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(54) COMPOSITION OF A STRUCTURE-FORMING AGENT

(57) A structure-forming composition for nonpolar hydrocarbons, comprising a compound of the general formula $M(OR)_3$ and a compound of the general formula M^1OR^1, where M is a metal of the main subgroup of Group III, M^1 is lithium or sodium, and R and R^1 are hydrocarbon radicals, and **characterized** in that the composition contains additionally a metal halide of the general formula M^1X, where X is chlorine, bromine, or iodine, in the form of a complex compound of the general formula $M^1OR^1 \cdot M^1X$ in concentrations of at least 0.5 mole per 1 mole of compound of the general formula $M(OR)_3$.

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Description

Field of the Invention

The present invention is in the field of chemistry, relating more specifically to chemicals used for thickening liquid hydrocarbons.

The invention can be utilized, principally, for environmental protection, thus, for eliminating accidental spillages of liquid hydrocarbons on water and on land, for preventing leakage of same from damaged reservoirs or pipelines, and in such other instances where a need may arise for thickening liquid hydrocarbons.

Prior Art

To be successfully utilized in practice, more particularly in emergency situations, thickening agents are expected to meet several requirements.

First and foremost, a thickening agent is to assure a fast and effective rice in the viscosity of a liquid product and high resistance to degrading environmental effects.

The highly probable danger of a fire in an emergency situation makes it a critical problem to reduce the the fire hazard associated with thickened products.

Also of vast importance is the provision in a thickening agent of such properties as would make the reprocessing of thickened products ecologically and economically advantageous.

There are known at present a great number of chemical compounds and compositions based thereupon, which can be used to achieve a substantial increase in the viscosity of a liquid hydrocarbon. In practice, however, not all thickening agents by far exhibit an optimal combination of properties.

Thus, many inorganic and organic adsorbents with a highly developed surface structure will effectively bind liquid hydrocarbons, but there may be serious difficulties to encounter in removing the resultant products from the cleaning zone and in the subsequent reprocessing of same.

Good thickening agents for liquid hydrocarbons are provided by compositions based on high molecular weight polymers capable of being ionically and coordinately cross - linked in solution - with, however, the required rate of gelation generally failing to be assured in the process.

In other cases, thus when using polyhexamethyleneimines with an average molecular weight of 500 to 20,000, the limiting factor is the dependence of the thickening process upon the amount of water, in excess of water leading to the formation of a stable emulsion.

The indispensable requirements can be largely met by thikening agents based on metal alkoxides, which are called structure - forming agents owing to their capability to form densely packed hypomolecular structures in nonpolar hydrocarbons.The formation of such structures is due to polyassociation of alkoxyl compounds in a three - dimensional space.

There is known a structure - forming composition comprising a trialkoxide of a metal of the main subgroup of Group III, $M(OR)_3$, and alkali metal alkoxide, M^1OR^1 (US, A, 3,615,285: SU, A, 1,661,369).

Adding the components of the structure - forming agents to a hydrocarbon solution of low permittivity (ε = 1 - 8) will lead to the system undergoing rapid structuring to give a gelatinous product with thixotropic and viscoelstic properties.

Said structure - forming agent will effectively thicken hydrocarbons of varied structure during a period of time ranging from several seconds to 30 minutes.

The viscosity value is influenced by the nature of the alkali metal,the structure of the alkoxide substituent, the permittivity value, and the structural affinity between the hydrocarbon and the polyassociate.

One very important feature of the structured system is the ability to be rapidly decomposed by exposure to a polar liquid, e.g. an alcohol, with the hydrocarbon recovering its original properties and becoming suitable for use in its original function.

The preferred embodiment of the structure - forming composition under consideration is to use a trialkoxy borate, with the number of carbon atoms in the radical of 4 to 11, as compound $M(OR)_3$, and lithium tert - butylate as compound M^1OR^1.This embodiment has found applications in, e.g., the petroleum industry as a means to temporarily isolate petroleum-, gas- and water - bearing strata (seams) (SU, A, 1,661,369).

The composition loses its isolating properties when contacted with water for 1.5 to 2.5 hours or when contacted with petroleum for 5 to 6 days.

While being highly effective in thickening liquid hydrocarbons of varied structure and composition and allowing of these being rapidly regenerated, the applications of said structure - forming composition are limited due to structured products being highly sensitive to water and flammable (fire - hazardous).

Disclosure of the Invention

The present invention is based upon the objective of providing a structure - forming composition that would be capable of structuring nonpolar hydrocarbons rapidly and effectively while ensuring higher water resistance and lower flammability (fire hazard) in structured products.

The objective as stated above is achieved by providing that in the composition of a structure - forming agent comprising a compound of the general formula $M(OR)_3$ and a compound of the general formula M^1OR^1 , where M is a metal of the main subgroup of Group III, M^1 is lithium or sodium, and R and R^1 are hydrocarbon radicals, there is additionally included a metal halide of the general formula M^1X, where X is chlorine, bromine, or iodine, in the form of a complex compound of the general formula $M^1OR^1 \cdot M^1X$ in concentrations of at least 0,5 mole per 1 mole of compound of the general formula $M(OR)_3$.

Thus, the objective stated is achieved by incorporating into the structure - forming composition a lithium or sodium halide in the form of a lithium or sodium complex of an alkoxide of the same metal.

The formation of a hypomolecular structure in a hydrocarbon - metal alkoxide system is a complicated multi-stage process, of which the mechanism has not yet been fully studied.

It has been found experimentally that the introduction into the known two-component structure-forming agent of a lithium or sodium halide in the form of a complex compound comprising an alkoxide of the same metal, will lead to a substantial increase in the resistance of structered hydrocarbons to water while simultaneously reducing their flammability (the fire hazard associated therewith).

With all that, the introduction of said compound into the structure-forming composition will not produce any adverse effect upon the structuring processes and the physical and chemical properties of the resultant gels.

The hydrocarbone radicals in the $M(OR)_3$ and $M^1OR^1 \cdot M^1X$ compounds may have a saturated or unsaturated chain of varying structure (normal, branched, cyclic, or aromatic) and having a varying content of carbon atoms. The choice is dependent upon economics and structural affinity.

The halogen used in the M^1X compound may be chlorine, bromine, or iodine, the nature of the halogen having no bearing upon the properties of the structure-forming agents.

To achieve the desired characteristics in the structured product and the desired parameters in the structuring process, it is convenient for the composition to contain at least 0.5 mole of $M^1OR^1 \cdot M^1X$ complex per 1 mole of $M(OR)_3$ compound. Introducing less than 0.5 mole of said complex compound into the composition will not assure the required thickening rate. The upper limit of the complex content will depend on the economic factor only.

It is convenient that boron or aluminium be used as metal of the main subgroup of Group III.

For the best result to be obtained, it is convenient for the structure-forming composition to comprise a trialkoxy borate, $B(OR)^3$, with the number of carbon atoms in the radical of 4 to 11, as compound of the general formula $M(OR)_3$, lithium chloride as metal halide, and lithium tert-butylate as compound of the general formula M^1OR^1, with an equimolar ratio of the components.

The proposed structure-forming composition is effective in regard to a wide gamut of nonpolar liquides, including such complex products as petroleum (oil), diesel fuel, kerosene, petrol (gasoline), as well as in regard to halogen-containing hydrocarbons, e.g. carbon tetrachloride.

Structured products can be rapidly and easily regenerated when a polar liquid (e.g. an alcogol) or water is added thereto.

The Claimants have failed to find any sources of information that would be indicative of a technological solution identical with or equivalent to the proposed composition. In the Claimants' opinion, this makes the invention to conform to the novelty criterion (N).

The realization of the distinctive features of the invention makes the structure-forming composition manifest an important technological effect which consists in increased resistance of the structured product to water coupled with decreased flammability (fire hazard). The said novel features comprised in the invention make, in the Claimants' opinion, the proposed technological solution conform to the inventive height criterion (IS).

Utilization of the proposed technological solution will provide a range of favourable properties, viz.:

- high structuring rates;
- effective structuring of liquid nonpolar hydrocarbons even to the state of pseudosolid viscoelstic gel;
- high resistance of the structured product to water;
- lower flammability of the structured product (less fire danger);
- effective and rapid regenerability of the structured product; and
- wide range of functional applications.

Best Mode to Carry the Invention into Effect

Structure-forming compositions have been studied comprising trialkoxy borates, with the number of carbon atoms

in the radical of 4 to 11, and lithium chloride complex of lithium tert-butylate.

Complex compounds involving lithium or sodium alkoxides and lithium or sodium chloride were obtained conventionally, by reacting anhydrous lithium or sodium chloride dissolved in an appropriate aliphatic alcohol with lithium or sodium metals.

Also studied were structure-forming compositions comprising aluminium alkoxides and sodium chloride complexes of sodium alkoxide.

Said compositions were used to structure various hydrocarbons of low permittivity (ε = 1-8).

Test hydrocarbons were measured for dynamic viscosity, using a Rheotest viscometer, at the strain rate $\gamma = 0.3\ s^{-1}$ and at 25°C.

Within 5 to 10 minutes from the beginning of the structuring process, the viscosity value of all test hydrocarbons reached over 3000 Pa • s, which corresponded to a viscoelastic gel having been formed. Within 20 to 25 minutes, the viscosity value was over 5000 Pa • s, which corresponded to a solid gel having been formed.

Structured hydrocarbons were tested for resistance to water in the following manner.

A test gel was charged into a measuring cylinder, and the height of the gel column was marked. Then an equal volume of water was poured into the cylinder. The water resistance criterion used was the half-life (τ 1/2), i.e. the time it takes half the test product column to be destroyed.

Structured hydrocarbons were also tested for flammability (fire-hazardous characteristics), using a conventional method of determining the linear burning rate.

Examples are cited below of structuring hydrocarbons by using several specific structure-forming compositions, with relevant test results in a tabular form.

Example 1

Grade A-76 petrol (gasoline) was structured, using a composition comprising $Li(T\text{-}OC_4H_9) \cdot LiCl$ and $B(OC_8H_{17})_3$, with the components in an equimolar ratio.

To 1000 ml of petrol were added in succession, with stirring and at room temperature (T = 20-25°C), 19 g of $Li(T\text{-}OC_4H_9) \cdot LiCl$ dissolved in the same petrol and 61 g of $B(OC_8H_{17})_3$. The quantity of the structure-forming agent added was 10 wt.% of the weight of petrol.

For comparison, structuring was carried out under identical conditions, using a prior-art composition comprising $Li(T\text{-}OC_4H_9)$ and $B(OC_8H_{17})_3$.

The test results are tabulated below.

Example 2

lamp kerosene was structured, using the same composition and under the same conditions as described in Example 1.

The quantity of the structure-forming agent was 15 wt.% of the kerosene weight.

For comparison, structuring was carried out under identical conditions, using a prior-art composition comprising $Li(T\text{-}OC_4H_9)$ and $B(OC_8H_{17})_3$.

The test results are tabulated below.

Example 3

Carbon tetrachloride was structured, using the same composition and under the same conditions as described in Example 1.

The quantity the structure-forming agent added was 5 wt.% of the weight of carbon tetrachloride.

For comparison, struturing was done under identical conditions, using a prior-art composition comprising $Li(T\text{-}OC_4H_9)$ and $B(OC_8H_{17})_3$.

The tests results are tabulated below.

Example 4

Toluene was structured, using a composition comprising $Li(T\text{-}OC_4H_9) \cdot LiCl$ and $B(OC_{10}H_{21})_3$, with the components in an equimolar ratio.

The experimental conditions were as described in Example 1.

The quantity of the structure-forming agent added was 5 wt.% of the toluent weight.

For comparison, structuring was done under identical conditions, using a prior-art composition comprising $Li(T\text{-}OC_4H_9)$ and $B(OC_{10}H_{21})_3$.

The test results are tabulated below.

Example 5

Petroleum with a maximum tar content of 7 % was structured using a composition comprising Li(T-OC_4H_9) and trialkoxy borate, $B(OR)_3$, an industrial product obtained from the production wastes of C_4-C_{11} aliphatic alcohols (R, wt.% = C_4H_9-4.6; C_5H_{11}-0.9; C_6H_{13}-7.2; C_7H_{15}-25.0; C_8H_{17}-29.0; C_9H_{19}-25.0; $C_{10}H_{21}$-8.1; and $C_{11}H_{23}$-0.2).

The molar ratio of the components was 1.5:1. The quantity of the structure-forming agent added was 25 wt.% of the petroleum weight.

The experimental conditions were the same as described in Example 1.

For comparison, structuring was done under identical conditons, using a prior-art composition comprising Li(T-OC_4H_9) and $B(OR)_3$.

The gels thus obtained were tested. The test results are shown in the Table below.

Example 6

Diesel fuel structured using a composition comprising Li(T-OC_4H_9) • LiCl and $Al(OC_8H_{17})_3$, the molar ratio of the components being 0.8:1. The quantity of the structure-forming agent added was 20 wt.%.

The experimental conditions were as described in Example 1.

For comparison, structuring was done under identical conditions, using a prior-art composition comprising Li(T-OC_4H_9) and $Al(OC_8H_{17})_3$.

The test results are shown in the Table below.

Example 7

Hexan was structured using a composition comprising $Na(OC_8H_{17})$ • • NaCl and $B(OC_8H_{17})_3$, with the components in an equimolar ratio. The quantity of the structure-forming agent added was 20 wt.% of the hexane weight.

The experimental conditions were as described in Example 1.

For comparison, structuring was done under identical conditions, using a prior-art composition comprising $Na(OC_8H_{17})$ and $B(OC_8H_{17})_3$.

The test results are shown in the Table below.

Table

Results of structured hydrocarbon tests				
Example No.s.	τ 1/2, hrs		Linear burning rate, m/s x 10^{-6}	
	inventive composition	prior-art composition	inventive composition	prior-art composition
1	15	9	8.8	36
2	16	10	20	35
3	17	13	practically nonburning	practically nonburning
4	15	10	18	35
5	12	8	10	20
6	13	9	10	30
7	12	9	10	41

The test results manifest that the use of proposed structure-forming composition affords substantially increased water resistance in structured products while reducing their flammability (fire hazard involved).

Industrial Applicability

The proposed invention affords rapid and effective structuring of nonpolar hydrocarbons, as corroborated by experimental and on-site tests.

The invention can be used to best advantage in structuring fire-hazardous hydrocarbon liquids such as toluene, petrol (gasoline), diesel fuel, low-tar petroleum, or liquified natural gases. The high performance properties of the proposed structure-forming agent will provide for the formation of high-viscosity gels, such as will not flow from their con-

tainers, or of a structured mass, nondestructible and easy to remove from water or land surfaces, as well as for easy handling and safe elimination of accidental spillages and leakages.

Besides, the proposed structure-forming agent may be used to structure toxic organic liquids to form solid gels and thereby help in preventing environmental pollution.

Thus, the proposed invention may find an extensive scope of industrial applications.

The inventive structure-forming agent was tested during 1993-1994 at the Institute for Transport Problems of the Russian Academy of Sciences, the Shipbuilding University, and the Baltsudoproyekt Central Design Bureau in the city of Saint-Petersburg.

Claims

1. A structure-forming composition for nonpolar hydrocarbons, comprising a compound of the general formula $M(OR)_3$ and a compound of the general formula M^1OR^1, where M is a metal of the main subgroup of Group III, M^1 is lithium or sodium, and R and R^1 are hydrocarbon radicals, and **characterized** in that the composition contains additionally a metal halide of the general formula M^1X, where X is chlorine, bromine, or iodine, in the form of a complex compound of the general formula $M^1OR^1 \cdot M^1X$ in concentrations of at least 0.5 mole per 1 mole of the compound of the general formula $M(OR)_3$.

2. A composition as defined in Claim 1, **characterized** in that in the compound of the general formula $M(OR)^3$ M is aluminium or boron.

3. A composition as defined in claim 2, **characterized** in that it comprises a trialkoxy borate, with number of carbon atoms in the hydrocarbon radical of 4 to 11, as compound of the general formula $M(OR)_3$, lithium chloride as metal halide, and lithium tert-butylate as compound of the general formula M^1OR^1, with an equimolar ratio of the components.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU95/00049

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.6 . C07L 7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl.6 : C07L 7/02-7/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3775069, (ESSO RESEARCH AND ENGINEERING COMPANY), 27 November 1973 (27.11.73)	1-3
A	GB, A, 1352539, (ESSO RESEARCH AND ENGINEERING Co.), 8 May 1974 (08.05.74)	1-3
A	US, A, 3615285, (ESSO RESEARCH AND ENGINEERING Co.), 26 October 1971 (26.10.71)	1-3
A	DE, A, 1233840, (NATIONAL LEAD COMPANY), 9 February 1964 (09.02.64)	1
A	DE, A, 1444841, (GREGUOLI LAZZARO ALFREDO et al), 5 February 1970 (05.02.70)	1
A	US, A, 3539311, (USA AS REPRESENTED BY THE SECRETARY OF THE ARMY NO DRAWNING), 10 November 1970 (10.11.70)	1

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

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"&" document member of the same patent family

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