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[54] **HYDROCARBONS GELLED WITH ALKOXY COMPOUNDS CONTAINING TWO DIFFERENT METALS**
18 Claims, No Drawings

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[56] **References Cited**

UNITED STATES PATENTS

2,492,173	12/1949	Mysels	44/7 A
2,618,536	11/1952	Hunn	44/7 A
2,751,284	6/1956	Hill et al.	44/7 A
3,488,370	1/1970	Leary et al.	44/7 A

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ABSTRACT: Liquid hydrocarbons may be increased in viscosity to a desired degree by combining the liquid with a gelling composition of the general formula MOR and $M'(OR')_3$ where M is a Group I metal and M' is a group III metal. R and R' are independently selected from C_1 to C_{25} hydrocarbyl radicals.

HYDROCARBONS GELLED WITH ALKOXY COMPOUNDS CONTAINING TWO DIFFERENT METALS

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. In particular, there is need for paints which tend not to drip or spill readily.

In addition, the problem of oil spills has recently been given a great deal of attention. Leaks developing within tankers have caused destruction to nearby beaches. Utilizing the process of the instant invention, in which fuels may successfully be gelatinized so that their mobility is severely hindered in the event of any destruction in a tanker hull would certainly be important in our modern age. Needless to say, the same technique could be used to restrict fuel from flowing freely out of a puncture in any storage tank.

Thus, it is readily apparent, that a process is needed for gelatinizing a hydrocarbon which process will not suffer from the disadvantages of the prior techniques.

SUMMARY OF THE INVENTION

According to the instant invention, it has unexpectedly been discovered that when liquid hydrocarbons, either aromatic or aliphatic, are combined with a two-element gelling composition; one element of the general formula MOR and a second element having the general formula $M'(OR')_3$ where M is a Group 1A metal preferably selected from Na or Li, M' is a Group IIIA metal preferably selected from boron or aluminum and R and R' are independently selected from the group consisting of C_1 to C_{25} hydrocarbyl radicals. A composition results which will promptly be transformed into a gelatinous mass. The degree of viscosity of the mass may be controlled by the amount of reagents added to the hydrocarbon and the nature of the reagents added.

In more detail, the instant invention pertains to a method for gelatinizing liquid hydrocarbons. These hydrocarbons may be liquid under ambient conditions or may be liquified 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-heptane, 4-nonene, isooctane, n-octylcyclohexane, 1,4-di-n-butylcyclohexane, norbornane.

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. as well as naphtha boiling between 30° and 150° C.

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 have the general formulae MOR and $M'(OR')_3$. Both of the above compounds are necessary for the gelling to be effected within the hydrocarbon; that is to say, if either of the two compounds is not present 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 1A 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 percent of gelling reagents added to the hydrocarbon. M' may be any Group IIIA metal, preferably boron or aliminum.

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. Cycloalkyl radicals and cycloalkenyl 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.

The molar ratio of the two gelling compounds may be varied from 3:1 to 1:3 equivalents of MOR to $M'(OR')_3$. Preferably a 1:1 molar ratio is employed.

The weight percent of gelling reagents employed may be varied from one-fourth to 5 percent. The preferred range is one-half to 3 percent and the most preferred range is three-fourth to 2 percent 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, CH_3ONa, 2-C_8H_{17} ONa. The preferred compounds having the formula $M'(OR')_3$ are as follows: $B(OC_4H_9)_3$, $B(OC_6H_{11})_3$, $B(OC_{16}H_{33})_3$, $Al(O\text{-}sec\text{-}C_4H_9)_3$ $B(2OC_8H_{17})_{23}$, $Al(OCH(CH_3)_{23}$, $Al(OC_{16}H_{33})_3$.

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 1,000 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.

SPECIFIC EMBODIMENTS

Example 1

Utilizing a glass vial at ambient conditions, the following experiment was performed:

To 3 ml. of benzene was added 0.04 g. (1 mmole) of LiOMe, prepared by the reaction of 3 tetramethylethylenediamine $LiNMe_2$ and $B(OMe)_3$, and 0.23 g. (1 mmole) $B(OC_4H_9)_3$. The mixture was shaken and the LiOMe dissolved yielding a very viscous clear product. Upon inversion of the sample 30 seconds were required for the benzene to flow to the opposite end of a small vial. An air bubble required about 2.5 minutes to travel 1.5 inches in this product.

Example 2

A 2 mm. diameter applicator stick was used to remove about 0.4 g. of the viscous benzene prepared in example 1 and transfer it to a second clean vial. To the latter was added 3.5 ml. of reagent grade n-hexane. The benzene-hexane mixture was shaken for a few minutes and the entire contents of the vial became very viscous and gellike. The material flowed slowly and when the vial was tapped its contents vibrated. This behavior demonstrates that gels produced by means of this invention are viscoelastic and have an elastic structure over and above the normal elasticity of a liquid or of a solution of a polymer in a hydrocarbon.

The following experiments all took place in a 4- oz. glass jar at ambient conditions.

Example 3

Into 50 ml. of n-pentane was dispersed 0.0979 g. (2.58 mmole) of LiOMe and to the mixture was added a solution of 0.59 g. (2.58 mmole) of $B(OC_4H_9)_3$ in 27 ml. of pentane with stirring. A viscoelastic gel resulted which could be cut with a knife, was highly flammable and did not melt while burning. The concentration of gelling agent in this material was 0.033 molar or 1.43 wt. percent.

Example 4

A 0.1894 g. (5 mmole) portion of LiOMe was dispersed in 50 ml. of jet fuel. The jet fuel comprised paraffins 33.5%; monocycloparaffins 36.5%; dicycloparaffins 2.0%; alkyl benzenes 28.0% by weight and boiled between 30 and 225° C. 1.15 g. (5 mmole) of $B(OC_4H_9)_3$ was added and the mixture was diluted to 75 ml. with additional jet fuel with stirring. A soft, free-standing, solid gel resulted after the mixture was allowed to stand ½ hour. The total wt. percent of gelling agent used in this example was 2.33 percent. Thus, a liquid hydrocarbon mixture which is composed of many different components may be gelled by means of the invention.

Example 5

To 50 ml. of n-pentane was added 0.40 g. (5 mmole) of tert-BuOLi with stirring followed by 1.15 g. (5 mmole) $B(OC_4H_9)_3$ and an additional 25 ml. of pentane. Within 10 minutes the mixture set into a clear hard gel which vibrated when the side of the container was struck. The concentration of gelling reagents was 0.067 molar or 3.23 total wt. percent. Thus, a tertiary lithium alkoxide and a primary borate is an effective gelling combination for liquid hydrocarbons.

Example 6

0.69 g. (1.6 mmole) of n-BuLi solution was diluted with enough jet fuel from example 4 to make the total weight 14.66 g. To the solution was added 0.21 g. (1.6 mmole) of 1-octanol dissolved in 14.45 g. of jet fuel over a 5-minute period. A clear solution resulted to which was added 0.37 g. (1.6 mmole) of $B(OC_4H_9)B3$ as a solution in 28.94 g. of jet fuel. The mixture was stirred 10 seconds and allowed to stand at room temperature and a gel resulted. The concentration of the gelling reagent was 1 percent total wt./wt. Thus, MOR of the gelling composition may be prepared in situ. It is not necessary to prepare MOR separately and then add it to the hydrocarbon to be gelled.

Example 7

0.0971 g. (0.71 mmole) of $n\text{-}C_8H_{17}OLi$ was dissolved in 31.7 g. of the previously defined jet fuel and 0.22 g. (0.71 mmole) of tricyclohexyl borate was dissolved in a separate 31.7 g. portion of jet fuel. The borate solution was poured into the alkoxide solution and the whole was stirred 10 seconds and allowed to stand. After 10 minutes a clear viscous liquid was obtained. Thus, R' of $M'(OR')_3$ may be secondary cyclic alkyl radical.

Example 8

0.1876 g. (1.38 mmole) of $n\text{-}C_8H_{17}OLi$ was dissolved in 26.3 g. of the previously defined jet fuel and the solution was cooled to room temperature. To a separate 26.3 g. portion of jet fuel was added 0.34 g. (138 mmole) of $Al(O\text{-}sec\text{-}C_4H_9)_3$ and the two solutions were mixed and stirred for 10 seconds. A clear viscous liquid resulted at a total of 1 percent wt./wt. of gelling reagents. Thus, the gelling composition MOR and $M'(OR')_3$ may be composed of a primary lithium alkoxide and a secondary aluminate.

Example 9

By the same procedures as detailed in example 4, using the same jet fuel the following hydrocarbon gels were made:

Gelling reagents	Mole ratio of MOR to $M'(OR')_3$	Concentration total wt. percent	Hydrocarbon	Appearance
tert-BuOLi, $B(OC_6H_{11})_3$	1:1	1	Jet fuel	Granular gel.
LiOMe, $B(O\text{-}C_4H_9)_3$	1:1	½	do	Slightly thickened liquid.
tert-BuOLi, $B(OMe)_3$	1:1	1	Pentane	Do.
LiOMe, $B(O\text{-}C_4H_9)_3$	1:1	2	Tetrahydromethyldicyclopentadiene.	Semisolid gel.
tert-BuOLi, $B(OC_4H_9)_3$	1:1	2	Butane	Very hard gel.
tert-BuOLi, $B(OC_4H_9)_3$	1:2	1.2	Jet fuel	Medium hard gel.
tert-BuOLi, $B(OC_4H_9)_3$	2:1	1.2	do	Do.
tert-BuOLi, $B(OC_4H_9)_3$	1:1	¼	do	Viscous liquid.
$n\text{-}C_8H_{17}OLi$, $B(OC_6H_{11})_3$	1:1	1	Heptane	Soft gel.
$nC_8H_{17}OLi$, $B(OC_6H_{11})_3$	1:1	1	Toluene	Viscous granular gel.
$n\text{-}C_8H_{17}OLi$, $B(OC_6H_{11})_3$	1:1	1	Methylcyclohexane	Medium hard gel.
$n\text{-}C_{16}H_{33}OLi$, $B(OC_4H_9)_3$	1:1	1	Jet fuel	Medium soft gel.
$n\text{-}C_8H_{17}OLi$, $B(OC_6H_{11})_3$	1:1	1	Tetralin	Hard gel.
$n\text{-}C_8H_{17}OLi$, $B(OC_6H_{11})_3$	1:1	1	Decalin	Do.
$C_6H_{11}OLi$, $B(OC_6H_{11})_3$	1:1	1	Jet fuel	Viscous liquid.
sec-$C_8H_{17}OLi$, $B(OC_4H_9)_3$	1:1	1	do	Medium gel.
2-ethylhexylOLi, $B(OC_4H_9)_3$	1:1	1	do	Do.
Iso-hexadecylOLi, $B(OC_4H_9)_3$	1:1	1	do	Very viscous liquid.
$n\text{-}C_{16}H_{33}OLi$, $B(O\text{-}n\text{-}C_{16}H_{33})_3$	1:1	1	do	Moderately visccus liquid.
$n\text{-}C_{16}H_{33}OLi$, tri-2-octyl borate	1:1	1	do	Very viscous liquid.
$n\text{-}C_{16}H_{33}OLi$, $B(O\text{-}n\text{-}C_{16}H_{33})_3$	1:1	1	do	Very slight visous liquid.
tert-C_4H_9ONa, $B(OC_4H_9)_3$	1:1	1	do	Very viscous liquid.

Gelling reagents	Mole ratio of MOR to $M'(OR')_3$	Concentration total wt. percent	Hydrocarbon	Appearance
$n\text{-}C_8H_{17}OLi$, $Al(O\text{-}CH(CH_3)_2)_3$	1:1	1	do	Do.
$n\text{-}C_8H_{17}OLi$, Al (o-sec-butyl)$_3$	1:1	1	do	Do.
$n\text{-}C_{16}H_{33}OLi$, Al (o-sec-butyl)$_3$	1:1	1	do	Do.
LiO-2-octyl, Al(o-sec-butyl)	1:1	1	do	Soft gel.
CH_3ONa, $B(OC_4H_9)_3$	1:1	1	do	Moderately viscous liquid.
Li salt of l-menthol, $B(OC_4H_9)_3$	1:1	2	do	Very hard gel.

Example 10

0.3892 g. (4.86 mmole) of t-butyl OLi was dissolved in 36.5 ml. of pentane. To the solution was added 46 microliters of $(CH_3)_3COH$ (0.5 mmole) or 10 percent of an equivalent. To a separate 36.5 ml. portion of pentane was added 1.12 g. of $B(OC_4H_9)B3$ (4.86 mmole) and the two solutions were combined with stirring for 10 seconds. A clear hard gel resulted. Similarly gels were prepared which contained 20 percent and 30 percent of an added equivalent of $(CH_3)_3COH$ based on the quantity of lithium alkoxide present. All three runs were 1 percent total wt./wt. and all were gels. Thus an alkoxide used to gel a hydrocarbon by means of this invention need not be entirely free of carbinol.

Example 11

0.1330 g. (1.66 mmole) of $(CH_3)_3COLi$ was dissolved in 26 g. of the jet fuel of example 4 and to the solution was added 3 microliters of water (0.17 mmole of 10 percent of 1 equivalent of the alkoxide). To a separate 26 g. portion of jet fuel was added 0.38 g. (1.66 mmole) of $B(OC_4H_9)_3$, the two solutions were mixed and stirred for 10 seconds. After 10 minutes a soft gel was obtained. A run was also made using the same quantities of reagents, but the water was added to the borate solution before final mixing. A soft gel was also obtained in 10 minutes. In both runs the concentration of gelling reagents was 1 percent wt./wt. Thus an alkoxide or a borate used to gel a hydrocarbon by means of this invention need not be anhydrous.

What is claimed is:

1. A composition of matter comprising a gelatinous hydrocarbon containing a minor amount of compounds having the general formula MOR and $M'(OR')_3$ wherein M is selected from the group consisting of Group 1A metals, M' is selected from the group consisting of Group IIIA metals and R and R' are independently selected from the group consisting of C_1 to C_{25} hydrocarbyl radicals.

2. The composition of claim 1 wherein M' is selected from the group consisting of boron and aluminum.

3. The composition of claim 1 wherein R and R' are alkyls independently selected from the group consisting of C_4 to C_{16}.

4. The composition of claim 1 wherein said hydrocarbon boils between 30° and 350° C.

5. The composition of claim 1 wherein M is selected from the group consisting of Li and Na.

6. The composition of claim 5 wherein R is selected from the group consisting of C_8 to C_{12} alkyl radicals.

7. The composition of claim 6 wherein R is selected from the group consisting of C_4 to C_8 alkyl radicals and M' is selected from the group consisting of B and Al.

8. The composition of claim 1 wherein said hydrocarbon boils substantially between 30° and 350° C., MOR is $n\text{-}C_{16}H_{33}OLi$ and $M'(OR')_3$ is $B(OC_4H_9)_3$.

9. A process for manufacturing a gelatinous hydrocarbon which comprises adding to a liquid hydrocarbon a minor amount of each of the following: (a) a compound having the general formula MOR and (b) a compound having the general formula $M'(OR')_3$ wherein M is selected from the group consisting of Group 1A metals, M' is selected from the group consisting of Group IIIA metals and R and R' are independently selected from the group consisting of C_1 to C_{25} hydrocarbyl radicals and recovering a gelatinized hydrocarbon.

10. The process of claim 9 wherein M' is selected from the group consisting of boron and aluminum.

11. The process of claim 10 wherein R and R' are alkyl radicals selected from C_4 to C_{16}.

12. The process of claim 11 wherein M is selected from the group consisting of Na and Li.

13. The process of claim 12 wherein said hydrocarbon is a mixture boiling between about 30° and 350° C.

14. The process of claim 12 wherein said hydrocarbon is a mixture boiling within the kerosene range.

15. The process of claim 12 wherein said hydrocarbon is butane.

16. The process of claim 14 wherein MOR is $n\text{-}C_4H_9OLI$ and $M'(OR')_3$ is $B(OC_4H_9)_3$.

17. The process of claim 14 wherein the molar ration of MOR to $M'(OR')_3$ is 1:1.

18. The process of claim 14 wherein said addition takes place at about 20° to 30° C.

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