straight chain or branched, suitably the former.

A fuel formulation according to the invention may contain a mixture of two or more ≥C6 DACs. The mixture may have been produced from a mixture of two or more alcohols: for example, ethanol and butanol together may

be used to prepare a mixture of DEC and DBC, or of DEC, BEC and DBC.

In an embodiment of the invention, the DAC is selected from DBC, BEC and mixtures thereof. In an embodiment, the DAC is DBC, in particular when the fuel formulation is a diesel fuel formulation.

In particular where the formulation is a gasoline fuel formulation, it may be preferred for the ≥C6 DAC to contain fewer than 9 carbon atoms, or fewer than 8 carbon atoms. In general, lower molecular weight DACs are likely to have boiling points within the normal gasoline range.

In particular where the formulation is a gasoline fuel formulation, the ≥C6 DAC may be selected from PrEC, BEC, DPrC, DiPrC and mixtures thereof. It may be selected from PrEC, BEC, DPrC and mixtures thereof.

In particular although not necessarily when the formulation is a gasoline fuel formulation, it may be preferred for the ≥C6 DAC not to be PrEC, or for the PrEC to be included at a concentration of less than 10% v/v or of 9 or 8 or 7 or 6% v/v or less.

In particular where the formulation is a diesel fuel formulation, it may be preferred for the ≥C6 DAC to contain at least 7 carbon atoms, or at least 8 carbon atoms. In general, higher molecular weight DACs are likely to have higher viscosities and higher flash points, thus making them more suitable for use as diesel fuel components; they are also more likely to have boiling points within the normal diesel range.

In particular where the formulation is a diesel fuel formulation, the ≥C6 DAC may be selected from BEC, DPrC, DiPrC, DBC and mixtures thereof. It may be selected from BEC, DPrC, DBC and mixtures thereof, or (in particular where the DAC concentration is 8 or 9 or 10% v/v or

greater) from DPrC, DBC and mixtures thereof. It may be selected from di(n-alkyl) carbonates having 7 or more carbon atoms, and mixtures thereof. It may be selected from BEC, DBC and mixtures thereof. In an embodiment, it is DBC.

In an embodiment, in particular where the formulation is a diesel fuel formulation, it may be preferred for the ≥C6 DAC to be selected from PrEC, DiPrC and mixtures thereof, or for the ≥C6 DAC to be PrEC, or for the ≥C6 DAC to be an asymmetric DAC.

Where the formulation is a gasoline fuel formulation, the ≥C6 DAC suitably has a boiling point (ASTM D86) of from 0 to 250ºC. Where the formulation is a diesel fuel formulation, the ≥C6 DAC suitably has a boiling point (ASTM D86) of from 150 or 180 to 360ºC.

The ≥C6 DAC may be included in the fuel formulation at a concentration of 0.5% v/v or greater, or of at least 1 or 2 or 3 or 4 or 5 or 6 or 7 or 8 or 9 or 10% v/v. Its concentration may in some embodiments be 25 or 50 or 75% v/v or greater. It may be included at a concentration of up to 100% v/v, or of up to 99 or 98% v/v; in other words, the ≥C6 DAC may itself be used as a fuel, or may represent the major proportion of a fuel formulation which may optionally contain minor amounts of fuel additives and/or additional fuel components.

The ≥C6 DAC may be included in the fuel formulation of the invention at a concentration of up to 95 or 90 or 80 or 70 or 60% v/v. In embodiments, it may be included at a concentration of up to 50% v/v, or of up to 40 or 30% v/v, or of up to 25 or 20 or 18 or 15 or 12 or 10% v/v. Its concentration may for instance be from 5 to 20% v/v or from 5 to 10% v/v. In particular where the DAC is DBC and the formulation is a diesel fuel formulation,

the DAC may be included at a concentration of up to 15 or 18 or 20% v/v or in cases of up to 30 or 40 or 50% v/v, or of up to 60 or 70 or 80 or 90 or 100% v/v.

The ≥C6 DAC may be obtained from any suitable source, of which many are available. It can for example be prepared by oxidative carbonylation of alcohols, or by transesterification of dimethyl carbonate with alcohols, or it may be generated as a co-product in the synthesis of monoethylene glycol from ethylene oxide and carbon dioxide via ethylene carbonate. The alcohols used in such processes may themselves be derived from biological sources.

In an embodiment, it may be preferred for the ≥C6 DAC not to have been synthesised using phosgene ($COCl_2$), as this may introduce undesirable impurities such as chlorides or carbonochloridic acid derivatives. Such impurities may contribute to deposit, stability and corrosion problems in a fuel formulation.

A fuel formulation according to the invention may contain other fuel components, as desired. Where it is a gasoline fuel formulation, for example, it may contain one or more gasoline fuel components, which are typically liquid hydrocarbon distillate fuel components containing hydrocarbons which boil in the range from 0 to 250°C (ASTM D86 or EN ISO 3405). A gasoline fuel component suitably has a research octane number (RON) (ASTM D2699) of from 85 to 115 or from 95 to 115 and/or a motor octane number (MON) (ASTM D2700) of from 75 to 95 or from 85 to 95.

Where the formulation is a diesel fuel formulation, it may contain one or more diesel fuel components, which are typically liquid hydrocarbon middle distillate fuel components (for example gas oils) containing hydrocarbons

which boil in the range from 150 or 180 to 360°C (ASTM D86 or EN ISO 3405). A diesel fuel component suitably has a measured cetane number (ASTM D613) of from 40 to 70 or from 40 to 65 or from 51 to 65 or 70.

Such additional fuel components may be derived from any suitable source. They may for example be petroleum derived. Alternatively they may be synthetic products such as from a Fischer-Tropsch synthesis. Additional fuel components may also be derived from biological sources. They may be or include oxygenates such as alcohols (in particular C1 to C3 aliphatic alcohols, more particularly ethanol) or fatty acid methyl esters (FAMEs) such as rapeseed methyl ester or palm oil methyl ester.

The formulation of the invention may contain one or more lower molecular weight DACs, for example selected from DMC, DEC and mixtures thereof, in addition to the ≥C6 DAC.

Where the formulation is a gasoline fuel formulation, it will suitably comply with applicable current standard gasoline fuel specification(s) such as for example EN 228 in the European Union. By way of example, the overall formulation may have a density from 0.720 to 0.775 kg/m^3 at 15°C (ASTM D4052 or EN ISO 3675); a final boiling point (ASTM D86 or EN ISO 3405) of 210ºC or less; a RON (ASTM D2699) of 95.0 or greater; and/or a MON (ASTM D2700) of 85.0 or greater. Relevant specifications may however differ from country to country and from year to year, and may depend on the intended use of the formulation. Moreover a formulation according to the invention may contain fuel components with properties outside of these ranges, since the properties of an overall blend may differ, often significantly, from those of its individual constituents.

Where the formulation is a diesel fuel formulation, it will suitably comply with applicable current standard diesel fuel specification(s) such as for example EN 590 (for Europe) or ASTM D975 (for the USA). By way of example, the overall formulation may have a density from 820 to 845 kg/m^3 at 15°C (ASTM D4052 or EN ISO 3675); a T95 boiling point (ASTM D86 or EN ISO 3405) of 360°C or less; a measured cetane number (ASTM D613) of 51 or greater; a kinematic viscosity at 40°C (ASTM D445 or EN ISO 3104) from 2 to 4.5 centistokes; a sulphur content (ASTM D2622 or EN ISO 20846) of 50 mg/kg or less; and/or a polycyclic aromatic hydrocarbons (PAH) content (IP 391(mod)) of less than 11% w/w. Relevant specifications may however differ from country to country and from year to year, and may depend on the intended use of the formulation. Moreover a formulation according to the invention may contain individual fuel components with properties outside of these ranges.

A fuel formulation according to the invention may contain standard fuel or refinery additives, in particular additives which are suitable for use in automotive gasoline or diesel fuels. Many such additives are known and commercially available. The formulation may for example contain a corrosion inhibitor, since DACs – in common with many other oxygenates – are known to be slightly corrosive and may reduce the performance of standard anti-corrosion additives. Suitable corrosion inhibitors include alkyl phosphates, esters, amine salts of alkenyl succinic acids, alkyl phosphoric acids and aryl sulphonic acids: commercially available examples include the products DCI™ 4a and 6a (ex. Innospec), Hitec™ 580 (ex. Afton), Nalco™ 5403 and 5405 (ex. Nalco), Spec-Aid™ 8Q22 (ex. GE Betz), and Tolad™ 351 and 4410

(ex. Baker Petrolite). They may be included at a concentration of up to 25 ppmw (parts per million by weight): slightly higher than usual treat rates may be required due to the presence of the DAC.

In an embodiment, the formulation contains a lubricity enhancing additive, although as discussed below the lubricity-enhancing properties of the ≥C6 DAC may make this unnecessary, or may make possible the use of lower levels of such additives.

The preparation of a fuel formulation according to the invention, involves blending together a DAC having 6 or more carbon atoms and one or more additional fuel components such as those described above. The additional fuel component(s) may for example be gasoline or diesel base fuels. The ≥C6 DAC and the additional fuel component(s) may also be mixed with one or more fuel additives. The process may be used to produce at least 1,000 litres of the fuel formulation, or at least 5,000 or 10,000 or 25,000 litres, or at least 50,000 or 75,000 or 100,000 litres.

A method of operating an internal combustion engine, and/or a vehicle which is driven by an internal combustion engine, involves introducing into a combustion chamber of the engine a fuel formulation described in the first aspect of the invention. The engine may be a spark ignition (petrol) engine. It may be a compression ignition (diesel) engine.

According to the first aspect of the invention there is provided the use of a DAC having 6 or more carbon atoms, in a fuel formulation, for the purpose of

improving the lubricity of the formulation. The formulation is suitably a diesel fuel formulation.

In the context of the first aspect of the invention, it may be preferred for the DAC to be an asymmetric DAC. In an embodiment, it may be selected from PrEC, BEC and mixtures thereof.

The lubricity of a fuel formulation can be assessed by any suitable method. One such method involves measuring the wear scar produced on an oscillating ball from contact with a stationary plate whilst immersed in the formulation. This "wear scar" may be measured for example using the test described in Example 3 below.

An "improvement" in the lubricity of a formulation may be manifested for example by a lower degree of wear scar, or of other friction-induced damage, in two relatively-moving components which are exposed to the formulation. The invention may be used to achieve any degree of improvement in the lubricity of the fuel formulation, and/or for the purpose of achieving a desired target lubricity.

A second aspect of the invention provides the use of a DAC having 6 or more carbon atoms, in a fuel formulation, for the purpose of reducing the concentration of a lubricity-enhancing additive in the formulation. Again the formulation is suitably a diesel fuel formulation.

In the context of this second aspect of the invention, the term "reducing" embraces any degree of reduction, including reduction to zero. The reduction may for instance be 10% or more of the original lubricity-enhancing additive concentration, or 25 or 50 or 75 or 90% or more. The reduction may be as compared to the concentration of lubricity-enhancing additive which

would otherwise have been incorporated into the fuel formulation in order to achieve the properties and performance required and/or desired of it in the context of its intended use. This may for instance be the concentration of lubricity-enhancing additive which was present in the formulation prior to the realisation that a ≥C6 DAC could be used in the way provided by the present invention, and/or which was present in an otherwise analogous fuel formulation intended (e.g. marketed) for use in an analogous context, prior to adding a ≥C6 DAC to it in accordance with the invention.

The reduction in lubricity-enhancing additive concentration may be as compared to the concentration of lubricity-enhancing additive which would be predicted to be necessary to achieve a desired target lubricity for the formulation in the absence of the ≥C6 DAC.

The lubricity-enhancing additive may be any additive which is capable of, or intended to, improve the lubricity of the formulation. Many such additives are known; they include for example R655™ (an ester-based additive ex. Infineum) and LZ 539C™ (an acid-based additive ex. Lubrizol).

A third aspect of the invention provides the use of a first DAC having 6 or more carbon atoms, in a fuel formulation, for the purpose of replacing all or part of a second DAC having fewer carbon atoms than the first DAC which is, or would otherwise have been, included in the formulation, whilst at the same time reducing the elastomer damaging effects (in particular the elastomer swelling effects) of the formulation due to the presence of the DAC(s).

The second DAC may be a DAC having 5 or fewer carbon atoms. It will typically be selected from dimethyl

carbonate (DMC), diethyl carbonate (DEC) and mixtures thereof. It may have been included, or intended to be included, in the formulation for any purpose, for example as an oxygenate, to increase the bioenergy content of the fuel, or as a combustion improver, or to reduce pollution levels caused by combustion of the fuel.

The first DAC may have 7 or more carbon atoms, or 8 or 9 or more carbon atoms.

The third aspect of the invention allows a higher molecular weight DAC to be used in place of a lower molecular weight DAC such as DMC or DEC, in order to reduce the elastomer damaging effects which can be caused by the use of DMC and DEC in fuel formulations. This mitigation of elastomer damaging - in particular elastomer swelling - effects can allow higher concentrations of DAC to be included in a formulation. It therefore allows a fuel to benefit from the advantages of including a DAC, but with less of an increase in the elastomer damaging effects of the overall formulation than would be caused by including the same concentration of DMC or DEC alone.

The first DAC (which has 6 or more carbon atoms) may therefore be used, in a DAC-containing fuel formulation, for the purpose of increasing the overall DAC concentration whilst maintaining the elastomer damaging effects of the formulation within a desired specification, and/or for the purpose of reducing the elastomer damaging effects of the formulation relative to those that would be caused by the inclusion of the same amount of a second DAC which typically has 5 or fewer carbon atoms.

Thus the present invention is able to provide more optimised methods for formulating biofuel-containing fuel

formulations, in particular to achieve target levels of elastomer damage and/or lubricity.

In the context of the third aspect of the invention, an elastomer damaging effect may be any effect which reduces the ability of an elastomeric material to function correctly in a fuel-consuming system and/or in the presence of a fuel formulation. It may comprise swelling of the elastomer when in contact with the fuel formulation. It may comprise a change (typically a reduction) in the hardness and/or flexibility of the elastomer when in contact with the fuel formulation.

Elastomer swell measurements in particular provide a measure of the compatibility of elastomeric materials, such as are used in fuel pump seals and other engine components, with a fuel component or formulation or additive. Generally this compatibility is evaluated by assessing changes in the properties of an elastomer due to its immersion in a test fluid. The elastomer swelling effects of a fuel formulation may for instance be assessed by measuring the increase or percentage increase in volume of an elastomeric material on immersion in the formulation for a predetermined period of time. A smaller volume increase indicates a reduction in elastomer swelling effects. This assessment may for example be carried out for nitrile and/or fluorocarbon elastomers, suitably both. A suitable assessment method is described in Example 1 below. Alternatively a standard test method such as ISO 1817:1998 may be used to measure elastomer swell effects.

Changes in the hardness and/or flexibility of an elastomeric material may be assessed using standard test methods such as the Shore hardness test or TMS 556.

In the context of the present invention, "use" of a DAC in a fuel formulation means incorporating the DAC into the formulation, typically as a blend (i.e. a physical mixture) with one or more other fuel components. The DAC will conveniently be incorporated before the formulation is introduced into an engine or other system which is to be run on the formulation. Instead or in addition the use of a DAC may involve running a fuel-consuming system, typically an internal combustion engine, on a fuel formulation containing the DAC, typically by introducing the formulation into a combustion chamber of an engine.

"Use" of a DAC in the ways described above may also embrace supplying the DAC together with instructions for its use in a fuel formulation to achieve the purpose(s) of any of the first to the third aspects of the invention, for instance to improve the lubricity of the formulation. The DAC may itself be supplied as part of a composition which is suitable for and/or intended for use as a fuel additive, in which case the DAC may be included in such a composition for the purpose of influencing its effects on the lubricity and/or elastomer damaging effects of a fuel formulation.

Use of a DAC in a fuel formulation for a particular purpose may also embrace using the DAC itself as a fuel for the relevant purpose, optionally together with minor amounts of one or more fuel additives.

Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of the words, for example "comprising" and "comprises", mean "including but not limited to", and do not exclude other moieties, additives, components, integers or steps. Moreover the singular encompasses the

plural unless the context otherwise requires: in particular, where the indefinite article is used, the specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

Preferred features of each aspect of the invention may be as described in connection with any of the other aspects. Other features of the invention will become apparent from the following examples. Generally speaking the invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims and drawings). Thus features, integers, characteristics, compounds, chemical moieties or groups described in conjunction with a particular aspect, embodiment or example of the invention are to be understood to be applicable to any other aspect, embodiment or example described herein unless incompatible therewith. Moreover unless stated otherwise, any feature disclosed herein may be replaced by an alternative feature serving the same or a similar purpose.

The present invention will now be further described with reference to the following non-limiting examples.

Example 1

Gasoline fuel formulations were prepared by blending a number of DACs, each at both 5% v/v and 10% v/v, with a gasoline base fuel GBF. The base fuel was a commercially available EN 228-compliant unleaded gasoline with 95 RON (ex. Shell).

The DACs tested were dimethyl carbonate (DMC), diethyl carbonate (DEC), n-propyl ethyl carbonate (PrEC), n-butyl ethyl carbonate (BEC), di-n-propyl carbonate (DPrC) and di-isopropyl carbonate (DiPrC). Their

properties are summarised in Table 1 below. Table 1 also shows the properties of di-n-butyl carbonate (DBC), which was used in Examples 2 to 5.

Table 1

Property	DMC	DEC	PrEC	BEC	DPrC	DiPrC	DBC
Molecular weight	90	118	132	146	146	146	174
Symmetric (S) or asymmetric (A)	S	S	A	A	S	S	S
Research octane no. (RON)	>120	>120	n.d.	n.d.	n.d.	n.d.	n.d.
Motor octane no. (MON)	>118	105.7	n.d.	n.d.	n.d.	n.d.	n.d.
Cetane no. (CN)	<20	<20	n.d.	n.d.	n.d.	n.d.	n.d.
Flash point (°C)	16.5	34.5	29	53	59	45.5	89
Boiling point (°C)	90	126	175	174	175	150	215
Density @ 15°C (g/cm^3)	1.076	0.981	0.966	0.945	0.949	0.927	0.929
Water solubility (g/L)	151	29	19	9	5	14	5
Kinematic viscosity @ 40°C (cSt)	0.48	0.66	0.849	0.976	1.097	0.967	1.462
Lower heating value (LHV) (MJ/kg)	14.5	21.6	22.9	25.0	25.1	25.4	28.2

n.d. = not determined

Properties were measured using the test methods indicated in Table 2 below.

Table 2

Property	Test method
RON	ASTM D2699
MON	ASTM D2700
CN	ASTM D613
Flash point	IP 34
Boiling point (& other distillation properties)	IP 123
Density @ 15ºC	IP 365
Water solubility	Internal method (see Example 4)
Kinematic viscosity @ 40ºC	IP 71
LHV	IP 12

Table 3 summarises some of the physicochemical properties of the gasoline base fuel GBF and of blends of the base fuel with DMC and DEC at both 5 and 10% v/v. Table 3 also shows, where applicable, the values required by the European gasoline specification EN 228.

Table 3

Parameter	GBF	EN 228 min	EN 228 max	GBF + 5% DMC	GBF + 10% DMC	GBF + 5% DEC	GBF + 10% DEC
RON	96.1	95.0	-	96.6	97.3	96.5	97.5
MON	85.5	85.0	-	86.0	86.7	85.8	86.7
Density @ 15°C (g/cm^3)	0.7430	0.720	0.775	0.7582	0.7738	0.7545	0.7660
Distillation:							
IBP	30.40			28.60	30.60	29.80	29.30
10% rec	46.10			45.60	45.80	47.20	45.20
50% rec	101.90			95.60	91.80	104.90	108.00
90% rec	160.60			156.50	157.40	157.20	154.80
FBP	202.00		210	201.20	203.50	201.70	203.70
E70	29.90	20	48	31.40	31.20	28.20	25.70
E100	48.80	46	71	53.00	56.70	46.70	44.00

Table 4 summarises some of the physicochemical properties of blends of GBF with the higher molecular weight dialkyl carbonates PrEC, BEC, DPrC and DiPrC, again at both 5 and 10% v/v.

Table 4

Parameter	GBF + 5% PrEC	GBF + 10% PrEC	GBF + 5% BEC	GBF + 10% BEC	GBF + 5% DPrC	GBF + 10% DPrC	GBF + 5% DiPrC	GBF + 10% DiPrC
RON	95.8	96.5	95.4	95.8	95.9	96.4	96.2	97.1
MON	85.9	87.5	86.0	86.7	86.7	87.0	86.3	87.1
Density @ 15ºC (g/cm^3)	0.753	0.763	0.752	0.761	0.752	0.762	0.753	0.758
Distillation:								
IBP	30.1	31.0	27.5	31.3	30.2	31.6	30.0	26.2
10% rec	44.0	45.7	44.3	43.4	46.1	44.3	51.6	46.0
50% rec	105.0	108.5	105.3	108.6	106.2	108.9	107.1	108.7
90% rec	156.7	156.3	163.1	164.9	162.8	164.0	158.2	155.2
FBP	202.3	200.0	200.9	196.8	200.8	198.5	201.9	197.5
E70	25.9	24.4	25.8	25.1	24.7	24.7	21.5	23.9
E100	45.0	42.3	45.2	42.8	44.2	42.4	42.4	42.0

It can be seen from Table 4 that all of the blends containing ≥C6 DACs were compliant with the EN 228 gasoline specification in terms of their octane numbers and densities. Indeed, the DACs increased the octane numbers of the base fuel, the ≥C6 DACs performing generally better in this respect than DMC and DEC and also in many cases reducing the fuel sensitivity (RON - MON) better than DMC and DEC. Although the blends containing ≥C6 DACs had E100 values below the EN 228 minimum, it is expected that such issues could be resolved fairly readily by minor adjustments to base fuel specifications prior to the addition of a ≥C6 DAC.

The elastomer damaging effects caused by each of the GBF/DAC blends, and by the base fuel itself and the neat DACs, were then assessed using the following test method, which is a modified version of the standard test method ISO 1817:1998. Two elastomeric materials were tested: a hydrogenated nitrile elastomer ("Elast-o-Lion™" 280) and a fluorocarbon tetrapolymer elastomer ("Viton™" LR 6316), both ex. James Walker & Co Ltd, UK. The volumes of elastomer samples of initial dimensions 50 mm x 25 mm x 3 mm were measured after immersion in 100 ml of the relevant test fluid at ambient temperature and pressure for 24 hours. After immersion, the samples were quickly dried, and weighed in air and in water (within 8 hours of removal from the test fluid). Percentage changes in volume were then calculated.

Shore hardness values were also measured for the elastomer samples both before and after immersion in the test fluids; hardness was measured at ambient temperature using a Type A Shore Durometer™ (ex. Shore Instruments, Instron Corp, USA).

The results are shown in Tables 5a (DMC and DEC) and 5b (other DACs) below. FC refers to tests on the fluorocarbon elastomer, Ni to tests on the nitrile elastomer. In each cell of the table, the first figure is the percentage change in elastomer volume, and the second the percentage change in elastomer hardness. DMC and DEC were also tested at 2% v/v in the base fuel.

C EC	Ni PrEC	FC BEC	Ni BEC	FC DPrC	Ni DPrC	FC DiPrC	Ni DiPrC
0/- .7	27.2/- 20.2	2.0/- 1.7	27.2/- 20.2	2.0/- 1.7	27.2/- 20.2	2.0/- 1.7	27.2/- 20.2
9/- .9	29.1/- 2.9	3.3/- 2.1	28.4/- 20.2	2.9/- 2.5	3.9/- 2.9	3.2/- 3.0	26.3/- 19.7
9/- .3	31.5/- 20.6	4.7/- 2.9	30.6/- 19.6	4.3/- 2.9	29.9/- 20.3	4.7/- 3.5	26.4/- 19.3
2/- .8	53.2/- 29.1	82.0/- 23.3	50.6/- 30.6	78.2/- 23.0	41.3/- 25.6	104.6/- 18	14.9/- 9.4

The data in Tables 5a and 5b show that at any given concentration, the ≥C6 DACs (PrEC, BEC, DPrC and DiPrC) cause less elastomer damage (swelling and reductions in hardness) than the lower molecular weight DACs, DMC and DEC. For the ≥C6 DACs, nitrile elastomer swell levels were well within the "normal" range (a 20-30% volume change) recorded for a selection of available gasoline base fuels, at both 5 and 10% v/v. In contrast, DMC at 10% v/v caused a nitrile elastomer swell which was well above the normal base fuel range. In the fluorocarbon elastomer tests, the ≥C6 DACs performed mostly in line with the normal base fuel range (a 1-4% volume change), whilst DMC and DEC caused significantly higher swell at both 5 and 10% v/v.

Thus, DMC and DEC can cause elastomer damage problems when blended in gasoline fuels, even at 5% v/v. However, ≥C6 DACs may be used in gasoline fuel formulations in place of either DMC or DEC, in order to reduce such problems. They may be incorporated at concentrations of at least 10% v/v without undue concerns over elastomer damage issues.

Example 2

Diesel fuel formulations were prepared by splash-blending a number of DACs, each at both 5% v/v and 10% v/v, with a diesel base fuel DBF. The base fuel was a commercially available, EN 590-compliant zero sulphur diesel (ex. Shell).

The DACs tested were those used in Example 1, and in addition di-n-butyl carbonate (DBC). Their properties are summarised in Table 1 above.

Table 6 summarises some of the physicochemical properties of the diesel base fuel DBF and of blends of the base fuel with DMC and DEC at both 5 and 10% v/v.

Table 6 also shows, where applicable, the values required by the European diesel specification EN 590.

Table 6

Parameter	DBF	EN 590 min	EN 590 max	DBF + 5% DMC	DBF + 10% DMC	DBF + 5% DEC	DBF + 10% DEC
CN	55.1	51.0	-	54.2	52.7	54.2	52.2
Density @ 15ºC (g/cm^3)	0.8389	0.820	0.845	0.8488	0.8594	0.8451	0.8515
Flash point (ºC)	65.5	55.0	-	<40 (28.5)	<40 (24.5)	50.5	44.0
Distillation:							
IBP	161.4	-	-	91.4	85.8	130	127.6
10% rec	213	-	-	194.8	118.9	184.7	153.1
50% rec	281.9	-	-	278.5	276	278.8	276
90% rec	333.5	-	-	330.8	330.5	330.7	329.7
95% rec	347.6	-	360	344.3	344.5	343.9	343.5
FBP	358.2	-	-	355.9	357.7	355.4	357.4

Table 7 summarises some of the physicochemical properties of blends of DBF with the higher molecular weight dialkyl carbonates PrEC, BEC, DPrC, DiPrC and DBC, again at both 5 and 10% v/v.

Table 7

Parameter	DBF + 5% PrEC	DBF + 10% PrEC	DBF + 5% BEC	DBF + 10% BEC	DBF + 5% DPrC	DBF + 10% DPrC	DBF + 5% DiPrC	DBF + 10% DiPrC	DBF + 5% DBC	DBF + 10% DBC
CN	53.4	51.4	54.3	52.2	52.6	51	53.8	51.6	54.7	51.3
Density @ 15ºC (g/cm^3)	0.8357	0.8418	0.835	0.8402	0.8351	0.8404	0.834	0.8328	0.8343	0.8386
Flash point (ºC)	54	48	59	55	61.5	59.5	57	53	66	67
Distillation:										
IBP	153.6	144.5	165.4	160	167.6	163.1	148.9	142.6	180.4	179.3
10% rec	192.8	173.9	196.5	184.5	196.5	184.9	189.7	170.1	209.4	207.6
50% rec	271.6	268.4	271.5	268.3	271.8	267.4	270.9	267	241.8	266.4
90% rec	335.6	334.2	335.5	333.8	336.2	334	335.8	333.9	335.9	333.7
95% rec	351.3	349.7	350.9	350	352.1	350.4	352.1	350	351.2	349.2
FBP	362.4	361.9	362.1	362.2	363.4	362.3	361.4	361.4	362.3	361.6

Table 7 shows that all of the blends containing ≥C6 DACs were compliant with the EN 590 diesel fuel specification in terms of their distillation curves, cetane numbers and densities. At 5% v/v DAC, all but one of the ≥C6 DAC blends (that containing PrEC) were compliant with the EN 590 flash point specification. The BEC-, DPrC- and DBC-containing blends were also EN 590 compliant (in terms of their flash points) at 10% v/v. Base fuels having higher initial flash points could be used in order to ensure EN 590 compliance with all of the tested ≥C6 DACs. All the blends were also found to be EN 590-compliant in terms of their viscosities (individual data not shown).

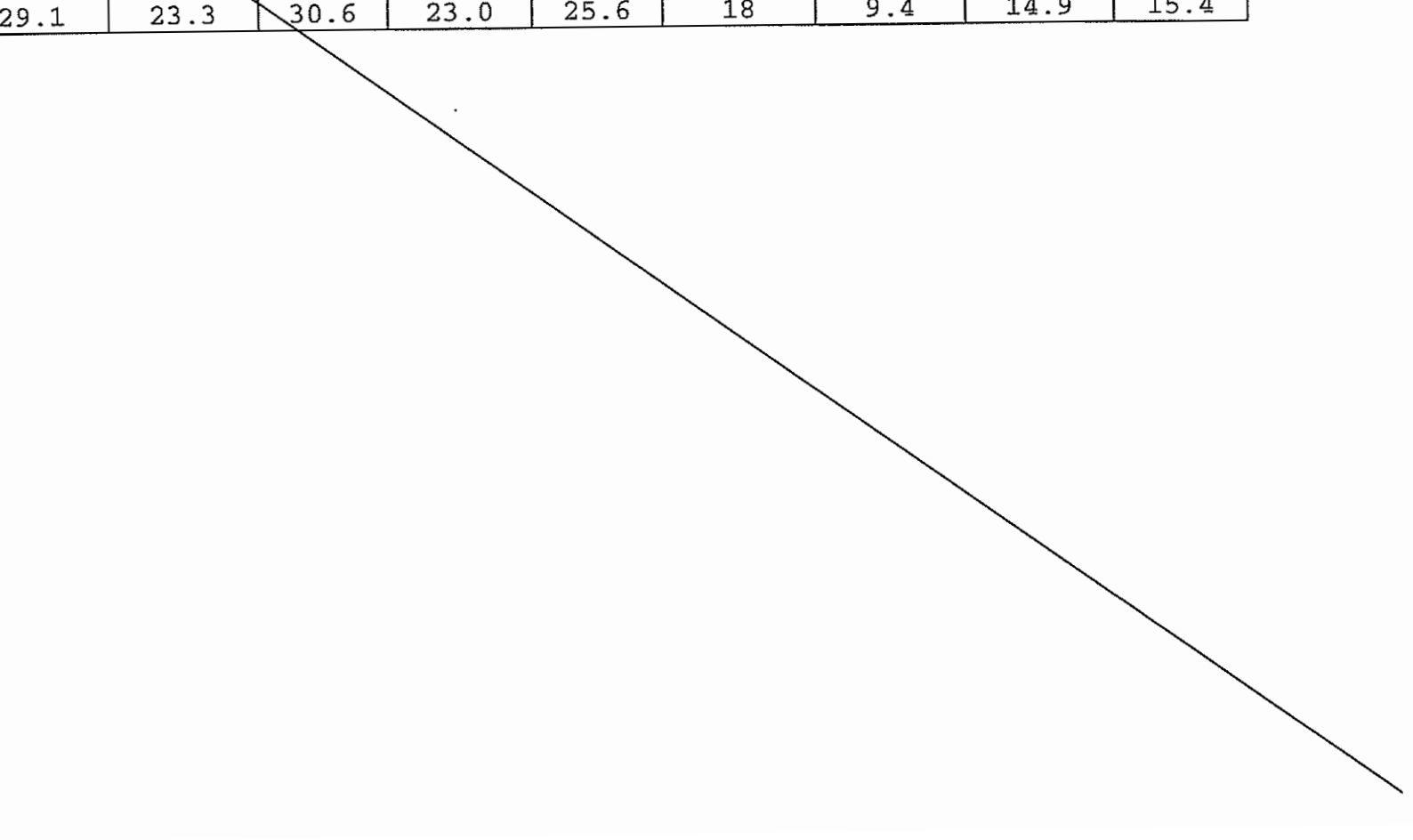
The elastomer damaging effects of each of the DBF/DAC blends, and of the base fuel itself and the neat DACs, was then assessed using the Example 1 test method, but immersing the elastomer samples in the test fluids for 7 days at 70°C. Shore hardness values were measured at 70°C.

The results are shown in Tables 8a (DMC and DEC) and 8b (other DACs) below. FC refers to tests on the fluorocarbon elastomer, Ni to tests on the nitrile elastomer. In each cell of the table, the first figure is the percentage change in elastomer volume, and the second the percentage change in elastomer hardness. Again, DMC and DEC were also tested in 2% v/v blends.

Table 8a (DMC & DEC)

DAC conc^{n} (% v/v)	FC DMC	Ni DMC	FC DEC	Ni DEC
0	0.0/-0.6	1.7/-1.6	0.0/-0.6	1.7/-1.6
2	2.5/-4	5.3/-6	0.6/0	3.0/-3.0
5	9.0/-11.0	12.4/-12.3	2.4/-7.2	4.8/-4.8
10	21.7/-19.0	27.3/-21	6.8/-3	9.1/-8.3
100	82.9/-35	58.3/-28.7	111.2/-36.3	54.6/-28.5

29.1	23.3	30.6	23.0	25.6	18	9.4	14.9	15.4



The data in Tables 8a and 8b show that at any given blend ratio, the ≥C6 DACs cause less elastomer damage (both swelling and reductions in hardness) than the lower molecular weight DACs, DMC and DEC. For the ≥C6 DACs both nitrile and fluorocarbon elastomer swell levels were well within the "normal" ranges (2-12% volume change for the nitrile elastomer; 0-4% volume change for the fluorocarbon) recorded for a selection of available diesel base fuels, at both 5 and 10% v/v. In contrast, DMC at 10% v/v caused a nitrile elastomer swell which was well above the normal base fuel range, and even at 5% v/v caused a higher than average elastomer swell. In the fluorocarbon elastomer tests, both DMC and DEC gave rise to elastomer swell levels well above the normal base fuel range at 10% v/v, as did DMC at 5% v/v.

Thus, DMC and DEC can cause elastomer damage problems when blended in diesel fuels. However, ≥C6 DACs may be used in diesel fuel formulations in place of either DMC or DEC, in order to reduce such problems. For this purpose they can be incorporated at concentrations of at least 10% v/v.

Example 3

Diesel fuel formulations were prepared by blending together a second diesel base fuel DBF2 and the DACs which were tested in Example 2. All blends contained 10% v/v of the relevant DAC.

DBF2 was a commercially available Swedish Class I diesel fuel. It had a density at 15ºC (ASTM D4052) of 813.7 kg/m^3, an initial boiling point (ASTM D86) of 181ºC, a T95 boiling point (ASTM D86) of 286ºC, a final boiling point (ASTM D86) of 294ºC, a measured cetane number (ASTM D613) of 56.3 and a kinematic viscosity at 40ºC (ASTM D445) of 1.96 mm^2/s.

The lubricity of each DBF2/DAC blend, and of the base fuel itself, was then assessed using the following test method, which is a HFRR (high friction reciprocating rig) wear scar test based on EN ISO 12156-1. A sample of the fuel or blend under test was placed in a test reservoir which was maintained at a specified test temperature. A fixed steel ball was held in a vertically mounted chuck and forced against a horizontally mounted stationary steel plate with an applied load. The test ball was oscillated at a fixed frequency and stroke length while the interface with the plate was fully immersed in the fluid reservoir. The metallurgies of the ball and plate, and the temperature, load, frequency, and stroke length were as specified in EN ISO 12156-1. The ambient conditions during the test were then used to correct the size of the wear scar generated on the test ball to a standard set of ambient conditions, again as per EN ISO 12156-1. The corrected wear scar diameter provides a measure of the test fluid lubricity.

The lubricity results are shown in Table 9 below.

Table 9

Fuel/blend	Wear scar (µm)
DBF2	670.5
+ 10% DMC	613
+ 10% DEC	496
+ 10% PrEC	403.5
+ 10% BEC	414.5
+ 10% DPrC	477.5
+ 10% DiPrC	466.5
+ 10% DBC	492
MAX 460 µm	460

It can be seen that the addition of 10% v/v of a ≥C6 DAC significantly improves the lubricity of the base fuel, bringing the wear scar close to or even below the

EN 590 maximum specification of 460 μm. It is expected that the addition of suitable lubricity additives, at standard or indeed below standard treat rates, will bring the lubricity of all the DBF2/≥C6 DAC blends above specification (ie the wear scar will be below the maximum).

Of note is the fact that the lubricity enhancing effects of the DACs do not vary linearly with molecular weight. Although all of the ≥C6 DACs outperform both DMC and DEC, in this respect PrEC seems to increase lubricity the best of all the ≥C6 DACs tested, whilst DiPrC performs slightly better than, and BEC much better than, the same molecular weight DPrC.

Thus, ≥C6 DACs may be used to improve the lubricity of a diesel base fuel or fuel formulation, either with or without lubricity additives. Instead or in addition they may be used to reduce the concentration of lubricity-enhancing additives necessary in a diesel fuel formulation, without or without undue reduction in overall lubricity. Improvements in lubricity may also be accompanied by improvements in fuel economy when a fuel-consuming system is run on a fuel formulation according to the invention.

Example 4

The water tolerance of the DAC/base fuel blends prepared in Examples 1 and 2 was assessed using the following method.

Distilled water was added to a sample of the relevant blend, in incremental amounts, and the sample agitated by hand until a slight haze persisted. The volume of added water at this point was converted to a mass M (in grams) using an appropriate density. The water tolerance W = M/400 (g/mL). Water was added to further

samples of the blend in amounts sufficient to give water contents of 0.25W, 0.5W, W, 2W and 4W g/mL. The moisture content of the organic phase in each of these samples was tested using the standard test method IP 386, and its phase transition temperature was measured according to ASTM D2386.

All the gasoline blends were found to have good water tolerance. On addition of further water, the water content of the organic fuel phase was generally maintained (indicating effective phase separation of the added water), as was the DAC content in the organic phase (indicating that the DAC had not migrated into the added water). Thus, in this respect the DACs behave better than ethanol which does separate into water phases when present. This water-rejecting effect also highlights the potential for DACs, in particular ≥C6 DACs, to be incorporated into gasoline/alcohol fuel blends in order to stabilise the alcohol in the organic phase. They may also be used to allow the incorporation of hydrous alcohols into gasoline fuels, the hydrous alcohols requiring less energy to produce than their anhydrous counterparts.

There were no water tolerance issues with any of the diesel fuel blends.

Example 5

The effects of neat DACs on both nitrile and fluorocarbon elastomers were assessed using the same method as in Examples 1 and 2. The results are shown in Table 10; the figures are percentages increases in volume/changes in hardness.

Table 10

DAC	Nitrile	Fluorocarbon
DMC	58.3/-28.7	82.9/-35
DEC	54.6/-28.5	111.2/-36.3
PrEC	53.2/-29.1	88.2/-23.8
BEC	50.6/-30.3	82.0/-23.3
DPrC	41.3/-25.3	78.2/-25.6
DiPrC	14.9/-9.4	104.6/-18.0
DBC	18.6/-15.4	24.2/-14.9

These results confirm those found for the DAC-containing fuel blends. The ≥C6 DACs in general show a reduced tendency to cause elastomer damage. This means that the ≥C6 DACs are likely to be easier to store and transport, as well as causing fewer problems when used in automotive fuel formulations.

However, these data, together with those from Examples 1 and 2, also show that elastomer damaging effects do not vary linearly with DAC molecular weight. Although the ≥C6 DACs all outperform DMC and DEC, it is of note that in the neat DACs, for example, fluorocarbon elastomer swell is markedly greater in DiPrC than in DPrC. Thus, performance in fuel formulations cannot necessarily be predicted from the elastomer damaging properties of the neat DACs, or solely from the DAC molecular weight, although it has now been found that using DACs of 6 or more carbon atoms can yield consistent advantages over the more conventionally used DMC and DEC.

C L A I M S

1. Use of a DAC having 6 or more carbon atoms, in a fuel formulation, for the purpose of improving the lubricity of the formulation.

2. Use according to claim 1, which is in a gasoline fuel formulation.

3. Use according to claim 1, which is in a diesel fuel formulation.

4. Use according to any one of the preceding claims, wherein the DAC is selected from di-n-propyl carbonate (DPrC), di-isopropyl carbonate (DiPrC), di-n-butyl carbonate (DBC), di-n-pentyl carbonate (DPeC), di-n-hexyl carbonate (DHexC), di-n-heptyl carbonate (DHeptC), and mixtures thereof.

5. Use according to any one of the preceding claims, wherein the DAC is selected from butyl ethyl carbonate (BEC), DBC and mixtures thereof.

6. Use according to claim 5, wherein the DAC is DBC.

7. Use according to any one of the preceding claims, wherein the concentration of the DAC in the formulation is 5% v/v or greater.

8. Use according to any one of the preceding claims , wherein the DAC is an asymmetric DAC.

9. Use of a DAC having 6 or more carbon atoms, in a fuel formulation, for the purpose of reducing the concentration of a lubricity-enhancing additive in the formulation.

10. Use, in a fuel formulation, of a first DAC having 6 or more carbon atoms, for the purpose of replacing all or part of a second DAC having fewer carbon atoms than said first DAC which is, or would otherwise have been, included in the formulation, whilst at the same time reducing the elastomer damaging effects of the formulation due to the presence of the DAC(s).

11. Use according to claim 10, wherein the second DAC is selected from dimethyl carbonate (DMC), diethyl carbonate (DEC) and mixtures thereof.

FUEL FORMULATIONS

Field of the Invention

This invention relates to fuel formulations, their preparation and their use, and to the use of certain materials in fuel formulations for new purposes.

Background to the Invention

In the interests of the environment, and to comply with increasingly stringent regulatory demands, it is necessary to increase the amount of biofuels used in automotive fuels.

Biofuels are combustible fuels, typically derived from biological sources, which result in a reduction in "well-to-wheels" (i.e. from source to combustion) greenhouse gas emissions. In gasoline fuels for use in spark ignition engines, the most common biofuels are alcohols, in particular ethanol. These are typically blended with more traditional gasoline fuel components. For use in diesel engines, fatty acid methyl esters (FAMEs) such as rapeseed methyl ester and palm oil methyl ester are the biofuels most commonly blended with conventional diesel fuel components.

Dialkyl carbonates, in particular the lower dialkyl carbonates dimethyl carbonate (DMC) and diethyl carbonate (DEC) are also biofuels which have in the past been added to both gasoline and diesel fuels. DMC and DEC have been used for instance as oxygenates, as combustion improvers and to reduce pollution levels. However, there are a number of practical constraints on the concentrations at which DMC and DEC can be included in automotive fuels. In particular, they appear to cause undesirable swelling of elastomeric engine components such as fuel pump seals, an effect which can reach unacceptable levels at as low as

5% v/v for DEC. In gasoline formulations, oxygen content specifications limit DMC and DEC concentrations to around 5% v/v. In diesel fuels, at least for use in the European Union, flash point and density specifications tend to limit DMC concentrations to less than 2% v/v and DEC concentrations to around 3% v/v. As a result, dialkyl carbonates have received little attention as fuel components other than at relatively low levels.

It would be desirable to provide new biofuel-containing fuel formulations which could overcome or at least mitigate the above problems.

Statements of the Invention

According to a first aspect of the present invention there is provided a fuel formulation containing a dialkyl carbonate (DAC) having 6 or more carbon atoms selected from the group consisting of di-n-hexyl carbonate, di-n-heptyl carbonate, hexyl ethyl carbonate, heptyl ethyl carbonate, and any combination thereof.

It has surprisingly been found that higher molecular weight DACs can cause less elastomer damage than DMC and DEC in blends with both gasoline and diesel fuels. It has also surprisingly been found that these DACs can improve the lubricity of gasoline and diesel fuels. The use of a higher molecular weight DAC as a replacement for either DMC or DEC can therefore provide fuel benefits. Their reduced elastomer damaging effects can also allow the higher molecular weight DACs to be included in fuels at higher concentrations, thus providing increased bioenergy contents.

There can be a number of advantages to the use of DACs in fuel formulations, which advantages can be increased if the DACs can be included at higher concentrations. DACs for instance have low toxicity and

are biodegradable. They have good octane blending properties, making them suitable for use in gasoline fuels. Unlike ethanol, which at blend ratios less than 7% v/v typically requires base fuel modification to compensate for undesirable RVP (Reid vapour pressure) boost, DACs do not significantly impact on the RVP of the base fuel blend at any blend ratios, making it easier to control evaporative emissions when they are used as components of gasoline formulations.

The use of DACs in diesel fuels can cause less environmental impact than the more traditional use of FAME biofuel components. DACs also show resistance to phase separation in hydrocarbon-water mixtures, which makes them less likely to migrate into water which may be present in wet storage tanks; they can also therefore help to stabilise ethanol-containing fuels.

DACs can be produced from renewable ingredients (carbon dioxide and bio-alcohols). DEC in particular can be produced from azeotropic ethanol, thus avoiding the energy penalty associated with breaking the azeotropic ethanol/water mix to produce anhydrous ethanol. DACs can thus provide a route to including an alcohol-based (in particular ethanol-based) oxygenate in a fuel, but with less carbon consumption.

A fuel formulation according to the invention may be suitable for use in an internal combustion engine. It may in particular be an automotive fuel formulation. In an embodiment, it is a gasoline fuel formulation which is suitable and/or adapted for use in a spark ignition (petrol) engine. In an alternative embodiment it is a diesel fuel formulation which is suitable and/or adapted for use in a compression ignition (diesel) engine. In further embodiments it may be suitable and/or adapted for

use as an industrial gas oil, or as a domestic heating oil.

The DAC used in a fuel formulation according to the invention has 6 or more carbon atoms, including the carbonate (-C(O)O-) carbon, and is selected from the group consisting of di-n-hexyl carbonate, di-n-heptyl carbonate, hexyl ethyl carbonate, heptyl ethyl carbonate, and any combination thereof. It is referred to herein as a "≥C6 DAC".

A fuel formulation according to the invention may contain a mixture of two or more ≥C6 DACs. The mixture may have been produced from a mixture of two or more alcohols: for example, ethanol and butanol together may be used to prepare a mixture of DEC and DBC, or of DEC, BEC and DBC.

In general, higher molecular weight DACs are likely to have higher viscosities and higher flash points, thus making them more suitable for use as diesel fuel components; they are also more likely to have boiling points within the normal diesel range.

Where the formulation is a gasoline fuel formulation, the ≥C6 DAC suitably has a boiling point (ASTM D86) of from 0 to 250°C. Where the formulation is a diesel fuel formulation, the ≥C6 DAC suitably has a boiling point (ASTM D86) of from 150 or 180 to 360°C.

The ≥C6 DAC may be included in the fuel formulation at a concentration of 0.5% v/v or greater, or of at least 1 or 2 or 3 or 4 or 5 or 6 or 7 or 8 or 9 or 10% v/v. Its concentration may in some embodiments be 25 or 50 or 75% v/v or greater. It may be included at a concentration of up to 100% v/v, or of up to 99 or 98% v/v; in other words, the ≥C6 DAC may itself be used as a fuel, or may represent the major proportion of a fuel formulation

which may optionally contain minor amounts of fuel additives and/or additional fuel components.

The ≥C6 DAC may be included in the fuel formulation of the invention at a concentration of up to 95 or 90 or 80 or 70 or 60% v/v. In embodiments, it may be included at a concentration of up to 50% v/v, or of up to 40 or 30% v/v, or of up to 25 or 20 or 18 or 15 or 12 or 10% v/v. Its concentration may for instance be from 5 to 20% v/v or from 5 to 10% v/v. In particular where the DAC is DBC and the formulation is a diesel fuel formulation, the DAC may be included at a concentration of up to 15 or 18 or 20% v/v or in cases of up to 30 or 40 or 50% v/v, or of up to 60 or 70 or 80 or 90 or 100% v/v.

The ≥C6 DAC may be obtained from any suitable source, of which many are available. It can for example be prepared by oxidative carbonylation of alcohols, or by transesterification of dimethyl carbonate with alcohols, or it may be generated as a co-product in the synthesis of monoethylene glycol from ethylene oxide and carbon dioxide via ethylene carbonate. The alcohols used in such processes may themselves be derived from biological sources.

In an embodiment, it may be preferred for the ≥C6 DAC not to have been synthesised using phosgene ($COCl_2$), as this may introduce undesirable impurities such as chlorides or carbonochloridic acid derivatives. Such impurities may contribute to deposit, stability and corrosion problems in a fuel formulation.

A fuel formulation according to the invention may contain other fuel components, as desired. Where it is a gasoline fuel formulation, for example, it may contain one or more gasoline fuel components, which are typically liquid hydrocarbon distillate fuel components containing

hydrocarbons which boil in the range from 0 to 250°C (ASTM D86 or EN ISO 3405). A gasoline fuel component suitably has a research octane number (RON) (ASTM D2699) of from 85 to 115 or from 95 to 115 and/or a motor octane number (MON) (ASTM D2700) of from 75 to 95 or from 85 to 95.

Where the formulation is a diesel fuel formulation, it may contain one or more diesel fuel components, which are typically liquid hydrocarbon middle distillate fuel components (for example gas oils) containing hydrocarbons which boil in the range from 150 or 180 to 360°C (ASTM D86 or EN ISO 3405). A diesel fuel component suitably has a measured cetane number (ASTM D613) of from 40 to 70 or from 40 to 65 or from 51 to 65 or 70.

Such additional fuel components may be derived from any suitable source. They may for example be petroleum derived. Alternatively they may be synthetic products such as from a Fischer-Tropsch synthesis. Additional fuel components may also be derived from biological sources. They may be or include oxygenates such as alcohols (in particular C1 to C3 aliphatic alcohols, more particularly ethanol) or fatty acid methyl esters (FAMEs) such as rapeseed methyl ester or palm oil methyl ester.

The formulation of the invention may contain one or more lower molecular weight DACs, for example selected from DMC, DEC and mixtures thereof, in addition to the ≥C6 DAC.

Where the formulation is a gasoline fuel formulation, it will suitably comply with applicable current standard gasoline fuel specification(s) such as for example EN 228 in the European Union. By way of example, the overall formulation may have a density from 0.720 to 0.775 kg/m^3 at 15°C (ASTM D4052 or EN ISO 3675);

a final boiling point (ASTM D86 or EN ISO 3405) of 210°C or less; a RON (ASTM D2699) of 95.0 or greater; and/or a MON (ASTM D2700) of 85.0 or greater. Relevant specifications may however differ from country to country and from year to year, and may depend on the intended use of the formulation. Moreover a formulation according to the invention may contain fuel components with properties outside of these ranges, since the properties of an overall blend may differ, often significantly, from those of its individual constituents.

Where the formulation is a diesel fuel formulation, it will suitably comply with applicable current standard diesel fuel specification(s) such as for example EN 590 (for Europe) or ASTM D975 (for the USA). By way of example, the overall formulation may have a density from 820 to 845 kg/m^3 at 15°C (ASTM D4052 or EN ISO 3675); a T95 boiling point (ASTM D86 or EN ISO 3405) of 360°C or less; a measured cetane number (ASTM D613) of 51 or greater; a kinematic viscosity at 40°C (ASTM D445 or EN ISO 3104) from 2 to 4.5 centistokes; a sulphur content (ASTM D2622 or EN ISO 20846) of 50 mg/kg or less; and/or a polycyclic aromatic hydrocarbons (PAH) content (IP 391(mod)) of less than 11% w/w. Relevant specifications may however differ from country to country and from year to year, and may depend on the intended use of the formulation. Moreover a formulation according to the invention may contain individual fuel components with properties outside of these ranges.

A fuel formulation according to the invention may contain standard fuel or refinery additives, in particular additives which are suitable for use in automotive gasoline or diesel fuels. Many such additives are known and commercially available. The formulation may

for example contain a corrosion inhibitor, since DACs - in common with many other oxygenates - are known to be slightly corrosive and may reduce the performance of standard anti-corrosion additives. Suitable corrosion inhibitors include alkyl phosphates, esters, amine salts of alkenyl succinic acids, alkyl phosphoric acids and aryl sulphonic acids: commercially available examples include the products DCI™ 4a and 6a (ex. Innospec), Hitec™ 580 (ex. Afton), Nalco™ 5403 and 5405 (ex. Nalco), Spec-Aid™ 8Q22 (ex. GE Betz), and Tolad™ 351 and 4410 (ex. Baker Petrolite). They may be included at a concentration of up to 25 ppmw (parts per million by weight): slightly higher than usual treat rates may be required due to the presence of the DAC.

In an embodiment, the formulation contains a lubricity enhancing additive, although as discussed below the lubricity-enhancing properties of the ≥C6 DAC may make this unnecessary, or may make possible the use of lower levels of such additives.

According to a second aspect of the present invention, there is provided a process for the preparation of a fuel formulation, which process involves blending together a DAC having 6 or more carbon atoms selected from the group consisting of di-n-hexyl carbonate, di-n-heptyl carbonate, hexyl ethyl carbonate, heptyl ethyl carbonate, and any combination thereof and one or more additional fuel components such as those described above. The additional fuel component(s) may for example be gasoline or diesel base fuels. The ≥C6 DAC and the additional fuel component(s) may also be mixed with one or more fuel additives. The process may be used to produce at least 1,000 litres of the fuel formulation, or

at least 5,000 or 10,000 or 25,000 litres, or at least 50,000 or 75,000 or 100,000 litres.

A third aspect of the invention provides a method of operating an internal combustion engine, and/or a vehicle which is driven by an internal combustion engine, which method involves introducing into a combustion chamber of the engine a fuel formulation according to the first aspect of the invention. The engine may be a spark ignition (petrol) engine. It may be a compression ignition (diesel) engine.

According to a fourth aspect of the invention there is provided a method for improving the lubricity of a fuel formulation, the method comprising adding to the formulation a DAC having 6 or more carbon atoms selected from the group consisting of di-n-hexyl carbonate, di-n-heptyl carbonate, hexyl ethyl carbonate, heptyl ethyl carbonate, and any combination thereof. The formulation is suitably a diesel fuel formulation.

The lubricity of a fuel formulation can be assessed by any suitable method. One such method involves measuring the wear scar produced on an oscillating ball from contact with a stationary plate whilst immersed in the formulation. This "wear scar" may be measured for example using the test described in Example 3 below.

An "improvement" in the lubricity of a formulation may be manifested for example by a lower degree of wear scar, or of other friction-induced damage, in two relatively-moving components which are exposed to the formulation. The invention may be used to achieve any degree of improvement in the lubricity of the fuel formulation, and/or for the purpose of achieving a desired target lubricity.

A fifth aspect of the invention provides a method for improving the lubricity of a fuel formulation, the method comprising adding to the formulation a DAC having 6 or more carbon atoms selected from the group consisting of di-n-hexyl carbonate, di-n-heptyl carbonate, hexyl ethyl carbonate, heptyl ethyl carbonate, and any combination thereof. Again the formulation is suitably a diesel fuel formulation.

In the context of this fifth aspect of the invention, the term "reducing" embraces any degree of reduction, including reduction to zero. The reduction may for instance be 10% or more of the original lubricity-enhancing additive concentration, or 25 or 50 or 75 or 90% or more. The reduction may be as compared to the concentration of lubricity-enhancing additive which would otherwise have been incorporated into the fuel formulation in order to achieve the properties and performance required and/or desired of it in the context of its intended use. This may for instance be the concentration of lubricity-enhancing additive which was present in the formulation prior to the realisation that a ≥C6 DAC could be used in the way provided by the present invention, and/or which was present in an otherwise analogous fuel formulation intended (e.g. marketed) for use in an analogous context, prior to adding a ≥C6 DAC to it in accordance with the invention.

The reduction in lubricity-enhancing additive concentration may be as compared to the concentration of lubricity-enhancing additive which would be predicted to be necessary to achieve a desired target lubricity for the formulation in the absence of the ≥C6 DAC.

The lubricity-enhancing additive may be any additive which is capable of, or intended to, improve the

lubricity of the formulation. Many such additives are known; they include for example R655™ (an ester-based additive ex. Infineum) and LZ 539C™ (an acid-based additive ex. Lubrizol).

A sixth aspect of the invention provides a method for reducing the elastomer damaging effects of a fuel formulation due to the presence of DAC(s), the method comprising adding to the formulation a first DAC having 6 or more carbon atoms selected from the group consisting of di-n-hexyl carbonate, di-n-heptyl carbonate, hexyl ethyl carbonate, heptyl ethyl carbonate, and any combination thereof for the purpose of replacing all or part of a second DAC having fewer carbon atoms than the first DAC which is, or would otherwise have been, included in the formulation.

The second DAC may be a DAC having 5 or fewer carbon atoms. It will typically be selected from dimethyl carbonate (DMC), diethyl carbonate (DEC) and mixtures thereof. It may have been included, or intended to be included, in the formulation for any purpose, for example as an oxygenate, to increase the bioenergy content of the fuel, or as a combustion improver, or to reduce pollution levels caused by combustion of the fuel.

The sixth aspect of the invention allows a higher molecular weight DAC to be used in place of a lower molecular weight DAC such as DMC or DEC, in order to reduce the elastomer damaging effects which can be caused by the use of DMC and DEC in fuel formulations. This mitigation of elastomer damaging - in particular elastomer swelling - effects can allow higher concentrations of DAC to be included in a formulation. It therefore allows a fuel to benefit from the advantages of including a DAC, but with less of an increase in the

elastomer damaging effects of the overall formulation than would be caused by including the same concentration of DMC or DEC alone.

The first DAC (which has 6 or more carbon atoms) may therefore be used, in a DAC-containing fuel formulation, for the purpose of increasing the overall DAC concentration whilst maintaining the elastomer damaging effects of the formulation within a desired specification, and/or for the purpose of reducing the elastomer damaging effects of the formulation relative to those that would be caused by the inclusion of the same amount of a second DAC which typically has 5 or fewer carbon atoms.

Thus the present invention is able to provide more optimised methods for formulating biofuel-containing fuel formulations, in particular to achieve target levels of elastomer damage and/or lubricity.

In the context of the sixth aspect of the invention, an elastomer damaging effect may be any effect which reduces the ability of an elastomeric material to function correctly in a fuel-consuming system and/or in the presence of a fuel formulation. It may comprise swelling of the elastomer when in contact with the fuel formulation. It may comprise a change (typically a reduction) in the hardness and/or flexibility of the elastomer when in contact with the fuel formulation.

Elastomer swell measurements in particular provide a measure of the compatibility of elastomeric materials, such as are used in fuel pump seals and other engine components, with a fuel component or formulation or additive. Generally this compatibility is evaluated by assessing changes in the properties of an elastomer due to its immersion in a test fluid. The elastomer swelling

effects of a fuel formulation may for instance be assessed by measuring the increase or percentage increase in volume of an elastomeric material on immersion in the formulation for a predetermined period of time. A smaller volume increase indicates a reduction in elastomer swelling effects. This assessment may for example be carried out for nitrile and/or fluorocarbon elastomers, suitably both. A suitable assessment method is described in Example 1 below. Alternatively a standard test method such as ISO 1817:1998 may be used to measure elastomer swell effects.

Changes in the hardness and/or flexibility of an elastomeric material may be assessed using standard test methods such as the Shore hardness test or TMS 556.

In the context of the present invention, "use" of a DAC in a fuel formulation means incorporating the DAC into the formulation, typically as a blend (i.e. a physical mixture) with one or more other fuel components. The DAC will conveniently be incorporated before the formulation is introduced into an engine or other system which is to be run on the formulation. Instead or in addition the use of a DAC may involve running a fuel-consuming system, typically an internal combustion engine, on a fuel formulation containing the DAC, typically by introducing the formulation into a combustion chamber of an engine.

"Use" of a DAC in the ways described above may also embrace supplying the DAC together with instructions for its use in a fuel formulation to achieve the purpose(s) of any of the fourth to the sixth aspects of the invention, for instance to improve the lubricity of the formulation. The DAC may itself be supplied as part of a composition which is suitable for and/or intended for use

as a fuel additive, in which case the DAC may be included in such a composition for the purpose of influencing its effects on the lubricity and/or elastomer damaging effects of a fuel formulation.

Use of a DAC in a fuel formulation for a particular purpose may also embrace using the DAC itself as a fuel for the relevant purpose, optionally together with minor amounts of one or more fuel additives.

Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of the words, for example "comprising" and "comprises", mean "including but not limited to", and do not exclude other moieties, additives, components, integers or steps. Moreover the singular encompasses the plural unless the context otherwise requires: in particular, where the indefinite article is used, the specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

Preferred features of each aspect of the invention may be as described in connection with any of the other aspects. Other features of the invention will become apparent from the following examples. Generally speaking the invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims and drawings). Thus features, integers, characteristics, compounds, chemical moieties or groups described in conjunction with a particular aspect, embodiment or example of the invention are to be understood to be applicable to any other aspect, embodiment or example described herein unless incompatible therewith. Moreover unless stated otherwise, any feature disclosed herein may

be replaced by an alternative feature serving the same or a similar purpose.

The present invention will now be further described with reference to the following non-limiting examples.

Example 1

Gasoline fuel formulations were prepared by blending a number of DACs, each at both 5% v/v and 10% v/v, with a gasoline base fuel GBF. The base fuel was a commercially available EN 228-compliant unleaded gasoline with 95 RON (ex. Shell).

The DACs tested were dimethyl carbonate (DMC), diethyl carbonate (DEC), n-propyl ethyl carbonate (PrEC), n-butyl ethyl carbonate (BEC), di-n-propyl carbonate (DPrC) and di-isopropyl carbonate (DiPrC). Their properties are summarised in Table 1 below. Table 1 also shows the properties of di-n-butyl carbonate (DBC), which was used in Examples 2 to 5.

Table 1

Property	DMC	DEC	PrEC	BEC	DPrC	DiPrC	DBC
Molecular weight	90	118	132	146	146	146	174
Symmetric (S) or asymmetric (A)	S	S	A	A	S	S	S
Research octane no. (RON)	>120	>120	n.d.	n.d.	n.d.	n.d.	n.d.
Motor octane no. (MON)	>118	105.7	n.d.	n.d.	n.d.	n.d.	n.d.
Cetane no. (CN)	<20	<20	n.d.	n.d.	n.d.	n.d.	n.d.
Flash point (°C)	16.5	34.5	29	53	59	45.5	89
Boiling point (°C)	90	126	175	174	175	150	215
Density @ 15°C (g/cm^3)	1.076	0.981	0.966	0.945	0.949	0.927	0.929

Property	DMC	DEC	PrEC	BEC	DPrC	DiPrC	DBC
Water solubility (g/L)	151	29	19	9	5	14	5
Kinematic viscosity @ 40°C (cSt)	0.48	0.66	0.849	0.976	1.097	0.967	1.462
Lower heating value (LHV) (MJ/kg)	14.5	21.6	22.9	25.0	25.1	25.4	28.2

n.d. = not determined

Properties were measured using the test methods indicated in Table 2 below.

Table 2

Property	Test method
RON	ASTM D2699
MON	ASTM D2700
CN	ASTM D613
Flash point	IP 34
Boiling point (& other distillation properties)	IP 123
Density @ 15°C	IP 365
Water solubility	Internal method (see Example 4)
Kinematic viscosity @ 40°C	IP 71
LHV	IP 12

Table 3 summarises some of the physicochemical properties of the gasoline base fuel GBF and of blends of the base fuel with DMC and DEC at both 5 and 10% v/v. Table 3 also shows, where applicable, the values required by the European gasoline specification EN 228.

ec	101.90			95.60	91.80	104.90	108.00
ec	160.60			156.50	157.40	157.20	154.80
	202.00		210	201.20	203.50	201.70	203.70
	29.90	20	48	31.40	31.20	28.20	25.70
0	48.80	46	71	53.00	56.70	46.70	44.00

Table 4 summarises some of the physicochemical properties of blends of GBF with the higher molecular weight dialkyl carbonates PrEC, BEC, DPrC and DiPrC, again at both 5 and 10% v/v.

Table 4

Parameter	GBF + 5% PrEC	GBF + 10% PrEC	GBF + 5% BEC	GBF + 10% BEC	GBF + 5% DPrC	GBF + 10% DPrC	GBF + 5% DiPrC	GBF + 10% DiPrC
RON	95.8	96.5	95.4	95.8	95.9	96.4	96.2	97.1
MON	85.9	87.5	86.0	86.7	86.7	87.0	86.3	87.1
Density @ 15°C (g/cm^3)	0.753	0.763	0.752	0.761	0.752	0.762	0.753	0.758
Distillation:								
IBP	30.1	31.0	27.5	31.3	30.2	31.6	30.0	26.2
10% rec	44.0	45.7	44.3	43.4	46.1	44.3	51.6	46.0
50% rec	105.0	108.5	105.3	108.6	106.2	108.9	107.1	108.7
90% rec	156.7	156.3	163.1	164.9	162.8	164.0	158.2	155.2
FBP	202.3	200.0	200.9	196.8	200.8	198.5	201.9	197.5
E70	25.9	24.4	25.8	25.1	24.7	24.7	21.5	23.9
E100	45.0	42.3	45.2	42.8	44.2	42.4	42.4	42.0

It can be seen from Table 4 that all of the blends containing ≥C6 DACs were compliant with the EN 228 gasoline specification in terms of their octane numbers and densities. Indeed, the DACs increased the octane numbers of the base fuel, the ≥C6 DACs performing generally better in this respect than DMC and DEC and also in many cases reducing the fuel sensitivity (RON - MON) better than DMC and DEC. Although the blends containing ≥C6 DACs had E100 values below the EN 228 minimum, it is expected that such issues could be resolved fairly readily by minor adjustments to base fuel specifications prior to the addition of a ≥C6 DAC.

The elastomer damaging effects caused by each of the GBF/DAC blends, and by the base fuel itself and the neat DACs, were then assessed using the following test method, which is a modified version of the standard test method ISO 1817:1998. Two elastomeric materials were tested: a hydrogenated nitrile elastomer ("Elast-o-Lion™" 280) and a fluorocarbon tetrapolymer elastomer ("Viton™" LR 6316), both ex. James Walker & Co Ltd, UK. The volumes of elastomer samples of initial dimensions 50 mm x 25 mm x 3 mm were measured after immersion in 100 ml of the relevant test fluid at ambient temperature and pressure for 24 hours. After immersion, the samples were quickly dried, and weighed in air and in water (within 8 hours of removal from the test fluid). Percentage changes in volume were then calculated.

Shore hardness values were also measured for the elastomer samples both before and after immersion in the test fluids; hardness was measured at ambient temperature using a Type A Shore Durometer™ (ex. Shore Instruments, Instron Corp, USA).

The results are shown in Tables 5a (DMC and DEC) and 5b (other DACs) below. FC refers to tests on the fluorocarbon elastomer, Ni to tests on the nitrile elastomer. In each cell of the table, the first figure is the percentage change in elastomer volume, and the second the percentage change in elastomer hardness. DMC and DEC were also tested at 2% v/v in the base fuel.

Table 5a (DMC & DEC)

DAC conc^{n} (% v/v)	FC DMC	Ni DMC	FC DEC	Ni DEC
0	2.4/-4.7	27.7/-21	2.4/-4.7	27.7/-21
2	4.4/-4	31.0/-18	2.5/-3	29.1/-18
5	13.3/-10.3	34.2/-23.9	6.2/-7.3	31.7-22.4
10	24.6/-19.7	40.3/-24	12.0/-11.4	33.9/-23.5
100	82.9/-35	58.3/-28.7	111.2/-36.3	54.6/-28.5

Table 5b (PrEC, BEC, DPrC & DiPrC)

DAC conc^{n} (% v/v)	FC PrEC	Ni PrEC	FC BEC	Ni BEC	FC DPrC	Ni DPrC	FC DiPrC	Ni DiPrC
0	2.0/-1.7	27.2/-20.2	2.0/-1.7	27.2/-20.2	2.0/-1.7	27.2/-20.2	2.0/-1.7	27.2/-20.2
5	3.9/-2.9	29.1/-2.9	3.3/-2.1	28.4/-20.2	2.9/-2.5	3.9/-2.9	3.2/-3.0	26.3/-19.7
10	6.9/-3.3	31.5/-20.6	4.7/-2.9	30.6/-19.6	4.3/-2.9	29.9/-20.3	4.7/-3.5	26.4/-19.3
100	88.2/-23.8	53.2/-29.1	82.0/-23.3	50.6/-30.6	78.2/-23.0	41.3/-25.6	104.6/-18	14.9/-9.4

The data in Tables 5a and 5b show that at any given concentration, the ≥C6 DACs (PrEC, BEC, DPrC and DiPrC) cause less elastomer damage (swelling and reductions in hardness) than the lower molecular weight DACs, DMC and DEC. For the ≥C6 DACs, nitrile elastomer swell levels were well within the "normal" range (a 20-30% volume change) recorded for a selection of available gasoline base fuels, at both 5 and 10% v/v. In contrast, DMC at 10% v/v caused a nitrile elastomer swell which was well above the normal base fuel range. In the fluorocarbon elastomer tests, the ≥C6 DACs performed mostly in line with the normal base fuel range (a 1-4% volume change), whilst DMC and DEC caused significantly higher swell at both 5 and 10% v/v.

Thus, DMC and DEC can cause elastomer damage problems when blended in gasoline fuels, even at 5% v/v. However, ≥C6 DACs may be used in gasoline fuel formulations in place of either DMC or DEC, in order to reduce such problems. They may be incorporated at concentrations of at least 10% v/v without undue concerns over elastomer damage issues.

Example 2

Diesel fuel formulations were prepared by splash-blending a number of DACs, each at both 5% v/v and 10% v/v, with a diesel base fuel DBF. The base fuel was a commercially available, EN 590-compliant zero sulphur diesel (ex. Shell).

The DACs tested were those used in Example 1, and in addition di-n-butyl carbonate (DBC). Their properties are summarised in Table 1 above.

Table 6 summarises some of the physicochemical properties of the diesel base fuel DBF and of blends of the base fuel with DMC and DEC at both 5 and 10% v/v.

Table 6 also shows, where applicable, the values required by the European diesel specification EN 590.

Table 6

Parameter	DBF	EN 590 min	EN 590 max	DBF + 5% DMC	DBF + 10% DMC	DBF + 5% DEC	DBF + 10% DEC
CN	55.1	51.0	-	54.2	52.7	54.2	52.2
Density @ 15°C (g/cm^3)	0.8389	0.820	0.845	0.8488	0.8594	0.8451	0.8515
Flash point (°C)	65.5	55.0	-	<40 (28.5)	<40 (24.5)	50.5	44.0
Distillation:							
IBP	161.4	-	-	91.4	85.8	130	127.6
10% rec	213	-	-	194.8	118.9	184.7	153.1
50% rec	281.9	-	-	278.5	276	278.8	276
90% rec	333.5	-	-	330.8	330.5	330.7	329.7
95% rec	347.6	-	360	344.3	344.5	343.9	343.5
FBP	358.2	-	-	355.9	357.7	355.4	357.4

Table 7 summarises some of the physicochemical properties of blends of DBF with the higher molecular weight dialkyl carbonates PrEC, BEC, DPrC, DiPrC and DBC, again at both 5 and 10% v/v.

Table 7

Parameter	DBF + 5% PrEC	DBF + 10% PrEC	DBF + 5% BEC	DBF + 10% BEC	DBF + 5% DPrC	DBF + 10% DPrC	DBF + 5% DiPrC	DBF + 10% DiPrC	DBF + 5% DBC	DBF + 10% DBC
CN	53.4	51.4	54.3	52.2	52.6	51	53.8	51.6	54.7	51.3
Density @ 15°C (g/cm^3)	0.8357	0.8418	0.835	0.8402	0.8351	0.8404	0.834	0.8328	0.8343	0.8386
Flash point (°C)	54	48	59	55	61.5	59.5	57	53	66	67
Distillation:										
IBP	153.6	144.5	165.4	160	167.6	163.1	148.9	142.6	180.4	179.3
10% rec	192.8	173.9	196.5	184.5	196.5	184.9	189.7	170.1	209.4	207.6
50% rec	271.6	268.4	271.5	268.3	271.8	267.4	270.9	267	241.8	266.4
90% rec	335.6	334.2	335.5	333.8	336.2	334	335.8	333.9	335.9	333.7
95% rec	351.3	349.7	350.9	350	352.1	350.4	352.1	350	351.2	349.2
FBP	362.4	361.9	362.1	362.2	363.4	362.3	361.4	361.4	362.3	361.6

Table 7 shows that all of the blends containing ≥C6 DACs were compliant with the EN 590 diesel fuel specification in terms of their distillation curves, cetane numbers and densities. At 5% v/v DAC, all but one of the ≥C6 DAC blends (that containing PrEC) were compliant with the EN 590 flash point specification. The BEC-, DPrC- and DBC-containing blends were also EN 590 compliant (in terms of their flash points) at 10% v/v. Base fuels having higher initial flash points could be used in order to ensure EN 590 compliance with all of the tested ≥C6 DACs. All the blends were also found to be EN 590-compliant in terms of their viscosities (individual data not shown).

The elastomer damaging effects of each of the DBF/DAC blends, and of the base fuel itself and the neat DACs, was then assessed using the Example 1 test method, but immersing the elastomer samples in the test fluids for 7 days at 70°C. Shore hardness values were measured at 70°C.

The results are shown in Tables 8a (DMC and DEC) and 8b (other DACs) below. FC refers to tests on the fluorocarbon elastomer, Ni to tests on the nitrile elastomer. In each cell of the table, the first figure is the percentage change in elastomer volume, and the second the percentage change in elastomer hardness. Again, DMC and DEC were also tested in 2% v/v blends.

Table 8a (DMC & DEC)

DAC conc^{n} (% v/v)	FC DMC	Ni DMC	FC DEC	Ni DEC
0	0.0/-0.6	1.7/-1.6	0.0/-0.6	1.7/-1.6
2	2.5/-4	5.3/-6	0.6/0	3.0/-3.0
5	9.0/-11.0	12.4/-12.3	2.4/-7.2	4.8/-4.8
10	21.7/-19.0	27.3/-21	6.8/-3	9.1/-8.3
100	82.9/-35	58.3/-28.7	111.2/-36.3	54.6/-28.5

9.1	23.3	30.6	23.0	25.6	18	9.4	14.9	15.4

The data in Tables 8a and 8b show that at any given blend ratio, the ≥C6 DACs cause less elastomer damage (both swelling and reductions in hardness) than the lower molecular weight DACs, DMC and DEC. For the ≥C6 DACs, both nitrile and fluorocarbon elastomer swell levels were well within the "normal" ranges (2-12% volume change for the nitrile elastomer; 0-4% volume change for the fluorocarbon) recorded for a selection of available diesel base fuels, at both 5 and 10% v/v. In contrast, DMC at 10% v/v caused a nitrile elastomer swell which was well above the normal base fuel range, and even at 5% v/v caused a higher than average elastomer swell. In the fluorocarbon elastomer tests, both DMC and DEC gave rise to elastomer swell levels well above the normal base fuel range at 10% v/v, as did DMC at 5% v/v.

Thus, DMC and DEC can cause elastomer damage problems when blended in diesel fuels. However, ≥C6 DACs may be used in diesel fuel formulations in place of either DMC or DEC, in order to reduce such problems. For this purpose they can be incorporated at concentrations of at least 10% v/v.

Example 3

Diesel fuel formulations were prepared by blending together a second diesel base fuel DBF2 and the DACs which were tested in Example 2. All blends contained 10% v/v of the relevant DAC.

DBF2 was a commercially available Swedish Class I diesel fuel. It had a density at 15°C (ASTM D4052) of 813.7 kg/m^3, an initial boiling point (ASTM D86) of 181°C, a T95 boiling point (ASTM D86) of 286°C, a final boiling point (ASTM D86) of 294°C, a measured cetane number (ASTM D613) of 56.3 and a kinematic viscosity at 40°C (ASTM D445) of 1.96 mm^2/s.

The lubricity of each DBF2/DAC blend, and of the base fuel itself, was then assessed using the following test method, which is a HFRR (high friction reciprocating rig) wear scar test based on EN ISO 12156-1. A sample of the fuel or blend under test was placed in a test reservoir which was maintained at a specified test temperature. A fixed steel ball was held in a vertically mounted chuck and forced against a horizontally mounted stationary steel plate with an applied load. The test ball was oscillated at a fixed frequency and stroke length while the interface with the plate was fully immersed in the fluid reservoir. The metallurgies of the ball and plate, and the temperature, load, frequency, and stroke length were as specified in EN ISO 12156-1. The ambient conditions during the test were then used to correct the size of the wear scar generated on the test ball to a standard set of ambient conditions, again as per EN ISO 12156-1. The corrected wear scar diameter provides a measure of the test fluid lubricity.

The lubricity results are shown in Table 9 below.

Table 9

Fuel/blend	Wear scar (µm)
DBF2	670.5
+ 10% DMC	613
+ 10% DEC	496
+ 10% PrEC	403.5
+ 10% BEC	414.5
+ 10% DPrC	477.5
+ 10% DiPrC	466.5
+ 10% DBC	492
MAX 460 µm	460

It can be seen that the addition of 10% v/v of a ≥C6 DAC significantly improves the lubricity of the base fuel, bringing the wear scar close to or even below the

EN 590 maximum specification of 460 μm. It is expected that the addition of suitable lubricity additives, at standard or indeed below standard treat rates, will bring the lubricity of all the DBF2/≥C6 DAC blends above specification (ie the wear scar will be below the maximum).

Of note is the fact that the lubricity enhancing effects of the DACs do not vary linearly with molecular weight. Although all of the ≥C6 DACs outperform both DMC and DEC, in this respect PrEC seems to increase lubricity the best of all the ≥C6 DACs tested, whilst DiPrC performs slightly better than, and BEC much better than, the same molecular weight DPrC.

Thus, ≥C6 DACs may be used to improve the lubricity of a diesel base fuel or fuel formulation, either with or without lubricity additives. Instead or in addition they may be used to reduce the concentration of lubricity-enhancing additives necessary in a diesel fuel formulation, without or without undue reduction in overall lubricity. Improvements in lubricity may also be accompanied by improvements in fuel economy when a fuel-consuming system is run on a fuel formulation according to the invention.

Example 4

The water tolerance of the DAC/base fuel blends prepared in Examples 1 and 2 was assessed using the following method.

Distilled water was added to a sample of the relevant blend, in incremental amounts, and the sample agitated by hand until a slight haze persisted. The volume of added water at this point was converted to a mass M (in grams) using an appropriate density. The water tolerance W = M/400 (g/mL). Water was added to further

samples of the blend in amounts sufficient to give water contents of 0.25W, 0.5W, W, 2W and 4W g/mL. The moisture content of the organic phase in each of these samples was tested using the standard test method IP 386, and its phase transition temperature was measured according to ASTM D2386.

All the gasoline blends were found to have good water tolerance. On addition of further water, the water content of the organic fuel phase was generally maintained (indicating effective phase separation of the added water), as was the DAC content in the organic phase (indicating that the DAC had not migrated into the added water). Thus, in this respect the DACs behave better than ethanol which does separate into water phases when present. This water-rejecting effect also highlights the potential for DACs, in particular ≥C6 DACs, to be incorporated into gasoline/alcohol fuel blends in order to stabilise the alcohol in the organic phase. They may also be used to allow the incorporation of hydrous alcohols into gasoline fuels, the hydrous alcohols requiring less energy to produce than their anhydrous counterparts.

There were no water tolerance issues with any of the diesel fuel blends.

Example 5

The effects of neat DACs on both nitrile and fluorocarbon elastomers were assessed using the same method as in Examples 1 and 2. The results are shown in Table 10; the figures are percentages increases in volume/changes in hardness.

Table 10

DAC	Nitrile	Fluorocarbon
DMC	58.3/-28.7	82.9/-35
DEC	54.6/-28.5	111.2/-36.3
PrEC	53.2/-29.1	88.2/-23.8
BEC	50.6/-30.3	82.0/-23.3
DPrC	41.3/-25.3	78.2/-25.6
DiPrC	14.9/-9.4	104.6/-18.0
DBC	18.6/-15.4	24.2/-14.9

These results confirm those found for the DAC-containing fuel blends. The ≥C6 DACs in general show a reduced tendency to cause elastomer damage. This means that the ≥C6 DACs are likely to be easier to store and transport, as well as causing fewer problems when used in automotive fuel formulations.

However, these data, together with those from Examples 1 and 2, also show that elastomer damaging effects do not vary linearly with DAC molecular weight. Although the ≥C6 DACs all outperform DMC and DEC, it is of note that in the neat DACs, for example, fluorocarbon elastomer swell is markedly greater in DiPrC than in DPrC. Thus, performance in fuel formulations cannot necessarily be predicted from the elastomer damaging properties of the neat DACs, or solely from the DAC molecular weight, although it has now been found that using DACs of 6 or more carbon atoms can yield consistent advantages over the more conventionally used DMC and DEC.

C L A I M S

1. A fuel formulation comprising a dialkyl carbonate (DAC) having 6 or more carbon atoms selected from the group consisting of di-n-hexyl carbonate, di-n-heptyl carbonate, hexyl ethyl carbonate, heptyl ethyl carbonate, and any combination thereof.

2. A fuel formulation according to claim 1, which is a gasoline fuel formulation.

3. A fuel formulation according to claim 1, which is a diesel fuel formulation.

4. A fuel formulation according to any one of the preceding claims, wherein the concentration of the DAC in the formulation is 5% v/v or greater.

5. A process for the preparation of a fuel formulation, which process involves blending together a DAC having 6 or more carbon atoms selected from the group consisting of di-n-hexyl carbonate, di-n-heptyl carbonate, hexyl ethyl carbonate, heptyl ethyl carbonate, and any combination thereof, and one or more additional fuel components.

6. A method of operating an internal combustion engine, and/or a vehicle which is driven by an internal combustion engine, which method involves introducing into a combustion chamber of the engine a fuel formulation according to any one of claims 1 to 4.

7. A method for improving the lubricity of a fuel formulation, the method comprising adding to the formulation a DAC having 6 or more carbon atoms selected from the group consisting of di-n-hexyl carbonate, di-n-heptyl carbonate, hexyl ethyl carbonate, heptyl ethyl carbonate, and any combination thereof.

8. A method for reducing the concentration of a lubricity-enhancing additive in a fuel formulation, the method comprising adding to the formulation a DAC having 6 or more carbon atoms selected from the group consisting of di-n-hexyl carbonate, di-n-heptyl carbonate, hexyl ethyl carbonate, heptyl ethyl carbonate, and any combination thereof.

9. The method according to any one of claims 7 to 8, wherein the fuel formulation is a diesel fuel formulation.

10. A method for reducing the elastomer damaging effects of a fuel formulation due to the presence of DAC(s), the method comprising adding to the formulation a first DAC having 6 or more carbon atoms selected from the group consisting of di-n-hexyl carbonate, di-n-heptyl carbonate, hexyl ethyl carbonate, heptyl ethyl carbonate, and any combination thereof, for the purpose of replacing all or part of a second DAC having fewer carbon atoms than said first DAC which is, or would otherwise have been, included in the formulation.

11. The method according to claim 10, wherein the second DAC is selected from dimethyl carbonate (DMC), diethyl carbonate (DEC) and mixtures thereof.