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SOLIDIFICATION OF LIQUID FUEL

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The invention described herein, if patented, may be manufactured and used by or for the Government for governmental purposes, without the payment to us of any royalty thereon.

This invention relates to the solidification of liquid hydrocarbon fuels.

The solidification of liquid hydrocarbon fuels by emulsifying the same in alginic acid or in a water-soluble salt of alginic acid, followed by congealing in an aqueous solution of a calcium salt has been described in the foreign patent literature, e. g., in British Patent No. 450,206, De Granville, and British Patent No. 481,392, Pouettre. The solidified bodies obtained by the methods set forth in these patents burn with a slow flame without exploding, and are reconverted into liquid hydrocarbon fuel by squeezing, shredding, or similar mechanical operations.

Alginic acid is a product found in nature and has up to now defied synthesis. The natural product is principally extracted from kelp, varies greatly in quality, depending e. g. upon the method of extraction, the species and age of the kelp and the location of its growth. Consequently, the solidified product made by the use of alginic acid or alginate lacks uniformity with regard to gasoline content of the solidified body, syneresis (release of water after congealing), storage stability, etc.

We have found that liquid hydrocarbon fuel can be solidified by emulsifying it in an aqueous solution of a water-soluble synthetic polymer characterized by repeating —$CH_2.CH<$ groups, and congealing the emulsion by converting the dispersant phase into a water-insoluble and substantially hydrocarbon-insoluble complex, e. g. by contact with an aqueous bath of a calcium salt such as calcium chloride.

Thus, it is an object of our invention to solidify a hydrocarbon fuel by means of a synthetic polymer.

Another object of our invention is a solidified hydrocarbon fuel having uniform properties of low flammability, storage life and being mechanically reconvertible into liquid hydrocarbon.

A further object of our invention is a reliable and inexpensive method of preparing liquid hydrocarbon fuel for stockpiling and transportation for military and civilian purposes.

Other objects and advantages of our invention will appear from the following detailed description of a preferred example of carrying the same into practice.

We have found that liquid hydrocarbon fuel emulsions suitable for the purpose of our invention may be obtained by dispersing the gasoline in an aqueous solution of a water-soluble polymeric substance characterized by repeating —$CH_2.CH<$ groups capable of forming water-insoluble and gasoline-insoluble calcium complexes by reacting with a calcium salt containing congealing bath. Thus, the continuous phase of the liquid gasoline emulsion is converted into a solidified gel serving as a supporting structure wherein the liquid hydrocarbon phase is dispersed as tiny droplets. Among suitable water-soluble polymeric substances are alkali and other monovalent salts of polyacrylic acid, of polymeric crotonic acid or of polymeric vinyl acetic acid, e. g., sodium polyacrylate, potassium polyacrylate, ammonium polyacrylate, sodium polyvinyl acetate, sodium polycrotonate.

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Sodium polyacrylate (e. g., the commercial product now sold by Rohm and Haas under the name of "RHotex") is prepared either by polymerizing sodium acrylate, e. g., with hydrogen peroxide or potassium persulfate as low temperature polymerization catalysts, or by converting polymerized acrylic acid into its sodium salt by methods well known to the art. Sodium polyacrylate is water-soluble even in the highly polymerized state.

The preparation of other polymeric monovalent salts (e. g. alkali metal salts or ammonium salts) of acrylic acid, vinyl acetic acid, crotonic acid and of other starting materials characterized by the $CH_2{:}CH—$ (vinyl) configuration are prepared similarly either by polymerizing the monomeric salt or by converting the polymerized acid into the corresponding salt.

Copolymers of the above polymeric substances with compatible water-soluble monomers are within the contemplation of our invention; thus, the polymeric sodium salt of acrylic acid copolymerized with vinyl methyl ether may be used as the dispersant for the gasoline. The dispersant for the gasoline may also consist of a mixture of the above-mentioned polymeric substances with each other and/or with alginic acid or alkali metal alginate.

The following specific example illustrates a method of carrying our invention into practice by the use of sodium polyacrylate as dispersant for gasoline; it will be understood, however, that our method may be carried out by the use of the above-mentioned other synthetic water-soluble polymeric monovalent compounds as well.

Example

Gasoline (e. g. a commercial mixture of hydrocarbons predominantly comprising heptane) is emulsified by stirring in an approximately equal volume of a 2% water solution of sodium polyacrylate until all the gasoline has been dispersed.

The resulting emulsion is then introduced into a 10% aqueous solution of calcium chloride, wherein it immediately gels. We prefer to introduce the emulsion into the congealing bath dropwise, so as to obtain pellets of substantially uniform size.

The resulting solidified body, e. g. of pellet shape, loses a substantial amount of water during the next few hours. It also gives off gasoline vapors immediately after congealing and therefore should be "aged" in a chamber equipped with gasoline vapor recovery means. After "aging" the gasoline content of the body remains substantially uniform during prolonged storage; its dispersed gasoline content is up to about 75%. The solidified body is non-explosive, burns with a slow flame, and yields most of its gasoline content by squeezing; a nearly complete gasoline recovery can be obtained by shredding and pressing.

The strength of the emulsifying sodium polyacrylate solution may be varied; for instance, within the strength range of the order of 1% to 2% and preferably less than 3%. Lesser strengths are feasible but result in the introduction of an undesired quantity of water in the solidified gel structure; conversely, an excessively strong sodium polyacrylate solution lowers the proportion by weight of dispersed gasoline and thus may prove less economical for storage and transport. Likewise, the relative proportions by volume of gasoline and emulsifying bath may be varied within suitable limits.

Instead of a 10% aqueous solution of calcium chloride for the congealing bath, aqueous solutions of different strengths and of different calcium salts, e. g. calcium nitrate or calcium sulfate may be used, as long as there are enough positive calcium ions in the congealing bath to convert the water-soluble dispersant phase of the gasoline-containing emulsion into a water-insoluble and substantially hydrocarbon-insoluble complex. Thus, good results have been obtained with a 30% strength calcium chloride congealing bath, and even greater strengths up to the saturation point may be employed (solubility of calcium chloride in cold water 59.5 g. per 100 ml.). If a calcium nitrate bath is employed lesser strength, say 5%, and preferably not above 10%, ought to be employed, and excess nitrate should be removed from the gels because of the flammability of nitrate complexes. Gels formed in calcium sulfate congealing baths are not as strong as those formed in calcium chloride baths. Likewise, the corresponding salts of other alkaline earth metals having a higher molecular weight than calcium (e. g. of strontium or barium) may be used in the congealing bath instead of a calcium salt.

Variations from and modifications of the specific example of our invention, above set forth, will readily occur to the expert without, however, departing from the spirit of our invention. Such variations and modifications are therefore to be deemed with the scope of our invention, which we define by the appended claims.

We claim:

1. The process of making a solidified hydrocarbon gel, comprising emulsifying liquid hydrocarbon in an aqueous solution of a water-soluble polymeric monovalent salt being a member of the group consisting of alkali metal salts and ammonium salts and characterized by repeating

$$-CH_2.CH<$$

groups, and reacting the liquid dispersant phase with a member of the group consisting of alkaline earth chlorides, alkaline earth nitrates and alkaline earth sulfates, to convert said phase into a water-insoluble and hydrocarbon-insoluble solid alkaline earth complex.

2. The process of making solidified hydrocarbon gel, comprising emulsifying liquid hydrocarbon in an aqueous solution of a polymeric water-soluble monovalent salt being a member of the group consisting of alkali metal salts and ammonium salts and characterized by repeating

$$-CH_2.CH<$$

groups, and reacting the liquid dispersant phase with an alkaline earth chloride to convert said phase into a water-insoluble and hydrocarbon-insoluble soild alkaline earth complex.

3. The process of making solidified hydrocarbon gel, comprising emulsifying liquid hydrocarbon in an aqueous solution of a polymeric water-soluble monovalent salt being a member of the group consisting of alkali metal salts and ammonium salts and characterized by repeating

$$-CH_2.CH<$$

groups, and reacting the liquid dispersant phase with an alkaline earth nitrate to convert said phase into a water-insoluble and hydrocarbon-insoluble solid alkaline earth complex.

4. The process of making solidified hydrocarbon gel, comprising emulsifying liquid hydrocarbon in an aqueous solution of a polymeric water-soluble monovalent alkali metal salt characterized by repeating

$$-CH_2.CH<$$

groups, and reacting the liquid dispersant phase with an alkaline earth sulfate to convert said phase into a water-insoluble and hydrocarbon-insoluble solid alkaline earth complex.

5. The process of making solidified hydrocarbon gel, comprising emulsifying liquid hydrocarbon in an aqueous solution of a polymeric water-soluble monovalent sodium salt characterized by repeating

$$-CH_2.CH<$$

groups, and reacting the liquid dispersant phase with calcium chloride to convert said phase into a water-insoluble and hydrocarbon-insoluble solid calcium complex.

6. The process of making a solidified hydrocarbon gel, comprising emulsifying liquid hydrocarbon in an aqueous solution of a water-soluble alkali metal polyacrylate, and reacting the liquid dispersant phase with a member of the group consisting of alkaline earth chlorides, alkaline earth nitrates and alkaline earth sulfates, to convert said phase into a water-insoluble and hydrocarbon-insoluble solid alkaline earth polyacrylate complex.

7. The process of making solidified hydrocarbon gel, comprising emulsifying liquid hydrocarbon in an aqueous solution of sodium polyacrylate, and reacting the liquid dispersant phase with a member of the group consisting of alkaline earth chlorides, alkaline earth nitrates and alkaline earth sulfates, to convert said phase into a water-insoluble and hydrocarbon-insoluble solid alkaline earth polyacrylate complex.

8. The process of making solidified hydrocarbon gel, comprising emulsifying liquid hydrocarbon in an aqueous solution of sodium polyacrylate of a strength of from about 1% to about 2%, and reacting the liquid dispersant phase with a member of the group consisting of alkaline earth chlorides, alkaline earth nitrates and alkaline

earth sulfates, to convert said phase into a water-insoluble and hydrocarbon-insoluble solid alkaline earth polyacrylate complex.

9. The process of making solidified hydrocarbon gel, comprising emulsifying liquid hydrocarbon in an aqueous solution of sodium polyacrylate, and reacting the liquid dispersant phase with calcium chloride to convert said phase into a water-insoluble and hydrocarbon-insoluble solid calcium polyacrylate complex.

10. The process of making solidified hydrocarbon gel, comprising emulsifying liquid hydrocarbon in an aqueous solution of sodium polyacrylate, and reacting the dispersant phase of said emulsion with an aqueous solution of calcium chloride to form a water-insoluble and hydrocarbon-insoluble calcium polyacrylate complex.

11. The process of making solidified hydrocarbon gel, comprising emulsifying liquid hydrocarbon in an aqueous solution of sodium polyacrylate, and reacting the dispersant phase of said emulsion with an aqueous solution of calcium chloride of about 10% strength to form a water-insoluble and hydrocarbon-insoluble calcium polyacrylate complex.

12. The process of making solidified hydrocarbon gel, comprising emulsifying liquid hydrocarbon in an aqueous solution of sodium polyacrylate of a strength of from about 1% to about 2% and reacting the continuous phase of said emulsion with an aqueous solution of calcium chloride of about 10% strength to form a water-insoluble and hydrocarbon-insoluble calcium polyacrylate complex.

13. A solidified non-explosive hydrocarbon-containing gel essentially comprising a dispersion of droplets of gasoline in a solidified water-insoluble and hydrocarbon-insoluble solid alkaline earth polymeric dispersant phase, said dispersant phase being the reaction product of (1) a member of the group consisting of alkaline earth chlorides, alkaline earth nitrates and alkaline earth sulfates with (2) the liquid dispersant phase of a liquid emulsion of said gasoline as the dispersed phase in an aqueous solution of a water-soluble polymeric monovalent salt being a member of the group consisting of alkali metal salts and ammonium salts and characterized by repeating

$$-CH_2.CH<$$

groups as the dispersant phase.

14. A solidified non-explosive hydrocarbon body comprising a dispersion of gasoline in a solidified dispersant phase essentially comprising the water-insoluble and substantially hydrocarbon-insoluble reaction product of (1) a member of the group consisting of alkaline earth chlorides, alkaline earth nitrates and alkaline earth sulfates with (2) the liquid dispersant phase of a liquid emulsion of gasoline as the dispersed phase in an aqueous solution of a water-soluble alkali metal polyacrylate as the dispersant phase.

15. A solidified non-explosive hydrocarbon body comprising a dispersion of gasoline in a solidified dispersant phase essentially comprising the water-insoluble and substantially hydrocarbon-insoluble reaction product of calcium chloride with the liquid dispersant phase of a liquid emulsion of gasoline as the dispersed phase in an aqueous solution of a water-soluble alkali metal polyacrylate as the dispersant phase.

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