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PROCESS FOR GELLING DISTILLATE HYDROCARBON FUELS

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No Drawing. Application August 28, 1956
Serial No. 606,581

6 Claims. (Cl. 44-7)

This invention is directed to a process for preparing gelled liquid hydrocarbons by the formation, in situ, of certain cuprous mercaptides as gelling agents.

Many substances are known which are capable of gelling (solidifying) liquid hydrocarbons. Included among these are: rubber to thicken or gel gasoline and similar hydrocarbons for use as fillings for incendiary munitions; metallic soaps of high molecular weight carboxylic acids, such as the alkali metal, alkaline-earth metal, aluminum and other polyvalent metal, salts of stearic, oleic and palmitic acids, naphthenic acids and acids derived from coconut oil; salts or polymeric carboxylic acids such as sodium polyacrylate. In almost all cases rather large quantities, e. g., 10 to 20% of gelling agent is employed, and to produce a firm gel special mixing and heating techniques are required as well as a waiting period for the gel to form and cure.

It is the object of the present invention to provide a simple and inexpensive method for gelling liquid hydrocarbons for safe and convenient stock-piling and transporting.

It is a further object of the present invention to provide a gelling process which does not require any special chemical, thermal or mechanical treatment for the conversion of a liquid fuel such as gasoline, naphtha, petroleum ether, aromatic hydrocarbons, jet fuel, kerosene, diesel oil, furnace fuel and the like, into a solid fuel.

It is another object of the present invention to provide a process for producing in the liquid hydrocarbon to be gelled certain cuprous mercaptides as gelling agents.

More specifically, the present invention is directed to a process for gelling liquid hydrocarbon fuels boiling in the gasoline and fuel oil range which consists of incorporating into said fuels (a) at least 0.05% by weight of cupric copper as a fuel-soluble cupric carboxylate and (b) at least 0.05% by weight of mercaptan sulfur in the form of a primary aliphatic mercaptan having at least 4 carbon atoms, or, a mixture of said aliphatic mercaptan with an aromatic mercaptan, said mixture containing at least about an equal part of primary aliphatic mercaptan based on mercaptan sulfur.

The process of the present invention produces gelled hydrocarbon fuels which may be used to ignite combustible materials.

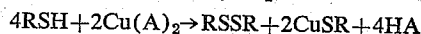
The present invention is based on the discovery that certain cuprous mercaptides are excellent gelling agents for liquid hydrocarbons. According to the method of this invention, the cuprous mercaptide is formed in situ by reacting cupric copper with select primary aliphatic or mixed aliphatic and aromatic mercaptans as defined. Produced in this way, relatively minute quantities of cuprous mercaptide are sufficient to cause rapid, in most cases immediate, gelation of rather large quantities of liquid hydrocarbons. The liquid hydrocarbons are those which boil in the gasoline and distillate fuel oil range; these liquid hydrocarbons may be individual aliphatic, naphthenic or aromatic hydrocarbons such as isooctane and xylene, or they may be mixtures such as occurring in

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distillate hydrocarbons, e. g., petroleum ether, naphtha, gasoline, jet fuel, kerosene, Stoddard solvent, diesel fuel, burner oil, furnace oil, etc. The distillate hydrocarbon fuels may be straight run, i. e., essentially free of olefinic unsaturation (or may be cracked hydrocarbon stocks as produced by thermal- or catalytic-cracking of petroleum crudes, or may be mixtures of straight run and cracked stocks, e. g., blended gasolines and fuel oils. For maximum storage stability of the gelled fuels it is preferred that the liquid fuels themselves be essentially free of olefinic components, that is, straight run distillates or chemically purified crudes, such as "deodorized" kerosene.

In preparing gels from these liquid hydrocarbons, the cupric salt and the mercaptan are introduced into the hydrocarbon to be gelled, preferably by mixing separate solutions of each of these components. The solutions can be poured together, stirred together or shaken. Gelation occurs rapidly, almost immediately in most cases, even at room temperatures, and seldom requires more than an hour to be complete. No other reagent is necessary and no special mixing, heating, or curing operations have to be employed to obtain satisfactory solid gels. The cupric copper and mercaptan reactants and the liquid hydrocarbon may be anhydrous but need not be. This gelling process does not depend upon the presence or absence of peroxides in the hydrocarbon. Water as well as peroxide may be present in quantities normally associated with water-saturated hydrocarbon fuels and with hydrocarbons that have been stored in presence of air for long periods of time.

While the exact mechanism of the gelling process itself is not known, gelation depends upon the formation, in the fuel, of cuprous mercaptide. The reaction of the cupric copper compound with mercaptan can be followed visually by the color change associated with the conversion of cupric copper to cuprous mercaptide and by the more or less rapid gelation of the liquid hydrocarbon. The following equation represents the principle oxidation-reduction reaction of the subject process:



Cu(A)_2 represents a cupric salt, preferably a cupric salt of a carboxylic acid, particularly fuel-soluble cupric carboxylates. Thus Cu(A)_2 may be cupric acetate but is preferably a higher molecular weight carboxylate as represented by cupric oleate and cupric naphthenate. RSH represents a primary aliphatic mercaptan having at least 4 carbon atoms or a mixture of such a mercaptan with an aromatic thiol. Thus R stands for a primary aliphatic or aromatic radical. Primary aliphatic mercaptans are those having the thiol ($-\text{SH}$) group attached via a methylene group to an aliphatic radical. The aliphatic mercaptans are preferably straight chain compounds, and particularly they are primary n-alkylthiols having 4 to 18 carbon atoms, e. g., n-butyl mercaptan, n-octadecyl mercaptan. These may be employed singly or as mixtures. Suitable mixtures of primary aliphatic mercaptans are available from branched chain or straight chain alcohols which are derived synthetically as by the "Oxo process" or naturally as from coconut oil and which are readily converted by known methods into the corresponding thiols. Xylyl mercaptan and beta-thionaphthol are representative aromatic thiols which may be employed in combination with primary aliphatic mercaptans.

According to the stoichiometry of the oxidation-reduction reaction given in the equation above, one-half of the mercaptan sulfur and all of the cupric copper is converted into cuprous mercaptide, the active gelling agent. Since the ratio of the atomic weights of copper to sulfur is very nearly two, approximately equal weights of cupric copper and mercaptan sulfur satisfy the stoichiometry. The cupric salt and the mercaptan will normally be em-

ployed in quantities providing from about 0.05 to 1 weight percent, preferably about 0.1 to 0.5 weight percent, based on the fuel to be gelled, of cupric copper and mercaptan sulfur, will produce sufficient quantities of cuprous mercaptide for rapid and substantially complete gelation of the fuel. Lesser quantities do not always produce satisfactory gels. Greater quantities of reactants, being unnecessary, are wasteful. Either of the two reactants, $\text{Cu}(\text{A})_2$ and RSH, may be used in excess so long as from 0.05 to 1% by weight of each as cupric copper and as mercaptan sulfur is present in the fuel to be gelled.

As stated above, the process requires that the major sulfur-containing component be a primary aliphatic mercaptan. Although secondary and tertiary aliphatic mercaptans in general also undergo oxidation-reduction reactions with cupric copper, they are unsatisfactory reagents for producing gelled hydrocarbons. When employing mercaptan sulfur in the small quantities (0.05 to 1%) given above, it is preferred that the primary mercaptan that supplies these quantities of mercaptan sulfur be substantially free of secondary and tertiary mercaptans. It is also preferred, under these conditions, that the primary aliphatic mercaptan or mixture of mercaptans be substantially free of branched structures, i. e., free of tertiary and quaternary carbon atoms elsewhere in the aliphatic group. When mixtures of aliphatic primary mercaptan and aromatic mercaptan are employed, at least one-half of the total mercaptan sulfur content will be preferably in the aliphatic form.

The gels produced by the formation in situ of copper mercaptides from cupric copper and the mercaptan sulfur, as defined, are usually pale yellow to light brown solids of varying consistency. Some are soft and jelly-like; others are firm, almost waxy. They may be clear, turbid or opaque depending on the fuel type and the particular reactants employed. All are characterized in having a greatly decreased hydrocarbon vapor pressure compared to the original liquid. They may be heated to relatively high temperatures, e. g., to as high as 150–200° F. in the case of gelled No. 2 fuel oil, without running or melting and may be cooled to well below 0° F. without becoming embrittled. The gels are combustible; as they consist almost entirely of hydrocarbon components.

The following examples illustrate the process of this invention. The gelled hydrocarbons were prepared at room temperatures in conventional chemical equipment.

Example 1

Cupric oleate was dissolved in No. 2 fuel oil to give a 0.2 weight percent solution of cupric copper. Equal parts of mercaptan sulfur as n-dodecyl and xylyl mercaptans were dissolved in No. 2 fuel oil to produce a solution containing 0.2 weight percent mercaptan sulfur. On mixing the two solutions immediate and complete gelation occurred to yield a clear firm product.

Example 2

A firmly gelled No. 2 fuel oil containing 0.05 weight percent copper (essentially as cuprous mercaptide) was prepared by mixing a fuel oil sample containing 0.1 weight percent copper (present as added cupric naphthenate) with an equal part of a fuel oil sample containing 0.1 weight percent mercaptan sulfur which was present in the fuel as added technical dodecyl mercaptan.

Example 3

To 15 parts of No. 2 fuel oil containing 0.13 weight percent mercaptan sulfur of which equal parts based on mercaptan sulfur were present as xylyl and dodecyl mercaptans was added with agitation 5 parts of No. 2 fuel oil containing 0.4 weight percent copper present as cupric naphthenate. Within 10 minutes after the two fuels were mixed the entire mass had set to a firm solid gel.

Example 4

A fuel containing 0.1 weight percent copper as cupric naphthenate was prepared by dissolving 7.2 grams of copper naphthenate containing 10% copper in 800 ml. of No. 2 fuel oil. To this fuel was added 1.2 grams of xylyl mercaptan, 5 grams of dodecyl mercaptan and 1 gram of water. The mixture was shaken vigorously in a capped jar for a few seconds whereupon the mixture completely gelled.

Example 5

Samples of No. 2 fuel oil containing 0.2 weight percent of mercaptan sulfur were made up by dissolving therein various mercaptans or mixtures of mercaptans. To each of these fuel samples was added an equal volume of a 0.2 weight percent solution of cupric naphthenate in No. 2 fuel oil. Each mixture was then immediately shaken briskly for a few seconds in a capped container and set aside for observation.

The results obtained with various mercaptans are summarized below:

Test	Mercaptan	Result
1.-----	n-butyl.-----	Turbid gel formed immediately.
2.-----	n-hexyl.-----	Opaque gel formed immediately.
3.-----	n-heptyl.-----	Clear gel formed immediately.
4.-----	n-dodecyl.-----	Do.
5.-----	n-tetradecyl.-----	Do.
6.-----	n-octadecyl.-----	Complete gelation after 0.5 hour.
7.-----	xylyl+heptyl, (1/1 mixture).	Immediate gelation of fuel.
8.-----	xylyl+dodecyl, (1/1 mixture).	Do.
9.-----	thio-beta-naphthol+dodecyl, (1/1 mixture).	Do.
10.-----	thio-beta-naphthol+dodecyl, (1/3 mixture).	Do.

In contrast, no gels were formed on using secondary aliphatic mercaptans, tertiary aliphatic mercaptans, aromatic mercaptans, or mixtures of any of these in the above tests. Sec-butyl and cyclohexyl mercaptans produced turbid fluids rather than gels; tert-butyl, tert-octyl, and tert-tetradecyl mercaptans either did not react or reacted only very slowly with the copper compound, no gel being formed. While a 3 to 1 mixture of n-dodecyl mercaptan and sec-butyl produced gel in one hour in the above test, mixtures of primary with secondary or tertiary aliphatic mercaptans were generally unsatisfactory for gelling fuels.

The above primary aliphatic mercaptans may be employed singly or as mixtures to produce completely gelled fuels.

Example 6

The results presented below show the applicability of the gelation process to various hydrocarbon fuels. A 0.4 weight percent solution of cupric copper, present as added cupric naphthenate, in each of the fuels listed below, was added to and mixed with an equal volume of the same fuel containing 0.4 weight percent mercaptan sulfur which was dissolved in the fuel as a 1:1 mixture (equal parts) of n-dodecyl and xylyl mercaptans.

Test	Hydrocarbon Fuel	Result on mixing the copper-containing with the mercaptan-containing portion of the fuel
11.-----	Isooctane.-----	Gelled immediately and completely.
12.-----	Gasoline.-----	Do.
13.-----	JP-4 Jet Fuel.-----	Do.
14.-----	Kerosene.-----	Do.
15.-----	Xylene.-----	Completely gelled within 5 min.
16.-----	Cetane.-----	Completely gelled within 30 min.

Rapid, complete gelation of the fuel is also obtained on mixing any of the copper-containing solutions with any other mercaptan-containing solution, that is, the hydrocarbon portions can be the same or different.

Example 7

A. A firm gel was prepared, following the methods described earlier, by mixing equal volumes of (a) a "deodorized" kerosene containing 0.2 weight percent copper (dissolved in the fuel as cupric naphthenate) and (b) the same base fuel containing 0.2 weight percent mercaptan sulfur (dissolved in the kerosene as a 1:1 mixture, based on the mercaptan sulfur, of xylyl and dodecyl mercaptans).

B. A lump of this gel was ignited by holding a lit match to it, said gel burned at a steady rate, the burning taking place on the surface of the gel, and, the lump continued to burn, while retaining its shape, until substantially consumed. A small residue remained. Considering that such gels consist almost entirely of hydrocarbons which are normally liquid, it is surprising that the burning gel does not melt or run, but stays in its place and retains its shape well.

C. A charcoal fire was started by placing several portions of the above-gelled kerosene on a mound of charcoal briquets and then holding a lit match to said gel. The charcoal subsequently caught fire and burned in the normal manner.

In addition to the above use, igniting a combustible material, the gelled fuels, such as gelled gasoline, kerosene and fuel oil No. 2 may also be used as a convenient source of portable canned heat; that is, they may be transported in lidded cans and burned, when desired, in the open cans.

For the purposes indicated, the gelled fuels, in being solid and having therefore a lower hydrocarbon vapor pressure, are safer and more convenient to handle and store. The solid gel burns at a somewhat slower rate and stays where it is placed, thereby providing for controlled burning. Handling of the liquid fuels, on the other hand, because of the high volatility of said fuels, entails the danger of accidental flash fires and the danger that the fire may extend beyond the confines of the intended area due to the accidental leakage or spillage.

The present method of gelling liquid hydrocarbons affords the advantage of being able to reconvert the solid gel into the mobile liquid state by the use of certain alkylene diamines as degelling agents. Thus, liquid hydrocarbon fuels are easily and rapidly gelled and degelled when desired.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A process for gelling liquid hydrocarbon fuels boiling in the gasoline and fuel oil range, which process consists of incorporating into said fuel at least 0.05% by weight of cupric copper, said copper being added as a fuel-soluble cupric carboxylate, and, at least 0.05% by weight of mercaptan sulfur, said sulfur being taken from the group consisting of a primary aliphatic mercaptan of at least 4 carbon atoms and a mixture of said aliphatic mercaptan with an aromatic mercaptan, said mixture containing at least about an equal part of primary aliphatic mercaptan sulfur.

2. The process of claim 1 wherein the primary aliphatic mercaptan is dodecyl mercaptan.

3. The process of claim 1 wherein said cupric copper is present as cupric oleate.

4. The process of claim 1 wherein said cupric copper is present as cupric naphthenate.

5. The process of claim 1 wherein the mercaptan providing said mercaptan sulfur is a mixture of dodecyl mercaptan and xylyl mercaptan, said mixture containing at least about an equal part of dodecyl mercaptan sulfur.

6. A process for gelling liquid hydrocarbon fuels boiling in the gasoline and fuel oil range, which process consists of incorporating into said fuel at least 0.05 to 1% by weight of cupric copper, said copper being added as a fuel-soluble cupric carboxylate, and, at least 0.05 to 1% by weight of mercaptan sulfur, said mercaptan providing the mercaptan sulfur being taken from the group consisting of n-alkyl mercaptans having 4 to 18 carbon atoms, and, a mixture of said n-alkyl mercaptans and xylyl mercaptans, said mixture containing at least about an equal part of n-alkyl mercaptan sulfur.

References Cited in the file of this patent

UNITED STATES PATENTS

1,749,171	Wall et al. _____	Mar. 4, 1930
2,350,544	Zimmer et al. _____	June 6, 1944