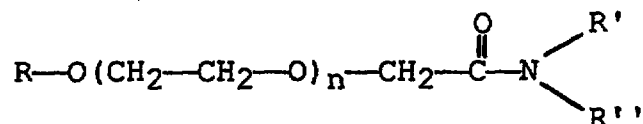


ALKOXY ACETIC ACID DERIVATIVES

This invention relates to alkoxy acetic acid derivatives, processes for their preparation, and their incorporation in additive concentrates and fuel compositions for internal combustion engines.

- 5 FR-A-2 407 258 (Rhone-Poulenc) discloses fuel compositions comprising a motor fuel and at least one alkylpolyglycol acetic acid amide having the formula:-



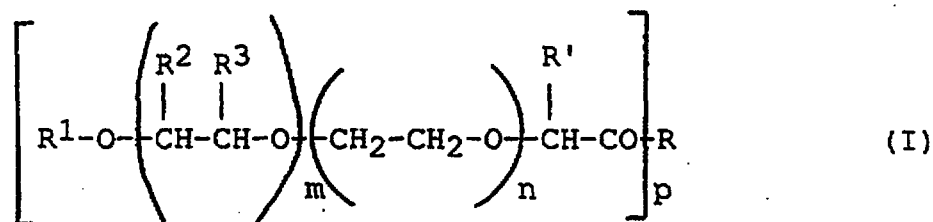
- wherein R represents a saturated or unsaturated C₈-20, preferably C₁₂-18, aliphatic radical, R' represents hydrogen or a saturated or unsaturated aliphatic radical of at least 3, preferably 4 to 18, carbon atoms, and R'' represents a saturated or unsaturated aliphatic radical of at least 3, preferably 4 to 18, carbon atoms. In the examples, there are described additives of the above formula in the form (1) of the N,N-dibutylamide of the acid derived from a 45:55 mixture of polyethoxylated cetyl and oleyl alcohols (C₁₆ saturated and C₁₈ unsaturated alcohols) wherein n is 6.3, (2) of the N-dodecylamide of the acid derived from a 75:25 mixture of polyethoxylated dodecyl and tetradecyl alcohols wherein n is 4.5 and (3) of the N,N-dibutylamide of the acid from which (2) is derived. The amides are said to impart improved detergency, anti-corrosion, anti-pollution and anti-icing properties to hydrocarbon fuels.

25 There has now been discovered a novel class of alkoxyacetic acid derivatives which may be incorporated

- 2 -

in fuel compositions for internal combustion engines, members of which class have been found to give rise to advantageous engine cleanliness effects.

According to the present invention there are provided alkoxy acetic acid derivatives of general formula I:-



wherein R is the residue of an amine, an aminoalcohol or a polyol linked to the or each -CHR'CO- moiety via an amide or ester linkage;

R' is hydrogen or C₁₋₄ alkyl;

R¹ is an optionally substituted hydrocarbyl group of 1 to 300 carbon atoms;

one of R² and R³ is independently selected from hydrogen and optionally substituted hydrocarbyl of 1 to 10 carbon atoms, the other of R² and R³ being independently selected from optionally substituted hydrocarbyl of 1 to 10 carbon atoms;

m is from 3 to 200;

n is from 0 to 20, provided that m/n is at least 1;

and

p is from 1 to 5.

It is considered that the combination of features that m is at least 3 and that n is not greater than m are essential to the attainment of improved properties relative to otherwise comparable prior art compounds.

Whilst R' may be hydrogen or a C₁₋₄ alkyl group, e.g. a methyl, ethyl or n-propyl group, R' is preferably a hydrogen atom.

The value of p is preferably in the range 1 to 3, advantageously 1 or 2.

- 3 -

The value of m is preferably from 3 to 150, more preferably 3 to 120, advantageously 3 to 50, and especially 3 to 30. Values of n from 0 to 10 are preferred. Preferably m/n is at least 2, more preferably at least 3.

As used herein, the term "hydrocarbyl" represents a radical formed by the removal of one or more hydrogen atoms from a carbon atom of a hydrocarbon (not necessarily the same carbon atom). Useful hydrocarbyls are aliphatic, acyclic or cyclic. Preferably, the hydrocarbyls are aryl, alkyl, alkenyl or cycloalkyl and are straight-chain or branched-chain. Representative hydrocarbyls include methyl, ethyl, butyl, pentyl, methylpentyl, hexenyl, ethylhexyl, dimethylhexyl, octamethylene, octenylene, cyclooctylene, methylcyclooctylene, dimethylcyclooctyl, isooctyl, dodecyl, hexadecenyl, octyl, eicosyl, hexacosyl, triacontyl and phenylethyl. When the hydrocarbyl is substituted, it contains a functional group such as carbonyl, carboxyl, nitro, tertiary amino (no N-H linkages), oxy, cyano, sulfonyl and sulfoxyl. The majority of the atoms, other than hydrogen, in substituted hydrocarbyls are carbon, with the heteroatoms (e.g. oxygen, nitrogen and sulphur) representing only a minority, 33% or less, of the total non-hydrogen atoms present.

Those skilled in the art will appreciate that functional groups such as nitro and cyano in a substituted hydrocarbyl group will displace one of the hydrogen atoms of the hydrocarbyl, whilst functional groups such as carbonyl, carboxyl, tertiary amino (-N-), oxy, sulfonyl and sulfoxyl in a substituted hydrocarbyl group will displace a -CH- or -CH₂- moiety of the hydrocarbyl. In "optionally substituted hydrocarbyl of 1 to 300 carbon atoms", "1 to 300 carbon

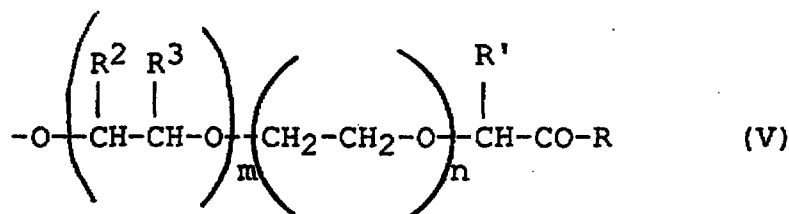
- 4 -

atoms" represents the total number of carbon atoms in the optionally substituted hydrocarbyl group. The same applies to "optionally substituted hydrocarbyl" of lower numbers of specified carbon atoms.

- 5 In derivatives of general formula I wherein p is 1, R¹ may contain one or more, e.g. 1 to 3, substituents of formula IV:-

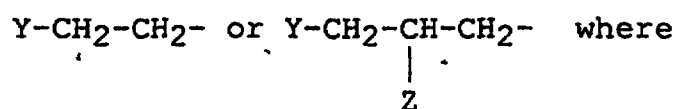


or one or more, e.g. 1 to 3, substituents of formula V:-



- 10 wherein R, R¹, R², R³, m and n are as defined above in relation to formula I, subject to the total number of carbon atoms in R¹ being not more than 300.

Thus, for example R¹ may be of the formula:-



- 15 Y is of formula IV or V above and Z is of formula IV or V above.

- 20 R¹ is preferably a hydrocarbyl group of 1 to 300 carbon atoms, more preferably a hydrocarbyl group of 1 to 100 carbon atoms. When R¹ is hydrocarbyl of a relatively high number of carbon atoms, i.e. greater than about 50 carbon atoms, R¹ may conveniently be a polymeric hydrocarbyl such as polyisobutylene, polybutene, polypropylene or polyalphaolefin. In particularly preferred derivatives of formula I, R¹

- 5 -

represents a C₁-20 alkyl group, a phenyl or benzyl group or a (C₁-15 alkyl) phenyl or (C₁-15 alkyl) benzyl group. R¹ may very conveniently represent a C₁₀-18 alkyl group, e.g. a C₁₂-15 alkyl group.

5 Preferably one of R² and R³ is independently selected from hydrogen and hydrocarbyl of 1 to 10, preferably 1 to 4 carbon atoms, the other of R² and R³ being independently selected from hydrocarbyl of 1 to 10, preferably 1 to 4, carbon atoms. Conveniently, one
10 of R² and R³ is hydrogen, the other being hydrocarbyl, preferably a C₁-3 alkyl group. Preferably, one of R² and R³ is hydrogen and the other is a methyl or ethyl group, the moieties -CHR²-CHR³-O- then being derived from propylene oxide and/or butylene oxide (1,2-
15 epoxybutane). When the moieties -CHR²-CHR³-O- contain two or more different R² and/or R³ groups, the moiety -(CHR²-CHR³-O)_m- may represent a block copolymeric group or a random copolymeric group. Derivatives of formula I wherein one of R² and R³ is hydrogen and the
20 other is a methyl group have been found to be very suitable.

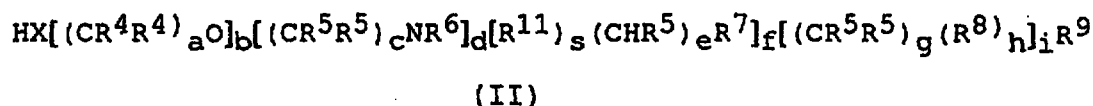
The amines, aminoalcohols and polyols of which R in formula I represents the residue are known in the art or may be prepared by analogous methods to those used
25 for preparing the known amines, aminoalcohols and polyols. For example, various amines and their preparation are described in US Patents Nos. 3,275,554, 3,438,757, 3,454,555, 3,565,804, 3,755,433 and 3,822,209. Complex amines such as "Starburst" (trade
30 mark) dendrimers may be used, e.g. the compound of formula [CH₂N((CH₂)₂CONH(CH₂)₂NH₂)₂]₂.

Examples of polyols include ethylene glycol, glycerol, trimethylolethane, trimethylolpropane, 1,2-
butanediol, 2,3-hexanediol, 2,4-hexanediol, pinacol,
35 erythritol, arabitol, sorbitol, mannitol,

- 6 -

pentaerythritol, dipentaerythritol and tripentaerythritol.

Preferred derivatives of formula I are those wherein the compound of R(H)p, of which R represents the residue, has the general formula II:-



wherein X is O or NR⁶,

each R⁴ independently represents hydrogen, hydrocarbyl of 1 to 10 carbon atoms or hydrocarbyl of 1 to 10 carbon atoms substituted by at least one hydroxy group,

each R⁵ independently represents hydrogen or hydrocarbyl of 1 to 10 carbon atoms,

each R⁶ independently represents hydrogen or hydrocarbyl of 1 to 10 carbon atoms,

R⁷ represents a C₅₋₇ cycloalkanediyl-NH- or 1,4-piperazinediyl moiety optionally substituted by one or more hydrocarbyl groups of 1 to 10 carbon atoms,

each R⁸ independently represents NR¹⁰ or CHR¹⁰,

R⁹ represents hydrogen, hydrocarbyl of 1 to 30 carbon atoms or a -C(=O)(CHOH)_t(CR⁵R⁵)_j(NR⁵)_k(CR⁵R⁵)_lOH group,

R¹⁰ represents a -(CR⁵R⁵)_rNR⁶R⁹ group,

R¹¹ represents a C₅₋₇ cycloalkanediyl moiety optionally substituted by one or more hydrocarbyl groups of 1 to 10 carbon atoms,

a is 1 to 10,

b is 0 to 10,

c is 1 to 10,

d is 0 to 10,

e is 1 to 10,

f is 0 or 1,

- 7 -

g is 1 to 10,
 h is 0 or 1
 i is 0 to 10
 j is 1 to 10,
 5 k is 0 or 1,
 l is 1 to 10,
 r is 1 to 10,
 s is 0 or 1, and
 t is 0 or 1

10 and integers b, d, f and i indicate numbers of associated moieties present, and the various moieties $[(CR^4R^4)_aO]$, $[(CR^5R^5)_cNR^6]$, $[(CHR^5)_eR^7]$ and $[(CR^5R^5)_g(R^8)_h]$ may be in any linear order.

15 Preferably in formula II X is O or NR^6 , each R^4 independently represents hydrogen, C_{1-4} alkyl or C_{1-4} hydroxyalkyl, each R^5 independently represents hydrogen or C_{1-4} alkyl, each R^6 represents hydrogen or methyl, R^7 represents a 1,4-piperazinediyl moiety or a cyclohexanediyl-NH- moiety optionally substituted by up
 20 to three methyl groups, each R^8 independently represents NR^{10} or CHR^{10} , R^9 represents hydrogen, methyl or a $-CO(CHOH)_t(CHR^5)_j(NR^5)_k(CHR^5)_lOH$ group, R^{10} represents a $-(CHR^5)_rNHR^9$ group, R^{11} represents a cyclohexanediyl moiety optionally substituted by up to
 25 three methyl groups, a is 1 to 5, b is 0 to 5, c is 1 to 6, d is 0 to 5, e is 1 to 5, f is 0 or 1, g is 1 to 5, h is 0 or 1, i is 0 to 5, j is 1 to 5, k is 0 or 1, l is 1 to 5, r is 1 to 5, s is 0 or 1 and t is 0 or 1.

30 Advantageously, X is O or NH, each R^4 independently represents hydrogen, methyl or hydroxymethyl, each R^5 independently represents hydrogen or methyl, each R^6 represents hydrogen or methyl, R^7 represents a 1,4-piperazinediyl moiety or a cyclohexanediyl-NH- moiety optionally substituted by up to 3 methyl groups, each
 35 R^8 independently represents NR^{10} or CHR^{10} , R^9

- 8 -

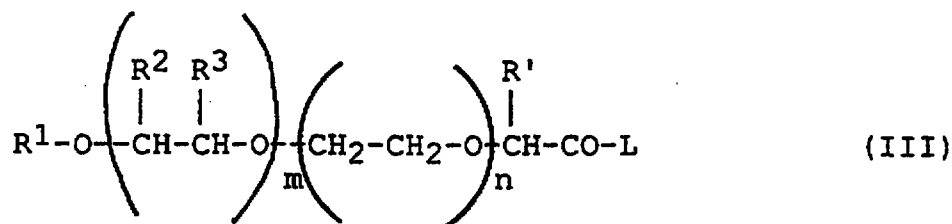
represents hydrogen, methyl, or a
 $\text{CO}(\text{CHOH})_t(\text{CHR}^5)_j(\text{NR}^5)_k(\text{CHR}^5)_l\text{OH}$ group, R^{10} represents a
 $(\text{CHR}^5)_r\text{NHR}^9$ group, a is 2 or 3, b is 0 to 3, c is 2 to
 6, d is 0 to 4, e is 3, f is 0 or 1, g is 2 or 3, h is
 1, i is 0 or 1, j is 1 to 4, k is 0 or 1, l is 1 to 4,
 5 r is 1 or 2, s is 0 or 1 and t is 0 or 1.

Examples of preferred such moieties R are the
 following:-

- $\text{NHCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$, $-\text{O}(\text{CH}_2\text{C}(\text{CH}_2\text{OH})_2)_b\text{H}$ where b is
 10 1 to 3, preferably 1, $-\text{NH}(\text{CH}_2\text{CH}_2\text{NH})_d\text{H}$ where d is 1 to
 4, $-\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH}$, $-\text{NH}(\text{CH}_2)_c\text{NH}_2$, where c is 2 to
 6, preferably 2 to 4, $-\text{NH}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{NH}_2$,
 $-\text{NH}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2\text{CH}_2\text{NH}_2$, $-\text{NH}(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$,
 $-\text{NH}(\text{CH}_2)_3(1,4\text{-piperazinediyl})(\text{CH}_2)_3\text{NH}_2$, $-\text{NH}(1,4\text{-}$
 15 $\text{cyclohexanediyl})\text{CH}_2(1,4\text{-cyclohexanediyl})\text{NH}_2$,
 $-\text{NHCH}_2(1,3,3\text{-trimethyl-5-aminocyclohexyl})$,
 $-\text{NH}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH})_2\text{H}$, $-\text{NH}(\text{CH}_2)_3\text{CH}(\text{CH}_2\text{NH}_2)(\text{CH}_2)_4\text{NH}_2$,
 $-\text{NHCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NHCO}(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{OH})_2$,
 $-\text{NHCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NHCOCH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH})_2$,
 20 $-\text{NHCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NH}_2$, $-\text{NH}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$ (all when p = 1);
 and $-\text{NH}(\text{CH}_2\text{CH}_2\text{NH})_3$ - and $-\text{NHCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)\text{CH}_2\text{CH}_2\text{NH}-$
 (when p = 2).

Most preferably, R(H)_p is selected from the group
 consisting of pentaerythritol, triethylenetetramine and
 25 tris(2-aminoethyl)amine.

The present invention further provides a process
 for preparing an alkoxy acetic acid derivative of
 general formula I as defined above which comprises
 reacting a compound of general formula III:-



- 9 -

wherein R' , R^1 , R^2 , R^3 , m and n are as defined above and L represents a leaving group, with a compound of general formula $R(H)_p$, wherein R is as defined above in molar ratio compound of formula III : compound of formula $R(H)_p$ of substantially $p:1$, optionally followed by converting the resulting acid derivative of formula I into another acid derivative of formula I with different group R as defined above.

Although the leaving group L may be, for example, a halogen atom, such as chlorine or bromine atom, L is preferably a hydroxy group.

Reaction between the compound of formula III and the compound of formula $R(H)_p$ may conveniently be effected in the presence of an inert solvent, e.g. an aromatic hydrocarbon such as toluene or xylene.

When L is a hydroxy group, the reaction may conveniently be effected at a temperature in the range from 100°C to the reflux temperature of the reaction mixture. Water may advantageously be removed, e.g. by means of a Dean-Stark extractor and condenser. When $R(H)_p$ is a polyol, advantageously an acid, such as para-toluene sulphonic acid, is present.

Conversion of one R group into a different R group as defined above is most likely to be done when the desired final product of formula I as defined above contains one or more R^9 moieties, wherein R^9 is a $-\text{CO}(\text{CHOH})_t(\text{CHR}^5)_j(\text{NR}^5)_k(\text{CHR}^5)_l\text{OH}$ group. For example, a compound of formula I wherein R^9 is hydrogen may be converted into a compound of formula I wherein R^9 is a $\text{CO}(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{OH}$ group, a $\text{COCH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$ group or a $\text{CO}(\text{CHOH})\text{C}(\text{CH}_3)_2\text{CH}_2\text{OH}$ group respectively by reaction with gamma-valerolactone, N-methylmorpholinone or pantolactone.

Compounds of formula III as defined above wherein L is other than a hydroxy group can be prepared in known

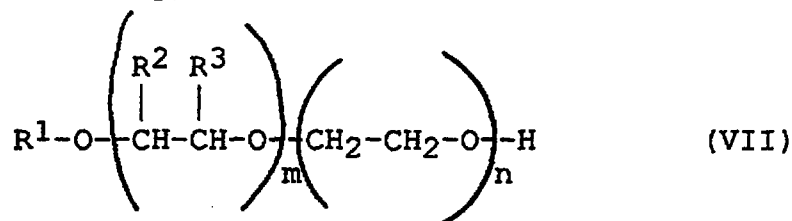
- 10 -

manner from the corresponding compound of formula III wherein L is a hydroxy group.

Compounds of formula III wherein L is a hydroxy compound may be prepared by reaction of an alpha-halo carboxylic acid of general formula VI:-



or an alkali metal salt thereof, wherein R' is as defined above and Q is a halogen, preferably chlorine, atom with a compound of formula VII:-



where R¹, R², R³, m and n are as defined above, in the presence of a suitable base and an inert solvent.

Suitable bases include sodium and potassium hydrides and amides, for which solvents such as tetrahydrofuran and xylene are suitable, and potassium tertiary butoxide, for which tertiary butanol is suitable as solvent. In an aprotic solvent, sodium metal may be used to generate suitably basic conditions. When n is 1 to 20 (i.e. greater than 0), milder bases can be employed, such as sodium and potassium hydroxides, e.g. using toluene as solvent.

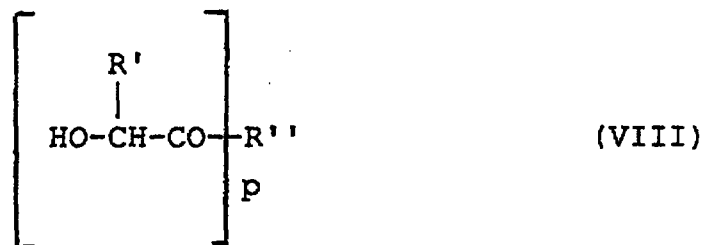
Compounds of formula VII wherein n is 1 to 20 may be generated by reacting a compound of formula VII wherein n is 0 with ethylene oxide in molar ratio compound of formula VII : ethylene oxide 1:n.

A compound of formula VII wherein n is 1 to 20 may be converted into an alkoxyacetic acid of general formula III wherein L is a hydroxy group, R' is

- 11 -

hydrogen and n is 0 to 19 by a process similar to that described in US Patent No. 5,380,930. In such a process, the compound of formula VII wherein n is 1 to 20 is conveniently reacted with a stable free radical nitroxide, such as piperidine-1-oxyl, in the presence of nitric acid and an oxidising agent, e.g. air or gaseous oxygen, in the presence or absence of a solvent.

Alkoxy acetic acid derivatives of formula I may alternatively, in principle, be prepared by reacting a compound of general formula VIII:-



where R' and p are as defined above and R'' is R as above or a protecting group with appropriate alkylene oxides in suitable order, followed by end-capping the resulting product in order to produce the desired alkoxyacetic acid derivative of formula I, or when R'' is a protecting group, with reaction with a compound R(H)_p as defined above to displace the protecting group and finally obtain the desired alkoxy acetic acid derivative of formula I.

The present invention further provides a fuel composition comprising a major amount of a fuel for an internal combustion engine and a minor amount of an acid derivative of formula I as defined above, and an additive concentrate suitable for addition to fuel for an internal combustion engine which comprises a fuel-compatible diluent and an acid derivative of formula I as defined above.

The alkoxy acetic acid derivatives of formula I have useful application both in fuel compositions for

- 12 -

spark-ignition engines (gasoline compositions) and in fuel compositions for compression ignition engines (diesel fuel compositions).

The "minor amount" referred to above is preferably less than 10% w of the composition, more preferably less than 1% w and advantageously less than 0.1% w (1000 ppmw) (parts per million by weight) of the composition. In preferred fuel compositions of the invention, the alkoxy acetic acid derivative is present in an amount in the range 50 to 1000 ppmw of the fuel composition.

For gasoline compositions, the fuel will be a fuel boiling in the gasoline boiling range, and it may consist substantially of hydrocarbons or it may contain blending components. Alternatively, e.g. in countries such as Brazil, the fuel may consist substantially of ethanol.

Suitable liquid hydrocarbon fuels of the gasoline boiling range are mixtures of hydrocarbon boiling in the temperature range from about 25°C to about 232°C, and comprise mixtures of saturated hydrocarbons, olefinic hydrocarbons and aromatic hydrocarbons. Preferred are gasoline mixtures having a saturated hydrocarbon content ranging from about 40% to about 80% by volume, an olefinic hydrocarbon content from 0% to about 30% by volume and an aromatic hydrocarbon content from about 10% to about 60% by volume. The base fuel is derived from straight run gasoline, polymer gasoline, natural gasoline, dimer and trimerized olefins, synthetically produced aromatic hydrocarbon mixtures, from thermally or catalytically reformed hydrocarbons, or from catalytically cracked or thermally cracked petroleum stocks, and mixtures of these. The hydrocarbon composition and octane level of the base fuel are not critical. The octane level,

- 13 -

$(R+M)/2$, will generally be above about 85 (where R is Research Octane Number and M is Motor Octane Number).

Any conventional base gasoline can be employed in the practice of the present invention. For example, hydrocarbons in the gasoline can be replaced by, up to a substantial amount of conventional alcohols or ethers, conventionally known for use in fuels. The base gasolines are desirably substantially free of water since water could impede a smooth combustion.

Normally, the gasolines to which the invention is applied may be leaded or unleaded, although are preferably substantially lead-free, and may contain minor amounts of one or more blending agents such as methanol, ethanol, tertiary butanol, ethyl tertiary butyl ether, methyl tertiary butyl ether, and the like, at from about 0.1% by volume to about 25% by volume of the base fuel, although larger amounts (e.g. up to 40%v) may be utilised. The gasolines can also contain conventional additives including antioxidants such as phenolics, e.g. 2,6-di-tert-butylphenol or phenylenediamines, e.g. N,N'-di-sec-butyl-p-phenylenediamine, dyes, metal deactivators, dehazers such as polyester-type ethoxylated alkylphenol-formaldehyde resins. Corrosion inhibitors, such as that commercially sold by Rhein Chemie, Mannheim, Germany as "RC 4801", or a polyhydric alcohol ester of a succinic acid derivative having on at least one of its alpha-carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group having from 20 to 500 carbon atoms, for example, pentaerythritol diester of polyisobutylene-substituted succinic acid, the polyisobutylene group having an average molecular weight of about 950, in an amount from about 1 ppmw to about 1000 ppmw, may also be present. The fuels can also contain antiknock compounds such as methyl

- 14 -

cyclopentadienylmanganese tricarbonyl, tetraethyl lead or other lead-containing compounds, and ortho-azodiphenol as well as co-antiknock compounds such as benzoyl acetone.

5 A preferred gasoline composition of the invention may additionally contain a minor amount of at least one additional additive compound selected from the group consisting of polyalkenyl amines, Mannich amines, polyalkenyl succinimide, poly(oxyalkylene)amines, 10 poly(oxyalkylene)carbamates, and poly(alkenyl)-N-substituted carbamates.

An effective amount of one or more acid derivatives of formula I are introduced into the combustion zone of the engine in a variety of ways to prevent build-up of 15 deposits, or to accomplish the reduction of intake valve deposits or the modification of existing deposits that are related to octane requirement. As mentioned, a preferred method is to add a minor amount of one or more acid derivatives of formula I to the gasoline. 20 For example, one or more acid derivatives of formula I are added directly to the gasoline or are blended with one or more carriers and/or one or more hydrocarbon-soluble alkali metal or alkaline earth metal salts and/or one or more additional detergents before being 25 added to the gasoline.

The amount of acid derivative of formula I used will depend on the particular variation of formula I used, the engine, the fuel, and the presence or absence of carriers, additional detergents and diluents.

30 The carrier, when utilised, may conveniently have an average molecular weight from about 250 to about 5000. Suitable carriers, when utilised, include hydrocarbon based materials such as polyisobutylenes (PIB's), polypropylenes (PP's) and polyalphaolefins 35 (PAO's), all of which may be hydrogenated or

- 15 -

unhydrogenated but are preferably hydrogenated; polyether based materials such as polybutylene oxides (poly BO's), polypropylene oxides (poly PO's), polyhexadecene oxides (poly HO's) and mixtures thereof (i.e. both (poly BO) + (poly PO) and poly-BO-PO)); and mineral oils such as those sold by member companies of the Royal Dutch/Shell group under the designations "HVI" and "XHVI" (trade mark), Exxon Naphthenic 900 sus mineral oil and high viscosity index oils in general. The carrier is preferably selected from PIB's, poly BO's and poly PO's with poly PO's being the most preferred.

A particularly prepared carrier fluid comprises a combination of a polyalphaolefin having a viscosity at 100°C in the range 2×10^{-6} to 2×10^{-5} m²/s (2 to 20 centistokes) being a hydrogenated oligomer containing 18 to 80 carbon atoms derived from at least one alphaolefinic monomer containing from 8 to 16 carbon atoms, and a polyoxyalkylene compound selected from glycols, mono- and diethers thereof, having number average molecular weight (M_n) in the range 400 to 3000, the weight ratio polyalphaolefin: polyoxyalkylene compound being in the range 1:10 to 10:1.

The polyalphaolefins are primarily trimers, tetramers and pentamers, and synthesis of such materials is outlined in Campen et al., "Growing use of synlubes", Hydrocarbon Processing, February 1982, pages 75 to 82. The polyalphaolefin is preferably derived from an alphaolefinic monomer containing from 8 to 12 carbon atoms. Polyalphaolefins derived from decene-1 have been found to be very effective. The polyalphaolefin preferably has viscosity at 100°C in the range of 6×10^{-6} to 1×10^{-5} m²/s (6 to 10 centistokes). Polyalphaolefin having a viscosity at

- 16 -

100°C of $8 \times 10^{-6} \text{ m}^2/\text{s}$ (8 centistokes) has been found to be very effective.

Preferred polyoxyalkylene compounds for use in combination with these polyalphaolefins are described in EP-A-588429 (Applicants reference T 5677).

The carrier concentration in the final fuel composition is up to about 1000 ppm weight. When a carrier is present, the preferred concentration is from about 50 ppm by weight to about 400 ppm by weight, based on the total weight of the fuel composition. Once the carrier is blended with one or more compounds of formula I and any other desired components, the blend is added directly to the fuel or packaged for future use.

The hydrocarbon-soluble alkali metal or alkaline earth metal salt, when utilised, may be one of those described in WO 87/01126, and the compounds of formula I are particularly suitable for incorporation, as additional component, in fuel compositions as described in WO 87/01126. Preferred hydrocarbon-soluble alkali metal or alkaline earth metal salts are, however, alkali metal or alkaline earth metal salts of a succinic acid derivative. Such a salt of a succinic acid derivative, when utilised, will have as a substituent on one of its alpha-carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group having from 20 to 200 carbon atoms. Alternatively, the succinic acid derivative will have as a substituent on one of its alpha-carbon atoms an unsubstituted or substituted hydrocarbon group having from 20 to 200 carbon atoms which is connected to the other alpha-carbon atom by means of a hydrocarbon moiety having from 1 to 6 carbon atoms, forming a ring structure. Suitable such salts are described for example in EP-A-207560 and in EP-A-491439.

- 17 -

The salts of the succinic acid derivative can be monobasic or dibasic. Monobasic salts in which the remaining carboxylic acid group has been transformed into an amide or ester group may also be used.

5 Suitable alkali metal salts of a partial ester of an alkyl polyether alcohol with a succinic acid derivative are described in EP-A-491439.

 Suitable metal salts include lithium, sodium, potassium, rubidium, caesium and calcium salts.
10 Particularly preferred salts are described in EP-A-207560.

 The aliphatic hydrocarbon substituent(s) of the succinic acid derivative is suitably derived from a polyolefin, the monomers of which have 2 to 6 carbon
15 atoms. Thus, convenient substituents include polyethylene, polypropylene, polybutylenes, polypentenenes, polyhexenes or mixed polymers. Particularly preferred is an aliphatic hydrocarbon group which is derived from polyisobutylene.

20 The hydrocarbon group may include an alkyl and/or an alkenyl moiety and may contain substituents. One or more hydrogen atoms may be replaced by another atom, for example halogen, or by a non-aliphatic organic group, e.g. an (un)substituted phenyl group, a hydroxy,
25 ether, ketone, aldehyde or ester. A very suitable substituent in the hydrocarbon group is at least one other metal succinate group, yielding a hydrocarbon group having two or more succinate moieties.

 The aliphatic hydrocarbon group should contain 20
30 to 200, preferably 35-150, carbon atoms. When a polyolefin is used as substituent the chain length is conveniently expressed as the number average molecular weight. The number average molecular weight of the substituent, e.g. determined by osmometry, is
35 advantageously from 400 to 2000.

- 18 -

The succinic acid derivative may have more than one C₂₀-200 aliphatic hydrocarbon group attached to one or both alpha-carbon atoms, but preferably it has one C₂₀-200 aliphatic hydrocarbon group on one of its alpha-carbon atoms and on the other alpha-carbon atom either no substituent or a hydrocarbon of only a short chain length, e.g. C₁₋₆ group. The latter group can be linked with the C₂₀-200 hydrocarbon group forming a ring structure.

The gasoline compositions of the present invention may also contain one or more additional detergents. When additional detergents are utilised, the gasoline composition will comprise a mixture of a major amount of hydrocarbons in the gasoline boiling range as described hereinbefore, a minor amount of one or more compounds of formula I as described hereinbefore and a minor amount of an additional detergent selected from polyalkenyl amines, e.g. polybutyleneamines, such as "KEROCOM" polyisobutyleneamine, available ex BASF, Mannich amines, polyalkenyl succinimides, poly(oxyalkylene)amines, poly(oxyalkylene) carbamates, poly(alkenyl)-N-substituted carbamates, and mixtures thereof. As noted above, a carrier as described hereinbefore may also be included. The "minor amount" is preferably less than about 10% by weight of the total fuel composition, more preferably less than about 1% by weight of the total fuel composition and yet more preferably less than about 0.1% by weight of the total fuel composition.

The polyalkenyl amine detergents utilised comprise at least one monovalent hydrocarbon group having at least 50 carbon atoms and at least one monovalent hydrocarbon group having at most five carbon atoms bound directly to separate nitrogen atoms of a diamine. Preferred polyalkenyl amines are polyisobutenyl amines.

- 19 -

Polyisobutenyl amines are known in the art and representative examples are disclosed in various US Patents including US Patent No. 3,753,670, US Patent No. 3,756,793, US Patent No. 3,574,576 and US Patent No. 3,438,757. Particularly preferred polyisobutenyl amines for use in the present fuel composition include N-polyisobutenyl-N', N'-dimethyl-1,3-diaminopropane (PIB-DAP), OGA-472 (a polyisobutenyl ethylene diamine available commercially from Oronite), N-polyisobutenyl diethylene triamine (PIB-DETA) and N-polyisobutenyl triethylene tetramine (PIB-TETA).

The Mannich amine detergents utilised comprise a condensation product of a high molecular weight alkyl-substituted hydroxyaromatic compound, an amine which contains an amino group having at least one active hydrogen atom (preferably a polyamine), and an aldehyde. Such Mannich amines are known in the art and are disclosed in US Patent No. 4,231,759. Preferably, the Mannich amine is an alkyl substituted Mannich amine.

The polyalkenyl succinimide detergents comprise the reaction product of a dibasic acid anhydride with either a polyoxyalkylene diamine, a hydrocarbyl polyamine or mixtures of both. Typically the succinimide is substituted with the polyalkenyl group but the polyalkenyl group may be found on the polyoxyalkylene diamine or the hydrocarbyl polyamine. Polyalkenyl succinimides are also known in the art and representative examples are disclosed in various patent references including US Patent No. 3,443,918, EP-A-208560, DE-OLS 3,126,404, US Patent No. 4,234,435, US Patent No. 4,810,261, US Patent No. 4,852,993, US Patent No. 4,968,321, US Patent No. 4,985,047, US Patent No. 5,061,291 and US Patent No. 5,147,414.

- 20 -

Particularly effective succinimide detergents are those obtained by reacting at least one amine, with a polyalkenyl derivative of a monoethylenically unsaturated C₄-10 dicarboxylic acid material in which the ratio of dicarboxylic acid moieties per polyalkenyl chain is not greater than 1.2:1 and the number average molecular weight (Mn) of the polyalkenyl chain is in the range from 1600 to 5000, e.g. as described in EP-A-587250 (Applicants reference T1665).

Amines employed in the preparation of said succinimide detergents are preferably C₁-30, more preferably C₁-18, and especially C₈-12, amines containing 1 to 8 nitrogen atoms. Such amines may be branched or unbranched, saturated aliphatic, primary or secondary amines, containing 1 to 8 nitrogens, preferably mono- or diamines, such as ethylamine, butylamine, sec. butylamine, diethylamine and 3-dimethylamino-1-propylamine, but including higher polyamines such as alkylene polyamines, wherein pairs of nitrogen atoms are joined by alkylene groups of 2 to 4 carbon atoms.

Poly(oxyalkylene)amines are described, for example, in US Patents Nos. 4,985,047 and 4,332,595, in EP-A-440 248, EP-A-310 875, EP-A-208 978 and WO-A-85 01956. The poly(oxyalkylene) carbamate detergents comprise an amine moiety and a poly(oxyalkylene) moiety linked together through a carbamate linkage, i.e.,



(IX)

These poly(oxyalkylene) carbamates are known in the art and representative examples are disclosed for example in US Patent No. 4,191,537, US Patent No. 4,160,648, US Patent No. 4,236,020, US Patent No. 4,270,930, US Patent No. 4,288,612 and US Patent No. 4,881,945. Particularly preferred poly(oxyalkylene)

- 21 -

carbamates for use in the present fuel composition include OGA-480 (a poly(oxyalkylene) carbamate which is available commercially from Oronite).

The poly(alkenyl)-N-substituted carbamate
5 detergents utilised are of the formula:



in which R is a poly(alkenyl) chain; R¹ is a hydrocarbyl or substituted hydrocarbyl group; and A is an N-substituted amino group. Poly(alkenyl)-N-substituted carbamates are known in the art and are
10 disclosed in US Patent No. 4,936,868.

The one or more additional detergents are added directly to the fuel boiling in the gasoline boiling range, blended with one or more carriers, blended with one or more acid derivatives of formula I, or blended
15 with one or more acid derivatives of formula I and one or more carriers before being added to the fuel.

The concentration of the one or more additional detergents in the final fuel composition is generally up to about 1000 ppmw for each additional detergent.
20 When one or more additional detergents are utilised, the preferred concentration for each additional detergent is from about 10 ppmw to about 400 ppmw, based on the total weight of the fuel composition, even more preferably from about 25 ppmw to about 250 ppmw,
25 based on the total weight of the fuel composition.

Additive components can be added separately to the gasoline or can be blended with one or more diluents, forming an additive concentrate, and added to the gasoline together. Suitable gasoline-compatible
30 diluents are hydrocarbons and mixtures of hydrocarbons with alcohols or ethers, such as methanol, ethanol,

- 22 -

propanol, 2-butoxyethanol, methyl tert-butyl ether, or higher alcohols such as "Dobanol 91", (Trade Mark) available from member companies of the Royal Dutch/Shell group.

5 Preferably the diluent is an aromatic hydrocarbon solvent such as toluene, xylene, mixtures thereof or mixtures of toluene or xylene with an alcohol. Additionally preferred diluents include "Shellsol AB", "Shellsol R", (Trade Marks) and low aromatic white
10 spirit (LAWS), which are available from member companies of the Royal Dutch/Shell group.

For diesel fuel compositions, the fuel will be a diesel oil, which may be a hydrocarbon fuel (a middle distillate fuel oil), which may be a conventional fuel
15 or a low-sulphur fuel having a sulphur concentration below 500 ppmw, preferably below 50 ppmw, advantageously below 10 ppmw. Diesel fuels typically have initial distillation temperature about 160°C and 90% point of 290-360°C, depending on fuel grade and
20 use. Vegetable oils may also be used as diesel fuels per se or in blends with hydrocarbon fuels.

Low-sulphur fuels will typically require a lubricity additive to reduce fuel pump wear.

Additive concentrates suitable for incorporating in
25 diesel fuel compositions will contain the acid derivative of formula I and a fuel-compatible diluent, which may be a non-polar solvent such as toluene, xylene, white spirits and those sold by member companies of the Royal Dutch/Shell Group under the
30 Trade Mark "SHELLSOL", and/or a polar solvent such as esters and , in particular, alcohols, e.g. hexanol, 2-ethylhexanol, decanol, isotridecanol and alcohol mixtures such as those sold by member companies of the Royal Dutch/Shell Group under the Trade Mark "LINEVOL",
35 especially "LINEVOL" 79 alcohol which is a mixture of

- 23 -

C₇₋₉ primary alcohols, or the C₁₂₋₁₄ alcohol mixture commercially available from Sidobre Sinnova, France under the Trade Mark "SIPOL".

5 Additive concentrates and diesel fuel compositions prepared therefrom may additionally contain additional additives such as low molecular weight amine co-detergents, dehazers, e.g. alkoxyated phenol formaldehyde polymers such as those commercially available as "NALCO" (Trade Mark) 7D07 (ex Nalco), and
10 "TOLAD" (Trade Mark) 2683 (ex Petrolite; anti-foaming agents (e.g. the polyether-modified polysiloxanes commercially available as "TEGOPREN" (Trade Mark) 5851, Q 25907 (ex Dow Corning) or "RHODORSIL" (Trade Mark) (ex Rhone Poulenc)); ignition improvers (e.g. 2-
15 ethylhexyl nitrate, cyclohexyl nitrate, di-tertiary-butyl peroxide and those disclosed in US Patent No. 4,208,190 at Column 2, line 27 to Column 3, line 21); anti-rust agents (e.g. that commercially sold by Rhein Chemie, Mannheim, Germany as "RC 4801", or polyhydric
20 alcohol esters of a succinic acid derivative, the succinic acid derivative having on at least one of its alpha-carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group containing from 20 to 500 carbon atoms, e.g. the pentaerythritol diester of
25 polyisobutylene-substituted succinic acid), reodorants, anti-wear additives; anti-oxidants (e.g. phenolics such as 2,6-di-tert-butylphenol, or phenylenediamines such as N,N'-di-sec-butyl-p-phenylenediamine), metal deactivators and lubricity agents (e.g. those
30 commercially available as EC831 (ex Paramins) or "HITEC" (Trade Mark) 580 (ex Ethyl Corporation)).

Preferred low molecular weight amine co-detergents are C₁₀₋₂₀ alkylamines. Aliphatic primary monoamines, particularly linear aliphatic primary monoamines,
35 having 10 to 20 carbon atoms are particularly

- 24 -

preferred. The alkylamine preferably has 10 to 18, e.g. 12 to 18, more preferably 12 to 16 carbon atoms. Dodecylamine is particularly preferred.

Unless otherwise stated, the (active matter) concentration of each additive in the diesel fuel is preferably up to 1 percent by weight more preferably in the range from 5 to 1000 ppmw (parts per million by weight of the diesel fuel). The (active matter) concentration of the compound of formula I in the diesel fuel is preferably 50 to 1000 ppmw.

The (active matter) concentration of the dehazer in the diesel fuel is preferably in the range from 1 to 20, more preferably from 1 to 15, still more preferably from 1 to 10 and advantageously from 1 to 5 ppmw. The (active matter) concentrations of other additives (with the exception of the ignition improver and the lubricity agent) are each preferably in the range from 0 to 20, more preferably from 0 to 10 and advantageously from 0 to 5 ppmw. The (active matter) concentration of the ignition improver in the diesel fuel is preferably in the range from 0 to 600 and more preferably from 0 to 500 ppmw. If an ignition improver is incorporated into the diesel fuel, it is conveniently used in an amount of 300 to 500 ppmw. If a lubricity agent is incorporated into the diesel fuel, it is conveniently used in an amount of 100 to 500 ppmw.

The diesel oil itself may be an additised (additive-containing) oil or an unadditised (additive-free) oil. If the diesel oil is an additised oil, it will contain minor amounts of one or more additives, e.g. one or more additives selected from anti-static agents, pipeline drag reducers, flow improvers (e.g. ethylene/vinyl acetate copolymers or acrylate/maleic anhydride copolymers) and wax anti-settling agents

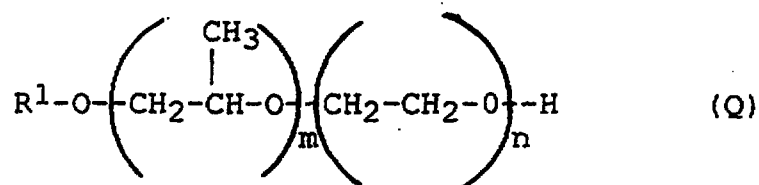
- 25 -

(e.g. those commercially available under the Trade Marks "PARAFLOW" (e.g. "PARAFLOW" 450; ex Paramins), "OCTEL" (e.g. "OCTEL" W 5000; ex Octel) and "DODIFLOW" (e.g. "DODIFLOW" V 3958; ex Hoechst).

5 The present invention still further provides a method of operating an internal combustion engine (e.g. a spark-ignition engine or a compression-ignition engine) which comprises introducing into the combustion chambers of said engine a fuel composition (e.g. a gasoline composition or diesel fuel composition, as
10 appropriate) as defined above.

Use of alkoxy acetic acid derivatives of formula I as additives in fuels for internal combustion engines may result in attaining one or more of a number of
15 effects such as inlet system cleanliness (intake valves, fuel injectors, carburettors), combustion chamber cleanliness (in each case either or both of keep clean and clean-up effects), anti-corrosion (including anti-rust) and reduction or elimination of
20 valve-stick.

The invention will be further understood from the following illustrative examples in which Examples I to V relate to the preparation of intermediate acids, and Examples I' to 24 to compounds of formula I. In the
25 examples, various polyether starting material of the general formula:



wherein R^1 represents a C_{12-15} alkyl group are designated as follows:-

Polyether A is a polyoxypropylene glycol hemiether
30 (monoether) corresponding to formula Q wherein m is in

- 26 -

the range 17 to 23 and n is 0, prepared using a mixture of C_{12-15} alcohols as initiator, and having M_n in the range 1200 to 1500 and a kinematic viscosity in the range 72 to 82 mm^2/s at 40°C according to ASTM D 445, available under the trade designation "SAP 949" from member companies of the Royal Dutch/Shell group;

Polyether B is a polyoxypropylene glycol hemiether (monoether) corresponding to formula Q wherein m is in the range 3.5 to 5.5 and n is 0, prepared using a mixture of C_{12-15} alkanols as initiator, and having M_n in the range 435 to 505 and a kinematic viscosity in the range 16 to 21 mm^2/s at 40°C according to ASTM D 445, available under the trade designation "OXILUBE 500" ("OXILUBE" is a registered trade mark) from member companies of the Royal Dutch/Shell group;

Polyether C is a polyoxypropylene glycol hemiether (monoether) corresponding to formula Q wherein m is about 120 and n is 0, prepared using a mixture of C_{12-15} alkanols as initiator, having a hydroxyl value of 0.14 milliequivalents per gram according to ASTM D 4274-88 and M_n calculated therefrom (on the basis of one hydroxyl group per molecule) of 7150, and a kinematic viscosity in the range of 2300 to 2400 mm^2/s at 40°C according to ASTM D 445;

Polyether D is a polyalkylene glycol hemiether (monoether) corresponding to formula Q wherein m is 19 and n is 5, prepared by reacting a sample of Polyether A with ethylene oxide in molar ratio 1:5 in the presence of potassium hydroxide as base, at 125°C , under pressure. Polyether D had hydroxyl value of 0.625 milliequivalents per gram according to ASTM D 4274-88 and a kinematic viscosity of 98.3 mm^2/s at 40°C according to ASTM D 445.

Various abbreviations are employed in the examples as follows:-

- 27 -

"AV" denotes acid value, and this was determined using a "Metrohm 670" (trademark) potentiometric titrometer according to a method based upon ASTM D 664-89 with modified solvent system (75% w toluene, 12.5% w acetonitrile, 12.5% w acetic acid);

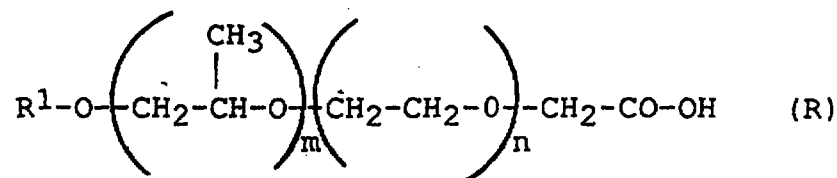
"TBN" denotes total basic nitrogen, and this was determined using a "Metrohm 670" (trade mark) potentiometric titrometer according to a method based upon ASTM D 2896 with modified solvent system (75% w toluene, 12.5% w acetonitrile, 12.5% w acetic acid);

"AM" denotes active matter content, and this was determined by separating inactive material from the desired active matter in obtained product on a silica column using hexane as eluant, and is expressed as a percentage relative to the obtained product.

"meqg⁻¹" denotes milliequivalents per gram.

In the examples and tests which follow, all parts and percentages are by weight unless stated otherwise, and temperatures are in degrees Celsius.

Intermediate acids, in the form of alkoxy acetic acids derivatives of general formula:



wherein R¹ represents a C₁₂₋₁₅ alkyl group, were prepared from the above polyether starting materials as follows:-

EXAMPLE I

Preparation of alkoxy acetic acid A

(m = 17 to 23, n = 0)

To a 3000 ml flask, equipped with mechanical stirrer and nitrogen purge, was added sodium hydride (88 g, 2.2 mol, 60% dispersion in oil) and

- 28 -

tetrahydrofuran (500 ml). To the resulting agitated mixture, a solution of Polyether A (1500g, 1 mol) in tetrahydrofuran (1500 ml) was added, gradually over a period of approximately 3 hours. The mixture was then heated to reflux, with stirring, for 3 hours, cooled to 40-50°C and a solution of chloroacetic acid (94.5 g, 1 mol) in tetrahydrofuran (100 ml) was added over approximately 2 hours. The reaction mixture was heated to reflux for 3 hours, cooled to ambient temperature (20°C) and then acidified with hydrochloric acid (2 N aqueous solution) (addition continued until sufficient to render the mixture acidic). The reaction mixture was extracted with diethylether (3 x 1 L) and the combined organic phase was washed with water (3 x 1 L). The organic phase was dried over MgSO_4 , filtered and evaporated to afford the desired product as 1560 g of a pale yellow oil, $\text{AV} = 0.596 \text{ meqg}^{-1}$, $\text{AM} = 85.5\%$.

This product was also prepared by variations of this process in which ethylchloroacetate or sodium chloroacetate were used instead of chloroacetic acid, wherein tertiary butanol or xylene were used as solvent instead of tetrahydrofuran and wherein potassium tertiary butoxide, sodamide or sodium metal (with xylene as solvent) were used instead of sodium hydride.

EXAMPLE II

Preparation of alkoxy acetic acid B

($m = 3.5$ to 5.5 , $n = 0$)

To a 3000 ml flask, equipped with mechanical stirrer and nitrogen purge, was added sodium hydride (88 g, 2.2 mol, 60% dispersion in oil) and tetrahydrofuran (500 ml). To this agitated mixture, a solution of Polyether B (555 g, 1 mol) in tetrahydrofuran (1000 ml) was added, gradually over a period of approximately 3 hours. The mixture was stirred, for 3 hours and a solution of chloroacetic

- 29 -

acid (108 g, 1.1 mol) in tetrahydrofuran (500 ml) was added over approximately 4 hours. The reaction mixture was heated to reflux for 14 hours, cooled and then acidified with hydrochloric acid (2 N aqueous solution). The reaction mixture was extracted with diethylether (3 x 1 L) and the combined organic phase was washed with water (3 x 1 L). The organic phase was dried over Na_2SO_4 , filtered and evaporated to afford the desired product as 604 g of a pale yellow oil, AV = 1.72 meqg⁻¹.

EXAMPLE III

Preparation of alkoxy acetic acid C (m = 120, n = 0)

To a 2000 ml flask, equipped with mechanical stirrer and nitrogen purge, was added sodium hydride (8.8 g, 0.22 mol, 60% dispersion in oil) and tetrahydrofuran (250 ml). This mixture was heated to reflux, with stirring, and a solution of Polyether C (460 g, 0.1 mol) in tetrahydrofuran (1000 ml) added dropwise over 2 hours. After 3 hours a solution of chloroacetic acid (10.4 g, 0.11 mol) in tetrahydrofuran (50 ml) was added and the mixture maintained under reflux, with stirring, for a further 4 hours. The mixture was cooled, acidified with hydrochloric acid (2 N aqueous solution) and extracted with ether (3 x 750 ml). The combined organic phase was washed with saturated aqueous sodium chloride solution (3 x 200 ml), dried over MgSO_4 , filtered and evaporated to afford 452 g of the desired product as a pale yellow oil, AV = 0.25 meqg⁻¹.

EXAMPLE IV

Preparation of alkoxy acetic acid D (m = 19, n = 5)

To a 500 ml flask equipped with Dean-Stark extractor and condenser, was added Polyether D (150 g, 0.09 mol), toluene (250 ml) and a solution of sodium

- 30 -

hydroxide (3.6 g, 0.1 mol) in water (20 ml). The mixture was heated at reflux temperature until all the water from the reaction mixture had been removed through the Dean-Stark extractor. The mixture was cooled sufficiently to allow the addition of the sodium salt of chloroacetic acid (11.6 g, 0.1 mol) and the mixture heated under reflux for 14 hours. The mixture was cooled, acidified with hydrochloric acid (2 N aqueous solution) and the phases separated. The organic phase was washed with saturated aqueous sodium chloride solution (2 x 50 ml), dried over MgSO_4 , filtered and evaporated to afford the desired product as 149 g of a pale yellow oil, $\text{AV} = 0.23 \text{ meqg}^{-1}$.

This product was also prepared by variations of this process wherein aqueous potassium hydroxide solution or potassium hydroxide pellets were used instead of aqueous sodium hydroxide solution, and wherein chloroacetic acid was used instead of the sodium salt of chloroacetic acid.

EXAMPLE V

Preparation of alkoxy acetic acid E (m = 19, n = 4)

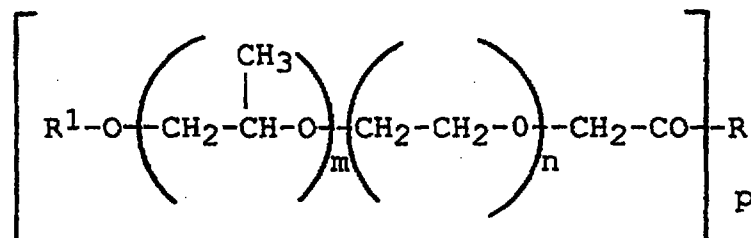
To a round-bottomed flask equipped with magnetic stirrer was added Polyether D (12 g), dichloromethane (25 ml), nitric acid (69%, 1 ml) and 2,2,6,6-tetramethylpiperidine-1-oxyl (0.3 g, 2.5% w/w, based on Polyether D). The resulting mixture was stirred at 35°C whilst oxygen was bubbled through at a rate of 30 ml/minute for 3 hours at ambient pressure. The mixture was then cooled to ambient temperature (20°C), washed with brine (3 x 50 ml), dried over MgSO_4 , filtered and evaporated to afford the desired product as 10.4 g of a pale yellow oil, $\text{AV} = 0.41 \text{ meqg}^{-1}$.

This product was also prepared by variations of this process in which 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl or 4-acetamido-2,2,6,6-

- 31 -

tetramethylpiperidine-1-oxyl were used instead of 2,2,6,6-tetramethylpiperidine-1-oxyl, wherein air was used instead of gaseous oxygen and in the absence of dichloromethane (solvent).

Alkoxy acetic acid derivations of general formula:



wherein R^1 represents a C_{12-15} alkyl group, were prepared from the above intermediate acids as follows:-

EXAMPLE 1 ($m = 17$ to 23 , $n = 0$, $p = 1$,

$R = -\text{NH CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$)

5 To a three litre flask, equipped with mechanical stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid A (1405 g, 0.9 mol), toluene (1500 ml) and tris(2-aminoethyl)amine (123.1 g, 0.84 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 10 16 hours whilst removing water evolved from the reaction mixture. The reaction mixture was then evaporated under high vacuum to afford the desired product as 1446 g of a pale brown oil, TBN = 1.76%N, AM = 89.7%.

EXAMPLE 2 ($m = 120$, $n = 0$, $p = 1$,

$R = -\text{NH CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$)

To a 500 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy 20 acetic acid C (150 g, 0.03 mol), xylene (250 ml) and tris(2-aminoethyl)amine (5.5 g, 0.038 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 8 hours whilst removing water evolved from the reaction

- 32 -

mixture. The resulting mixture was evaporated, dissolved in heptane (250 ml), washed with sodium chloride solution (2 x 100 ml, saturated), dried over MgSO_4 , filtered and evaporated under high vacuum to afford the desired product as 133 g of a pale brown oil, TBN = 0.27%N, AM = 83.3%.

EXAMPLE 3 ($m = 17$ to 23 , $n = 0$, $p = 1$,
 $R = -\text{NH}-(\text{CH}_2\text{CH}_2\text{NH})_2\text{H}$)

To a 500 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid A (115 g, 0.07 mol), xylene (250 ml) and diethylenetriamine (7.3 g, 0.07 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The resulting mixture was cooled, decanted and evaporated under high vacuum to afford the desired product as 117 g of a pale brown oil, TBN = 0.87%N.

EXAMPLE 4 ($m = 17$ to 23 , $n = 0$, $p = 1$,
 $R = -\text{NH}-(\text{CH}_2\text{CH}_2\text{NH})_3\text{H}$)

To a 1000 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid A (300 g, 0.18 mol), xylene (600 ml) and triethylenetetramine (23.6 g, 0.16 mol). The mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 8 hours whilst removing water evolved from the reaction mixture. The resulting mixture was cooled to ambient temperature (20°C), decanted and evaporated. The resulting product was dissolved in heptane (500 ml) and washed with sodium chloride (2 x 150 ml, saturated). The organic phase was then dried over MgSO_4 , filtered and evaporated under high vacuum to afford the desired product as 315 g of a pale brown oil, TBN = 0.75%N, AM = 69.6%.

- 33 -

EXAMPLE 5 ($m = 19$, $n = 5$, $p = 1$,
 $R = -NHCH_2CH_2N(CH_2CH_2NH_2)_2$)

To a 500 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy
5 acetic acid D (145 g, 0.09 mol), xylene (200 ml) and tris(2-aminoethyl)amine (10.2 g, 0.07 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 8 hours whilst removing water evolved from the reaction
10 mixture. The resulting mixture was cooled, filtered through "Celite" (trade mark) filter aid and evaporated. The resulting product was dissolved in heptane (500 ml), filtered through "Celite" filter aid and evaporated under high vacuum to afford the desired
15 product as 147 g of a pale brown oil, TBN = 0.61%N, AM = 78.9%.

EXAMPLE 6 ($m = 17$ to 23 , $n = 0$, $p = 1$,
 $R = -NHCH_2CH_2NHCH_2CH_2OH$)

To a 1000 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy
20 acetic acid A (200 g, 0.12 mol), xylene (300 ml) and 2-(2-aminoethylamino)ethanol (12.6 g, 0.12 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 6
25 hours whilst removing water evolved from the reaction mixture. The resulting mixture was cooled, decanted and evaporated under high vacuum to afford the desired product as 203 g of a pale brown oil, TBN = 0.76%N, AM = 88.5%.

30 EXAMPLE 7 ($m = 17$ to 23 , $n = 0$, $p = 1$,
 $R = -NHCH_2CH_2NH_2$)

To a 1000 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid A (200 g, 0.12 mol), xylene (300 ml) and

- 34 -

ethylenediamine (70 g, 1.16 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 8 hours whilst removing water evolved from the reaction mixture. The resulting mixture was cooled and evaporated under high vacuum to afford the desired product as 204 g of a pale brown oil, TBN = 0.71%N, AM = 86.6%.

EXAMPLE 8 (m = 17 to 23, n = 0, p = 1,
R = -OCH₂C(CH₂OH)₃)

To a 5000 ml flask, equipped with mechanical stirrer, Dean-Stark extractor and condenser, was added pentaerythritol (51 g, 0.37 mol), dimethylsulphoxide (300 ml), xylene (200 ml) and para-toluene sulphonic acid (2 g). The resulting mixture was heated, with stirring, to 140°C. A solution of alkoxy acetic acid A (300 g, 0.2 mol) in xylene (100 ml) was added gradually over 2 hours. The temperature was maintained at 140°C, with stirring for 5 hours whilst removing water evolved from the reaction mixture. The resulting mixture was cooled, filtered and evaporated. The resulting residue was dissolved in hexane (500 ml) and washed with aqueous sodium chloride solution (3 x 250 ml). The organic phase was dried over MgSO₄, filtered and evaporated to afford the desired product as 328 g of a pale yellow oil.

EXAMPLE 9 (m = 120, n = 0, p = 1,
R = -NH-(CH₂CH₂NH)₂H)

To a 1000 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid C (200 g, 0.04 mol), xylene (200 ml) and diethylenetriamine (5.16 g, 0.05 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The

- 35 -

resulting mixture was cooled and evaporated under high vacuum to afford the desired product as 204 g of a pale brown oil, TBN = 0.34%N.

EXAMPLE 10 (m = 17 to 23, n = 0, p = 1,

R = -NHCH₂CH₂N(CH₂CH₂NHCO(CH₂)₂CH(CH₃)OH)₂)

To a 250 ml flask, equipped with magnetic stirrer, was added a portion of the product of Example 1 (70 g, 0.04 mol) and gamma-valerolactone (8 g, 0.08 mol). The resulting mixture was heated, with stirring at 145-155°C for 5 hours. The resulting mixture was evaporated under high vacuum to afford the desired product as a pale brown oil, 76 g, TBN = 0.94.

EXAMPLE 11 (m = 17 to 23, n = 0, p = 1,

R = -NHCH₂CH₂N(CH₂CH₂NHCOCH₂N(CH₃)CH₂CH₂OH)₂)

To a 250 ml flask, equipped with magnetic stirrer, was added a portion of the product of Example 1 (70 g, 0.04 mol) and N-methylmorpholinone (9.2 g, 0.08 mol). The resulting mixture was heated, with stirring at 145-155°C for 4 hours. The resulting mixture was evaporated under high vacuum to afford the desired product as a pale brown oil, 78 g, TBN = 1.77%N, AM = 89%.

EXAMPLE 12 (m = 3.5 to 5.5, n = 0, p = 1,

R = -NH(CH₂CH₂NH)₂H)

To a 500 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid B (100 g, 0.16 mol), xylene (150 ml) and diethylenetriamine (17.8 g, 0.17 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The resulting mixture was evaporated under high vacuum to afford the desired product as 106g of a pale brown oil, TBN = 2.2%N, AM = 92.3%.

EXAMPLE 13 (m = 17 to 23, n = 0, p = 2,

- 36 -

R = -NH-(CH₂CH₂NH)₄-)

To a one litre flask, equipped with mechanical stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid A (100 g, 0.06 mol), xylene (150 ml) and tetraethylenepentamine (5.3 g, 0.03 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The resulting mixture was evaporated under high vacuum to afford the desired product as 103g of a pale brown oil, TBN = 0.86%N, AM = 65%.

EXAMPLE 14 (m = 17 to 23, n = 0, p = 1,

R = -NH-(CH₂CH₂NH)₄H)

To a one litre flask, equipped with mechanical stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid A (200 g, 0.12 mol), xylene (150 ml) and tetraethylenepentamine (20.4 g, 0.11 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The resulting mixture was evaporated under high vacuum to afford the desired product as 197g of a pale brown oil, TBN = 2.1%N, AM = 78%.

EXAMPLE 15 (m = 19, n = 4, p = 1,

R = -NHCH₂CH₂N(CH₂CH₂NH₂)₂)

To a one litre flask, equipped with mechanical stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid E (120 g, 0.08 mol), xylene (150 ml) and tris(2-aminoethyl)amine (7.8 g, 0.06 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The resulting mixture was evaporated under

- 37 -

high vacuum to afford the desired product as 103 g of a pale yellow oil, TBN = 0.99%N, AM = 60%.

EXAMPLE 16 (m = 17 to 23, n = 0, p = 1,
R = -NH(CH₂)₄NH₂)

5 To a one litre flask, equipped with mechanical stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid A (150 g, 0.09 mol), toluene (200 ml) and 1,4-diaminobutane (16 g, 0.18 mol). The resulting mixture was heated to reflux temperature and
10 maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The resulting mixture was evaporated, dissolved in chloroform (200 ml), washed with saturated aqueous sodium chloride solution (2 x 100 ml) and water
15 (100 ml). The organic phase was dried over MgSO₄, filtered and evaporated under high vacuum to afford the desired product as 142g of a pale yellow oil, TBN = 0.54%N, AM = 88%.

EXAMPLE 17 (m = 17 to 23, n = 0, p = 1,
20 R = -NH(CH₂)₃NH₂)

 To a one litre flask, equipped with mechanical stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid A (150 g, 0.09 mol), toluene (200 ml) and 1,4-diaminopropane (13.5 g, 0.18 mol). The
25 resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The resulting mixture was evaporated, dissolved in chloroform (200 ml), washed with saturated
30 aqueous sodium chloride solution (2 x 100 ml) and water (100 ml). The organic phase was dried over MgSO₄, filtered and evaporated under high vacuum to afford the desired product as 148g of a pale yellow oil, TBN = 0.58%N, AM = 87%.

- 38 -

EXAMPLE 18 (m = 17 to 23, n = 0, p = 1,
R = -NH-(CH₂CH₂O)₂-CH₂CH₂NH₂)

To a one litre flask, equipped with mechanical stirrer, Dean-Stark extractor and condenser, was added
5 alkoxy acetic acid A (150 g, 0.09 mol), toluene (200 ml) and 2,2'-ethylenedioxybis(ethylamine) (26.9 g, 0.18 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing water evolved
10 from the reaction mixture. The resulting mixture was evaporated, dissolved in chloroform (200 ml), washed with saturated aqueous sodium chloride solution (2 x 100 ml) and water (100 ml). The organic phase was dried over MgSO₄, filtered and evaporated under high
15 vacuum to afford the desired product as 137g of a pale yellow oil, TBN = 0.58%N, AM = 88%.

EXAMPLE 19 (m = 17 to 23, n = 0, p = 1,
R = -NH(CH₂)₃(1,4-piperazinediyl)(CH₂)₃NH₂)

To a one litre flask, equipped with mechanical stirrer, Dean-Stark extractor and condenser, was added
20 alkoxy acetic acid A (150 g, 0.09 mol), toluene (200 ml) and 1,4-bis(3-aminopropyl)piperazine (36.3 g, 0.18 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with
25 stirring, for 16 hours whilst removing water evolved from the reaction mixture. The resulting mixture was evaporated, dissolved in chloroform (200 ml), washed with saturated aqueous sodium chloride solution (2 x 100 ml) and water (100 ml). The organic phase was
30 dried over MgSO₄, filtered and evaporated under high vacuum to afford the desired product as 151g of a pale yellow oil, TBN = 1.85%N, AM = 88%.

EXAMPLE 20 (m = 17 to 23, n = 0, p = 1,
R = -NH-(CH₂-CH₂-O)₂H)

- 39 -

To a one litre flask, equipped with mechanical stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid A (30 g, 0.02 mol), toluene (50 ml) and 2-(2-aminoethoxy)ethanol (3.8 g, 0.04 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The resulting mixture was evaporated, dissolved in chloroform (100 ml), washed with saturated aqueous sodium chloride solution (2 x 50 ml) and water (50 ml). The organic phase was dried over MgSO_4 , filtered and evaporated under high vacuum to afford the desired product as 32g of a pale yellow oil, AM = 87%.

EXAMPLE 21 ($m = 17$ to 23 , $n = 0$, $p = 1$,

$R = -\text{NH}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{NH}_2$)

To a one litre flask, equipped with mechanical stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid A (30 g, 0.02 mol), toluene (50 ml) and N,N' -bis(3-aminopropyl)ethylenediamine (6.3 g, 0.04 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The resulting mixture was evaporated, dissolved in chloroform (100 ml), washed with saturated aqueous sodium chloride solution (2 x 50 ml) and water (50 ml). The organic phase was dried over MgSO_4 , filtered and evaporated under high vacuum to afford the desired product as 29g of a pale yellow oil, TBN = 1.17%N, AM = 87%.

EXAMPLE 22 ($m = 17$ to 23 , $n = 0$, $p = 1$,

$R = -\text{NH}-(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH})_2\text{H}$)

To a one litre flask, equipped with mechanical stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid A (30 g, 0.02 mol), toluene (50 ml)

- 40 -

and N-(3-aminopropyl)-1,3-propanediamine (4.8 g, 0.04 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The resulting mixture was evaporated, dissolved in chloroform (100 ml), washed with saturated aqueous sodium chloride solution (2 x 50 ml) and water (50 ml). The organic phase was dried over MgSO_4 , filtered and evaporated under high vacuum to afford the desired product as 33g of a pale yellow oil, TBN = 0.93%N, AM = 88%.

EXAMPLE 23 (m = 17 to 23, n = 0, p = 1,
R = $-\text{NH}-(\text{CH}_2)_3-\text{CH}(\text{CH}_2\text{NH}_2)(\text{CH}_3)_4\text{NH}_2$)

To a one litre flask, equipped with mechanical stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid A (150 g, 0.09 mol), toluene (200 ml) and 4-(aminomethyl)-1,8-octanediamine (30.7 g, 0.18 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The resulting mixture was evaporated, dissolved in chloroform (200 ml), washed with saturated aqueous sodium chloride solution (2 x 100 ml) and water (100 ml). The organic phase was dried over MgSO_4 , filtered and evaporated under high vacuum to afford the desired product as 159g of a pale yellow oil, TBN = 1.1%N, AM = 87%.

EXAMPLE 24 (m = 17 to 23, n = 0, p = 2,
R = $-\text{NH}-\text{CH}_2\text{CH}_2-\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)\text{CH}_2\text{CH}_2\text{NH}-$)

To a one litre flask, equipped with mechanical stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid A (150 g, 0.09 mol), toluene (150 ml) and tris(2-aminoethyl)amine (6.6 g, 0.04 mol). The resulting mixture was heated to reflux temperature and

- 41 -

maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The resulting mixture was diluted with toluene (150 ml) and washed with sodium chloride solution (1 x 500 ml, saturated). The organic phase was dried over MgSO_4 , filtered and evaporated under high vacuum to afford the desired product as 149 g of a pale yellow oil, TBN = 0.77%N, AM = 85%.

EXAMPLE 25 (m = 17 to 23, n = 0, p = 1, RH =

$[\text{CH}_2\text{N}((\text{CH}_2)_2\text{CONH}(\text{CH}_2)_2\text{NH}_2)_2]_2$

To a 250 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added "Starburst" (PAMAM, generation 0) dendrimer ("Starburst" is a trade mark) (ex Aldrich Chemical Company) (29 g, 0.01 mol, 20% solution in methanol) and xylene (100 ml). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 3 hours whilst removing methanol evolved from the reaction mixture. The resulting mixture was cooled to 90-100°C and a solution of alkoxy acetic acid A (20 g, 0.01 mol) in xylene (50 ml) was added over 30 minutes. The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The resulting mixture was evaporated, dissolved in heptane (100 ml), filtered through "Celite" (trade mark) filter aid and evaporated under high vacuum to afford the desired product as 21 g of a brown oil, TBN = 1.6%N, AM_S = 63%.

- 42 -

EXAMPLE 26 ($m = 17$ to 23 , $n = 0$, $p = 1$, $R = -NH-$
 $((CH_2)_2NH)_x-((CH_2)_2N(COCHOHC(CH_3)_2CH_2OH))_y-H$ where $x +$
 $y = 4$)

To a one litre autoclave equipped with mechanical
stirrer, was added toluene (500 ml), a portion of the
product of Example 14 (125 g, 0.07 mol) and
pantolactone (55 g, 0.42 mol). The autoclave was
sealed, flushed with nitrogen and heated, with
stirring, at 150-160°C for 15 hours. The resulting
mixture was evaporated, dissolved in heptane (750 ml),
washed with saturated aqueous sodium chloride solution
(2 x 200 ml), dried over $MgSO_4$, filtered and evaporated
under high vacuum to afford the desired product as
118 g of a brown oil. TBN = 0.68%N, AM = 85.2%

EXAMPLE 27 ($m = 19$, $n = 5$, $p = 1$, $R = -NH-(CH_2)_2NH_2$)

To a 150 ml flask, equipped with magnetic stirrer,
Dean-Stark extractor and condenser, was added alkoxy
acetic acid D (30 g, 0.02 mol), toluene (40 ml) and
ethylenediamine (1.95 g, 0.03 mol). The resulting
mixture was heated to reflux temperature and maintained
at that temperature, with stirring, for 8 hours whilst
removing water evolved from the reaction mixture. The
resulting mixture was cooled and evaporated. The
resulting residue was dissolved in chloroform (50 ml)
and washed with saturated aqueous sodium chloride
solution (2 x 25 ml) and water (25 ml). The organic
phase was dried over $MgSO_4$, filtered and evaporated to
afford the desired product as 32 g of a pale yellow
oil. TBN = 0.43%N

EXAMPLE 28 ($m = 19$, $n = 5$, $p = 1$, $R = -NH-(CH_2)_3NH_2$)

To a 150 ml flask, equipped with magnetic stirrer,
Dean-Stark extractor and condenser, was added alkoxy
acetic acid D (30 g, 0.02 mol), toluene (40 ml) and
propylenediamine (2.4 g, 0.03 mol). The resulting

- 43 -

5 mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 8 hours whilst removing water evolved from the reaction mixture. The resulting mixture was cooled and evaporated. The resulting residue was dissolved in chloroform (50 ml) and washed with saturated aqueous sodium chloride solution (2 x 25 ml) and water (25 ml). The organic phase was dried over MgSO_4 , filtered and evaporated to afford the desired product as 28 g of a pale yellow oil. TBN = 0.24%N

EXAMPLE 29 ($m = 19$, $n = 5$, $p = 1$, $R = -\text{NH}-(\text{CH}_2)_4\text{NH}_2$)

15 To a 150 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid D (30 g, 0.02 mol), toluene (40 ml) and butylenediamine (2.9 g, 0.03 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 8 hours whilst removing water evolved from the reaction mixture. The resulting mixture was cooled and evaporated. The resulting residue was dissolved in chloroform (50 ml) and washed with saturated aqueous sodium chloride solution (2 x 25 ml) and water (25 ml). The organic phase was dried over MgSO_4 , filtered and evaporated to afford the desired product as 30 g of a pale yellow oil. TBN = 0.56%N

EXAMPLE 30 ($m = 19$, $n = 5$, $p = 1$, $R = -\text{NH}-(\text{CH}_2)_5\text{NH}_2$)

30 To a 100 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid D (10 g, 0.006 mol), toluene (30 ml) and 1,5-pentanediamine (1.2 g, 0.01 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The resulting mixture was cooled and evaporated. The

- 44 -

resulting residue was dissolved in chloroform (50 ml) and washed with saturated aqueous sodium chloride solution (3 x 150 ml). The organic phase was dried over MgSO_4 , filtered and evaporated to afford the
5 desired product as 9 g of a pale yellow oil. TBN = 0.62%N

EXAMPLE 31 ($m = 19$, $n = 5$, $p = 1$, $R = -\text{NH}-(\text{CH}_2)_6\text{NH}_2$)

To a 100 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy
10 acetic acid D (10 g, 0.006 mol), toluene (30 ml) and 1,6-hexanediamine (1.3 g, 0.01 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The
15 resulting mixture was cooled and evaporated. The resulting residue was dissolved in chloroform (50 ml) and washed with saturated aqueous sodium chloride solution (3 x 150 ml). The organic phase was dried over MgSO_4 , filtered and evaporated to afford the
20 desired product as 10 g of a pale yellow oil. TBN = 0.53%N

EXAMPLE 32 ($m = 19$, $n = 5$, $p = 1$, $R = -\text{NH}-(\text{CH}_2\text{CH}_2\text{NH})_2-\text{H}$)

To a 150 ml flask, equipped with magnetic stirrer,
25 Dean-Stark extractor and condenser, was added alkoxy acetic acid D (30 g, 0.02 mol), toluene (40 ml) and diethylenetriamine (3.3 g, 0.03 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 8 hours whilst
30 removing water evolved from the reaction mixture. The resulting mixture was cooled and evaporated. The resulting residue was dissolved in chloroform (50 ml) and washed with saturated aqueous sodium chloride solution (2 x 25 ml) and water (25 ml). The organic

- 45 -

phase was dried over MgSO_4 , filtered and evaporated to afford the desired product as 28 g of a pale yellow oil. TBN = 0.89%N

EXAMPLE 33 (m = 19, n = 5, p = 1, R = $-\text{NH}-\text{CH}_2\text{CH}_2\text{NH}-\text{CH}_2\text{CH}_2\text{OH}$)

To a 150 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid D (30 g, 0.02 mol), toluene (40 ml) and 2-(2-aminoethylamino)ethanol (3.4 g, 0.03 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 8 hours whilst removing water evolved from the reaction mixture. The resulting mixture was cooled and evaporated. The resulting residue was dissolved in chloroform (50 ml) and washed with saturated aqueous sodium chloride solution (2 x 25 ml) and water (25 ml). The organic phase was dried over MgSO_4 , filtered and evaporated to afford the desired product as 27 g of a pale yellow oil. TBN = 0.53%N

EXAMPLE 34 (m = 19, n = 5, p = 1, R = $-\text{NH}-(\text{CH}_2\text{CH}_2\text{NH})_3-\text{H}$)

To a 150 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid D (30 g, 0.02 mol), toluene (40 ml) and triethylenetetraamine (4.7 g, 0.03 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 8 hours whilst removing water evolved from the reaction mixture. The resulting mixture was cooled and evaporated. The resulting residue was dissolved in chloroform (50 ml) and washed with saturated aqueous sodium chloride solution (2 x 25 ml) and water (25 ml). The organic phase was dried over MgSO_4 , filtered and evaporated to

- 46 -

afford the desired product as 33 g of a pale yellow oil. TBN = 1.15%N

EXAMPLE 35 (m = 19, n = 5, p = 1, R = -NH-(CH₂CH₂NH)₄-H)

5 To a 150 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid D (30 g, 0.02 mol), toluene (40 ml) and tetraethylenepentamine (6.1 g, 0.03 mol). The
10 resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 8 hours whilst removing water evolved from the reaction mixture. The resulting mixture was cooled and
15 evaporated. The resulting residue was dissolved in chloroform (50 ml) and washed with saturated aqueous sodium chloride solution (2 x 25 ml) and water (25 ml). The organic phase was dried over MgSO₄, filtered and
evaporated to afford the desired product as 30 g of a pale yellow oil. TBN = 1.65%N

20 EXAMPLE 36 (m = 19, n = 5, p = 1, R = -NH-(CH₂CH₂O)₂-CH₂CH₂NH₂)

To a 150 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid D (30 g, 0.02 mol), toluene (40 ml) and
2,2'-(ethylenedioxy)-bis(ethylamine) (4.8 g, 0.03 mol).
25 The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 8 hours whilst removing water evolved from the reaction mixture. The resulting mixture was cooled and
evaporated. The resulting residue was dissolved in
30 chloroform (50 ml) and washed with saturated aqueous sodium chloride solution (2 x 25 ml) and water (25 ml). The organic phase was dried over MgSO₄, filtered and
evaporated to afford the desired product as 27 g of a pale yellow oil. TBN = 0.42%N

- 47 -

EXAMPLE 37 ($m = 19$, $n = 5$, $p = 1$, $R = -NH-(CH_2CH_2CH_2NH)_2-H$)

To a 150 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy
5 acetic acid D (30 g, 0.02 mol), toluene (40 ml) and dipropyleneetriamine (4.3 g, 0.03 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 8 hours whilst removing water evolved from the reaction mixture. The
10 resulting mixture was cooled and evaporated. The resulting residue was dissolved in chloroform (50 ml) and washed with saturated aqueous sodium chloride solution (2 x 25 ml) and water (25 ml). The organic phase was dried over $MgSO_4$, filtered and evaporated to
15 afford the desired product as 33 g of a pale yellow oil. TBN = 0.64%N

EXAMPLE 38 ($m = 19$, $n = 5$, $p = 1$, $R = -NH-(CH_2)_3NH(CH_2N)_2NH(CH_2)_3NH_2$)

To a 150 ml flask, equipped with magnetic stirrer,
20 Dean-Stark extractor and condenser, was added alkoxy acetic acid D (30 g, 0.02 mol), toluene (40 ml) and N,N-bis(3-aminopropyl)ethylene diamine (5.6 g, 0.03 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with
25 stirring, for 8 hours whilst removing the water evolved from the reaction mixture. The resulting mixture was cooled and evaporated. The resulting residue was dissolved in chloroform (50 ml) and washed with saturated aqueous sodium chloride solution (2 x 25 ml)
30 and water (25 ml). The organic phase was dried over $MgSO_4$, filtered and evaporated to afford the desired product as 32 g of a pale yellow oil. TBN = 1.12%N

EXAMPLE 39 ($m = 19$, $n = 5$, $p = 1$, $R = -NH-(CH_2)_3(1,4\text{-piperazinediyl})(CH_2)_3NH_2$)

- 48 -

To a 150 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid D (30 g, 0.02 mol), toluene (40 ml) and 1,4-bis(3-aminopropyl)-piperazine (6.5 g, 0.03 mol).

5 The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 8 hours whilst removing water evolved from the reaction mixture. The resulting mixture was cooled and evaporated. The resulting residue was dissolved in
10 chloroform (50 ml) and washed with saturated aqueous sodium chloride solution (2 x 25 ml) and water (25 ml). The organic phase was dried over MgSO_4 , filtered and evaporated to afford the desired product as 30 g of a pale yellow oil. TBN = 0.97%N

15 EXAMPLE 40 ($m = 19$, $n = 5$, $p = 1$, $R = -\text{NH}-(4-(4\text{-aminocyclohexylmethyl})\text{-cyclohexyl})$)

To a 150 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid D (30 g, 0.02 mol), toluene (40 ml) and
20 4,4'-diaminodicyclohexylmethane (6.8 g, 0.03 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 8 hours whilst removing water evolved from the reaction mixture. The resulting mixture was cooled and
25 evaporated. The resulting residue was dissolved in chloroform (50 ml) and washed with saturated aqueous sodium chloride solution (2 x 25 ml) and water (25 ml). The organic phase was dried over MgSO_4 , filtered and evaporated to afford the desired product as 34 g of a
30 pale yellow oil. TBN = 0.86%N

EXAMPLE 41 ($m = 19$, $n = 5$, $p = 1$, $R = -\text{NH}-\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NH}_2$)

To a 150 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy

- 49 -

acetic acid D (30 g, 0.02 mol), toluene (40 ml) and 2,2-dimethylpropane-1,3-diamine (3.3 g, 0.03 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 8 hours whilst removing water evolved from the reaction mixture. The resulting mixture was cooled and evaporated. The resulting residue was dissolved in chloroform (50 ml) and washed with saturated aqueous sodium chloride solution (2 x 25 ml) and water (25 ml). The organic phase was dried over MgSO_4 , filtered and evaporated to afford the desired product as 31 g of a pale yellow oil. TBN = 0.53%N

EXAMPLE 42 ($m = 19$, $n = 5$, $p = 1$, $R = -\text{NH}-\text{CH}_2-1,3,3\text{-trimethyl-5-aminocyclohexyl}$)

To a 150 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid D (30 g, 0.02 mol), toluene (40 ml) and isophoronediamine (5.6 g, 0.03 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing the water evolved from the reaction mixture. The resulting mixture was cooled and evaporated. The resulting residue was dissolved in chloroform (100 ml) and washed with saturated aqueous sodium chloride solution (2 x 150 ml). The organic phase was dried over MgSO_4 , filtered and evaporated to afford the desired product as 27 g of a pale yellow oil. TBN = 0.91%N

EXAMPLE 43 ($m = 19$, $n = 5$, $p = 1$, $R = -\text{NH}-(\text{CH}_2)_3\text{CH}(\text{CH}_2\text{NH}_2)(\text{CH}_2)_4\text{NH}_2$)

To a 100 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid D (10 g, 0.006 mol), toluene (30 ml) and 4-aminomethyl-1,8-octanediamine (1.9 g, 0.01 mol). The

- 50 -

resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The resulting mixture was cooled and evaporated. The resulting residue was dissolved in chloroform (50 ml) and washed with saturated aqueous sodium chloride solution (3 x 50 ml). The organic phase was dried over MgSO_4 , filtered and evaporated to afford the desired product as 11 g of a yellow oil. TBN = 0.67%N

EXAMPLE 44 (m = 19, n = 5, p = 1, R = -NH-(CH₂)₃N(CH₃)₂)

To a 100 ml flask, equipped with magnetic stirrer, Dean-Stark extractor and condenser, was added alkoxy acetic acid D (10 g, 0.006 mol), toluene (30 ml) and N,N-dimethyl-1,3-diaminopropane (1.2 g, 0.01 mol). The resulting mixture was heated to reflux temperature and maintained at that temperature, with stirring, for 16 hours whilst removing water evolved from the reaction mixture. The resulting mixture was cooled and evaporated. The resulting residue was dissolved in chloroform (50 ml) and washed with saturated aqueous sodium chloride solution (3 x 100 ml). The organic phase was dried over MgSO_4 , filtered and evaporated to afford the desired product as 8 g of a pale yellow oil. TBN = 0.21%N

EXAMPLE 45 (m = 19, n = 5, p = 1, R = -(O-CH₂C(CH₂OH)₂CH₂)₂-OH)

To a 100 ml flask, equipped with a magnetic stirrer, Dean-Stark extractor and condenser, was added dipentaerythritol (3 g, 0.01 mol), dimethylsulphoxide (20 ml), xylene (30 ml) and para-toluene sulphonic acid (0.5 g). The resulting mixture was heated, with stirring, to 140°C. A solution of alkoxy acetic acid D

- 51 -

(10 g, 0.006 mol) in xylene (20 ml) was added dropwise over 20 minutes. The temperature was maintained at 140°C, with stirring, for 15 hours, whilst removing the water evolved from the reaction mixture. The resulting mixture was cooled and evaporated. The resulting residue was dissolved in hexane (50 ml) and washed with saturated aqueous sodium chloride solution (3 x 25 ml). The organic phase was dried over MgSO₄, filtered and evaporated to afford the desired product as 7 g of a pale yellow oil.

EXAMPLE 46 (m = 19, n = 5, p = 1, R = -(O-CH₂C(CH₂OH)₂CH₂)₃-OH)

To a 100 ml flask, equipped with a magnetic stirrer, Dean-Stark extractor and condenser, was added tripentaerythritol (4.3 g, 0.01 mol), dimethylsulphoxide (20 ml), xylene (40 ml) and para-toluene sulphonic acid (0.5 g). The resulting mixture was heated, with stirring, to 140°C. A solution of alkoxy acetic acid D (10 g, 0.006 mol) in xylene (20 ml) was added dropwise over 20 minutes. The temperature was maintained at 140°C, with stirring, for 15 hours, whilst removing water evolved from the reaction mixture. The resulting mixture was cooled and evaporated. The resulting residue was dissolved in hexane (50 ml) and washed with saturated aqueous sodium chloride solution (3 x 25 ml). The organic phase was dried over MgSO₄, filtered and evaporated to afford the desired product as 12 g of a yellow oil.

EXAMPLE 47 (m = 19, n = 5, p = 5, R(H)_p = HO(CH₂C(CH₂OH)₂CH₂-O)₃H)

To a 100 ml flask, equipped with a magnetic stirrer, Dean-Stark extractor and condenser, was added tripentaerythritol (0.4 g, 0.001 mol), dimethylsulphoxide (20 ml), xylene (40 ml) and para-toluene

- 52 -

5 sulphonic acid (0.5 g). The resulting mixture was heated, with stirring, to 140°C. A solution of alkoxy acetic acid D (8.5 g, 0.005 mol) in xylene (20 ml) was added dropwise over 20 minutes. The temperature was maintained at 140°C, with stirring, for 15 hours, whilst removing water evolved from the reaction mixture. The resulting mixture was cooled and evaporated. The resulting residue was dissolved in hexane (150 ml) and washed with saturated aqueous sodium chloride solution (3 x 50 ml). The organic phase was dried over MgSO₄, filtered and evaporated to afford the desired product as 7 g of a pale yellow oil.

EXAMPLE 48 (m = 19, n = 4, p = 1, R = -NH-(CH₂CH₂NH)₃-H)

15 To a 500 ml flask, equipped with magnetic stirrer, air sparge with 200 micron frit, Dean-Stark collector and condenser, was added alkoxy acetic acid E (200 g, 0.12 mol) and triethylenetetramine (15 g, 0.1 mole). The resulting mixture was heated to 90-110°C, with an air sparge rate of 100-200 ml/min and maintained at that temperature, with stirring, for 5 hours whilst removing water evolved from the reaction mixture. The resulting residue was dissolved in chloroform (350 ml) and washed with saturated aqueous sodium chloride solution (3 x 150 ml). The organic phase was dried over MgSO₄, filtered and evaporated to afford the desired product as 186 g of a brown oil. TBN = 0.76%N

COMPARATIVE EXAMPLE A (m = 0, n = 7, p = 1, R = -N(CH₂CH₂CH₂CH₃)₂) (corresponds closely to the N,N-dibutyl amide (1) of Examples 1 and 2 of FR-A-2407258)

30 As starting material there was employed "DOBANOL" ethoxylate 25-7 ("DOBANOL" is a registered trade mark), available from member companies of the Royal Dutch/Shell group, corresponding to the above formula

- 53 -

(Q) wherein m is 0, n is 7 and R¹ represents a C₁₂₋₁₅ alkyl group, having M_n 515 and a kinematic viscosity of 31 mm²/s at 40°C according to ASTM D 445.

5 To a one litre flask, equipped with mechanical stirrer and nitrogen purge, was added sodium hydride (64 g, 1.6 mol, 60% dispersion in oil) and tetrahydrofuran (100 ml). To this agitated mixture a solution of "DOBANOL" ethoxylate 25-7 (384 g, 0.76 mol) in tetrahydrofuran (500 ml) was added gradually over 2
10 hours. The resulting mixture was then heated to reflux temperature for 1 hour, cooled to 40-50°C and a solution of chloroacetic acid (75.6 g, 0.8 mol) in tetrahydrofuran (100 ml) was added gradually over 2 hours. The mixture was stirred at 20-30°C for 14 hours,
15 heated at reflux temperature for 1 hour, cooled and then acidified with hydrochloric acid (2 N aqueous solution). The resulting mixture was extracted with ether (3 x 500 ml) and the combined organic phase washed with saturated aqueous sodium chloride solution
20 (2 x 200 ml). The organic phase was dried over MgSO₄, filtered and evaporated to afford the desired intermediate acid corresponding to formula R wherein m is 0 and n is 7, as 406 g of a pale yellow oil. AV = 1.6 meqg⁻¹, AM = 78%.

25 To a one litre flask, equipped with magnetic stirrer and condenser, was added thionyl chloride (60 ml). To this the above intermediate acid (200 g, 0.04 mol) was added gradually over approximately 2 hours. The resulting mixture was heated to reflux for 1 hour
30 and excess thionyl chloride was removed by distillation. The resulting acid chloride was dissolved in toluene (100 ml) and added dropwise to a solution of dibutylamine (103 g, 0.8 mol) in toluene (200 ml) at such a rate as to maintain the reaction
35 temperature below 25°C. The mixture was stirred for 1

- 54 -

hour, filtered and evaporated to afford the desired product as 263 g of a pale brown oil.

The products of Examples 1 to 48 and Comparative Example A were subjected to at least one of the following tests in liquid fuels:-

(i) Intake Valve Deposit Simulator Test - Inclined Hot Plate Rig

(ii) Intake Valve and Combustion Chamber Deposits using 1.2L Opel Kadett Engine

(iii) Intake Valve Deposits using 2.3L Mercedes Benz M-102E Engine

(iv) Injector Fouling using 1.9L Fiat Regata Indirect Injection Diesel Engine

(i) Intake Valve Deposit Simulator Test - Inclined Hot Plate Rig

This simulator test corresponds closely to that described in SAE Paper 890215, Daneshgari et al., "The Influence of Temperature upon Gasoline Deposit Build-Up on the Intake Valves", Detroit, USA, 27 February to 3 March 1989. The test rig utilises four inclined plates in parallel. The plates are strips of sandblasted aluminium 50 cm long and 2.5 cm wide, having a central groove along their lengths 3 mm wide and 1 mm deep, mounted in the rig at an angle of 3 degrees relative to the horizontal. The temperature at the top end of each plate is maintained at 400°C and at the middle of each plate is maintained at 250°C.

Gasoline samples, containing test materials at a concentration of non-volatile matter of 100 parts per million by weight (ppmw) in base fuel, are prepared, and 100 ml portions of the gasoline samples are delivered at a rate of 0.6 ml/minute from glass syringes fitted with 20 gauge steel hypodermic Luer lock needles into the groove at the top end of each

- 55 -

plate. Once delivery is complete, after about 2 hours and 40 minutes, the plates are allowed to cool to ambient temperature (20°C) and are washed with n-heptane until the run-off liquid is clear, and are then left to dry before assessment of any deposit present.

Assessment is made using a "SEESCAN" (trade mark) Marker Image analyser with 512*512 image memory coupled to a "SONY"/"SEESCAN" (trade marks) CCD camera equipped with NIKON (trade mark) f55 Macro lens. Lighting of the plate being assessed is by two 12v Tungsten lamps mounted at a linear distance of 22 cm from the point on the plate upon which the camera is focused and at angles of 33 degrees and 147 degrees relative to the plate.

A clear portion of the plate is moved under the camera and an image thereof captured. The section of the plate containing deposit is then moved beneath the camera and an image thereof is captured. The image analyser divides, pixel by corresponding pixel, the deposit image by the clean image and automatically measures the area and optical density of deposit at the pixels contained within overall measuring frame, and calculates an integrated optical density for the image, the numerical value of which is recorded as a test rating.

Results of this test are given in Table 1 as follows:-

Table 1

Test material (Example No)	Rating
1	86
2	93
3	135
4	90

- 56 -

Table 1 (continued)

Test material (Example No)	Rating
5	71
6	58
7	84
8	114
9	174
10	94
11	140
12	187
13	171
14	55
15	69
16	63
17	211
18	46
19	75
20	214
21	114
22	61
23	75
24	79
25	124
26	71
27	30
28	162
29	53
30	49
31	46
32	25
33	32
34	23

- 57 -

Table 1 (continued)

Test material (Example No)	Rating
35	47
36	42
37	78
38	77
39	49
40	171
41	190
42	41
43	106
44	84
45	151
46	169
47	109
48	187
Comp. A	246
Base Fuel	266

In Table 1, the lower the rating the better. Accordingly, it can readily be seen that the results for all of the test materials of Examples 1 to 24 are superior both to that for Comparative Example A and for base gasoline.

(ii) Intake Valve and Combustion Chamber Deposits
using 1.2L Opel Kadett Engine

The test materials of a number of the Examples have been tested in a laboratory multicylinder engine to evaluate their intake valve and combustion chamber deposit control performance. This engine was a 1.2L twin carburettor four cylinder spark-ignition engine manufactured by General Motors' Opel subsidiary and is used in the published inlet system cleanliness test CEC

- 58 -

F-04-A-87. It has 79 mm bore, 61 mm stroke and is operated under a prescribed load and speed schedule representative of typical driving conditions as set forth in Table 2.

Table 2

Step	Time, sec	Load, Nm	Speed, r/min
1	30	0	1200
2	60	35	3000
3	60	29	1300
4	120	32	1850

5 In modifying the procedure, the air inlet was maintained at 25°C (+ or - 2 degrees) and no extra oil injection down the valve guides was used. The lubricating oil in the sump was "SHELL" "HELIX" 10 w/40 lubricating oil (API SG quality). The test duration
10 was 40 hours including 2 hour shutdowns after the first and second 12 hour running periods. A twin carburettor set up was used to enable two additives to be tested simultaneously. Consequently, intake valve and combustion chamber deposit weights are average values
15 from 2 cylinders.

All the tests were conducted on the same base gasoline representative of commercial unleaded fuel. This had a RON of 100.0 and a MON of 88.5, contained 57.1% v aromatics with 4.0% v olefins (ASTM D1319), and
20 had a final boiling point of 211°C (ASTM D86).

The test materials were all incorporated in the base gasoline together with a polyalphaolefin (PAO). The polyalphaolefin was a hydrogenated oligomer of decene-1 having a viscosity at 100°C of $8 \times 10^{-6} \text{ m}^2/\text{s}$ (8
25 centistokes). The concentration in the resulting gasoline compositions of the test materials was 500

- 59 -

ppmw (non-volatile matter), unless otherwise indicated, and of the polyalphaolefin was 500 ppmw.

Results of these tests are given in Table 3 following:

5

Table 3

Test material (Example No.)	Deposits in Opel Kadett Engine	
	Intake valve deposit (mg/valve)	Combustion Chamber Deposit (mg/cylinder)
1	2	1026
1 (no PAO)	0	1217
1 (250 ppmw)	17	1059
3	5	1265
4	6	1180
5	20	1051
6	36	1151
7	0	1238
8	68	1068
9	169	1326
10	3	1260
11	0	1034
12	9	1271
13	5	1167
14	13	1255
24	17	1100
Comp. A	51	1441
Base gasoline + 500 ppm PAO	179	1171
Base gasoline alone	280	1179

In tests on additional compounds a different base gasoline was used. This had a RON of 98.7 and a MON of 87.3, contained 48% v aromatics with 7.5% v olefins,

- 60 -

(ASTM D1319) and had a final boiling point of 208°C (ASTM D86).

Results of these tests are given in Table 3a following.

Table 3a

Test material (Example No.)	Deposits in Opel Kadett Engine	
	Intake valve deposit (mg/valve)	Combustion Chamber Deposit (mg/cylinder)
5	1	976
15	4	1269
16	4	1097
17	20	1121
18	2	1173
19	23	1011
23	24	1298
26	4	1126
34	0	930
Base gasoline + 500 ppm PAO	177	1112
Base gasoline alone	267	937

It will be noted that all of the gasoline compositions containing test materials of the present invention gave lower combustion chamber deposits than that containing the material of Comparative Example A, that all of the gasoline compositions containing test materials of the present invention also gave lower intake valve deposits than either the base gasoline or the base gasoline plus PAO, and that all but two of the gasoline compositions containing test materials of the present invention also gave lower intake valve deposits

- 61 -

than that containing the material of Comparative Example A.

5 A modification of the above procedure was used to investigate the clean-up potential of the test materials of the present invention. In a first phase a clean engine is run on base gasoline for 20 hours under the schedule of Table 2, with CEC RL-51 reference lubricating oil in the engine sump. The engine is then dismantled and the weight of intake valve deposit
10 measured. In the second phase the intake valves are replaced in their original orientation, without being cleaned, a new oil filter is fitted to the engine and the lubricating oil in the sump is changed to "SHELL" "HELIX" 10w/40 lubricating oil (API SG quality)
15 ("SHELL" and "HELIX" are registered trade marks). The engine is run using test fuel as above for 60 hours under the schedule of Table 2, and the weight of intake valve deposit is then measured and compared with that at the end of the first phase.

20 The clean-up test procedure was followed using (1) a gasoline composition containing 500 ppmw non-volatile matter) of the test material of Example 1 and, for comparison purposes, (2) using base gasoline.

25 At the end of the second phase, the intake valve deposits were found to be reduced by 48% in the case of the gasoline composition containing the test material of Example 1, whereas the intake valve deposits had increased by 35% in the case of the base gasoline.

30 (iii) Intake Valve Deposits using 2.3L Mercedes Benz Engine

The test material of Example 1 and that of Comparative Example A have also been tested in relation to intake valve deposits in a 2.3L Mercedes Benz 102E four cylinder spark-ignition engine according to the
-35 published test procedure CEC-F-05-A95.

- 62 -

The tests were effected using different base gasolines (Fuels I and II) due to availability reasons at the times when the tests were made. Fuel I had a RON of 98.6 and a MON of 86.2, contained 46% v aromatics with 9.4% v olefins (ASTM D 1319) and had initial boiling point of 29°C, 50% boiling temperature of 113°C and final boiling point of 203°C (ASTM D 86). Fuel II had a RON of 98.7 and a MON of 87.6, contained 52% v aromatics with 9.4% v olefins (ASTM D 1319) and had initial boiling point of 28°C, 50% boiling temperature of 121°C and final boiling point of 208°C (ASTM D86).

In some of the compositions, PAO and Polyether A were employed as carrier fluids. Quantities of the test materials are expressed in ppmw of non-volatile matter. Fuel compositions and test data are given in Table 4 following, wherein the rating is in accordance with CEC-F-05-A95, wherein 10 represents completely clean, and 0 completely blackened (i.e. the larger the value of the rating, the better).

Table 4

Test Material (Example No.)	2.3L Mercedes Benz Engine	
	Intake Valve Deposits (mg/valve)	Rating
Base Fuel I	452	7.3
Base Fuel plus 1 (200 ppmw)	5	9.8
1 (132 ppmw, + 200 ppmw PAO + 200 ppmw Polyether A)	0	9.8

- 63 -

Table 4 (continued)

Base Fuel II	359	7.5
Base Fuel II plus Comp. A (132 ppmw, + 200 ppmw PAO + 200 ppmw Polyether A)	93	8.8

It will be observed in Table 4 that not only are the various values in relation to gasoline compositions containing test material of Example 1 significantly superior to that containing test material of Comparative Example A, but these were achieved in a base gasoline (Base Fuel I) which had a greater tendency to foul the inlet valves than the base gasoline (Base Fuel II) used for comparison purposes.

(iv) Injector Fouling using 1.9L Fiat Regata Indirect Injection Diesel Engine

Diesel engine tests were performed using the test material of Example 1 dissolved at a concentration of 400 ppmw (non-volatile matter) in a base diesel fuel which was a blended diesel oil (without additives) in accordance with BS 2869, having cetane value in the range 50 to 53, and, for comparison purposes, with this same base diesel fuel per se.

These tests were performed according to the following method, employing a Fiat IDI (indirect injection) 1929 cc, type 149 Al.000, diesel engine as used in Fiat Regata diesel automobiles.

The engine was warmed up at 1500 rpm engine speed and 25 Nm dynamometer load for 20 mins. Injector nozzles were then changed to test nozzles.

The engine was then run at 2700 rpm and 75 Nm for 8.5 hours, after which the engine was switched off.

- 64 -

Coolant oil/water temperatures were maintained at $90 \pm 4^\circ \text{C}$.

Performance of each diesel fuel was assessed qualitatively by air-flow measurement of fouling levels produced in the engine's injector nozzles. The nozzles, of type Bosch DN 12 SD 1750, were placed in a Ricardo air-flow rig according to ISO 4010, and air-flow measurements were recorded at needle lifts of 0.1, 0.2 and 0.3 mm, with a vacuum pressure 600m Bar (60,000 Pa).

Build up of deposits in the nozzles causes a reduction in measured air-flow, and degree of nozzle fouling can be quantified by the formula:

$$\text{Nozzle Fouling} = \frac{\text{Flow (clean)} - \text{Flow (fouled)}}{\text{Flow (Clean)}} \times 100$$

where "clean" values were measured prior to engine test and "fouled" values were measured after engine test.

Average fouling level (averages of values at the three needle lift levels) were as follows:

<u>Fuel (Example)</u>	<u>Fouling level (%)</u>
1	2
Base Fuel	55 to 65

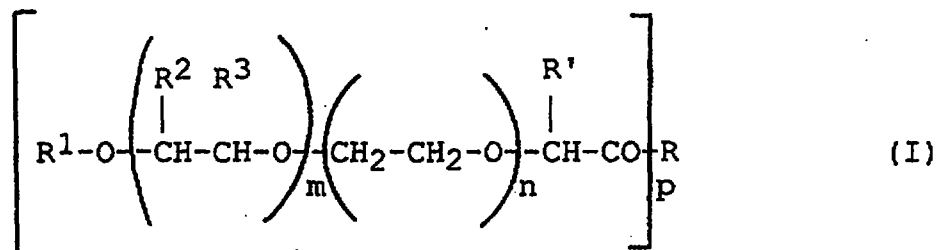
It can thus be seen that very much reduced fouling level resulted when the test material of Example 1 was employed.

In addition to the effects evidenced by the above tests, observations have suggested that products of formula I, in accordance with the invention, may promote flaking and removal of combustion chamber deposits in spark-ignition engines by spontaneous deadhesion of such deposits. At certain concentrations in fuels, products of formula I may confer a level of anti-rust protection.



C L A I M S

1. An alkoxy acetic acid derivative of general formula I:-



wherein R is the residue of an amine, an aminoalcohol or a polyol linked to the or each -CHR'-CO- moiety via an amide or ester linkage:

R' is hydrogen or C₁₋₄ alkyl;

R¹ is an optionally substituted hydrocarbyl group of 1 to 300 carbon atoms;

one of R² and R³ is independently selected from hydrogen and optionally substituted hydrocarbyl of 1 to 10 carbon atoms, the other of R² and R³ being independently selected from optionally substituted hydrocarbyl of 1 to 10 carbon atoms;

m is from 3 to 200;

n is from 0 to 20, provided that m/n is at least 1; and

p is from 1 to 5.

2. An acid derivative according to Claim 1 wherein R' is hydrogen.

3. An acid derivative according to Claim 1 or 2 wherein p is 1 or 2.

4. An acid derivative according to Claim 1, 2 or 3 wherein m is from 3 to 150 and n is from 0 to 10.

5. An acid derivative according to any one of Claims 1 to 4 wherein one of R² and R³ is hydrogen, the other being a C₁₋₃ alkyl group.

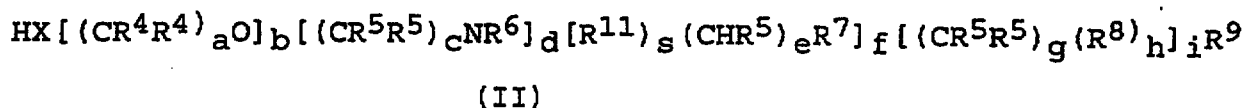


- 66 -

6. An acid derivative according to any of Claims 1 to 5 where R^1 represents a C_{1-20} alkyl group, a phenyl or benzyl group or a $(C_{1-15}$ alkyl) phenyl or $(C_{1-15}$ alkyl) benzyl group.

5 7. An acid derivative according to Claim 6 wherein R^1 represents a C_{10-18} alkyl group.

8. An acid derivative according to any one of Claims 1 to 7 wherein the compound of $R(H)_p$, of which R represents the residue, has the general formula II:-



10 wherein X is O or NR^6 ,

each R^4 independently represents hydrogen, hydrocarbyl of 1 to 10 carbon atoms or hydrocarbyl of 1 to 10 carbon atoms substituted by at least one hydroxy group,

15 each R^5 independently represents hydrogen or hydrocarbyl of 1 to 10 carbon atoms,

each R^6 independently represents hydrogen or hydrocarbyl of 1 to 10 carbon atoms,

20 R^7 represents a C_{5-7} cycloalkanediyl-NH- or 1,4-piperazinediyl moiety optionally substituted by one or more hydrocarbyl groups of 1 to 10 carbon atoms,

each R^8 independently represents NR^{10} or CHR^{10} ,

25 R^9 represents hydrogen, hydrocarbyl of 1 to 30 carbon atoms or a $-CO(CHOH)_t(CHR^5)_j(NR^5)_k(CHR^5)_lOH$ group,

R^{10} represents a $-(CR^5R^5)_rNR^6R^9$ group,

R^{11} represents a C_{5-7} cycloalkanediyl moiety optionally substituted by one or more hydrocarbyl groups of 1 to 10 carbon atoms,

30 a is 1 to 10,

b is 0 to 10,

- 67 -



c is 1 to 10,
d is 0 to 10,
e is 1 to 10,
f is 0 or 1,
5 g is 1 to 10,
h is 0 or 1
i is 0 to 10
j is 1 to 10,
k is 0 or 1,
10 l is 1 to 10,
r is 1 to 10,
s is 0 or 1, and
t is 0 or 1

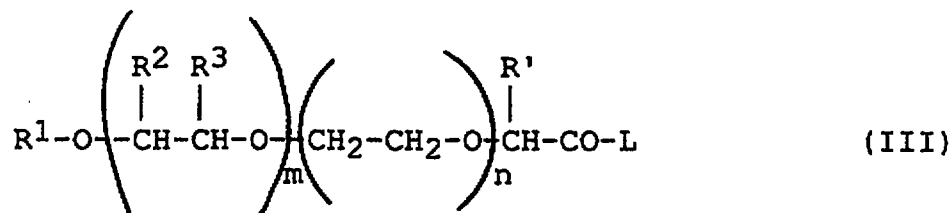
and integers b, d, f and i indicate numbers of
15 associated moieties present, and the various moieties
[(CR⁴R⁴)_aO], [(CR⁵R⁵)_cNR⁶], [(CHR⁵)_eR⁷] and
[(CR⁵R⁵)_g(R⁸)_h] may be in any linear order.

9. An acid derivative according to Claim 8 wherein in
formula II X is O or NR⁶, each R⁴ independently
20 represents hydrogen, C₁₋₄ alkyl or C₁₋₄ hydroxyalkyl,
each R⁵ independently represents hydrogen or C₁₋₄
alkyl, each R⁶ represents hydrogen or methyl, R⁷
represents a 1,4-piperazinediyl moiety or a
cyclohexanediyl-NH- moiety optionally substituted by up
25 to three methyl groups, each R⁸ independently
represents NR¹⁰ or CHR¹⁰, R⁹ represents hydrogen or a
-CO(CHOH)_t(CHR⁵)_j(NR⁵)_k(CHR⁵)_lOH group, R¹⁰ represents
a -(CHR⁵)_rNHR⁹ group, R¹¹ represents a cyclohexanediyl
moiety optionally substituted by up to three methyl
30 groups, a is 1 to 6, b is 0 to 5, c is 1 to 6, d is 0
to 5, e is 1 to 5, f is 0 or 1, g is 1 to 5, h is 0 or
1, i is 0 to 5, j is 1 to 5, k is 0 or 1, l is 1 to 5,
r is 1 to 5, s is 0 or 1 and t is 0 or 1.



10. An acid derivative according to Claim 9 wherein $R(H)_p$ is selected from the group consisting of pentaerythritol, triethylenetetramine and tris(2-aminoethyl)amine.

- 5 11. A process for preparing an acid derivative of formula I as defined in any one of Claims 1 to 10 which comprises reacting a compound of general formula III:-



- 10 wherein R' , R^1 , R^2 , R^3 , m and n are as defined in Claim 1 and L represents a leaving group, with a compound of general formula $R(H)_p$, wherein R is as defined in Claim 1 in molar ratio compound of formula III : compound of formula $R(H)_p$ of substantially $p:1$, optionally followed by converting the resulting acid derivative of formula I into another acid derivative of formula I with
- 15 different group R as defined in Claim 1.

12. An additive concentrate suitable for addition to fuel for an internal combustion engine which comprises a fuel-compatible diluent and an acid derivative of formula I as defined in any one of Claims 1 to 10.

- 20 13. A fuel composition comprising a major amount of a fuel for an internal combustion engine and a minor amount of an acid derivative of formula I as defined in any one of Claims 1 to 10.

- 25 14. A method of operating an internal combustion engine which comprises introducing into the combustion chambers of said engine a fuel composition according to Claim 13.



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07C 235/08, 235/10, 237/10, C07D 295/12, C07C 69/708	A1	(11) International Publication Number: WO 97/41092 (43) International Publication Date: 6 November 1997 (06.11.97)
(21) International Application Number: PCT/EP97/02238 (22) International Filing Date: 25 April 1997 (25.04.97) (30) Priority Data: 96302953.3 26 April 1996 (26.04.96) EP (34) Countries for which the regional or international application was filed: GB et al. 96308886.9 6 December 1996 (06.12.96) EP (34) Countries for which the regional or international application was filed: GB et al. (71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (72) Inventors: GRUNDY, Michael, John; Pool Lane, Ince, Chester, Cheshire CH1 3SH (GB). KENDALL, David, Roy; Pool Lane, Ince, Chester, Cheshire CH1 3SH (GB). NAISBY, Thomas, Webster; Pool Lane, Ince, Chester, Cheshire CH1 3SH (GB). SUTKOWSKI, Andrew, Czeslaw; Pool Lane, Ince, Chester, Cheshire CH1 3SH (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, (SG) SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.
(54) Title: ALKOXY ACETIC ACID DERIVATIVES (57) Abstract This invention provides alkoxy acetic acid derivatives of general formula (I) wherein R is the residue of an amine, an aminoalcohol or a polyol linked to the or each -CHR'-CO- moiety via an amide or ester linkage; R' is hydrogen or a C₁₋₄ alkyl group; R¹ is an optionally substituted hydrocarbyl group of 1 to 300 carbon atoms; one of R² and R³ is independently selected from hydrogen and optionally substituted hydrocarbyl of 1 to 10 carbon atoms, the other of R² and R³ being independently selected from optionally substituted hydrocarbyl of 1 to 10 carbon atoms; m is from 3 to 200; n is from 0 to 20, provided that m/n is at least 1; and p is from 1 to 5; a process for their preparation; and their incorporation in additive concentrates and fuel compositions for internal combustion engines. Derivatives of formula (I) give rise to advantageous engine cleanliness effects. $\left[\begin{array}{c} \text{R}^2 \quad \text{R}^3 \\ \quad \\ \text{R}^1\text{-O}-\text{CH}-\text{CH}-\text{O}-\left(\text{CH}_2-\text{CH}_2-\text{O} \right)_m-\left(\text{CH}_2-\text{CH}_2-\text{O} \right)_n-\text{CH}-\text{CO}-\text{R} \\ \quad \\ \text{R}' \quad \text{p} \end{array} \right] \quad (I)$		