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3,684,733

GELATION OF LIQUID HYDROCARBONS

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6 Claims

ABSTRACT OF THE DISCLOSURE

A method for gelling normally liquid hydrocarbons, and the compositions produced by the method, wherein normally liquid hydrocarbons are mixed with primary or secondary amines and reacted with carbon dioxide (in some cases requiring a catalytic amount of water).

CROSS REFERENCES TO RELATED APPLICATIONS

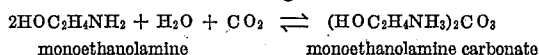
Applicants incorporate herein the disclosures of copending applications of Bannister, Pennace and Smith, entitled "Method for Separation and Purification of Aliphatic Amines," Ser. No. 73,633, and of Bannister, Pennace and Curby entitled "Device for Thickening, Igniting and Projecting Hydrocarbon Fuels," Ser. No. 73,556, both filed on the same day as the present application.

BACKGROUND OF THE INVENTION

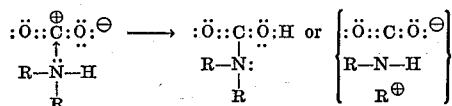
The field of the invention is solidification or gellation of normally liquid hydrocarbons for fuel and igniting devices; for facilitating the removal or collection of spills or other aggregates of such liquid hydrocarbons; and for the prevention of leakage or spills of such liquid hydrocarbons. The present invention is particularly concerned with gelled hydrocarbon compositions and the methods of gelling.

The state of the prior art of gelling liquid hydrocarbons, such as gasoline, may be ascertained by reference to the Kirk-Othmer "Encyclopedia of Chemical Technology," vol. 4 (1964), pages 893-894 under the section "Flame Agents," U.S. Pat. 2,606,107 of Feiser which issued Aug. 5, 1952, and U.S. Pat. 2,966,401 of Myerholtz which issued Dec. 27, 1970. The Feiser patent is the original "Napalm" patent and Myerholtz discloses "Napalm B" which makes use of "ABS" polymers.

That carbon dioxide reacts with amine and water is known from the Girbotol process as disclosed in Kirk-Othmer supra, vol. 4, page 362. The Girbotol process is used for the recovery of carbon dioxide from burned coke and the operation of the process depends upon the reversible nature of the following reaction:



That water is not always a necessary reactant, and that the product of the reaction of an amine and carbon dioxide is in the form of a carbamic acid or its salt is known from the work of F. Goodridge, Trans. Faraday Society 51, 1703 (1955):



The normally liquid hydrocarbon solvents that are gelled according to the present invention include petroleum hydrocarbons such as naphthas, gasoline, kerosene, fuel oil distillates and the like, pure hydrocarbons such as benzene, toluene, xylene, cyclohexane and the like, and higher boiling hydrocarbon fractions which contain substantial pro-

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portions of relatively low boiling hydrocarbons, for example, mixtures of crude oils containing lighter petroleum fractions.

The production of the amines useful in the present invention is disclosed in Kirk-Othmer supra, vol. 2, pages 99-116, under the section "Amines (Survey)," and pages 116-127 under the section "Amines (Lower Aliphatic)."

SUMMARY OF THE INVENTION

It has been discovered according to the present invention that the addition of small quantities of primary or secondary aliphatic or substituted aliphatic amines to saturated or unsaturated hydrocarbons (in certain cases with varying amounts of water also present for best results) and subsequent treatment with carbon dioxide in the gaseous or solid state results in the formation of solid and/or gelatinous compositions retaining their physical characteristics for long periods of time.

The amines useful in the present invention are aliphatic amines having 1 to 30 carbon atoms, though higher amines may also be useful. The amines are employed generally in the range of 0.1 to 10 percent by weight based upon the amount of liquid hydrocarbon being gelled.

The normally liquid hydrocarbons having amines therein which are then subjected to a reaction with carbon dioxide have particular utilities as listed below:

(1) As gel compositions for use in devices utilizing thickened fuel, including certain combustion engines; rocket engines; flame throwers, bombs, or other munitions; and similar devices.

(a) Relatively small concentrations of the amines are required. The addition of 1 part of n-butylamine to 100 parts by weight of gasoline, hexane, or similar hydrocarbon produces a rather loose slushy but still adaptable gel of sufficient consistency for use in flame throwers upon the addition of Dry Ice in excess quantity. The addition of 5 parts of the amine to 100 parts of fuel followed by Dry Ice treatment produces a very long lasting rigid gel of quite superior characteristics. In burning tests, the gels are known to retain the original consistency until the fuel has been consumed.

(b) The amines useful in the present invention are commercially available and many are disclosed in Kirk-Othmer supra (1963), vol. 2, pages 118-119.

(c) The amines are soluble in hydrocarbon fuels and facilitate the thorough and quick mixing of the thickening agents which gives rise to uniform consistencies of the thickened fuel. On the addition of carbon dioxide, gelation occurs over a range of time from almost instantaneous reaction to 5 minutes. It has been observed that the addition of about 1 part of water to 100 parts of amine accelerates the gelation in some cases.

(d) The amines are themselves flammable and in no way detract from the thermal value or flammability of the fuel. The small amount of carbon dioxide incorporated in the gel is inconsequential in terms of the possible effect on the flaming characteristics of the fuel.

(e) The gelled compositions are reversible upon the addition of water. Thus, thickened fuel is easily removed from munitions by the simple expedient of the addition of excess water, e.g. by hosing out. The fuel is unchanged by the overall gelling-degelling process and can be reclaimed for future use. Addition of dilute base (alkali carbonates or hydroxides, for example) or change to the hydrocarbon. Removal of the amine adducts with carbon dioxide can also be effected by centrifuging the gelled compositions, resulting in degelation.

(2) The hydrocarbon compositions admixed with amines are also useful as fuel thickeners for the preven-

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tion of spills, loss of fuel from leaking tanks or holds, and the general overcoming of free surface effects. The characteristics of the compositions, such as ease and speed of mixing uniform consistency of the gel, speed of gelation, gel rigidity and reversibility of gelations are useful for long term storage and transport of fuel and in damage control operations. A blanket of carbon dioxide gas provided in a container over the surface of a hydrocarbon fuel containing an amine is advantageous in the prevention of fires in all phases of storage.

(3) Certain amines, and in particular hydrophobic long chain aliphatic or substituted aliphatic primary and secondary amines, have been shown by the present invention to be quite useful in facilitating collection and removal of oil and other hydrocarbon spills over water surfaces. Thus, addition of less than 5 parts of cetylamine or octadecylamine per 100 parts of oil floating on water, followed by treatment with carbon dioxide, results in formation of waxy curds of a conglomerating nature, which can easily be collected together and subsequently removed, or which can be formed as floating rings effectively isolating hydrocarbon pools contained therein.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following amines were found to exhibit excellent gelling characteristics when admixed with liquid hydrocarbons and then reacted with carbon dioxide:

Benzylamine
Benzhydrylamine
N-benzyl-N-(2-cyanoethyl)amine
n-Butylamine
N-ethyl-N-butylamine
N-methyl-N-butylamine
N-hexadecylamine
N-dodecylamine
1-amino-2-hydroxyhexadecane

The following amines were also useful in the gelling of hydrocarbons when reacted with carbon dioxide:

Methylamine
n-Hexylamine
n-Dodecylamine
N-methyl-N-dodecylamine
Morpholine
Piperidine
Dimethylamine
1-amino-2-propanol
3-amino-1-propanol
n-Propylamine
1-propylamine
t-Butylamine
i-Butylamine
Diisobutylamine
1,6-hexanediamine
Ethylenediamine
2-methoxyethylamine

The concentration of the amines in the hydrocarbons ranges from 0.1 to 10 percent by weight amine based on the hydrocarbon and the preferred range is 1 to 5 percent.

Carbon dioxide is used in the solid, liquid or gaseous states; these reactants are always used in excess in order to insure complete reaction. For each mole of amine used, there must be more than a half mole of carbon dioxide.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent.

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EXAMPLE 1

A solution of 5 parts of benzylamine is mixed with 100 parts by weight of gasoline in a suitable container. Crushed Dry Ice is added with shaking for a few seconds, whereupon the solution immediately sets up in a gel. Treatment of the gel with water will reverse the gelling process and again make the gasoline available as a liquid when desired.

EXAMPLE 2

Example 1 is repeated in a container with a leak in the bottom. The gasoline leakage quickly slows and then stops.

EXAMPLE 3

A large flat vessel containing several gallons of salt water is layered with motor oil to a depth of 1/2 inch. A solution of cetylamine in benzene, corresponding to 4 parts of amine to 100 parts of motor oil, is evenly distributed over the oil layer. Another solution of carbon dioxide in benzene, with a calculated excess of carbon dioxide being used in a sufficient amount of benzene to provide a specific gravity less than 1.0, is evenly distributed over the oil layer containing the amine. A slushy gel immediately sets up, of loose consistency but still capable of holding its form to facilitate removal from the surface and/or entrapment of oil pools within enclosed areas. Because of its long chain character this gel tends to be hydrophobic and maintains its gel properties in the presence of water.

EXAMPLE 4

Example 1 is repeated using N-methyl-N-butylamine; upon the addition of 0.1 percent by weight of water, a gel of similar consistency is formed.

We claim:

1. A method for gelling a normally liquid hydrocarbon comprising admixing said hydrocarbon with about 0.1 to about 10 percent by weight of an aliphatic or substituted aliphatic amine having 1 to 30 carbon atoms and reacting the admixture with carbon dioxide in excess quantity.

2. The method of claim 1, wherein said amine concentration is about 1 to about 5 percent.

3. The method of claim 1, further comprising adding traces of water to facilitate gelation.

4. A gelled hydrocarbon consisting essentially of a normally liquid hydrocarbon, and the reaction product of about 0.1 to about 10 percent by weight of an aliphatic or substituted aliphatic amine having 1 to 30 carbon atoms and carbon dioxide in excess of 1 mole per 2 moles of said amine.

5. The gelled hydrocarbon of claim 4, wherein said amine concentration is about 1 to about 5 percent.

6. The gelled hydrocarbon of claim 4, wherein said amine is selected from the group consisting of benzylamine, benzhydrylamine, N-benzyl-N-(2-cyanoethyl)amine, n-butylamine, N-ethyl-N-butylamine, hexadecylamine, dodecylamine, and N-methyl-N-butylamine.

References Cited

UNITED STATES PATENTS

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2,958,665	11/1960	Stefcik et al.	252-316

RICHARD D. LOVERING, Primary Examiner

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44-7 C, 7 D; 166-294; 210-65, DIG. 21; 252-327