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POLYURETHANE BASE PRODUCTS AND PROCESSES

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ABSTRACT OF THE DISCLOSURE

Process for producing thixotropic hydrocarbon gels by reaction, in the hydrocarbon, of a dissolved unsaturated semipolymer having a molecular weight of at least 1000, and being terminated with isocyanate reactive groups, with an organic polyisocyanate in the presence of a Lewis acid, and the gelled compositions produced.

This invention relates to a novel method for rapidly gelling hydrocarbon liquids and to the novel products produced thereby.

Thixotropic hydrocarbon gels have important uses as rocket propellants, flame thrower fuels, napalm and other applications. The formation of hydrocarbon gels is also important as a safety device with regard to the handling, storage and use of various hydrocarbon fuels for vehicles, including land, marine and aviation vehicles.

One of the greatest dangers associated with the use of hydrocarbon fuels is their low viscosity. Spills, leaks and the like occur readily in their handling and pose serious flammability and explosion hazards. This problem is especially acute in the area of aviation fuels and especially jet and turbo-jet fuels. Perhaps the most dangerous single hazard in the event of aircraft accidents is the hazard of widespread fire and explosion caused by the rupture of fuel tanks and the resulting spillage of hydrocarbon fuels. The same potential danger also accompanies the use of hydrocarbon fuels as a power source for other vehicles.

Many of the dangers inherent in the use of hydrocarbon fuels can be eliminated or minimized by increasing their viscosity sufficiently so that they do not readily leak, spill, or fly about on impact. However, no technique previously described has proved fully satisfactory for accomplishing this end. It has been proposed to form hydrocarbon gels by dissolving a high polymer, such as polystyrene, in the hydrocarbon. This requires large quantities of polystyrene, typically an amount at least equal to the amount of hydrocarbon fuel. It is also time-consuming since the polystyrene dissolves slowly and often requires heating. The time required to form a gel in this manner renders it unconvenient for any application and totally useless for aviation use. If a hydrocarbon gelling technique is to be effective in averting fire hazards in aviation accidents, it is necessary that it be capable of forming a gel almost instantaneously so that the pilot can activate the gel-forming mechanism and the gel can be formed even when the accident is imminent.

It has also been suggested that fire hazards in aircraft

accidents might be reduced by injecting into the fuel tanks a mixture which forms, in situ, a polyurethane foam. This technique also presents serious problems. The formation of such foams is accompanied by rapid gas evolution which may contribute to the rupture of the fuel tank and the rapid spreading of its contents. Moreover, the cellular body which is formed is a solid which may completely plug fuel lines and starve the engine. Should the aircraft then avoid the anticipated danger, it would then still be in danger of crashing because of loss of power.

The continuing need for a convenient, practical method for gelling hydrocarbons is evidenced by such publications as "Inventions Wanted by the Armed Forces," No. 910, May 1959, published by the National Inventors Council; "Oil, Paint and Drug Reporter" of Apr. 18, 1966 and "Chemical and Engineering News" of Mar. 21, 1966.

It is an object of this invention to provide a technique for rapidly gelling a hydrocarbon fluid. It is a further object to provide a means for rapidly forming thixotropic gels from hydrocarbon fluids. It is a still further object to provide novel thixotropic gels.

In accordance with certain of its aspects, the novel process of this invention for rapidly increasing the viscosity of a normally liquid hydrocarbon to produce a thixotropic gelled composition comprises reacting, in said hydrocarbon, a semipolymer which is soluble therein and has a molecular weight of at least about 1,000; an organic polyisocyanate; and a Lewis acid; said semipolymer having at least two isocyanate-reactive groups and at least one reactive ethylenically unsaturated group per semipolymer molecule; to produce a final polymer having a molecular weight substantially higher than the molecular weight of said semicpolymer but not high enough to insolubilize said final polymer in said hydrocarbon.

The hydrocarbons which may be gelled by the process of this invention are those normally employed as fuels for jet, turbojet and internal combustion engines, flame thrower fuels, napalm bases, etc. They generally comprise mixtures of aliphatic, cycloaliphatic, aromatic and naphthenic hydrocarbons boiling within the range of about 20° C. to 400° C. under standard conditions. Gasoline fractions boiling in the range of about 20–220° C. are typically employed in internal combustion engines. Kerosene fractions boiling at about 100° C. to 300° C. are generally used for jet and turbojet engines. Diesel engines typically use fractions boiling at about 250° C. to 400° C. Any of these fractions may be enriched by the addition of lower-boiling hydrocarbons as ignition aids. These may have the effect of appreciably lowering the boiling point of the defined fractions.

The present invention is based upon the surprising finding that such hydrocarbons can be gelled in a very short time, virtually instantaneously in preferred embodiments, by reacting together therein an organic polyisocyanate, a Lewis acid, and a semipolymer which contains at least two isocyanate-reactive groups and at least one point of reactive ethylenic unsaturation per polymer molecule. Although the invention is not limited to any particular theory, it is believed that the Lewis acid effects further polymerization of the semipolymer through the points of residual unsaturation, and the organic polyisocyanate reacts with the isocyanate-reactive groups to cross-link the chain-extended semipolymer into a three-dimensional gel structure.

The preferred organic polyisocyanates are the aliphatic and aromatic polyisocyanates which are commercially available. Diisocyanates and triisocyanates are generally most suitable. The organic polyisocyanates which have been found most useful include tolylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, 4,4'-diphenylmethane diisocyanate, hydrogenated 4,4'-diphenylmethane diisocyanate, lysine diisocyanate, polymethylene polyphenyl isocyanate, dimer acid diisocyanate and the like. The most preferred polyisocyanates are tolylene diisocyanate and hexamethylene diisocyanate.

The useful Lewis acids are any of those which are known to have activity in promoting cationic-type polymerization of ethylenically unsaturated compounds. These include boron trifluoride and its complexes such as boron etherate and hydroxylamine adducts, tin tetrachloride, antimony pentachloride, phosphoryl chloride ($POCl_3$), phosphorus pentachloride, aluminum chloride, titanium tetrachloride, silicon tetrachloride, etc. It is preferred that these be used in the anhydrous form. The preferred Lewis acids are boron trifluoride, boron trifluoride-etherate, boron trifluoride-hydroxylamine and tin tetrachloride.

The semipolymer which is employed will be a predominantly linear organic semipolymer or telomer which is soluble in the hydrocarbon to be gelled. For fastest gelling, it is desirable that the semipolymer have a molecular weight of at least about 1,000. Substantially lower molecular weights may undesirably increase the gelation time. Molecular weights substantially above about 10,000 generally do not contribute any additional advantages and may lead to solubility, viscosity or dispersion problems. The most suitable semipolymers are those having molecular weights in the range of about 1,000 to 10,000 and preferably about 1,500 to 4,000.

The semipolymer should contain at least two isocyanate-reactive groups per polymer molecule. The most suitable isocyanate-reactive groups are those having one or more replaceable or "active" hydrogen atoms. These include such functional groups as the carboxyl, hydroxyl, thiol, primary amine and secondary amine groups, typically those bearing alkyl substituents. It is preferred that the isocyanate-reactive group be highly accessible to the isocyanate and preferably it will be a terminal group. Such terminal groups are readily obtained by means of known telomerization techniques.

The semipolymer should also contain at least one reactive ethylenically unsaturated group per polymer molecule. A reactive ethylenically unsaturated group is one which contains a $>C=<$ moiety which is capable of undergoing addition polymerization under the influence of the Lewis acid. The unsaturated group may be of cis or trans configuration and may be present in the polymer backbone or as a pendant group. Pendant groups, such as pendant vinyl groups, are generally more accessible and are therefore preferred. Semipolymers containing the desired residual unsaturation are readily obtained, for example, by polymerization of various dienes such as butadiene, isoprene, etc. Semipolymers containing a plurality of reactive ethylenically unsaturated groups say 75–25 per molecule give faster gelling and are therefore preferred.

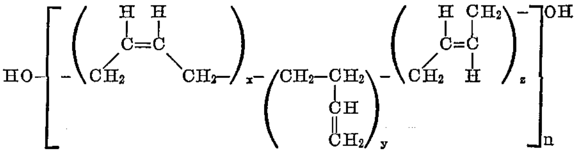
In preferred semipolymers, at least one of the ethylenically unsaturated groups will be situated so as to activate the isocyanate-reactive groups, e.g. in an allylic configuration.

A highly preferred class of semipolymers are hydroxyl-terminated homopolymeric and copolymeric telomers of butadiene containing predominantly primary allylic hydroxyl end-groups such as those prepared by the polymerization of butadiene and butadiene-styrene with an organic peroxide in the presence of allyl alcohol or propargyl alcohol. These materials are commercially available under the trademark "Sinclair Poly B–D." Representative materials of this type are described in Tables I through III.

TABLE I.—PROPERTIES OF HOMOPOLYMERIC BUTADIENE SEMIPOLYMERS

Semipolymer Type	Low viscosity	High viscosity
Average molecular weight	2,200	3,200
Brookfield viscosity (30° C. poise)	40–60	200–250
Average hydroxyl groups/molecule	2	2
Hydroxyl content, equiv./100 grams	0.1	0.07
Hydroxyl equivalent weight	1,100	1,600
Color Gardner	1	1
Moisture, percent	0.05	0.05
Anti-oxidant	None	None
Polybutadiene Microstructure:		
Percent cis	18–20	18–20
Percent trans	58–62	58–62
Percent vinyl	20–22	20–22

The materials described in Table I can be represented by the empirical structure.



$$HO-\left[\left(CH_2-CH=CH-CH_2\right)_x-\left(CH_2-\underset{\underset{CH_2}{\|}}{\overset{}{CH}}\right)_y-\left(CH_2-CH=CH-CH_2\right)_z\right]_n-OH$$

wherein:

$X=0.2$
$y=0.2$
$Z=0.6$, and
$n=40$ (for low viscosity Poly B–D), or
$n=55$ (for high viscosity Poly B–D)

TABLE II

Properties of "Poly B–D R–45" semipolymer

Non-volatile material, wt. percent	99.7
Weight per gallon pounds	7.5
Specific gravity, 60/60° F.	.904
Viscosity, poises @ 30° C.	45
Microstructure, infra-red:	
Trans-1,4, percent	60
Cis-1,4, percent	20
Cis-1,2, percent	20
Hydroxyl content, milliequivalents/gram	0.8
Water content, wt. percent, max.	0.09
Molecular weight, average	2,200

TABLE III.—PROPERTIES OF OTHER "POLY B-D" SEMIPOLYMERS

Semipolymer type	R–15M	Butadiene-styrene copolymer	Butadiene-acrylonitrile copolymer
Viscosity, poises at 30° C	50	258	464
Hydroxyl value, meg./gm	1.09	0.93	0.80
Water content, weight percent	0.04	0.04	0.17
Peroxide content, p.p.m., ceric method	50.0	18	242
KI	10.0	38	128

The most preferred semipolymer is the product sold under the trademark Sinclair Poly B–D R–15M, described above.

The proportions of semipolymer, Lewis acid and isocyanate may be varied considerably depending upon the materials selected and the result desired. The precise composition of the hydrocarbon to be gelled will also affect the quantities of reactants chosen, hydrocarbons containing a high percentage of aromatic components generally requiring less gelling mixture. The ratio of Lewis acid to semipolymer and isocyanate to semipolymer should be adjusted so that the final product is a fairly firm gel. Too much Lewis acid and/or isocyanate may lead to excessive cross-linking and too high a molecular weight polymer and the polymer formed may become insoluble in the hydrocarbon and precipitate therefrom instead of forming the desired gel. The proper ratios of reactants are, however, readily determined by a series of simple experiments using the chosen materials and the gels formed are easily and quickly evaluated by visual inspection, shaking, etc.

In general, the amount of semipolymer employed will be about 3–20 parts by weight per 100 parts by weight of hydrocarbon. Preferably, about 5–15 parts by weight will be employed. The organic polyisocyanate will preferably be present in amount sufficient to at least about one equivalent of isocyanate per isocyanate-reactive group. The Lewis acid will preferably be present in the amount of at least about one mole per molecule of semipolymer. It will be understood that the precise values chosen can vary considerably depending upon the materials used and the result desired, but the above represent convenient starting points for determining the optimum values for any system.

The order in which the individual reactants are added to the hydrocarbon to be gelled can be varied to suit particular purposes. They may also be added simultaneously. If desired, the semipolymer may be predissolved in the hydrocarbon and the Lewis acid and isocyanate added thereto at the desired time. In general, it will be found most convenient to add the semipolymer to the hydrocarbon prior to the Lewis acid and the isocyanate. Since the isocyanate will typically produce the most marked viscosity increase, it is generally added last to facilitate dispersion of the other reactants.

By varying the amounts of gelling agent employed, the gelling time may be varied from a few seconds to several minutes, the shorter times being preferred for vehicle fuel-safety systems and the longer times for the preparation of napalm, jellied fuels and the like. It is generally advisable to provide means for rapidly mixing the reactants, such as mixers, nozzles, etc.

Any of the noted reactants can be added as such or can be diluted with a suitable solvent, such as an aromatic hydrocarbon. Under some circumstances, it will be desirable to dispense the reactants from pressurized containers. The propellant may be a pressurized gas such as nitrogen or a low-boiling liquid such as the fluorinated hydrocarbons sold under the trademark Freon. The low-boiling liquid may also serve as a diluent for one or more of the reactants.,

It is desirable to maintain each of the noted reactants as anhydrous as is practically possible, since the isocyanate reacts readily with water with undesirable gas liberation.

If desired, the isocyanate reaction may be catalyzed by any of the known polyurethane-forming catalysts. The catalysts are soluble in the hydrocarbon. Typical catalysts which may be employed as polyurethane forming catalysts include dibutyl tin dilaurate, tin octoate, ferric acetonyl acetonate, N-alkyl morpholine, triethylene diamine (DABCO), tertiary piperazine derivatives and the like.

Practice of the specific embodiments of this invention may be observed from the following illustrative examples. It will be understood that the invention is not limited to the specific embodiments described but comprehends all such modifications as fall within its general scope.

Example 1

There is mixed together 180 kilograms of commercial automotive gasoline having an API-gravity of 62.5, an octane rating of 85, containing 40% aromatic hydrocarbons and distilling over the range of 86° F. to 410° F., with 28 kilograms of a solution of 20 kilograms of "Sinclair Poly B–D R–15M" semipolymer in 8 kilograms of toluene. Mixing is carried out as rapidly as possible. To this solution is successively added: 12 kilograms of a solution of 3 kilograms of anhydrous $SnCl_4$ in 9 kilograms of toluene; followed by 2.1 kilograms of tolylene diisocyanate. The gasoline immediately becomes reddish in color and its viscosity increases. In less than 10 minutes, it is converted to a transparent, clear, uniform gel suitable for use as a napalm composition.

Example 2

There is mixed together, with vigorous agitation, 21 kilograms of a solution of 15 kilograms of "Sinclair Poly B–D R–15M" in 6 kilograms of toluene and 180 kilograms of a commercial automotive gasoline having an API-gravity of 57, an octane rating of 91, containing 60% aromatic hydrocarbons, and distilling between 86° F. and 390° F. The so-prepared solution is storage-stable and can be used for making gelled gasoline on the spot. To gel the solution, there is added, in rapid sequence, 9 kilograms of a 20% by weight solution of tin tetrachloride in toluene, followed by 1.6 kilograms of tolylene diisocyanate. Vigorous mixing is carried out after each addition. Within 10 minutes, a clear, uniform, yellow gel is produced.

Alternatively, the gasoline is initially mixed with both the tin tetrachloride solution and the "Poly B–D" semipolymer to form a storage-stable, viscous, yellow composition. This composition is gelled when desired by adding thereto the tolylene diisocyanate, whereupon a firm gel is obtained within 10 minutes. These gels are suitable for use as napalm or gelled fuels.

Example 3

The process of Example 2 is followed, substituting 2 kilograms of a 20% BF_3-ether solution for the toluene solution of tin tetrachloride. A firm gel essentially identical to that of Example 2 is produced.

Example 4

In a large mixing vessel, there is placed 200 tons of moisture-free regular motor gasoline having physical and chemical properties as follows:

IPI-gravity		62
Distillation, ° F.:		
Beginning		92
10%		120
90%		350
End Point (97%)		418
Motor octane No.		86
Lead content, cc./gal.		1.7
S. content	percent	0.04
Aromatics	do	27
Paraffinic	do	33
Olefinic	do	24
Naphthenic	do	16

There is then added first 15 tons of "Sinclair Poly B–D R–15M" followed by one ton of anhydrous tin tetrachloride. The resulting substantially higher viscous yellow product is filled into canisters usually employed for napalm applications. Attached to each canister is a small pressurized container filled with hexamethylene diisocyanate in the amount 2% by weight of the total canister contents. Before the mission or even during the mission as soon as the hexamethylene diisocyanate is injected into the gasoline composition, it gels almost instantaneously to a firm gel.

Alternatively, the hexamethylene diisocyanate is replaced by tolylene diisocyanate and essentially identical results are obtained.

Example 5

A propeller-driven airplane, which employs aviation gasoline, is equipped with three pressurized small tanks: (1) one containing an 80% solution of Sinclair's Poly B–D R–15M resin in a mixture of "Freon" 12 (CF_2Cl_2) and "Freon" 13 (CF_3Cl), (2) the second containing gaseous boron trifluoride, (3) the third containing hexamethylene diisocyanate, pressurized with nitrogen. The relative amounts of the three ingredients to the full load of aviation gasoline expressed in parts by weight is: 100 parts of gasoline to 10 of (1) to 0.5 of (2) to 2.0 or (3). When the pilot believes that a hard landing or crash is impending, he activates, in sequence, the releasing valves of the three tanks which will inject the materials contained therein into the aviation gasoline tanks. The gasoline gels almost instantaneously, thus reducing the danger of explosion or widespread fires due to spreading gasoline.

Example 6

180 kilograms of "JP–4" jet fuel, comprising a mixture of 65% gasoline and 35% light petroleum distillate, is mixed with the gelling agents of Example 1, in the same amounts. Within 10 minutes the jet fuel is converted to a firm, pinkish gel.

Example 7

A jet aircraft is fitted with three separate pressurized containers containing, respectively: (1) an 80% solution of "Sinclair Poly B–D R–15M" in "Freon" 12; (2) boron trifluoride gas; and (3) an 80% solution of hexamethylene diisogyanate in "Freon" 12. The amounts of each of these materials, based on a full load of "JP–4" jet fuel are, in part by weight: 100 parts of jet fuel to 13 parts of (1) to 0.3 part of (2) to 1.5 parts of (3). In the event a potentially dangerous situation arises, the pilot energizes switches which cause the injection of the contents of the three separate tanks into the fuel tanks, whereupon the fuel is gelled almost instantaneously.

Example 8

Military jet fuel "JP–5", a refined kerosene having a flash point of about 140° F. and a viscosity of less than 10 centipoises is highly dangerous because of its low viscosity and high flammability. In order to reduce the hazards associated with the use of this fuel in aircraft, 10 parts by weight of "Sinclair Poly B–D R–15M" is added to each 100 parts by weight of "JP–5" and the aircraft is fitted with two separate small tank containing respectively gaseous boron trifluoride and hexamethylene diisocyanate under nitrogen pressure. Based on a full load of fuel, these tanks contain 0.25 part of boron trifluoride and 1.0 part of hexamethylene diisocyanate. The fuel mixture is capable of being burned in a jet engine because the semipolymer is essentially a hydrocarbon. In the event of danger, the pilot releases the contents of the two separate tanks into the fuel tank, either successively or simultaneously, whereupon the fuel is converted to a gel almost instantaneously.

What is claimed is:

1. The process for rapidly increasing the viscosity of a normally liquid hydrocarbon to produce a thixotropic gelled composition which comprises reacting, in said hydrocarbon, a semipolymer which is soluble therein and has a molecular weight of at least about 1,000; an organic polyisocyanate; and a Lewis acid; said semipolymer having at least two isocyanate-reactive groups and at least one reactive ethylenically unsaturated group per semipolymer molecule; to produce a final polymer having a molecular weight substantially higher than the molecular weight of said semipolymer but not high enough to insolubilize said final polymer in said hydrocarbon.

2. The process of claim **1** wherein said Lewis acid is selected from the group consisting of boron trifluoride, boron trifluoride complexes such as boron etherates, boron trifluoride-hydroxylamine adduct, tin tetrachloride, antimony pentachloride, phosphoryl chloride, phosphorus pentachloride, aluminum chloride, titanium tetrachloride and silicon tetrachloride.

3. The process of claim **1** wherein said Lewis acid is selected from the group consisting of boron trifluoride, boron trifluoride etherates, boron trifluoride-hydroxylamine adduct, and tin tetrachloride.

4. The process of claim **1** wherein said isocyanate-reactive groups are selected from the group consisting of carboxyl, hydroxyl, thiol, primary amine and secondary amine.

5. The process of claim **1** wherein said semipolymer is a hydroxyl-terminated butadiene polymer having a molecular weight between about 1,000 and 10,000.

6. A thixotropic gelled hydrocarbon composition containing a three-dimensional polymer structure prepared by reacting, in a normally liquid hydrocarbon, a semipolymer which is soluble in said hydrocarbon and has a molecular weight of at least about 1,000; an organic polyisocyanate; and a Lewis acid; said (semipolymer having at least two isocyanate-reactive groups and at least one reactive ethylenically unsaturated group per semipolymer molecule.

7. The composition of claim **6** wherein said Lewis acid is selected from the group consisting of boron trifluoride, boron trifluoride complexes such as boron etherates, boron trifluoride-hydroxylamine adduct, tin tetrachloride, antimony pentachloride, phosphoryl chloride, phosphorus pentachloride, aluminum chloride, titanium tetrachloride and silicon tetrachloride.

8. The composition of claim **6** wherein said Lewis acid is selected from the group consisting of boron trifluoride, boron trifluoride etherates, boron trifluoride-hydroxylamine adduct, and tin tetrachloride.

9. The composition of claim **6** wherein said isocyanate-reactive groups are selected from the group consisting of carboxyl, hydroxyl, thiol, primary amine and secondary amine.

10. The composition of claim **6** wherein said semipolymer is a hydroxyl-terminated butadiene polymer having a molecular weight between about 1,000 and 10,000.

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