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Whitney

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[54] **HYDROCARBON GELS**

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[21] Appl. No.: **386,950**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 231,746, March 3, 1972, Pat. No. 3,775,069.

[52] **U.S. Cl.** ..... **252/62.52,** 44/7 C, 44/7 D, 252/62.51, 252/62.53, 302/1

[51] **Int. Cl.** **H01f 1/28**

[58] **Field of Search** ..... 252/61.51, 62.52, 62.53; 44/7 C, 7 D

[56] **References Cited**

UNITED STATES PATENTS

3,505,374	4/1970	Monroe	260/439 R
3,531,413	9/1970	Rosensweig	252/62.51
3,615,285	10/1971	Whitney et al	44/7 C
3,700,595	10/1972	Kaiser	252/62.51

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[57] **ABSTRACT**

A composition of matter comprising a gelatinous hydrocarbon containing a minor amount of a compound having either the formula MOR or

$$R''_x(QA)_nOM$$
$$\quad\quad\quad|$$
$$\quad\quad(R''')_y$$

in combination with a compound having the formula $M'(OR')_3$ wherein M is one selected from the group consisting of Group IA metals; M' is one selected from the group consisting of Group IIIA metals; R and R' are independently selected from the group consisting of C_1–C_{25} straight or branched hydrocarbyl radicals; R'' and R''' are the same or different wherein each is a C_1–C_{16} straight or branched hydrocarbyl radical; Q is O or N; A is a hydrocarbyl group containing from 2 to 4 methylenic carbon atoms having 0 to 2 substituents, said substituents being one selected from the group consisting of C_1–C_6 alkyl, C_3–C_6 cycloalkyl, phenyl, C_2–C_6 alkenyl, C_2–C_6 alkynyl, Cl, Br, I; *n* is an integer ranging from 1 to 10 inclusive; *x* is an integer and is either 1 or 2 depending on the valence of Q; *y* is either 0 or 1 depending on the valence of Q; in combination with iron powder to provide the composition with magnetic properties.

3 Claims, No Drawings

HYDROCARBON GELS

CROSS REFERENCE TO RELATED CASE

This application is a continuation-in-part of application Ser. No. 231,746, filed Mar. 3, 1972, now U.S. Pat. No. 3,775,069.

BACKGROUND OF THE INVENTION

The gelatinization of hydrocarbons has been attempted repeatedly in the past. An almost endless variety of compounds have been utilized in order to effect the gelatinization; they include soap powder, beeswax, various alcohols, waxes, organic acids and bases, cellulose nitrate, soaps, high polymers, etc. These compounds have met with varying degrees of success but were deficient because generally a relatively large quantity of gelling agent was required to give satisfactory results and the hydrocarbon gels were quite temperature sensitive. In addition, the original fluidity of the hydrocarbon could not be restored.

There is a definite need for a technique to gelatinize hydrocarbons; the primary use for such gelatinized hydrocarbons would be in the fuels area. Specifically, helicopter fuels would have to be confined as much as possible if the fuel tank enclosing them were to be perforated. In the event that gasoline or jet fuel were to spray, the destruction caused by a fire would be increased several-fold.

There are, however, many areas outside of fuel consumption where it would be desirous to gelatinize a hydrocarbon such as in preparing a fluid for hydraulic gas or oil well fracturing or in greases, where it is required that the gels have a reduced water sensitivity. The preparation of the hydrocarbon gels are described in detail in U.S. Pat. No. 3,615,285. The subject inventive concept relates to an improvement in the composition by reducing its water sensitivity and providing it with magnetic properties.

SUMMARY OF THE INVENTION

A composition of matter comprising a gelatinous hydrocarbon containing a minor amount of a compound having either the formula MOR or

$$R''_x(QA)_nOM \quad \text{or} \quad \begin{matrix} R''_x(QA)_nOM \\ | \\ (R''')_y \end{matrix}$$

in combination with a compound having the formula $M'(OR')_3$ wherein M is one selected from the group consisting of Group IA metals; M' is one selected from the group consisting of Group IIIA metals; R and R' are independently selected from the group consisting of C_1–C_{25} straight or branched hydrocarbyl radicals; R'' and R''' are the same or different wherein each is a C_1-C_{16} straight or branched hydrocarbyl radical: Q is O or N; A is a hydrocarbyl group containing from 2 to 4 methylenic carbon atoms having 0 to 2 substituents, said substituents being one selected from the group consisting of C_1-C_6 alkyl, C_3-C_6 cycloalkyl, phenyl, C_2-C_6 alkenyl, C_2-C_6 alkynyl, Cl, Br, I; n is an integer ranging from 1 to 10 inclusive; preferably *n* is 1 to 3 inclusive; *x* is an integer and is either 1 or 2 depending on the valence of Q; *y* is either 0 or 1 depending on the valence of Q; in combination with either an effective amount of a dehydrating agent sufficient to prevent hydrolytic degelation or iron powder to provide the composition with magnetic properties. These hydrocarbons may be liquid under ambient

conditions or may be liquefied by means of pressure addition. The hydrocarbons may be aromatic or aliphatic which would include both saturated and unsaturated compounds as well as cyclic hydrocarbons. It is preferred that aromatics which are to be utilized be in the range of C_6 through C_{25} such as benzene, toluene, xylene, tetralin, alkyl tetralins, indane, indene, indole, etc. Substituted aromatics in which hydrogen is replaced with any of the following C_1 to C_{10} alkyl, alkenyl or naphthenic radical, Cl, Br, NO_2, CN, etc. may also be gelatinized effectively by the process of the instant invention. Regarding the aliphatic compounds, they include C_1 through C_{25} alkanes and alkenes, normal and branched chain as well as cyclic. Specific compounds which fall within these categories and would be preferred are the C_3 to C_{20} alkanes and alkenes as exemplified by the following: propane, butane, pentane, hexane, cyclohexane, cyclohexene, methylcyclopentane, decane, decalin, cetane, 1-heptene, 4-nonene, isooctane, n-octylcyclohexane, 1,4-di-n-butylcyclohexane, norbornene.

Substituted alkanes in which one or more hydrogens have been replaced by halogen such as Cl, Br, NO_2, CN, etc. may also be utilized.

Gelatinization of mixtures of various types of hydrocarbons are also intended to be within the scope of this invention. Thus, the hydrocarbon may encompass a kerosene fraction which boils between 150° and 350°C. or naphtha boiling between 30° and 150°C. or diesel fuel typically characterized as having a cetane number of 50, a boiling range of 180° to 350°C. and a gravity of 37. The hydrocarbon mixture may also be liquefied petroleum gas (LPG) which is generally about 95% C_3 hydrocarbons with the remaining 5% split half and half between C_2 and C_4 hydrocarbons.

In particular, jet fuels which may overlap both of the above ranges are intended to be included within the instant invention.

The two compositions needed to effect the gelling are either MOR or

$$R''_x(QA)_nOM \quad \text{or} \quad \begin{matrix} R''_x(QA)_nOM \\ | \\ (R''')_y \end{matrix}$$

in combination with $M'(OR')_3$. Such combination is necessary for the gelling to be effected within the hydrocarbon; that is to say, if either one of the two compounds are not present with the $M'(OR')_3$, the hydrocarbon will not gel. The degree of gelling within the hydrocarbon will be dependent upon the particular elements utilized within the formulae, this will be discussed in more detail below.

Turning to the gelling compositions M may be any group IA metal, i.e. lithium, sodium, or potassium. Lithium is preferred if it is desirous to have a more viscous hydrocarbon based on the total weight per cent of gelling reagents added to the hydrocarbon. M' may be any Group IIIA metal, preferably boron or aluminum.

R and R' are independently selected from the group consisting of C_1 to C_{25} hydrocarbyl radicals. Specifically, C_1 through C_{20} hydrocarbyl radicals are preferred. This would include C_6 through C_{20} aryl radicals, including anthracene and naphthalene. Other aryl radicals which may be utilized include the following: $C_6H_5CH_2$, $C_6H_5(CH_2)_n$ where $n = 2$ to 14.

Alkyl and alkenyl radicals may also be utilized for R and R', it is preferred that the alkyl and alkenyl radicals are C_4 to C_{16} radicals. Most preferred radicals for R are C_8 to C_{16} alkyl radicals either normal or branched; most preferred radicals for R' are the C_4 to C_8 alkyls normal and branched. Cyclo alkyl radicals and cyclo alkenyl radicals may also be utilized for R and R'. The cyclic radicals would fall within the range of C_3 to C_{15}, preferably C_5 to C_{10} and most preferably C_5 to C_6. Typical cyclic alkyl and alkenyl radicals which may be utilized are the following: cyclopentyl, cyclohexyl.

In the hydrocarbon gelling reagent having the general formula $ROM + M'(OR')_3$, R may also be derived from monoethers of polyalkyleneoxides such as polyethylene oxide, polypropylene oxide, polystyrene oxide, etc., as well as from amino alcohols. The alkoxides of the monoethers of polyalkylene oxides may be characterized by the formula

$$R''_x(QA)_nOM$$
$$(R''')_y$$

where Q is O or N, R'' and R''' are the same or different C_1 to C_{16} hydrocarbon radical straight or branched, A is a hydrocarbon group containing 2 to 4 methylenic carbon atoms having 0 to 2 substituents each containing 1 to 6 carbon atoms, M is a Group IA metal, preferably lithium or sodium, *n* is an integer ranging from 1 to 10 inclusive, preferably *n* is 1 to 3 inclusive; *x* is an integer and is either 1 or 2 depending on the valence of Q and *y* is either 0 or 1 depending on the valence of Q.

Alkoxides derived from monoethers of polyalkylene oxides can be liquid compounds having high hydrocarbon solubility. This property is particularly desirable for the convenience it lends to the preparation of thickened or gelled hydrocarbons. Such convenience is most desirable in field operations such as gas and oil well fracturing.

The molar ratio of the two gelling compounds may be varied from 3:1 to 1:3 equivalents of either MOR or

$$R''_x(QA)_nOM$$
$$(R''')_y$$

to $M'(OR')_3$. Preferably a 1:1 molar ratio is employed.

The weight per cent of gelling reagents employed may be varied from ¼ to 5%. The preferred range is ½ to 3% and the most preferred range is ¾ to 2% based on the total weight of hydrocarbon to be gelled.

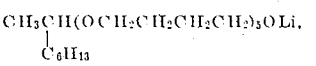
Thus, from the above preferred compounds having the designation MOR are as follows: n-—C_4H_9OLi, tert—C_4H_9OLi, n—$C_8H_{17}OLi$, 2—$C_8H_{17}OLi$, N—$C_{16}H_{33}OLi$, $C_6H_{11}OLi$, 2-ethylhexyl-OLi, iso-hexadecyl OLi, tert—C_4H_9ONa, 2—$C_8H_{17}ONa$.

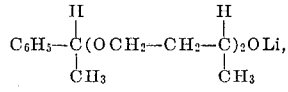
The preferred compounds having the formula $M'(OR')_3$ are as follows: $B(OCH(CH_3)_2)_3$, $B(OC4H_9)_3$, $B(OC_6H_{11})_3$, $B(OC_{16}H_{33})_3$, $Al(O—sec—C_4H_9)_3$, $B(2—OC_8H_{17})_3$, $Al(OCH(CH_3)_2)_3$, $Al(OC_{16}H_{33})_3$.

Preferred compounds having the designation

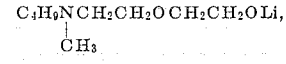
$$R''_x(QA)_nOM$$
$$(R''')_y$$

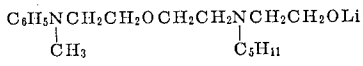
are as follows: $CH_3(CH_2)_3OCH_2CH_2OLi$, $CH_3(CH_2)_3OCH_2CH_2OCH_2CH_2OLi$, $CH_3OCH_2CH_2ONa$, $CH_3(CH_2)_3OCH_2CH(C_6H_5)OLi$, $CH_3(CH_2)_{15}OCH(CH_3)CH(CH_3)ONa$,





$CH_3(OCH_2CH_2)_{10}OLi$, $(CH_3)_2NCH_2CH_2OLi$,





The hydrocarbon gel may be prepared by combining separate solutions of the two compounds. The compound MOR may be suspended or dissolved in one part of the hydrocarbon to be gelled and the compound $M'(OR')_3$ is dissolved in a separate portion of the same or a different hydrocarbon and the two are combined with stirring at below or above ambient temperature. Pressure may vary from subatmospheric to superatmospheric but ambient pressure is preferred. Alternatively, the compound designated as MOR may be formed in situ by conversion of a hydrocarbon solution of a proper alcohol into its alkoxide by addition of an appropriate reagent such as n-butyl lithium and then adding to the hydrocarbon alkoxide solution or suspension the other compound either neat or as a solution in the same or a different hydrocarbon.

During the addition of the compounds to the hydrocarbon, temperatures should be between −80° and +200°C., preferably 0° to 120°C. and most preferably 20° to 30°C.

The gel takes from a few seconds to 30 minutes to form. Typically, the two compounds are added all at once with stirring.

In order to restore the original fluidity of the hydrocarbon the following technique is utilized:

To the gel is added a sufficient quantity (i.e. 5 to 1000 moles in excess of the quantity of MOR and $M'(OR')_3$ present in the gel) of a polar material such as water or methanol and the entire mixture is thoroughly mixed.

If it is desired to restore only part of the original fluidity of the hydrocarbon, a gel may be diluted with the same or a different hydrocarbon, with thorough mixing until the desired viscosity is obtained, or by addition of less than 5 moles polar material.

To make the improved hydrocarbon gel of the subject invention, a dehydrating agent in an amount sufficient to resist hydrolytic degelation is incorporated with the two gelling compounds described hereinabove. The dehydrating agent can be one selected from the group consisting of powdered $CaCl_2$, $MgSO_4$, Ca_2C, Na_2SO_4, CaO, NaOH, KOH, P_2O_5, boric anhydrides, $CaCO_3$, $ZnCl_2$ and BaO. It is to be understood that whatever is added to the gel would have to be compatible with the gel forming reagents and the gel network or else the gel would be destroyed. Those materials which have been found to not be compatible with the

gelling reagents are protonic acids such as H_2SO_4 and H_3PO_4, as well as reactive metals such as sodium and very strong oxidizing agents such as $Mg(ClO_4)_2$.

The added reagents or dehydrating agents will preferentially react with water or other polar materials thus affording the hydrocarbon gel an increased resistance to hydrolysis and/of reduction in viscosity. In addition, the dehydrating agent could also serve as a pore plugging agent in applications of the hydrocarbon gels for gas and oil well fracturing. Such a use wherein the components are MOR and $M'(OR')_3$ is described in a copending patent application bearing Ser. No. 231,525 filed on Mar. 3, 1972.

The same considerations apply to the use of the gels in secondary oil recovery applications.

The amount of the dehydrating agent employed in the gel ranges from 0.1 wt. to 90 wt. %, preferably from 0.5 wt. to 10 wt. % which depends upon how great an increased resistance to hydrolytic degelation is desired.

A gas or oil well fracturing fluid using the improved gels of this invention may be composed of from 1 to about 90% by weight of sand or other coarse solid material.

Another type of improved gel of this invention is a magnetic hydrocarbon gel which is prepared by incorporating iron powder or other ferromagnetic materials in a gel produced by the method described hereinabove. Such magnetic gels could have uses in electrical and electronic devices or in magnetic field displays. Other uses could include lifting or transporting hydrocarbons by means of magnetic and electric fields, fluids for magnetic clutches and fluids for sealing rotary motion feed-throughs into vacuum chambers. Another use for the magnetic hydrocarbon gels of this invention could be in the area of coating magnetic materials onto substrates using a hydrocarbon having a low boiling point such as pentane.

The amount of magnetic material such as iron filings contained in the gel may range from 0.1 to 95% by weight, preferably from 1% to 20% by weight.

The following examples are employed to demonstrate the applicability of the subject invention.

Example 1

To 24 grams of n-heptane was added 0.25 g of $C_{16}H_{33}OLi$ (1.0 mmole), the mixture was heated with stirring to 60°C. and 2.35 g of anhydrous Na_2SO_4 was added. To the alkoxide solution containing Na_2SO_4 was added a solution of 0.23 g (1 mmole) of $B(OC_4H_9)_3$ in enough heptane to make 24 g of solution. A gel was nearly instantly produced and the stirring bar was removed after 10 seconds leaving a soft gel with Na_2SO_4 evenly distributed. After 24 hours no settling of the Na_2SO_4 was evident. The Na_2SO_4 content of gel was 5 weight per cent.

The gel was aged for 46 days with frequent shaking in order to determine if the added Na_2SO_4 would have any deleterious effect on the gel properties. No such effect was detected.

Water, 0.5 ml, was then injected into the gel through a septum in the cap of the container and the whole was shaken vigorously for 15 minutes. The gel did not break down in that time. It did break down after about 1 hour of alternate periods of shaking and standing.

However, as compared to the control which was an identical heptane gel, the above gel was much more water resistant. The control gel upon addition of 0.5 ml of water followed by shaking broke down in several seconds.

EXAMPLE 2

A gel was prepared similar to that described in Example 1 except that 4.7 g of CaO was added to the alkoxide solution. (A separate gel was also prepared, but the CaO (4.7g) was added to the borate solution to demonstrate that gel formation would occur regardless of which reagent of the gelling reagents the dehydrating agent was added to.) The gel contained 10 per cent by weight of CaO.

The gel was aged 46 days and no change in its properties was noted. Water, 0.5 ml was then added and the mixture was vigorously shaken for 45 minutes. It did not break down in that time. After about 1 hour the gel did break down nevertheless it was much more stable toward water than an identical gel without added CaO.

EXAMPLE 3

A gel was prepared similar to that described in Example 1 except that 4.7 g of powdered $CaCl_2$ was incorporated in the gel. The gel was aged 46 days and no change in its properties was noted. To the gel was then added 0.75 ml of water and the whole was shaken for 2 hours. It became slightly less viscous but did not break down. After three days it did break down. However, the gel was very much more resistant to the effects of water than an identical gel without added $CaCl_2$.

EXAMPLE 4

Two separate samples of gelled heptane were prepared using $C_{16}H_{33}OLi$ and $B(OC_4H_9)_3$ as the gelling reagents at a 1 weight per cent level.

To one gel sample was added 4.7 g of $MgSO_4$ and to the other was added 4.7 g of Al_2O_3. Both samples were thoroughly mixed and each contained 10% by weight of the dehydrating agent. Both gel samples slowly ungelled upon standing and after 7 days the samples were no longer viscous.

This example demonstrates that not all dehydrating agents are compatible with the gelling reagents for a long period of time.

EXAMPLE 5

0.25 g (1 mmole) of $C_{16}H_{33}OLi$ was dissolved in 24 g of heptane heated to 60°C. and to the solution was added 4.7g of iron powder followed by 0.23g of $B(OC_4H_9)_3$ in 24 g of heptane. A gel formed instantly which was shaken well to get a good dispersion of the iron powder. The gel was attracted by a magnet and when the magnet was moved up the side of the glass jar containing the gel, the gel was pulled up far above its original level. The iron particles could be seen to align in the magnetic flux like iron filings on a sheet of paper over a magnet except that in the gel the particle pattern was three dimensional.

EXAMPLE 6

A gel was prepared as described in Example 5 except that benzene was the hydrocarbon and 15.67 g of iron powder was incorporated uniformly throughout the gel. The 4 oz. glass jar containing the gel could be lifted and held in midair by a small horseshoe magnet.

While the above Examples of improved gels having increased resistance to hydrolytic degelation employ particular weight per cents of dehydrating agents, this invention is not limited to those amounts. The amount of the dehydrating agent employed may be from 0.1 wt. per cent to 90 wt. per cent depending upon how great an increased resistance to hydrolytic degelation is desired.

In the case of the magnetic gels, the amount of magnetic material, such as iron filings, contained in the gel may range from 0.1 to 95 weight per cent.

Other dehydrating agents that may be used include NaOH, KOH, P_2O_5, boric anhydride, $ZnCl_2$, $CaSO_4$ and BaO. Those which cannot be used are protonic acids such as H_2SO_4 and H_3PO_4 as well as reactive metals such as sodium and very strong oxidizing agents such as $Mg(ClO_4)_2$.

A gas or oil well fracturing fluid using the improved gels of this invention may be composed of from 1 to ca. 90% by weight of sand or other coarse solid material.

EXAMPLE 7

To a solution of 1.83 g (15.5 mmoles) of 2-butoxyethanol ($CH_3(CH_2)_3OCH_2CH_2OH$) in 20 ml of pentane was added 15.5 mmoles of butyl lithium solution dropwise with stirring. The reaction mixture was stirred for one hour after addition of butyl lithium was complete and then the solvents were stripped off under reduced pressure leaving 1.87 g of clear, slightly viscous alkoxide.

A 0.18 g (1.47 mmole) portion of the above lithium alkoxide was dissolved in enough heptane to make 26 g of clear colorless solution. A solution of 0.34 (1.47 mmole) of $B(OC_4H_9)_3$ in 26 g of heptane was prepared and the two solutions were combined with stirring. A very viscous clear liquid resulted. After standing for 10 minutes the material was a soft gel containing 1 weight per cent of gelling reagents.

EXAMPLE 8

The lithium alkoxide of 2-(2-butoxyethoxy)-ethanol [i.e., $CH_3(CH_2)_3OCH_2CH_2OCH_2CH_2OLi$)], 2.54 g, was prepared from 2.51 g of 2-(2-butoxyethoxy)ethanol by the procedure described in Example 7.

A 0.22 g (1.31 mmole) portion of the alkoxide was dissolved in 26 g of heptane and to the solution was added 0.30 g (1.31 mmole) of $B(OC_4H_9)_3$ also dissolved in 26 g of heptane. Instant thickening occurred when the two solutions were combined and after 10 minutes a soft gel resulted.

EXAMPLE 9

The lithium alkoxide of $(CH_3)_2NCH_2CH_2OH$, 1.45 g, was prepared from 1.38 g of the amino alcohol by the procedure described in Example 7.

A 0.15 g portion of the alkoxide ($(CH_3)_2NCH_2CH_2OLi$) was dissolved in enough heptane of make, 26 g of solution. To the alkoxide solution was added a solution of 0.37 g of tri-n-butyl borate ($B(OC_4H_9)_3$) in 25.6 g of heptane with stirring. After 2 minutes, the heptane was a very viscous fluid.

What is claimed is:

1. A magnetic composition of matter comprising a gelatinous hydrocarbon containing an amount ranging from ¼ to 5 % by weight of said hydrocarbon, of a compound having either the formula MOR or

$$R''_x(QA)_nOM$$
$$|$$
$$(R''')_y$$

in combination with a compound having the formula $M'(OR')_3$ in a molar ratio ranging from 3:1 to 1:3 equivalents of either MOR or

$$R'_x(QA)_nOM$$
$$|$$
$$(R''')_y$$

to $M'(OR')_3$, wherein M is one selected from the group consisting of Group IA metals; M' is one selected from the group consisting of Group IIIA metals; R and R' are independently selected from the group consisting of C_1–C_{25} straight or branched hydrocarbyl radicals; R'' and R''' are the same or different wherein each is a C_1–C_{16} straight or branched hydrocarbyl radical; Q is O or N; A is a hydrocarbyl group containing from 2 to 4 methylenic carbon atoms having 0 to 2 substituents, said substituents being one selected from the group consisting of C_1–C_6 cycloalkyl, phenyl, C_2–C_6 alkenyl, C_2–C_6 alkynyl, Cl, Br, I; *n* is an integer ranging from 1 to 10 inclusive; *x* is an integer and is either 1 or 2 depending on the valence of Q; *y* is either 0 or 1 depending on the valence of Q; in combination with an iron powder or other ferromagnetic material to provide the composition with magnetic properties.

2. A composition of matter according to claim **1** wherein the minor compound has the formula

$$R''_x(QA)_nOM$$
$$|$$
$$(R''')_y$$

3. A composition according to claim **1** wherein the amount of the composition having the formula $M'(OR')_3$ is in a molar ratio of 1:1 equivalents of either MOR or

$$R'_x(QA)_nOM$$
$$|$$
$$(R''')_y$$

to $M'(OR')_3$.

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