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LIQUID GELLING AGENT

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The present invention relates to a novel liquid gelling agent for liquid hydrocarbons, such as the petroleum hydrocarbons.

This application is a continuation-in-part of our co-pending application, Serial No. 359,424, filed June 3, 1953, now abandoned.

The use of gelling agents for liquid hydrocarbons, such as gasoline, has probably been known for a decade or so. Beginning with World War II the so-called jellied gasoline bomb became a highly effective weapon in warfare, particularly aerial warfare. This weapon is still an effective one and is an important member of the arsenal of war. The gelling of petroleum hydrocarbons has also assumed great importance in peacetime pursuits, such as in breaking of rock formations in petroleum recovery from subterranean deposits.

Since the original success in the preparation of gelled liquid hydrocarbons, the technique has changed very little. The accepted practice is to mix with stirring a solid, powdered gelling agent into the liquid hydrocarbon. The powdered gelling agents with which the art is familiar are the metal salts of certain organic, including fatty acids. These salts include the magnesium, aluminum, calcium, barium, lithium, potassium, sodium, etc. (i. e., including the alkaline-earth and alkali-metal salts), salts of such acids as stearic, palmitic, lauric, naphthenic, oleic and 2-ethylhexoic or mixtures of these salts. One of these powdered gelling agents with which the general public is most familiar is the well-known napalm composition which is a mixture of salts of naphthenic, oleic and coconut-oil fatty acids; usually the aluminum salts of these acids.

The use of these solids, powdered gelling agents in the preparation of jellied liquid hydrocarbons results in serious disadvantages. The preparation of the jellied liquid hydrocarbon, such as gasoline, is usually conducted under field conditions, i. e., at advance air bases, aboard aircraft carriers, and the like. Under these far from ideal conditions, it has been difficult to consistently produce jellied hydrocarbon preparations having uniform, stable and stringy gels. Most of the solid, powdered gelling salts are substantially hygroscopic and present a storage problem; as moisture present in the liquid hydrocarbon or absorbed from the atmosphere makes the solid gelling agents "tacky" and interferes with their gelling properties. Even when substantially dry, the solid gelling agents of the prior art are uniformly mixed with the liquid hydrocarbons only with great difficulty and prolonged mixing. Where the gasoline must be jellied at lower temperatures, and such conditions are often encountered in military operations and during winter, proper gelling does not take place unless additional additives, such as cresylic acid, are present to peptize the composition. Compositions having these additives present produce gels having poor aging properties, as they gradually become thin with age and are affected by moisture.

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The use of solid gelling agents present other disadvantages of a mechanical nature. Solids are not conveniently proportioned with a liquid hydrocarbon and require prolonged mixing to disperse the gelling agent throughout the liquid hydrocarbon. It is inconvenient to measure the amount of solid gelling agent by weighing under field conditions, and yet, if a weighing operation is to be avoided, it is necessary to package the solid gelling agent in small or odd-sized containers of known content. Additionally, many of the solid gelling agents, such as napalm, require the presence of an oxidation inhibitor.

Those charged with overcoming the difficulties presented by the solid gelling agents of the prior art, including ourselves, have investigated many potential means of solving this problem. So far as we are presently advised, none of the prior attempts have met with more than a modicum of success.

It is an object of the present invention to provide a novel liquid gelling agent for liquid hydrocarbons.

It is also an object of the present invention to provide a novel process for gelling liquid hydrocarbons under wide variety of operating conditions to produce jellied hydrocarbon masses of superior properties.

It is an additional object of the present invention to provide a novel process for preparing the liquid gelling agents of the invention.

Other objects of the invention will be apparent to those skilled in the art upon reading the specification which follows:

The present invention is a novel liquid gelling agent for liquid hydrocarbons which comprises a suspension of a solid, finely-divided gelling agent for liquid hydrocarbons in a liquid suspending agent, which suspending agent is miscible with the liquid hydrocarbon to be gelled and which has a low freezing point. The solid, finely-divided gelling agent for hydrocarbons should be substantially insoluble in the liquid suspending agent. Preferably, the liquid suspending agent should aid the solid, hydrocarbon gelling agent in gelling liquid hydrocarbons, such as gasoline, at reduced temperatures, and have a freezing point below 0° C.

One unique composition of solid, finely-divided hydrocarbon gelling agent and its liquid suspending agent which satisfies the requirements of the present invention is a suspension of a metal salt of 2-ethylhexoic acid suspended in the monomethyl ether of ethylene glycol (the latter is sold to the trade under the trade names "Methyl Cellosolve" or "Dowanol 7"). After an extensive research investigation, this composition has been found to be particularly suitable for gelling liquid hydrocarbons, such as gasoline, under a wide variety of operating conditions and with maximum efficiency and satisfaction.

When the fatty acid soaps of the prior art are used alone, they gel gasoline to varying degrees depending upon the soap used and the temperature of the gasoline. To be effective, the gasoline must be at room temperature (about 25° C.) or above and the mixture with gasoline must be mixed continuously, or at least intermittently until the soap is completely dispersed in the gasoline in order to avoid lumping. This is often very time-consuming and very inconvenient. By the use of the compositions of the present invention, it is possible to rapidly gel gasoline under a wide range of operating conditions, including temperature ranges of 0° C. and below and of the ranges which are likely to be encountered in the field for use in military operations. Because of the fact that the gelling composition is a liquid, it may be measured easily by volume, rather than weighed, and introduced into the gasoline by simple liquid proportioning equipment with which the art is quite familiar. This makes it possible to ship and store the liquid gelling

agent in large containers of any size and withdraw only the amount required for immediate use. The gasoline is easily and rapidly jellied with a minimum of agitation and mixing. Only momentary mixing is required and yet lumping, and the formation of non-homogeneous globs of gel are avoided. What is more, no swelling in volume is produced.

The liquid gelling compositions of the present invention provide a number of other advantages over the solid acid salts of the prior art. These liquid gelling agents are not sensitive to highly humid atmosphere, thus the compositions may be stored for long periods of time without taking the exacting precautions necessary with the solid agents of the prior art to avoid lumping. Since gelling may be easily affected even at low temperatures, no additives need be stocked to enhance the gelling of gasoline at low temperatures. What is more, and what is quite important, is the fact that jellied gasolines prepared from the liquid gelling compositions of the present invention will maintain their higher viscosity for longer periods of time than gels prepared from solid soaps; thus jellied gasoline contained in bombs, etc., need not be used promptly, but may be stored for longer periods of time before use. The liquid gelling agents of the present invention appear to be immune to destructive oxidation; thus it is not necessary to add oxidation inhibitors as is the practice with the solid soaps of the prior art.

The liquid gelling agents of the present invention also provide space-saving features which are important in military operations. For example, about 45 pounds of liquid gelling composition according to the present invention may be stored in the same space as about 15 pounds of the more bulky solid soaps of the prior art. Because of what appears to be contributing properties of the liquid suspending agent, it is possible to obtain comparable gelled products, using the same weight of the liquid gelling compositions of the present invention as of the solid soaps of the prior art although the liquid gelling agents may only contain 25% by weight of active gelling soap.

The solid component of the liquid gelling agents of the present invention may desirably be of metal salt of 2-ethylhexoic acid, such as the salts of lithium, barium, calcium, magnesium, aluminum, zinc, etc. Aluminum di-(2-ethylhexoate) is preferred, based upon investigation to date. This aluminum salt of 2-ethylhexoic acid is known in the trade as aluminum octoate, but this preferred salt for use in the present invention is to be distinguished from the salt of n-octoic acid.

The liquid suspending component of the liquid gelling agents of the invention desirably contains the monomethyl ether of ethylene glycol. We have also investigated many alcohols, ethers and glycols, as well as other well-known organic solvents which we have found will suspend the aluminum di-(2-ethylhexoate) and aid in gelling gasoline at room temperature or higher, but none of these will provide a liquid gelling composition with all of the advantages of the preferred compositions of the present invention suspended in the monomethyl ether of ethylene glycol.

We have discovered that it is preferable that the liquid suspending component in which the solid gelling component is suspended have the same specific gravity as the solid soap hydrocarbon gelling component. Aluminum di-(2-ethylhexoate), for example, has a greater specific gravity than the monomethyl ether of ethylene glycol. We find that it is advantageous to add to the monomethyl ether of ethylene glycol an organic liquid which has a significantly higher specific gravity and which will also dissolve in the hydrocarbon, such as gasoline, to be gelled and in the suspending liquid, without having any untoward effect upon the gelling soap or its ability to gel the gasoline. Excellent results have been obtained by employing tricresyl phosphate for this purpose. The

chlorinated and the brominated hydrocarbons, the high specific gravity hydrocarbons, etc., may also be used. Among the brominated hydrocarbons are ethylene dibromide, acetylene tetrabromide, bromoform, methylene bromide, etc. The chlorinated and the brominated hydrocarbons are less desirable than tricresyl phosphate where the gelling agent is to be stored at elevated temperatures. For example, when acetylene tetrabromide is employed in the liquid suspending component and the gelling agent composition is stored at 160° F. for a period of about a month, thickening of the composition takes place with some decomposition of the components which makes the composition less desirable as a gelling agent.

It is important that the "weighting" component of the liquid suspending component have a sufficiently high specific gravity, that the specific gravity of the liquid suspending component will substantially equal that of the solid gelling component without reducing the concentration of monomethyl ether of ethylene glycol, for example, to less than 50%, and preferably not less than 60%, by volume, of the liquid suspending component. Tricresyl phosphate has a lower specific gravity than most of the brominated hydrocarbons and consequently must be used in greater concentrations than are required of the brominated hydrocarbons in the liquid suspending component. However, this slight disadvantage is overcome by the greater stability of the suspensions containing tricresyl phosphate when stored at elevated temperatures. When the specific gravity of the solid and liquid components of the liquid gelling agent are substantially equal it is not necessary to remix or agitate this agent before gelling the gasoline with it.

To date, best results have been obtained with a liquid gelling agent composed of from about 20% to 25% of aluminum di-(2-ethylhexoate) and about 75% to 80% (both by weight) of a liquid suspending component containing monomethyl ether of ethylene glycol and sufficient "weighting agent," such as tricresyl phosphate, to adjust the specific gravity of the monomethyl ether of ethylene glycol component to substantially the same as that of the aluminum salt of 2-ethylhexoic acid.

We have also discovered that it is advisable, where the liquid gelling agent is to be stored in ferrous containers, to incorporate a corrosion inhibitor into the composition to enhance the stability of the product. Morpholine in the amount of about 1% by volume based on the volume of liquid suspending component is satisfactory for this purpose.

The present invention also comprises the novel process of preparing the liquid gelling agents of the invention. This process comprises mixing a solid, finely-divided gelling agent for liquid hydrocarbons in a liquid suspending agent which is miscible with liquid hydrocarbons, which has a low freezing point and in which the solid gelling agent is substantially insoluble. Preferably, the liquid suspending agent is first blended with a liquid of substantially greater specific gravity than the suspending liquid until the specific gravity of the blend is substantially equal to that of the solid, finely-divided gelling agent. One specific process which has been found to be satisfactory is to mix gradually a metal soap of 2-ethylhexoic acid, such as the aluminum salt, with the monomethyl ether of ethylene glycol until the suspension contains from 20% to 25% by weight of aluminum di-(2-ethylhexoate) and from 75% to 80% by weight of a suspending liquid containing the monomethyl ether of ethylene glycol. The monomethyl ether of ethylene glycol may preferably be "weighted" previous to mixing with the soap of 2-ethylhexoic acid by blending it with a liquid of appreciably higher specific gravity, such as tricresyl phosphate, until the liquid blend or mixture shall have a specific gravity substantially equal to that of the soap of 2-ethylhexoic acid. The liquid blend or mixture of suspending agent should contain at least 50% by volume

of the monomethyl ether of ethylene glycol, and preferably above 60%.

The present invention also comprises the novel process of gelling liquid hydrocarbons, such as gasoline, with the novel liquid gelling agents of the invention. The process is performed simply, without the difficulties inherent to the prior art processes. Gelling may be accomplished with a minimum of mixing time by stirring lightly the liquid gelling agent into the liquid hydrocarbon. This can usually be done successfully by merely passing the two liquids in desirable proportions through a proportioning pump. For best results the liquid gelling agent should be mixed in with the liquid hydrocarbon in an amount of 6% or more, by volume, of the jellied hydrocarbon. The amount of liquid gelling agent shall preferably not exceed 15%. The amount of liquid gelling agent used will be somewhat dependent upon the degree of gelling required, the nature and temperature of the hydrocarbon to be gelled, and the concentration of and nature of the solid, finely-divided gelling agent suspended in the liquid gelling agent of the invention. However, for the sake of convenience, economy and reproducibility of results an amount of liquid gelling agent which is 6% by volume of the final jellied hydrocarbon has been found satisfactory.

In order to disclose more clearly the nature of the present invention, specific examples illustrating the invention will hereinafter be described. This is done solely by way of example and is intended neither to delineate the scope of the invention nor limit the ambit of the appended claims:

Example I

A suspension of aluminum di-(2-ethylhexoate) was prepared by mixing 20 pounds of the solid, finely-divided aluminum salt with 80 pounds of the monomethyl ether of ethylene glycol. The mixing was continued for several minutes until the components were thoroughly mixed. This suspension may be stored almost indefinitely without untoward results and used when desired, although slight remixing may be necessary if the aluminum salt settles out, to again obtain a uniform suspension. The liquid gelling agent prepared above was used to "jelly" gasoline by mixing in 6 parts by volume per 94 parts by volume of gasoline. Only slight mixing was required. The mixing may be effected by introducing the liquid gelling agent and the gasoline through a proportioning pump, with which the art is familiar, in the proportions above indicated. There was produced a jellied gasoline of a viscous, stringy nature having the characteristics desired for military purposes.

Example II

The procedure of Example I was repeated with the following modification: Prior to mixing the aluminum di-(2-ethylhexoate) and the monomethyl ether of ethylene glycol, the monomethyl ether of ethylene glycol was "weighted" by blending with enough tricresyl phosphate to constitute 35% by volume of the blend. The blend then had substantially the same specific gravity as the aluminum di-(2-ethylhexoate). About 75 pounds of the blend, which comprised the liquid suspending component, was mixed with 25 pounds of the aluminum salt and the mixture was heated to about 160°-175° F. and homogenized to aid dispersion. The composition had an attrac-

tive, translucent appearance, for the refractive indices of the solid and liquid phases were nearly identical. The product resembled a solution in appearance. This liquid gelling composition was stable when stored at 160° F. for periods of a month or more.

Example III

The procedure of Example I was repeated with the following modification: Prior to mixing the aluminum di-(2-ethylhexoate) and the monomethyl ether of ethylene glycol, the monomethyl ether of ethylene glycol was blended with enough acetylene tetrabromide to constitute 7% by volume of the blend, which increased the specific gravity of the monomethyl ether to substantially equal that of the aluminum di-(2-ethylhexoate). About 80 pounds of this blend was mixed with 20 pounds of aluminum di(2-ethylhexoate) and the mixture was heated to about 160°-175° F. and homogenized to aid dispersion. This produced a liquid gelling agent in which the aluminum salt did not settle out upon long standing and required no remixing prior to gelling the gasoline and which was reasonably stable when stored at temperatures approximating room temperature or less.

The terms and expressions which we have employed are used as terms of description and not of limitation, and we have no intention, in the use of such terms and expressions, of excluding any equivalents of the features shown and described or portions thereof, but recognize that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. A novel liquid gelling agent for liquid hydrocarbons consisting essentially of a solid, finely-divided, metal salt of a fatty acid containing at least 8 carbon atoms, suspended in the monomethyl ether of ethylene glycol, said metal being a member selected from the class consisting of alkali-metal, alkaline-earth metal, magnesium, aluminum and zinc metals, said metal salt comprising about 20% to 25% by weight of the composition.
2. A novel liquid gelling agent as defined by claim 1, in which the metal is aluminum.
3. A novel liquid gelling agent as defined by claim 1, in which the fatty acid is 2-ethylhexoic acid.
4. A novel liquid gelling agent as defined by claim 1, in which the metal salt is aluminum di-(2-ethylhexoate).
5. A novel liquid gelling agent for liquid hydrocarbons as defined by claim 1, wherein the mono-methyl ether of ethylene glycol is blended with a sufficient quantity of tricresyl phosphate to adjust the specific gravity of the liquid phase to substantially that of said metal salt.
6. A novel liquid gelling agent for liquid hydrocarbons as defined in claim 1, wherein there is also present morpholine as a corrosion inhibitor.

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