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London, WC2A 1AT(GB)(54) **Deposit control additives for hydrocarbon fuels and lubricants for use in internal combustion engines.**

(57) Additives for use in internal combustion engines are provided which particularly in unleaded fuels maintain cleanliness of the intake system without contributing to combustion chamber deposits. The additives are hydrocarbyl-terminated poly(oxyalkylene) polyamine ethanes comprising a hydrocarbyl-terminated poly(oxyalkylene) chain formed from 1 to 30 2-5 carbon oxyalkylene units bonded to an ethane or branched ethane chain containing from 2 to 8 carbon atoms in turn bonded to a nitrogen atom of a polyamine having from 2 to 12 amine nitrogens and from 2 to 40 carbon atoms with a carbon:nitrogen ratio between 1:1 and 10:1. The terminal hydrocarbyl group contains from 1 to 30 carbon atoms and the additive has a molecular weight in the range from 300 to 2500. The additive may be formulated as a concentrate in an inert oleophilic organic solvent or may be formulated as a lubricant composition for use in an internal combustion engine by incorporation in a lubricating oil.

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1 Deposit control additives for hydrocarbon fuels and
 lubricants for use in internal combustion engines

 This invention relates to deposit control
additives for hydrocarbon fuels and lubricants to be used
5 in internal combustion engines, especially internal combustion engines designed to run on unleaded gasoline.

 Numerous deposit-forming substances are inherent
in hydrocarbon fuels. These substances when used in
internal combustion engines tend to form deposits on and
10 around constricted areas of the engine contacted by the
fuel. Typical areas commonly and sometimes seriously
burdened by the formation of deposits include carburetor
ports, the throttle body and venturies, and engine intake
valves.

15 Deposits adversely affect the operation of the
engine. For example, deposits on the carburetor throttle
body and venturies increase the fuel to air ratio of the
gas mixture to the combustion chamber thereby increasing
the amount of unburned hydrocarbon and carbon monoxide
20 discharged from the chamber. The high fuel-air ratio
also reduces the gas mileage obtainable from the engine.

 Deposits on the engine intake valves when they get
sufficiently heavy, on the other hand, restrict the gas
mixture flow into the combustion chamber. This restriction
25 starves the engine of air and fuel and results in a
loss of power. Deposits on the valves also increase the
probability of valve failure due to burning and improper
valve seating. In addition, these deposits may break off
and enter the combustion chamber possibly resulting in
30 mechanical damage to the piston, piston rings, or engine
head.

 The formation of these deposits can be inhibited
as well as removed by incorporating an active detergent
into the fuel. These detergents function to cleanse
35 these deposit-prone areas of the harmful deposits,
thereby enhancing engine performance and longevity.
There are numerous detergent-type gasoline additives

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1 currently available which, to varying degrees, perform these functions.

A complicating factor has, however, recently arisen. With the advent of automobile engines that
5 require the use of unleaded gasolines (to prevent disablement of catalytic converters used therewith to reduce emissions), it has been found difficult to provide gasoline of high enough octane to prevent knocking and the concomitant damage which it causes. The chief
10 problem lies in the area of the degree of octane requirement increase, herein called "ORI", which is caused by deposits formed in the commercial gasoline.

The basis of the ORI problem is as follows:
each engine, when new, requires a certain minimum octane
15 fuel in order to operate satisfactorily without pinking and/or knocking. As the engine is operated on any gasoline, this minimum octane increases and, in most cases, if the engine is operated on the same fuel for a prolonged period, will reach an equilibrium. This is apparently
20 caused by an amount of deposits in the combustion chamber. Equilibrium is typically reached after 5000 to 15,000 miles (8047 to 24140 km) of automobile operation.

The octane requirement increase in particular engines used with commercial gasolines will vary at
25 equilibrium from 5 or 6 octane units to as high as 12 or 15 units, depending upon the gasoline compositions, engine design and type of operation. The seriousness of the problem is thus apparent. A typical automobile with a research octane requirement of 85, when new, may after
30 a few months of operation require 97 research octane gasoline for proper operation, and little unleaded gasoline of that octane is available. The ORI problem also exists in some degree with engines operated on leaded fuels.

The ORI problem is compounded by the fact that the
35 most common method for increasing the octane rating of unleaded gasoline is to increase its aromatic content. This, however, eventually increases even more the neces-

1 sary octane requirement. Moreover, some of the nitrogen-
containing compounds presently used as deposit-control
additives and their mineral oil or polymer carriers may
also significantly contribute to ORI in engines using
5 unleaded fuels.

It is, therefore, particularly desirable to
provide deposit control additives which effectively con-
trol the deposits in intake systems of engines, without
themselves eventually contributing to the problem.

10 According to the present invention there are
provided deposit control additives which, when incorp-
orated in hydrocarbon fuels, are effective in maintain-
ing the cleanliness of engine intake systems. The
additives are hydrocarbyl-terminated polyoxyalkylene
15 poly- amine ethanes soluble in hydrocarbon fuel boiling
in the gasoline range. The hydrocarbyl-terminated
polyoxyalkylene chain contains oxyalkylene units of from
2 to 5 carbon atoms. The polyoxyalkylene chain, which
preferably contains from 1 to 30 oxyalkylene units, is
20 bonded through a terminal carbon to an ethane or branched
ethane chain or connecting group which is in turn bonded
to the nitrogen atom of a polyamine having from 2 to 12
amine nitrogens and from 2 to 40 carbon atoms with a
carbon-nitrogen ratio in the range from 1:1 to 10:1. The
25 ethane moiety contains from 2 to 8 carbon atoms. The
hydrocarbyl-terminating group contains from 1 to 30
carbon atoms and is bonded to the polyoxyalkylene units
through an ether oxygen atom. The additives normally
have a molecular weight in the range from 300 to 2500,
30 preferably from 800 to 1500.

The polyoxyalkylene polyamine ethane additives of
the invention can be incorporated in a liquid hydrocarbon
fuel generally in an amount of from 30 to 10,000 ppm by
weight of said additive. Advantageously the additive
35 will be incorporated in the hydrocarbon fuel in the form
of an additive concentrate comprising the additive and an
inert stable oleophilic organic solvent. The additive

1 may also be incorporated in a lubricating oil composition for use as a lubricant in an internal combustion engine.

The additive consists of three parts or moieties. The first is the polyamine moiety, and the second the
5 poly(oxyalkylene) moiety comprising at least one hydrocarbyl-terminated polyoxyalkylene polymer, bonded through the third moiety, an ethane connecting group or linkage, connected in turn to the nitrogen atom of the polyamine.

As fuel additives, the polyoxyalkylene moiety, the
10 polyamine moiety, and the ethane moiety are selected to provide solubility in the fuel composition and deposit control activity without contributing to octane requirement increase (ORI). As lubricating oil additives, the moieties may be selected to provide solubility in
15 lubricating oil compositions and dispersant activity. The additives may be termed hydrocarbyl poly(oxyalkylene) polyamine ethanes or for convenience, "polyether polyamine ethanes". The additives may be prepared from the reaction of a suitable halogenating agent containing
20 the desired ethane moiety, such as ethylene chlorohydrin, with the appropriate substituted epoxide, polymerizing to the polyoxyalkylene chain. This is in turn reacted with the appropriate hydrocarbyl cap which is followed by reaction of the capped polyether chloride with the
25 appropriate polyamine to form the required additive.

Poly(oxyalkylene) Component

The polyoxyalkylene moiety is ordinarily prepared by the reaction of an appropriate chlorohydrin containing the desired ethane connecting group. In the preferred
30 embodiment ethylene chlorohydrin is used, which is reacted under polymerization conditions with the lower alkylene oxides or oxiranes such as propylene oxide or butylene oxide. In the polymerization reaction, a single type of alkylene oxide may be employed. Copolymers, how-
35 ever, are equally satisfactory and random copolymers are readily prepared by contacting the ethylene chlorohydrin compound with a mixture of alkylene oxides. Blocked co-

1 polymers of oxyalkylene units also provide satisfactory
polyoxyalkylene polymers for the practice of the present
invention. Blocked copolymers are prepared by reacting
the chlorohydrin with first one alkylene oxide and then
5 the other in any order, or repetitively, under polymeriz-
ation conditions.

The resulting polyoxyalkylene ethylene chloride is
then reacted with the suitable hydrocarbyl cap to
complete the precursor of the polyoxyalkylene moiety.
10 The hydrocarbyl cap (R-) contains from 1 to 30 carbon
atoms, preferably from 2 to 20 carbon atoms. The hydro-
carbyl group may be any straight chain or branched aliph-
atic, olefinic or alkyl aryl hydrocarbon chain. The
hydrocarbyl cap is added to the polyoxyalkylene precursor
15 by the addition of the desired compound group to the
polyoxyalkylene ethylene chloride in a catalyzed reaction
utilizing an acid ion exchange resin reaction.

The hydrocarbyl polyoxyalkylene ethane moiety
consists of one or more, preferably 1 or 2, more prefer-
20 ably one hydrocarbyl-terminated poly(oxyalkylene) poly-
mer, composed of oxyalkylene units containing 2 to 5,
preferably 3 or 4, carbon atoms. The poly(oxyalkylene)
polymer contains at least one oxyalkylene unit, generally
1 to 30 units, preferably 5 to 30 units and most prefer-
25 ably 10 to 25 oxyalkylene units.

The terminal carbon atom at the hydroxyl end of
the polyoxyalkylene chain is bound to the ethane or
branched ethane connecting group which is in turn bound
to the nitrogen atom of the polyamine.

30 In general, the poly(oxyalkylene) compounds are
mixtures of compounds that differ in polymer chain
length. However, their properties closely approximate
those of a polymer represented by the average composition
and molecular weight.

35 The ethane connecting group ordinarily consists of
a 2-carbon chain ethylene group or an ethylene group with
branched units extending from the carbons of the

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1 ethylene. The branches of the connecting group consists
of low molecular weight alkyl groups of up to 2 carbon
atoms. Additionally, in the present invention when the
ethylene connecting groups contain branched alkyl groups,
5 the branched groups will not generally contain the same
number of carbon atoms as those extending from the
oxyalkylene units of the polyoxyalkylene moiety.

The utilization of compounds containing the ethane
or branched ethane connecting groups enhances the
10 composition's use as a deposit control additive, ORI
inhibitor, or dispersant agent by providing the molecule
with less steric hindrance and greater polarity at the
amine moiety end of the molecule. This allows the
molecule to "bind" better to metal engine surfaces and/or
15 in the system and combustion chamber deposits thereby
enhancing its detergency effect.

Polyamine Component

The polyamine moiety of the polyether polyamine is
derived from a polyamine having from 2 to 12 amine
20 nitrogen atoms and from 2 to 40 carbon atoms. The
polyamine preferably has a carbon to nitrogen ratio of
from 1:1 to 10:1. The polyamine will contain at least 1
primary or secondary amine nitrogen atom. The polyamine
may be substituted with a substituent group selected from
25 (A) hydrogen; (B) hydrocarbyl groups of from 1 to 10
carbon atoms; (C) acyl groups of from 2 to 10 carbon
atoms; and (D) monoketo, monohydroxy, monocyano, lower
alkyl and lower alkoxy derivatives of (B) or (C).
"Lower", as used in lower alkyl and lower alkoxy, means a
30 group containing from 1 to 6 carbon atoms. "Hydrocarbyl"
denotes an organic radical composed of carbon and
hydrogen which may be aliphatic, alicyclic, aromatic or
combinations thereof, e.g. aralkyl. Preferably, the
hydrocarbyl group will be free of aliphatic unsaturation,
35 i.e. ethylenic and acetylenic, particularly acetylenic
unsaturation. The substituted polyamines used in the
present invention are generally, but not necessarily,

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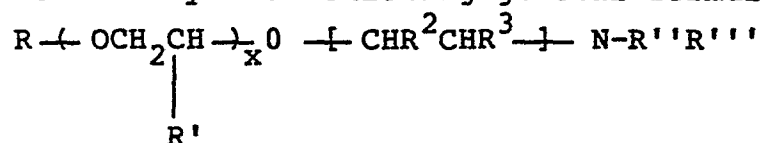
- 1 N-substituted polyamines. The acyl groups falling within
the definition of the aforementioned (C) substituents
are, for example, propionyl or acetyl. The more
preferred substituents are hydrogen, C₁ to C₆ alkyls, and
5 C₁-C₆ hydroxyalkyls.

The more preferred polyamines finding use in the
present invention are polyalkylene polyamines, including
alkylene diamine and including substituted polyamines,
e.g. alkyl and hydroxyalkyl substituted polyalkylene
10 polymines. Preferably the alkylene groups contain from 2
to 6 carbon atoms, there being preferably 2 or 3 carbon
atoms between the nitrogen atoms. Such groups are
exemplified by ethyleneamines and include ethylene
diamine, diethylene triamine, di(trimethylene) triamine,
15 dipropylene triamine and triethylenetetramine. Such
amines encompass isomers which are the branched-chain
polyamines and the previously mentioned substituted
polyamines, including hydroxy and hydrocarbyl-substituted
polyamines. Among the polyalkylene polyamines, those
20 containing 2 to 12 amine nitrogen atoms and 2 to 24
carbon atoms are especially preferred and the C₂ or C₃
alkylene polyamines are most preferred, in particular,
the lower polyalkylene polyamines, e.g. ethylene diamine
or tetraethylenepentamine.

25 In many instances a single compound will not be
used as reactant in the preparation of the additives of
this invention, in particular the polyamine component.
That is, mixtures will be used in which one or two
compounds will predominate with the average composition
30 indicated. For example, tetraethylene pentamine prepared
by the polymerization of aziridine or the reaction of
dichloroethylene and ammonia will have both lower and
higher amine numbers, e.g. triethylene tetramine,
substituted piperazines and pentaethylene hexamine, but
35 the composition will be mainly tetraethylene pentamine
and the empirical formula of the total amine composition
will closely approximate that of tetraethylene pentamine.

1 The final compositions comprising the additives of
the present invention are prepared by the reaction on the
hydrocarbonyl capped polyoxyalkylene-ethane moiety
containing a reactable chlorine or other halogen with the
5 appropriately selected amine or polyamine. The basic
substitution reaction yields the attachment of the
polyamine to the polyoxyalkylene and the elimination of
the hydrogen halide.

The class of preferred polyether polyamine ethanes
10 may be defined by the following general formula:



wherein R = C₁ to C₃₀ aliphatic, olefinic or
15 alkylaryl hydrocarbon;

R' = hydrogen, CH₃ or C₂H₅;

R'' and R''' = hydrogen, (-CH₂CH₂NH)_x wherein

x = 0 to 5, or C₁ to C₁₀;

R² and R³ = H, or low molecular alkyl groups up to
20 5 carbons, and where R' = R² and/or R³; and

x = 1 to 30 oxyalkylene units.

The polyether ethylene amines can be used as add-
itives in hydrocarbon distillate fuel and, in
particular, unleaded gasoline. The concentration of the
25 additive necessary in order to achieve the desired
deposit control effect or carburetor detergency is
dependent upon a variety of factors, including for
instance the type of fuel used and the presence of other
detergents or dispersants or other additives. Generally,
30 however, the range of concentration of the additive in
the base fuel is 30 to 10,000 weight parts per million,
preferably from 30 to 2,000 weight parts per million, and
most preferably from 100 to 700 parts per million of
polyether polyamine ethane per part of base fuel. If
35 other detergents are present, a lesser amount of
polyether polyamine ethane may be used.

1 The oils which find use in producing lubricating
oil compositions containing the additives of this
invention are generally oils of lubricating viscosity
derived from petroleum or synthetic sources. Oils of
5 lubricating viscosity normally have viscosities in the
range from 35 to 50,000 Saybolt Universal Seconds (SUS)
at 100°F (37.8°C) and more usually from 50 to 10,000 SUS
at 100°F (37.8°C). Examples of such base oils are
naphthenic bases, paraffin base and mixed base mineral
10 oils, synthetic oils, for example, alkylene polymers,
such as the polymers of propylene or butylene, and
mixtures thereof.

Usually included in the oils in addition to the
additives of the invention are one or more of such
15 additives as dispersants/detergents, rust inhibitors,
antioxidants, oiliness agents, foam inhibitors, viscosity
index improvers and pour point depressants. Usually,
these other additives will be present in amounts of from
0.5 to 15 weight percent of the total composition.
20 Generally, each of the additives will be present in the
range from 0.01 to 5 weight percent of the total
composition.

It is also contemplated that the polyether
polyamine ethanes may be used as concentrates, and could
25 be used as additive to fuels or lubricating oils
subsequent to their preparation. In concentrates, the
weight percent of these additives will usually range from
0.3 to 50, preferably 10 to 50, weight percent. The
concentrate would ordinarily comprise an inert stable
30 oleophilic organic solvent generally boiling in the range
from 150 to 400°F (65.6 to 204.4°C) and the concentrate
would preferably contain from 10 to 50 weight percent of
the polyether polyamine ethane compound.

The following Example illustrates the preparation
35 of an additive in accordance with the invention.

Example

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Preparation of 1-butyl-capped
polyoxyalkylene-2-N'-ethylene diamine ethane

5 To an ice-cold solution of 2 mls (3 mmoles) ethylene chlorohydrin in 30 mls of CH_2Cl_2 was added 0.5 ml (3.8 mmoles) of boron trifluoride:diethylether (undis-
tilled) in one portion under a nitrogen atmosphere. The
cooling bath was removed and butylene oxide added
dropwise. The temperature rose rapidly to approximately
10 40°C . An additional 30 mls (348 mmoles) of butylene
oxide was added at such a rate as to maintain an even
refluxing, i.e. approximately 2 drops per second. After
the addition was complete, the reaction product was
allowed to cool to room temperature over a four-hour
15 period and was diluted with additional CH_2Cl_2 . The
solution was extracted with cold water, then with a
saturated solution of sodium bicarbonate and then with
additional water. The product was stripped without
drying and afforded 23.4 grams of a translucent oil after
20 pumping with high vacuum. The product was redried in
diethylether over anhydrous magnesium sulphate and was
stripped to afford 22.6 grams of polyoxyalkylene ethane
chloride.

To a solution of 1.73 grams (2.2 mmoles) of the
25 polyoxyalkylene ethane chloride and 1.07 grams (5.4 meq)
Amberlyst cation ion exchange resin (H^+ form) in 5 ml of
hexane cooled in dry ice and under a nitrogen atmosphere,
was transferred 2.0 ml (2.21 mmoles) of isobutylene. The
reaction mixture was warmed to room temperature with
30 stirring.

After 88 hours, the reaction product was diluted
with hexane, filtered and stripped to afford 1.7 grams of
a clean oil. The crude product was taken up in diethyl-
ether and washed three times with water, dried over
35 magnesium sulphate and stripped to afford 1.4 grams of a
clean oil.

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1 To an ice-cold solution of 15 ml (224 mmoles) of
ethylene diamine was added 1.0 gram of the above product
dropwise. The mixture was placed under a nitrogen
atmosphere and brought to 80°C. After 23 hours the
5 reaction was cooled, the aliquot removed, diluted with
diethylether and washed with distilled water several
times, using methanol to keep emulsions down. After
neutrality was reached, as indicated by pH paper, using
water washings, the ether layer was washed three more
10 times with water, dried over anhydrous potassium
carbonate and stripped to afford 0.9 gram of a yellow oil
which was the desired product. The basic nitrogen of the
resulting product was 2.35%.

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1 CLAIMS:

1 1. A deposit control additive for use in an
internal combustion engine which is a hydrocarbyl-
terminated polyoxyalkylene polyamine ethane having a
5 molecular weight in the range from 300 to 2500, wherein
the hydrocarbyl group contains from 1 to 30 carbon atoms,
the polyoxyalkylene moiety comprises from 1 to 30
oxyalkylene units each having from 2 to 5 carbon atoms,
the ethane moiety contains from 2 to 8 carbon atoms and
10 the polyamine moiety comprises from 2 to 12 amine
nitrogen atoms and from 2 to 40 carbon atoms with a
carbon:nitrogen ratio in the range from 1:1 to 10:1.

 2. An additive as claimed in Claim 1, wherein
the oxyalkylene units are selected from oxyalkylene units
15 having 3 or 4 carbon atoms.

 3. An additive as claimed in Claim 1 or 2,
wherein said hydrocarbyl-terminated polyoxyalkylene poly-
amine ethane has a molecular weight in the range from 800
to 1500.

20 4. An additive as claimed in Claim 1, 2 or 3,
wherein said hydrocarbyl group contains from 2 to 20
carbon atoms.

 5. An additive as claimed in Claim 1, 2, 3 or
4, wherein said ethane moiety contains from 2 to 4 carbon
25 atoms.

 6. An additive as claimed in any preceding
claim, wherein said ethane moiety contains branched units
which do not contain the same number of carbons as the
branches of the oxyalkylene units of the polyoxyalkylene
30 moiety.

 7. An additive as claimed in any preceding
claim, wherein said polyamine moiety is derived from a
lower polyalkylene polyamine and contains at least one
primary or secondary amine nitrogen atom.

35 8. An additive as claimed in Claim 7, wherein
said lower polyalkylene polyamine is ethylene diamine or
diethylene triamine.

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1 9. A hydrocarbon fuel composition for use in an
internal combustion engine, comprising a hydrocarbon
boiling in the gasoline range and a deposit control
additive as claimed in any one of Claims 1 to 8.

5 10. A fuel composition as claimed in Claim 9,
wherein the additive is present in an amount of from 30
to 10,000 ppm by weight.

 11. A fuel composition as claimed in Claim 9 or
10, wherein said hydrocarbon is an unleaded gasoline.

10 12. An additive concentrate comprising an inert
stable oleophilic organic solvent and an additive as
claimed in any one of Claims 1 to 8.

 13. A concentrate as claimed in Claim 12,
wherein the organic solvent boils in the range from 150
15 to 400°F (65.6 to 204.4°C) and contains from 10 to 50
weight percent of the additive.

 14. A lubricating oil composition for use in an
internal combustion engine, comprising an oil of lubri-
cating viscosity and a deposit control additive as
20 claimed in any one of Claims 1 to 8.

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