



(22) Date de dépôt/Filing Date: 1998/10/15

(41) Mise à la disp. pub./Open to Public Insp.: 1999/04/16

(45) Date de délivrance/Issue Date: 2007/10/02

(30) Priorité/Priority: 1997/10/16 (US08/951,388)

(51) Cl.Int./Int.Cl. *C09K 8/64* (2006.01),
C08G 65/327 (2006.01), *C08G 65/335* (2006.01),
E21B 43/26 (2006.01)

(72) Inventeurs/Inventors:
JONES, CRUISE K., US;
TAYLOR, GRAHAME N., US

(73) Propriétaire/Owner:
ONDEO NALCO ENERGY SERVICES, L.P., US

(74) Agent: SMART & BIGGAR

(54) Titre : AGENT GELIFIANT POUR HYDROCARBURES LIQUIDES ET METHODE D'UTILISATION

(54) Title: GELLING AGENT FOR HYDROCARBON LIQUID AND METHOD OF USE

(57) **Abrégé/Abstract:**

A gelling agent for gelling hydrocarbon liquids comprises (a) a minor amount of a high molecular weight diphosphate ester acid or salt thereof synthesized using high molecular weight polyalkylene glycol and (b) a major amount of a phosphate diester acid or salt thereof synthesized from mixed C₁-C₂₄ alcohols, preferably C₆ to C₁₀ alcohols. The preferred high molecular weight gelling agent additive is an aluminum or ferric salt of an ester prepared from a polypropylene glycol having a molecular weight in the range of 6,000 to 26,000.

ABSTRACT OF THE PRESENT INVENTION

A gelling agent for gelling hydrocarbon liquids comprises (a) a minor amount of a high molecular weight diphosphate ester acid or salt thereof synthesized using high molecular weight polyalkylene glycol and (b) a major amount of a phosphate diester acid or salt thereof synthesized from mixed C_1 - C_{10} alcohols, preferably C_6 to C_{10} alcohols. The preferred high molecular weight gelling agent additive is an aluminum or ferric salt of an ester prepared from a polypropylene glycol having a molecular weight in the range of 6,000 to 26,000.

GELLING AGENT FOR HYDROCARBON LIQUID AND METHOD OF USE

(CASE NO. 5465)

FIELD OF INVENTION

The present invention relates generally to the fracturing of subterranean formations using gelled hydrocarbons. In one aspect, it relates to a novel oil base composition (and method of manufacturing) for fracturing subterranean formations. In another aspect, the invention relates to the use of a novel phosphate salt gelling agent. In still another aspect, the invention relates to a novel gelling agent additive synthesized from high molecular weight polyalkylene glycols.

DESCRIPTION OF THE PRIOR ART

Hydraulic fracturing has been widely used as a means for improving the rates at which fluids can be injected into or withdrawn from subterranean formations surrounding oil wells and similar boreholes. The methods employed normally involve the following steps: injection of a viscous fracturing fluid having a low fluid loss value into the well at a rate sufficient to generate a fracture in the exposed formation, the introduction of fluid containing suspended propping agent particles into the resultant fracture, and the subsequent shutting in of the well until the formation is closed on the injected particles. This results in the formation of vertical, high-conductivity channels through which fluids can thereafter be injected or produced. The conductivity in the propped fracture is the function of the fracture dimensions and the permeability of the bed of propping agent particles within the fracture.

In order to generate the fracture of sufficient length, height, and width and to carry the propping agent particles into the fracture, it is necessary for the fluid to have relatively high viscosity. This requires the use of gelling agents in the fracturing fluid.

Fracturing fluids are generally water or oil-based liquids gelled with polymers. However, the water-based liquids cannot be used in the fracturing of many water sensitive formations. Fracturing in these formations requires the use of oil-based liquids.

The most common gelling agent for oil-based fracturing fluids has been aluminum salts of phosphate esters. The following references disclose phosphate ester gelling agents:

- (a) U.S. Patent 4,104,173 discloses gelling agents prepared by
 - (i) reacting phosphorous pentoxide with monohydric alcohols and
 - (ii) reacting this product with a basic aluminum compound.
- (b) The gelling agent disclosed in U.S. Patent 4,316,810 is prepared by
 - (i) reacting phosphorous pentoxide with ethereal alcohols prepared by reacting ethylene oxide or propylene oxide with selected aliphatic alcohols to form a phosphate ester and
 - (ii) reacting phosphate ester with an aluminum compound to form the aluminum salt of the phosphate ester.
- (c) U.S. Patent 4,787,994 discloses the use of an oil with a gelling agent prepared by reacting an orthophosphate ester with an aluminum activator. The acid is mixed with the orthophosphate ester prior to the addition of the activator.
- (d) In U.S. Patent 4,877,894 and 5,057,233, gelling agents are prepared by

- (i) reacting triethyl phosphate with phosphorous pentoxide to form a polyphosphate intermediate.
 - (ii) reacting the polyphosphate intermediate with a mixed aliphatic alcohol.
This product is then reacted with an aluminum activator to form the aluminum alkylphosphate ester gelling agent.
- (e) U.S. Patent 5,190,675 discloses a metal phosphate diester prepared by reacting a triester phosphate with P_2O_5 to form a polyphosphate which is reacted with an alcohol to produce a phosphate diester. The diester is then contacted with an aluminum source (in the hydrocarbon liquid) to form the aluminum phosphate diester.
- (f) U.S. Patent 5,202,035 discloses a gelling agent similar to that disclosed in 5,057,233, except that an aluminum sulfate was used as a mixture with the aliphatic alcohol.
- (g) U.S. Patent 5,514,645 discloses a gelling agent comprising two components to be added to the liquid hydrocarbon:
- (i) an alkyl orthophosphate acid ester partially neutralized with an alkali metal hydroxide, and
 - (ii) a source of aluminum or ferric ions.
- (h) U.S. Patents 5,417,287; 5,571,315; 5,614,010; and 5,647,900 disclose organic phosphate gelling agents and (i) ferric salts, or (ii) ferric ammonium citrate, or (iii) ferric ions, an amine, and polycarboxylic acid, or (iv) a ferric salt reacted with a low molecular weight amine.

- (i) U.S. Patent 4,200,540 discloses gelling agents made from reacting low molecular weight alcohols with phosphorous pentoxide, which in turn is reacted with a basic aluminum compound.

One of the problems associated with oil based gelling agents is that they generate viscosity slowly, which means that the viscosified oil must be premixed by a batch process. In some fracturing operations, it would be highly desirable and economical to carryout the fracturing operations by a continuous process wherein the oil is viscosified "on the fly." The continuous operation requires the use of a fast acting gelling agent.

SUMMARY OF THE INVENTION

A main purpose of the compositions and method of the present invention is to rapidly viscosify an oil base fracturing fluid using a high molecular weight gelling agent additive. The rapid viscosification or gelling of the fracturing fluid aids in the process for the addition and suspension of the propping agent during the fracturing operations.

The compositions of the present invention fall into two broad categories:

- (a) a high molecular weight gelling agent additive which, when combined with another conventional gelling agent component or components, is an effective gelling agent for hydrocarbon liquids, and
- (b) a gelling agent composition comprising the aluminum or ferric salt of (i) a high molecular weight additive and (ii) a low molecular weight component.

The two gelling agent components are referred to herein as HMW additive (also HMW component) and LMW component.

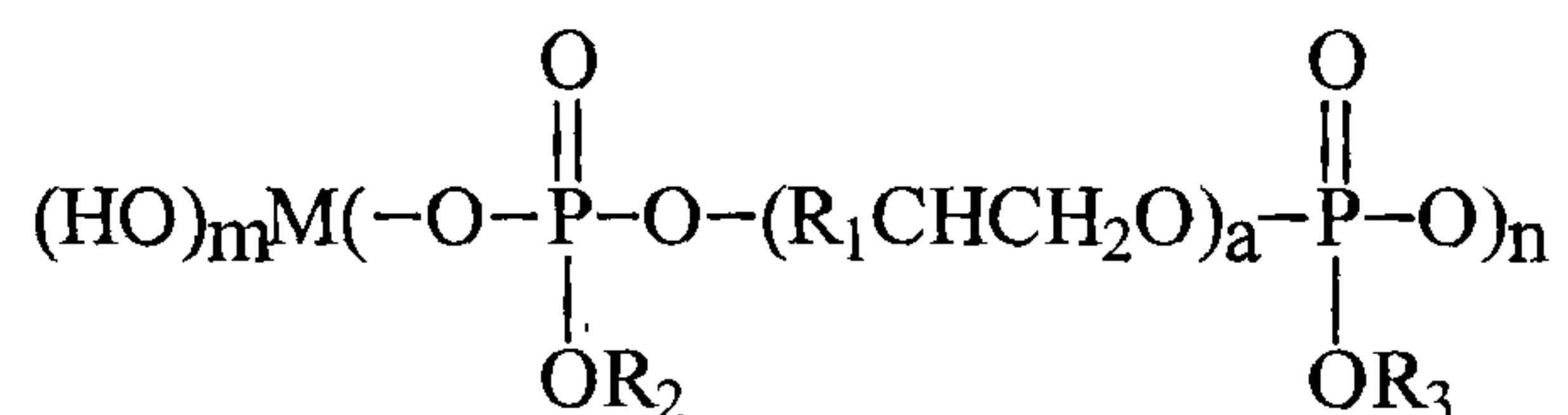
76340-9

The method of the present invention involves the use of the HMW additive and the gelling agent composition in a hydrocarbon liquid at the proper apparent pH. The term "apparent pH" means the measured pH of a hydrocarbon
 5 continuous liquid.

The HMW additive is produced by reacting a high molecular weight polyalkylene glycol with (a) P₂O₅ or (b) the reaction product of P₂O₅ and a trialkyl phosphate.

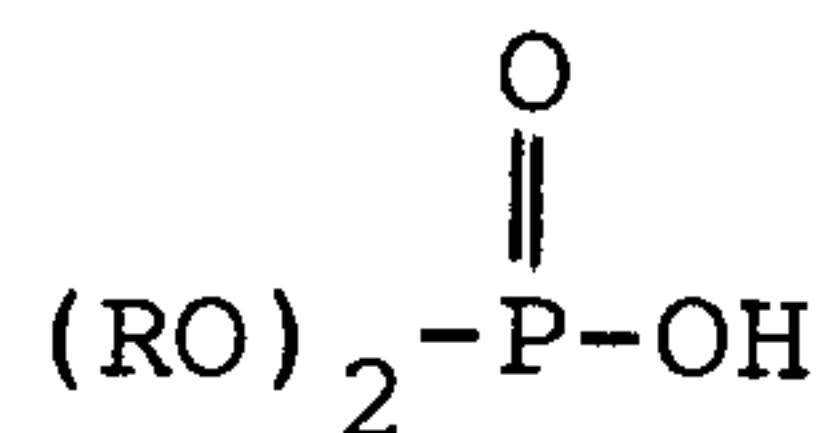
According to one aspect of the present invention,
 10 there is provided a gelling agent additive for hydrocarbon liquid which comprises the reaction product of (a) a polyalkylene glycol having a molecular weight of 1,000 to 26,000 and wherein the alkylene repeating unit comprises 3 to 4 carbon atoms and (b) phosphorus sources selected from
 15 the group consisting of (α) P₂O₅ or (β) a polyphosphate intermediate prepared by reacting triethyl phosphate with P₂O₅.

According to a further aspect of the present invention, there is provided a gelling agent composition for
 20 hydrocarbon liquids comprising (a) from 0.05 to 20 wt% of a compound having the following formula:



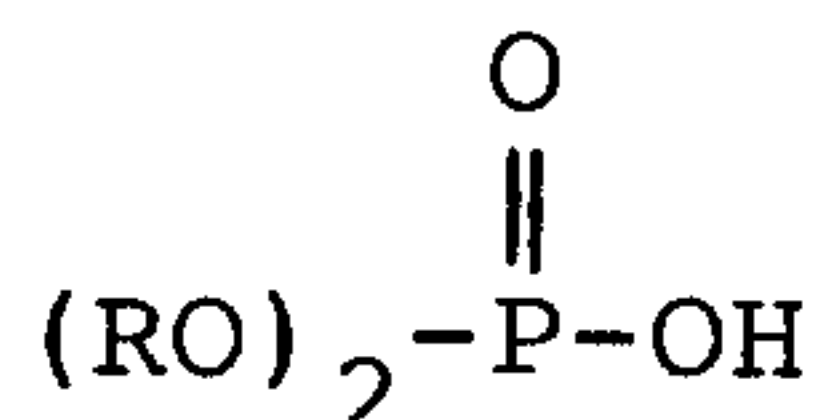
a is an integer ranging from 13 to 450, m + n = 3, m = 0 to 2,
 25 n = 1 to 3, R₁ is CH₃ or C₂H₅, M is Al⁺⁺⁺ or Fe⁺⁺⁺, R₂ is an alkyl or aryl group containing from 1 to 24 carbon atoms, R₃ is an alkyl or aryl

group containing from 1 to 24 carbon atoms; and (b) from 80 to 99.95 wt% of a compound having the following formula:



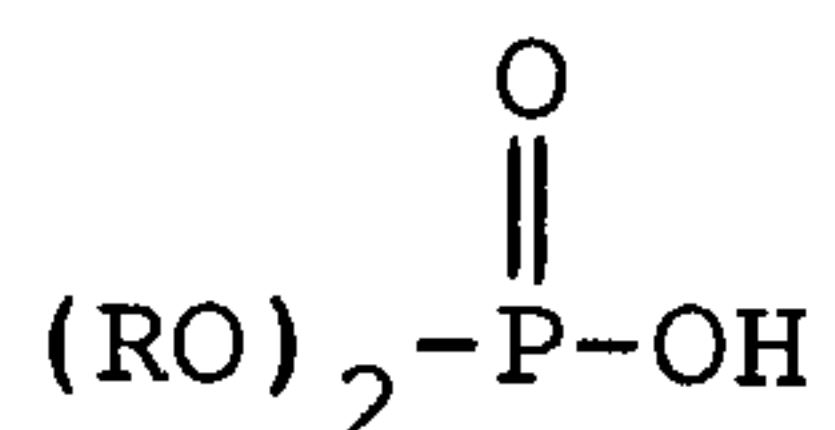
where R is independently a C₁ to C₂₄ alkyl or aryl group.

According to another aspect of the present invention, there is provided a gelled hydrocarbon liquid comprising (a) a hydrocarbon liquid, (b) a gelling agent comprising (i) from 0.1 to 10 wt% of the additive defined above, and (ii) 90 to 99.9 wt% of low molecular weight diester phosphate having the following
10 formula:



where R is a C₁ to C₂₄ alkyl or aryl group; and (c) a basic compound selected from aluminum and ferric compounds.

According to a still further aspect of the present invention, there is provided a method of preparing a gelled hydrocarbon liquid comprising the steps of (a) preparing the ester additive as defined above by reacting a C₃ or C₄ poly-alkylene glycol having a molecular weight of 1,000 to 26,000 with P₂O₅; (b) preparing a diester phosphate acid having the
20 following formula:



where R is an alkyl group having from 1 to 24 carbon atoms; (c) reacting the additive of step (a) with the diester acid of step

(b) to form mixed esters; (d) reacting the product of step (c) with a basic compound containing aluminum and ferric ions; and (e) adding the product of step (c) to the hydrocarbon liquid before or after reaction of step (d) in sufficient amounts to substantially increase the viscosity of the liquid.

The gelling agent composition may be made by combining the HMW additive with the LMW component in the presence of a metallic compound selected from Group II or Group III metals. Such compounds include ammonium citrate, sodium aluminate, aluminum sulfate, alumina, ferric sulfate, ferric sulfate reacted with a low molecular weight amine such as triethanolamine, and the like. The reaction of the three components may be in a batch process wherein the three components are reacted simultaneously, or by sequence wherein the HMW and LMW components are first reacted forming an ester or diester, followed by the ester or diester reaction with the metal compound to form a salt of the ester or diester, preferably an iron or aluminum salt.

The gelling agent may be preformulated for addition to the oil base fracturing fluid, or formed in situ in the fracturing fluid.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The gelling agent composition of the present invention comprises (a) a novel high molecular weight component synthesized using high molecular weight polyalkylene glycol (PAG) and (b) a low molecular weight component comprising a conventional

phosphate diester. (As used herein, molecular weight (MW) means number average molecular weight; and the term "ester"

76340-9

is sometimes used in the generic sense, meaning mono- and di-esters, and mixed esters.) Each of these components and their use are described below.

High Molecular Weight Component

5 The high molecular weight component (HMW additive for the gelling agent composition), is a diphosphate compound made by reacting a high molecular weight PAG with either (a) phosphorous pentoxide or (b) the reaction product of trialkyl phosphate and phosphorous pentoxide.

10 The PAG is either polypropylene glycol or polybutylene glycol (or co- or ter-polymers containing ethylene glycol links), with the former being preferred, and having a molecular weight of 1,000 to 26,000, preferably 6,000 to 26,000, and most preferably 8,000 to 18,000. The
15 alkylene repeating units of these PAGs have alkylene repeating units of 3 to 4 carbon atoms.

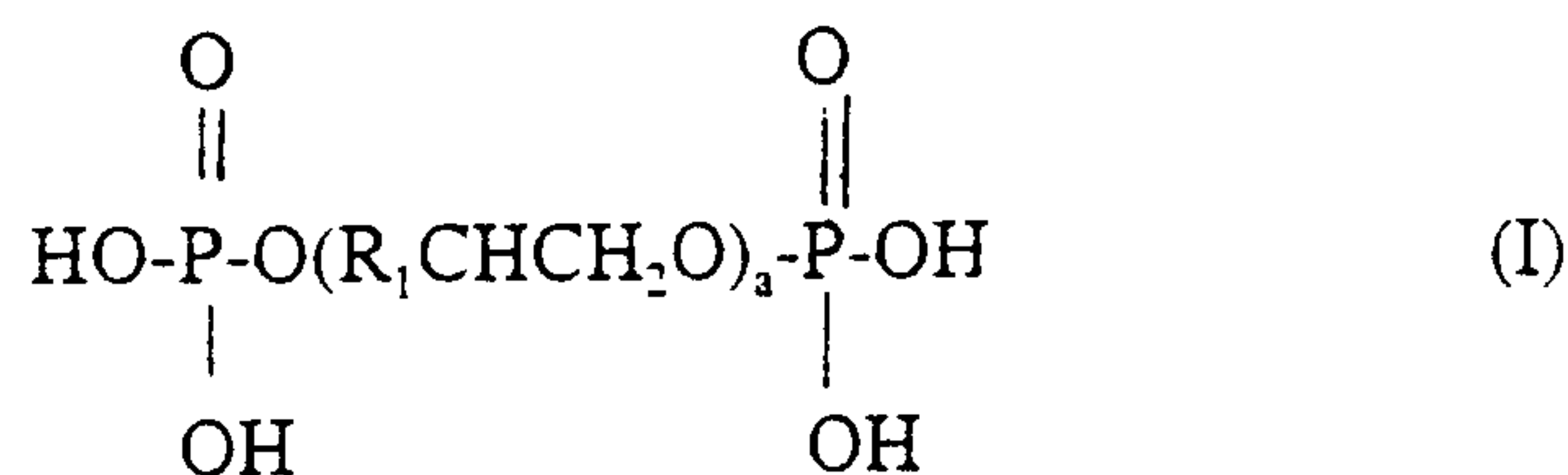
 The alkyl groups of the trialkyl phosphate may range from 1 to 6 carbon atoms, preferably 2 to 4 carbon atoms. The preferred phosphate is triethyl phosphate (TEP).

20 Selected PAGs for incorporation into the high molecular weight additive of the present invention may be prepared using a catalyst selected from the group consisting of barium, strontium and their oxides, hydroxides, hydrated hydroxides, or monohydroxide salts, or mixtures thereof or a
25 double metal cyanide complex compound wherein one of the metals of said complex compound is selected from the group consisting of Zn(II), Fe(II), Fe(III), Co (II), Ni(II), Mo(IV), Al(III), V(IV), V(V), Sr(II), W(IV), W(VI), Mn(II), and Cr(III) and mixtures thereof, and wherein the other
30 metal of said complex compound is a metal selected from the

76340-9

group consisting of Fe(II), Fe(III), Co(II), Co(III), Cr(II), Cr(III), Mn(II), Mn(III), V(IV), V(V), and mixtures thereof. These methods are described in detail in U.S. Patent 5,010,187.

A particularly effective PAG for use in the present invention is polypropylene glycol (PPG) of number average molecular weight 8,000 to 14,000. The reaction of PAG with phosphorous pentoxide, at the proper stoichiometry, produces an ester having the general formula I.



where

R_1 is CH_3 or C_2H_5

a is an integer ranging from 13 to 450

The preferred ranges of " a " will be determined by the preferred molecular weight ranges of the starting material PAG, as described above. For example if R_1 is CH_3 and the preferred molecular weight range is 6,000 to 26,000, then " a " will be from about 103 to about 450. If R_1 is C_2H_5 for the same molecular weight range, " a " will be from about 83 to about 360. The value of " a " for the other specified ranges may be similarly calculated.

The preferred method of synthesizing the HMW additive of Formula I is by reacting PAG with P_2O_5 . This may be carried out as follows: a slurry of about 4 wt% P_2O_5 , about 70 wt% PAG, and about 24 wt% of a solvent such as heptane is prepared, and permitted to react at room temperature.

Low Molecular Weight Component

The LMW component of the gelling agent composition is a phosphate diester acid having the following formula (II):

76340-9



Where

Each R is independently an alkyl or aryl group
 5 having from 1 to 24 C atoms, preferably alkyl groups having
 from 6 to 10 C atoms.

The preferred low molecular weight phosphate
 diester acid is made from reacting a polyphosphate
 intermediate (produced by the reaction of TEP and P₂O₅) with
 10 a mixture of aliphatic alcohols having from 6 to 10 carbon
 atoms.

The synthesis of the low molecular weight
 component is well known in the art. See for example U.S.
 Patents 4,877,894, 5,057,233, and 5,110,485.

15 In practice, the LMW phosphate ester may be
 prepared by reacting first phosphorous pentoxide with
 triethyl phosphate in the presence of a solvent (xylene) to
 form a polyphosphate intermediate. Temperature maximum to
 this point in the procedure is carefully controlled not to
 20 exceed about 85 Celsius. Subsequently a mixture of
 alcohols, preferably ranging from carbon number 6 through
 10, are added and heated to about 120 Celsius to form a
 predominantly phosphate diester. A representative feed
 composition of this process is given below:

25	<u>Material</u>	<u>Wt%</u>
	Triethylphosphate (TEP)	about 25
	Phosphorous Pentoxide	about 15
	C-6-10 Alcohol	about 35
	xylene	about 25.

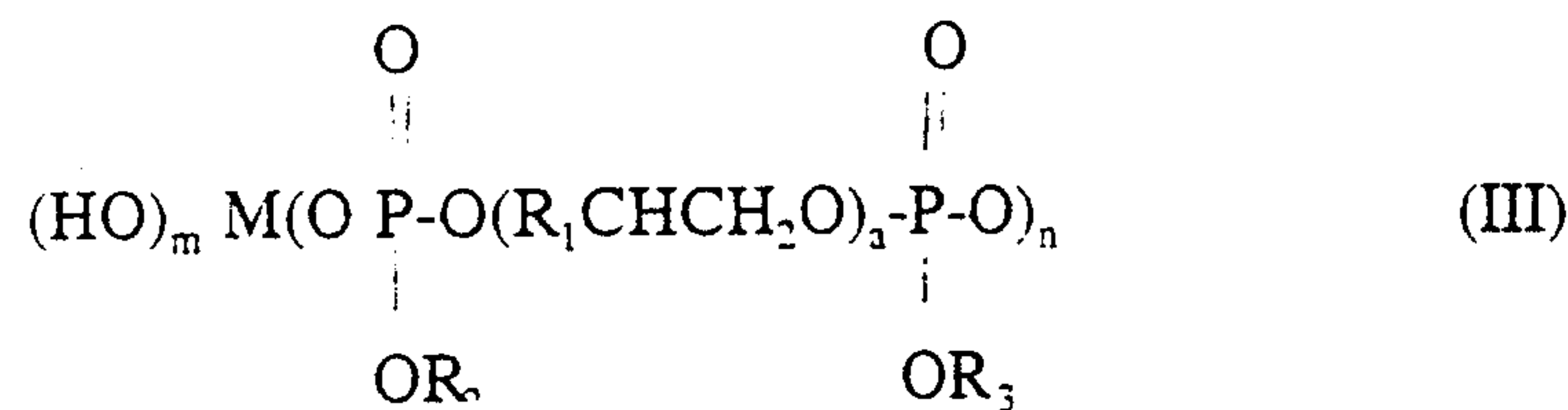
Formation of the Gelling Agent

The gelling agent composition of the present invention is prepared by reacting the three components:

- (a) the HMW ester, (Formula I)
- (b) the LMW diester, and (Formula II)
- (c) a metallic source such as Al^{+++} and Fe^{+++}

forming mixed salts.

The mixed salts have the following formulas (III and IV):



where a and R_1 are as defined in Formula I.

M is Al^{+++} or Fe^{+++}

$m+n = 3$

$m=0$ to 2 , preferably 0

$n=1$ to 3 , preferably 3

R_2 is H , or an alkyl or aryl group having from 1 to 24 C atoms, preferably a mixed C_2 to C_{10} alkyl group, with substantial amount of C_6 to C_{10} alkyl groups present

R_3 is the same or different from R_2 and is H or an alkyl or aryl group having from 1 to 24 C atoms, preferably mixed C_2 to C_{10} alkyl groups, with substantial amount of mixed C_6 to C_{10} alkyl groups.



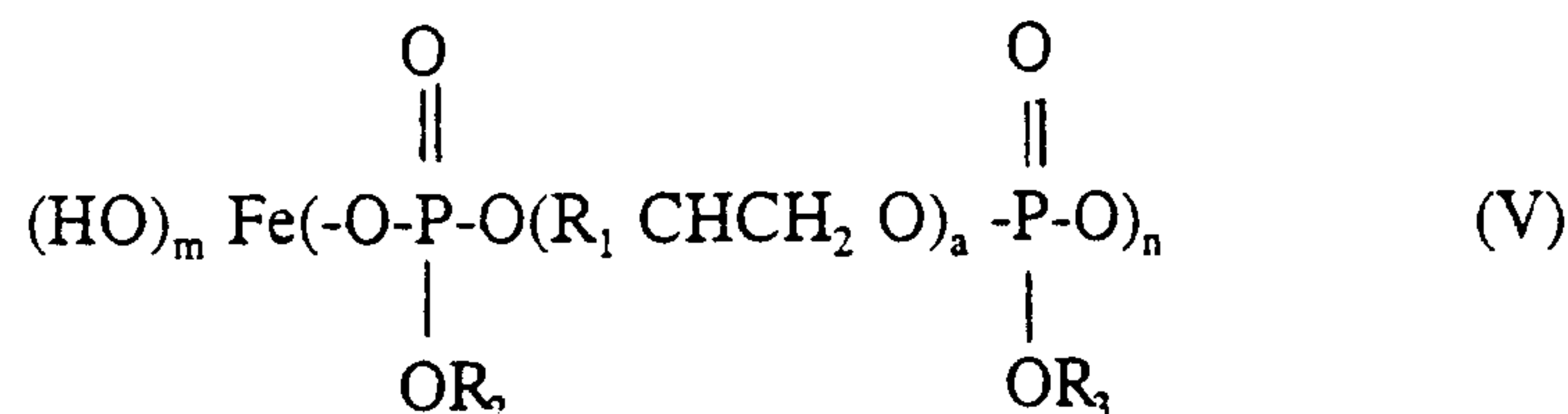
Where R is H , or C_1 to C_{24} alkyl or aryl groups, preferably a mixed C_2 to C_{10} alkyl groups, with substantial amounts of C_6 to C_{10} alkyl groups present.

M is an aluminum or ferric ion
 $x = 1$ to 3 , preferably 3 .
 $y = 0$ to 2 , preferably 0 .
 $x + y = 3$

The sources of the aluminum and ferric ions include metal compounds such as those described previously.

When the HMW additive (Formula I) is mixed with the LMW component (Formula II), transesterification occurs wherein some of the R alkyl groups transpose with the R_2 and R_3 groups. The HMW component thus has the general formula represented by Formula III and the LMW component has the general formula Formula IV. In practice, the molecules of Formulas III and IV will contain mixed alkyl groups or H at the R, R_2 and R_3 positions.

In one embodiment, the metal ion is iron and the preferred R, R_2 and R_3 groups are C_1 to C_{24} alkyl groups, wherein the HMW and LMW components of the gelling agent composition may be represented by Formulas V and VI (herein referred to as HMW iron salt and LMW iron salt, respectfully):



Where a, m, and n are defined in Formula III, x and y are defined in Formula IV, and R, R_2 and R_3 are independently C_1 to C_{24} alkyl groups, preferably C_2 to C_{10} alkyl groups with substantial amounts of C_6 to C_{10} alkyl groups, most preferably C_6 to C_{10} mixed alkyl groups.

When using an iron source (Fe^{++}), it is preferred to premix the HMW ester (Formula III) with the LMW diester (Formula IV) at a weight ratio wherein the HMW component constitutes not more than 20 wt%, and preferably more than 10 wt%, and most preferably not more than 6 wt%. The ester mixture is then added to the hydrocarbon liquid along with a source of iron such as the reaction product of ferric sulfate and triethanolamine in an aqueous solution. The ester mixture may be added to the hydrocarbon liquid before or after the addition of source of the iron.

When using an aluminum source (Al^{+++}), the preferred procedure is to add an aluminum source such as aluminum sulfate tetradecahydrate to the mixture of the mixed esters (HMW ester and LMW ester) in the proper stoichiometry, to form aluminum salts of the esters. Representative starting materials are as follows:

phosphate esters (LMW and HMW)	55-60 wt%
aluminum sulfate tetradecahydrate	15-20 wt%
solvent (e.g. xylene and heptane)	20-30 wt%

The weight ratio of the HMW salt and the LMW salt comprising the gelling agent composition, may range within relatively wide ranges, with the following being representative:

Table I

	<u>HMW Salt</u>	<u>LMW Salt</u>
Broad Range	0.05 to 20 wt%*	80 to 99.95 wt%
Preferred Range	0.1 to 10 wt%	90 to 99.90 wt%
Most Preferred Range	0.5 to 6 wt%	94 to 99.50 wt%

*% being based on the combined weights of the HMW and LMW salts

OPERATIONS

As indicated above, there are two modes for forming the gelling agent composition of the present invention: (1) preformulation and subsequent addition into the hydrocarbon liquid, and (2) in-situ formation in the hydrocarbon liquid. Each mode is described below:

Preformulation

In the preformulation mode, the HMW additive (Formula I) is reacted with the LMW compound (Formula II) and a metal compound (source of Al^{+++} or Fe^{+++}) to form the gelling agent composition having the formulas of III and IV in the weight concentrations of Table I. The reactions may be carried out in the presence of from 10 to 50 wt% of a solvent such as xylene, heptane, and the like.

The preformulated gelling agent composition may be added to the hydrocarbon liquid at the well site. The hydrocarbon liquids may be any of those currently used in oil base fracturing, including crude oil, diesel, fuel oil, refined oil, condensate, and the like.

In practice the gelling agent composition will be added as a formulation in a solvent such as diesel, kerosene or aromatic, wherein the gelling agent composition will constitute from about 50 to 90 wt%, preferably 60 to 80 wt% of the formulation.

The concentration of the gelling agent in the hydrocarbon liquid, of course, will depend on the viscosity desired. Generally, concentrations in the range of 0.1 to 3.0 weight percent based on the weight of the fracturing fluid will generate sufficient viscosity for purposes of the present invention: At least 50 cp at 100°F and 118 rpm as measured with a Fann 50C viscometer at 4b₅ rotor/bob configuration.

Also added to the hydrocarbon liquid is a basic activator to adjust the apparent pH to between about 3 and 5. The activator base may include aqueous solutions of an alkali metal hydroxide (e.g. KOH) or a low molecular weight amine such as triethanolamine or polyamine along with about 0.1 to 3 wt% water.

In-Situ Formation of the Gelling Agent Composition

In this mode, the HMW component (Formula I) and the LMW component (Formula II) are premixed (in the weight ratios described above) and added to the oil. The appropriate amounts of the metal compound, preferably an aqueous solution of the metal base, along with an organic base such as triethanolamine for pH control (3 to 5) are also added to the oil. The preferred order of addition is first the two gelling agent components, with agitation, followed with the aqueous base solution, also with agitation.

As described previously, when using the ferric salts of the HMW and LMW esters, it is preferred to use the in situ gelling procedure.

With either the preformulation mode or the in-situ formulation mode, the gelled hydrocarbon liquid is pumped into the formation at a rate and pressure sufficient to fracture the formation. Propping agents are carried in the gelled fracturing fluid and placed in the fracture. Following the fracturing treatment, the well is shut in.

The gelling and pumping operation may be by the batch process but preferably is by the continuous process. The rapid viscosification of the oil by the compositions of the present invention offer advantages in both types of operations. Preferably fracturing liquid will contain a breaker, or viscosity reducer, to controllably deliver proppant to the formation followed by subsequent proppant deposition, accomplished generally by viscosity reduction, i.e. decreasing

the ability of the hydrocarbon to suspend solids. Hydrocarbon de-viscosification after fracture also facilitates well cleanup in many instances. The viscosity reducers, normally referred to as "breakers", consist of many types though most function through apparent pH modification. In alkyl phosphate ionic complexes in hydrocarbon, inorganic base breakers are generally used, for example sodium carbonate, bicarbonate, calcium hydroxide or magnesium hydroxide. Organic bases such as alkylamines are also used. Acidic breakers such as aromatic acids, i.e. benzoic acid, toluene sulfonic acid are effective though not generally commercially used.

Typical hydrocarbon fracturing fluid compositions generally consist of viscosifiers, breakers, corrosion inhibitors, surfactant, CO₂ and wetting agents to perform specific functions designed to enhance the probability of success of the fracturing treatment.

EXAMPLES

Samples:

A low molecular weight phosphate ester "control" sample (Sample C-1) and its aluminum salt (Sample C-2) were synthesized from the raw materials described in Table II.

The phosphate ester was prepared by reacting first phosphorous pentoxide with triethyl phosphate in a xylene solvent to form a polyphosphate intermediate. Temperature maximum to this point in the procedure was carefully controlled not to exceed about 85 Celsius. Subsequently a mixture of alcohols ranging from carbon number 6 through 10 was added and heated to about 120 Celsius to form a predominantly phosphate diester. C-1 was added to Kerosene containing a basic iron salt and tested as Test #1.

The aluminum salt sample (C-2) of the above composition (C-1) was prepared by adding the C-1 sample to aluminum sulfate tetradecahydrate with xylene and heptane, following by

heating to azeotropically remove water via an equipped Dean Stark trap. Maximum temperature of the flask contents was 116 Celsius. This composition was tested in Test #2.

Table II - Comparative Samples

<u>Sample C-1 (LMW diester)</u>	<u>Raw Materials</u> <u>(wt percent)</u>	<u>Sample C-2 (LMW Al Salt)</u>	<u>Raw Materials</u> <u>(wt percent)</u>
Triethylphosphate (TEP)	24	Sample C-1	56
Phosphorous Pentoxide	14	Aluminum Sulfate Hydrate	16
C-6/10 Mixed alcohols	37	Xylene and heptane	28
Xylene and heptane	25		

Analogous gelling agents of the present invention were prepared from the feed compositions shown in Table III.

Table III

	<u>Sample A</u> <u>HMW and LMW esters</u> <u>(wt percent)</u>	<u>Sample B</u> <u>HMW and LMW esters</u> <u>(wt percent)</u>
Triethylphosphate (TEP)	23	23
Phosphorous Pentoxide	14	14
C6/10 Mixed alcohols	36	35
Xylene and heptane	26	24
PPG*	1.0	4.0

*molecular weight between 8,000 and 14,000

The aluminum salt of Sample A was prepared, the composition of the raw materials is shown in Table IV.

Table IV

	<u>Sample C (Al HMW and LMW Salts)</u> <u>Raw Materials</u> <u>(wt percent)</u>
Sample A	56
Aluminum Sulfate Hydrate	16
Xylene and heptane	28

The compositions of Samples A and B were each prepared by (a) reacting TEP with P_2O_5 in the solvent containing C_5 - C_{10} mixed alcohols and (b) reacting P_2O_5 with PPG. The reaction products of (a) and (b) were added to the kerosene containing the basic iron salt aqueous solution. The iron salt of Sample A and Sample B thus were formed in situ. The gelling compositions in the two samples constuted about 1 and 5 wt%, respectively of the HMW salt in the Kerosene. These compositions were tested as Test #3 and #5.

The Sample C composition was preformulated by preparing Sample A as described above and reacting Sample A with aluminum sulfate; and tested as Test #4.

Rheological properties of the above described compositions were determined on a Fann 50C viscometer equipped with r_1b_5 rotor bob configuration and measured at 118 rpm at 150 °F. Sample preparation was conducted as follows:

To a quart baffle design 3-blade propeller design Waring pitcher was added:

- 200 mls kerosene
- gellant composition
- activator solution

The amounts of each gellant and activator solution and type are given in Table V. The compositions in the pitcher were stirred for 60 seconds at low constant stir and placed on the Fann 50C for constant shear evaluation.

Table V

<u>Test #</u>	<u>Gellant Type (Sample)</u>	<u>Gellant Dosage. mls (in 200mls kerosene)</u>	<u>Activator Type</u>	<u>Dosage. mls</u>
1.	C-1 diester	2.0	Basic Iron Salt* (aqueous)	3.0
2.	C-2 Salt (Al)	2.0	17.0wt% KOH (aqueous)	0.80
3.	A mixed esters	2.0	Basic Iron Salt* (aqueous)	3.0
4.	C Salt (Al)	2.0	17.0wt% KOH (aqueous)	0.80
5.	B mixed esters	2.0	Basic Iron Salt* (aqueous)	3.0

*Basic Iron Salt aqueous solution prepared by adding 9 parts of 20wt% $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ solution to 1 part triethanolamine and mixing briefly to form solution.

Table VI presents the rheological data comparing the aluminum salt of a prior art composition to the aluminum salt of a composition of the present invention.

Table VI

<u>Elapsed Time (mins)</u>	<u>Temperature (°F)</u>	<u>Viscosity in Centipoise (+/-5cps error)</u>	
		<u>Test #2 Sample C-2 (Alum. Salt)</u>	<u>Test #4 Sample C (Alum. Salt)</u>
5	76	116	217
15	104	139	261
30	134	138	361
60	150	159	391

From observation of the data in Table VI, it is clear that incorporation of the HMW PAG additive into the gelling composition greatly enhances viscosity under the test conditions. Moreover, the Test #4 (Sample C) gels in the pitcher (within about 15.20 secs) which is particularly advantageous for continuous mix injection of very rapidly fracturing additives into a wellbore.

Table VII compares the rheological data comparing in-situ activated gelling agents of a prior art geller with those of the present invention.

Table VII

<u>Time</u> <u>(mins)</u>	<u>Temperature</u> <u>(°F)</u>	<u>Viscosity in Centipoise</u> <u>(+/-5cps error)</u>		
		<u>Test #1</u> <u>Sample C-1</u> LMW Fe Salt	<u>Test #3</u> <u>Sample A</u> Mixed Iron Salts	<u>Test #5</u> <u>Sample B</u> Mixed Iron Salts
5	87	588	649	897
10	99	615	860	740
15	116	715	838	718
30	142	857	835	1003
45	152	914	911	1009

As demonstrated by the Table VII data, the iron salts were synthesized using HMW PAG (Tests #3) and gelled the kerosene much faster than prior art geller (Test #1). Gelation in the Waring pitcher under the test conditions was approximately 10-15 seconds with the PPG additives.

SUMMARY

The various embodiments of the present invention involve:

- (a) a novel HMW additive (a phosphate ester acid prepared from HMW PAG);
- (b) a novel salt of the HMW additive;

(c) a gelling agent composition comprising mixed HMW and LMW salts. and method of formulating:

(d) a liquid hydrocarbon gelled with the composition of (c). and

(e) a method of fracturing a subterraneous formation using the gelling agent composition of (c).

76340-9

CLAIMS:

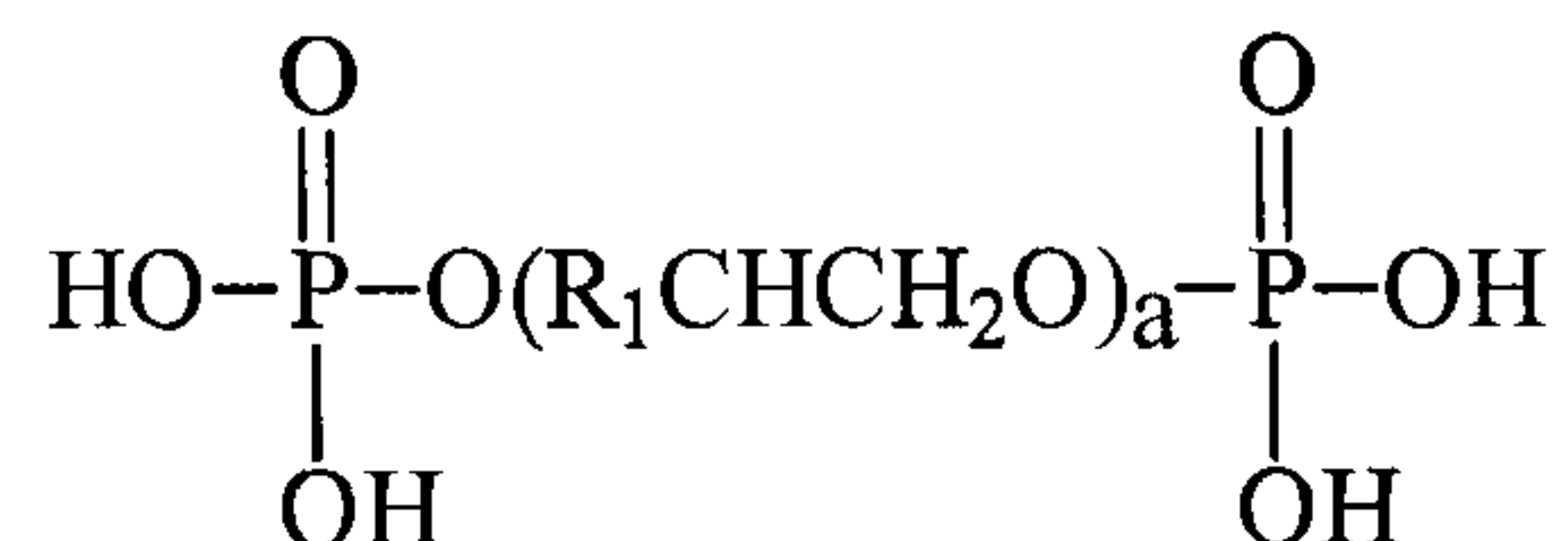
1. A gelling agent additive for a hydrocarbon liquid, which comprises the reaction product of: (a) a polyalkylene glycol having a molecular weight of 1,000 to 26,000 and
 5 wherein the alkylene repeating unit comprises 3 to 4 carbon atoms; and (b) a phosphorus source selected from the group consisting of:

(α) P₂O₅, and

(β) a polyphosphate intermediate prepared by
 10 reacting triethyl phosphate with P₂O₅.

2. The gelling agent additive of claim 1, wherein the polyalkylene is polypropylene glycol having a molecular weight of 6,000 to 26,000.

3. The gelling agent additive of claim 1, wherein the
 15 reaction product has the following general formula:

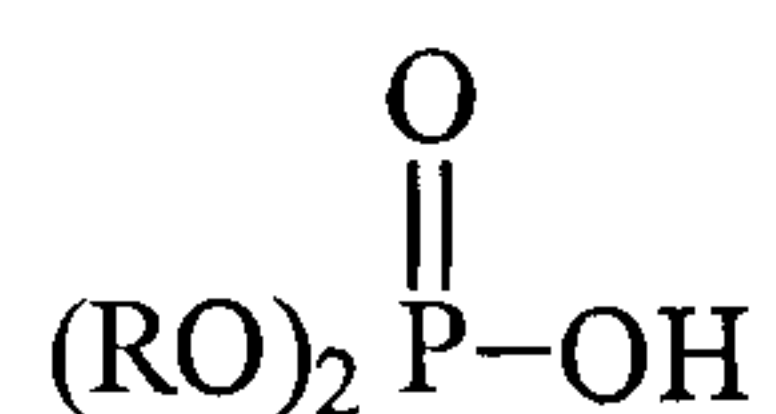


wherein:

R₁ is CH₃ or C₂H₅; and

20 a is an integer ranging from 13 to 450.

4. A gelling agent composition comprising the additive of any one of claims 1 to 3, reacted with a low molecular weight phosphate ester acid having the following general formula:

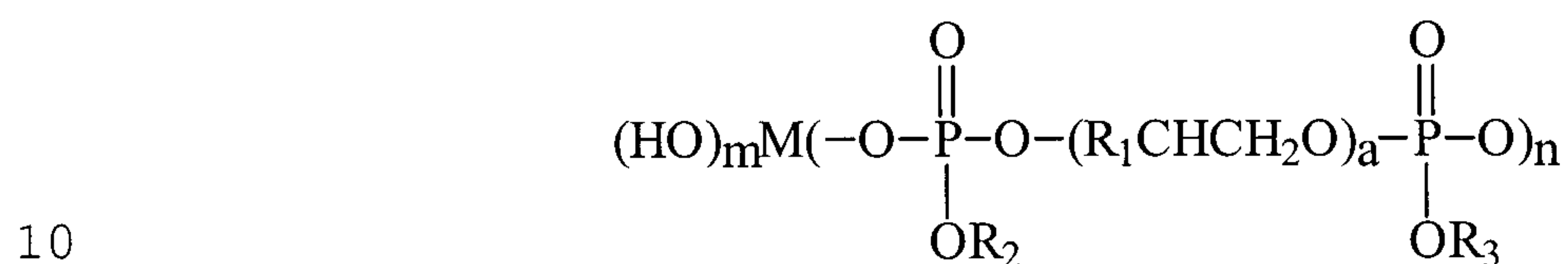


76340-9

wherein R is an alkyl or aryl group having up to 24 carbon atoms, the product of which is further reacted with a base selected from the group consisting of aluminum and ferric compounds.

- 5 5. A gelling agent composition for a hydrocarbon liquid, comprising:

(a) from 0.05 to 20 wt% of a compound having the following general formula:



wherein:

a is an integer ranging from 13 to 450,

m + n = 3,

m = 0 to 2,

15 n = 1 to 3,

R₁ is CH₃ or C₂H₅,

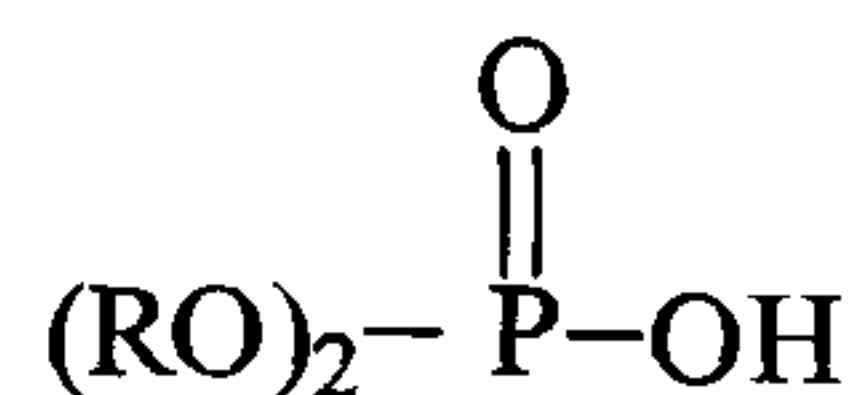
M is Al⁺⁺⁺ or Fe⁺⁺⁺,

R₂ is H, or an alkyl or aryl group having up to 24 carbon atoms, and

20 R₃ is H, or an alkyl or aryl group having up to 24 carbon atoms; and

(b) from 80 to 99.95 wt% of a compound having the following general formula:

76340-9



wherein R is an alkyl or aryl group having up to 24 carbon atoms.

5 6. The gelling agent composition of claim 5, wherein M is Al⁺⁺⁺, and R₂ and R₃ are independently C₂ to C₁₀ alkyl groups.

7. The gelling agent composition of claim 5 or 6, wherein compound (a) comprises from 0.5 to 6.0 wt% of the
10 gelling agent and compound (b) comprises from 99.5 to 94 wt% of the gelling agent.

8. The gelling agent composition of any one of claims 5 to 7, wherein m = 2 and n = 1.

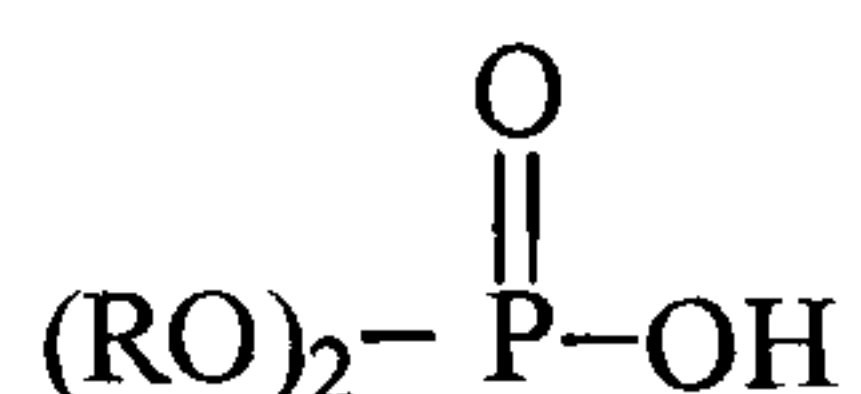
9. A gelled hydrocarbon liquid, comprising:

15 (a) a hydrocarbon liquid;

(b) a gelling agent, comprising:

(i) from 0.1 to 10 wt% of the additive of any one of claims 1 to 3, and

(ii) 90 to 99.9 wt% of low molecular weight
20 diester phosphate having the following general formula:



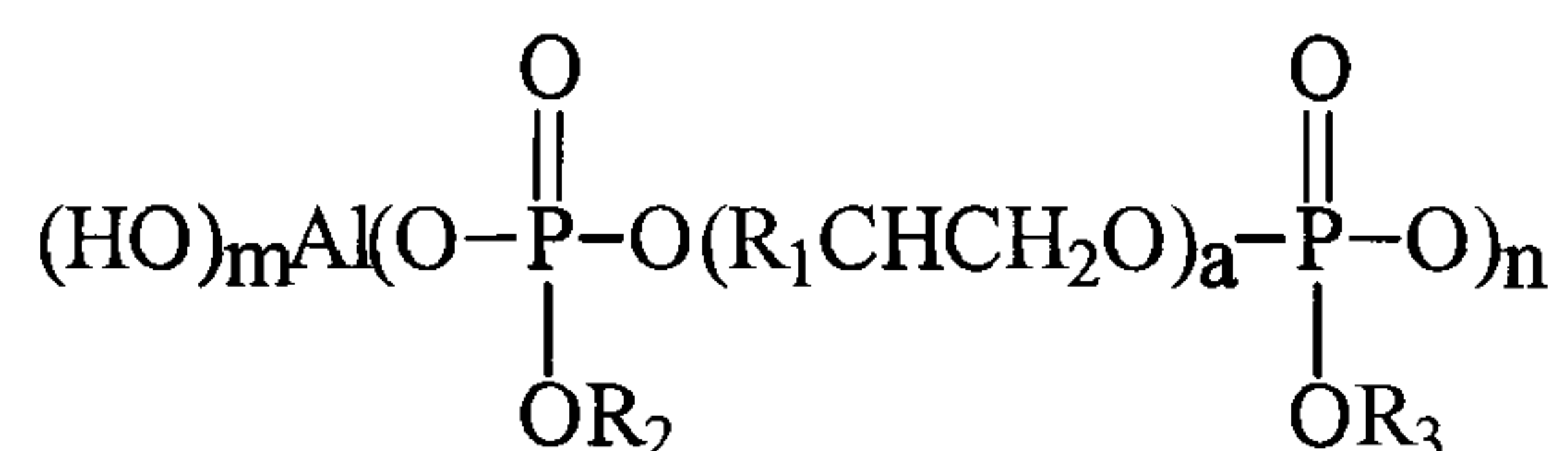
wherein R is an alkyl or aryl group having up to 24 carbon atoms; and

25 (c) a basic compound selected from the group consisting of aluminum and ferric compounds.

76340-9

10. The gelled hydrocarbon of claim 9, wherein R is a C₆ to C₁₀ alkyl group, or a mixture of C₆ to C₁₀ alkyl groups.

11. The gelled hydrocarbon liquid of claim 9, wherein the basic compound is an Al⁺⁺⁺ source, wherein the reaction
5 product of the additive and the Al⁺⁺⁺ source produces a salt having the following general formula:



wherein:

10 a is an integer having a value sufficient to provide the additive of claim 1 with a molecular weight of 6,000 to 26,000,

$$m + n = 3,$$

$$m = 0 \text{ to } 2,$$

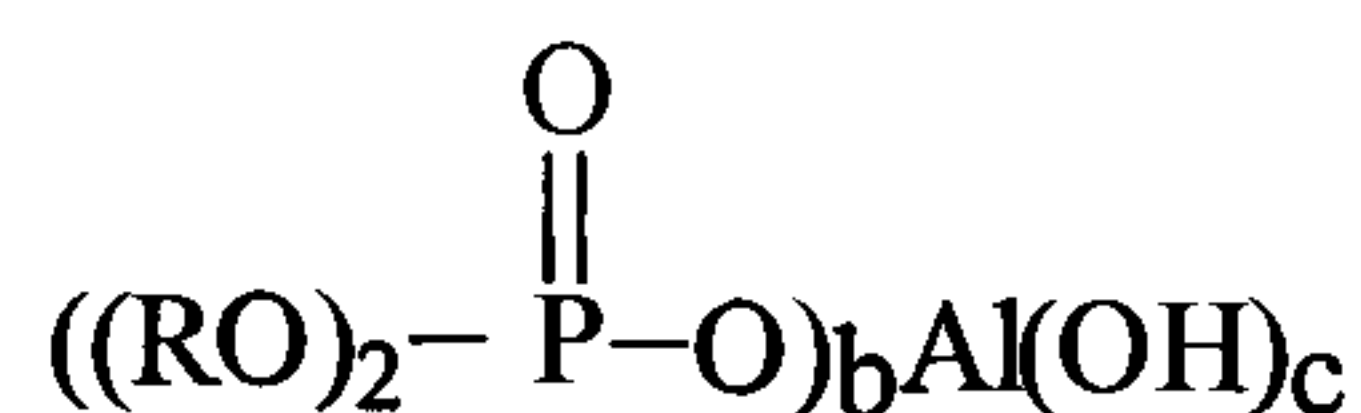
15 $n = 1 \text{ to } 3,$

R₁ is CH₃ or C₂H₅,

R₂ is H or a C₂ to C₁₀ alkyl group, and

R₃ is H or a C₂ to C₁₀ alkyl group; and

the low molecular weight diester reacts with the Al⁺⁺⁺ source
20 to produce a salt having the following general formula:



wherein:

$$b \text{ is } 1 \text{ to } 3,$$

76340-9

c is 0 to 2,

b + c = 3, and

R is a mixture of C₆ to C₁₂ alkyl groups.

12. The gelled hydrocarbon liquid of claim 11, wherein
5 n is 2.

13. The gelled hydrocarbon liquid of any one of
claims 9 to 12, wherein the gelling agent is present in the
hydrocarbon liquid in a sufficient amount to provide the
hydrocarbon liquid with a viscosity of at least 50 cps at
10 100°F when measured at 118 rpm with a Fann 50 C viscometer
at r₁b₅ rotor/bob configuration.

14. A method of preparing a gelled hydrocarbon liquid,
comprising the steps of:

(a) preparing the ester additive of claim 1, by
15 reacting a C₃ or C₄ polyalkylene glycol having a molecular
weight of 1,000 to 26,000 with P₂O₅;

(b) preparing a diester phosphate acid having the
following general formula:



wherein R is an alkyl group having up to 24 carbon
atoms;

(c) reacting the additive of step (a) with the
diester acid of step (b) to form a mixed ester;

25 (d) reacting the product of step (c) with a basic
compound containing aluminum or ferric ions; and

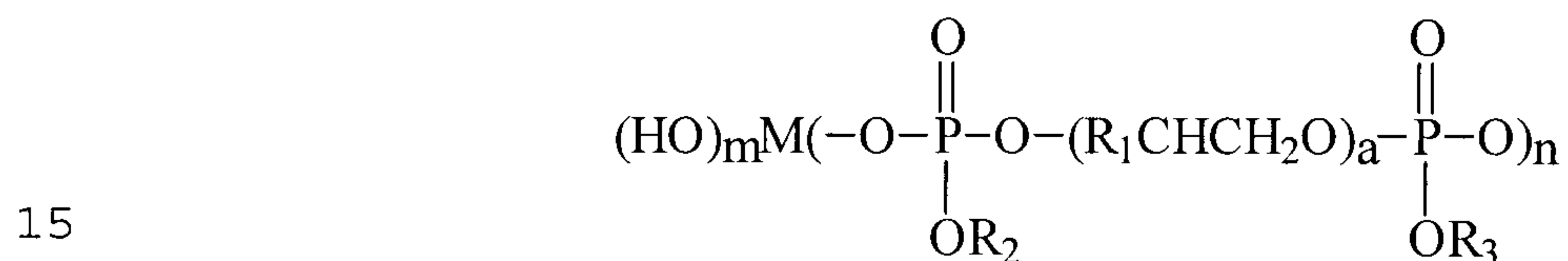
76340-9

(e) adding the product of step (c) to the hydrocarbon liquid before or after the reaction of step (d) in a sufficient amount to substantially increase the viscosity of the liquid.

5 15. The method of claim 14, wherein the reaction of step (d) is carried out before introduction into the hydrocarbon liquid.

16. The method of claim 14, wherein the reaction of step (d) is carried out after introduction into the
10 hydrocarbon liquid.

17. The method of any one of claims 14 to 16, wherein the mixed ester comprises 0.1 to 10 wt% of an ester having the following general formula:



wherein:

a is an integer ranging from 13 to 450,

m + n = 3,

m = 0 to 2,

20 n = 1 to 3,

R₁ is CH₃ or C₂H₅,

M is Al⁺⁺⁺ or Fe⁺⁺⁺,

R₂ is H, or an alkyl or aryl group having up to 24 carbon atoms, and

76340-9

R_3 is H, or an alkyl or aryl group having up to 24 carbon atoms.

18. The method of claim 17, wherein M is Fe^{+++} .

19. The method of claim 17, wherein M is Al^{+++} .

5 20. The method of any one of claims 17 to 19, wherein R_2 and R_3 comprise C_6 to C_{10} alkyl groups.

SMART & BIGGAR

OTTAWA, CANADA

PATENT AGENTS