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SOLIDIFIED NORMALLY LIQUID
HYDROCARBONS

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This invention relates to new and useful im-
provements in solidified normally liquid hydro-
carbons.

The normally liquid hydrocarbons in accord-
ance with the invention are of the combustible
type and preferably of the combustible fuel type.
One example is, for instance, a petroleum distil-
late. Another example is a mixture of hydro-
carbons of the benzene series. Although such
normally liquid hydrocarbons as used for fuel
ordinarily contain numerous hydrocarbons, the
term "hydrocarbons" as used herein includes the
limiting case in which only one hydrocarbon is
present. As a normally liquid hydrocarbon, I
may, for instance, use gasoline, although I pre-
fer a petroleum distillate of closer boiling point.
Also benzol or a light coal tar distillate consist-
ing predominantly of benzol homologues may be
used. The normally liquid hydrocarbons in ac-
cordance with my invention are preferably for
ordinary use readily inflammable and preferen-
tially then possess a flash point not substantially
above normal temperature so that combustion
may be started by means of a match or similar
lighter while the fuel is at normal temperature.

In accordance with the invention a voluminous
gel of a metallic soap substantially insoluble or
limitedly soluble in the hydrocarbon to be solid-
ified is created, in situ, in such hydrocarbon by
reacting a hydrocarbon solution of a suitable or-
ganic compound, saponifiable to yield a volumi-
nous metallic soap, with a suitable saponifica-
tion agent suspended in the hydrocarbon solu-
tion in substantially dry pulverulent form, under
conditions substantially assuring finest commin-
ution of the soap products formed.

The saponification reaction may be either one
of acid neutralization or of double decomposition.
The saponification agent should be maintained in
suspension during the reaction, i. e., no appre-
ciable segregation of suspended particles should
occur. This, as a rule, may be accomplished by
agitation or by the procurement of finest dis-
persion of saponification agent in the hydrocar-
bon to be solidified and preferably with the aid
of a suitable dispersion device such as a colloid
mill, ball mill or the like.

Comminution of the soap products formed dur-
ing the reaction may be accomplished in accord-
ance with the invention by agitation. The com-
minution may be carried out or enhanced by the
use of a suitable comminuting or dispersing de-
vice such as a colloid mill, ball mill or the like.
When proceeding in this manner, the resulting
products are of a heavily viscous to petrolatum-

like consistency depending upon the amount of
soap products present. The solidified hydrocar-
bon products of a consistency approaching or
simulating that of petrolatum are, as a rule, pre-
ferred as they cannot be poured under normal
conditions and are usually possessed of a high
degree of homogeneity.

I have discovered that it is sometimes of ad-
vantage in the production of products of rela-
tively high consistency, such as those approach-
ing or simulating petrolatum consistency, to use
dispersing or peptizing agents of a type substan-
tially soluble in the hydrocarbon to be solidified.

In some cases, it is of advantage to initiate or
expedite the saponification reaction by heating
the hydrocarbon solution containing the react-
ants to a temperature of above normal or alter-
natively procure the mixing of the reactants at
such temperature. Depending upon the react-
ants used, the temperature requirements may
vary. In some cases, a temperature of about
40° C. may suffice, while in other cases, higher
temperatures must be resorted to. In most cases,
once the saponification reaction has been satis-
factorily initiated, the heating may be discon-
tinued. In some cases, it may be of advantage
to continue the heating until the substantial
completion of the saponification reaction.

The organic compound of the afore-mentioned
type is preferably one of the aliphatic acid or
acid salt series, carrying at least one carboxyl
or carboxyl metal group in aliphatic chain link-
age, the aliphatic chain in either case having
preferably at least 12 carbon atoms in said chain.
The organic compound in accordance with the
invention may thus comprise either an organic
acid salt or free organic acid of the above-men-
tioned type and nature. If the same is an or-
ganic acid, the saponification reaction is one of
neutralization of the acid with the saponifica-
tion agent. On the other hand, if the organic
compound is a salt, the saponification reaction
will be one of double decomposition between the
organic acid salt and the saponification agent.
Organic acids useful in accordance with the in-
vention are, for instance, stearic acid, oleic acid,
palmitic acid and the like. In many instances
the commercial forms of these acids may be used,
such as, for instance the products obtained by
the splitting of fats and containing a mixture of
palmitic, stearic and oleic acids in varying pro-
portions. Commercial products of this type are,
for instance, coconut oil fatty acids, peanut oil
fatty acids, palm oil fatty acids and the like.
For best results, I have found it of advantage

to use stearic acid. Organic salts that may be used in the practice of my invention are, for instance, the metal salts of any of the herein enumerated organic acids or mixtures of organic acids in which the metal is capable of exchange with the metal of the saponification agent.

The saponification agent of the type hereinabove referred to may be any agent which is capable of neutralizing the organic acid present in the hydrocarbon solution or reacting with a suitable salt of such organic acid by way of double decomposition as the case may be. The saponification agent should in all cases be such as is capable of forming with the organic compound in accordance with the invention a voluminous metallic soap gel insoluble or limitedly soluble in the liquid material to be solidified. Good results are preferably obtained with hydroxides and alcoholates and suitable saponification agents of this type, useful in accordance with the invention are, for example, sodium hydroxide, sodium alcoholates and the like. It is sometimes of advantage and desirable to initiate or expedite the saponification reaction by passing the reaction mix containing both the organic compound and the saponification agent through a suitable dispersion device. In accordance with the preferred practice of my invention, the saponification agent is added to the hydrocarbon solution of the organic compound in the form of a fine suspension in a portion of the hydrocarbon to be solidified.

The alcoholates are preferably the salts of monohydric and polyhydric alcohols carrying the hydroxyl group in aliphatic chain linkage. Examples of such alcohols are, for instance, the simple alcohols of the aliphatic series, such as methyl, ethyl, propyl, iso-propyl, butyl, iso-butyl, and the like alcohols. Examples of suitable polyhydric alcohols, are, for instance, the glycols. The alcoholate formation may be accomplished by the dissolution of a suitable metal such as metallic sodium in the alcohol. Whenever possible, however, such as in the case of the simple aliphatic alcohols, as for instance, methyl alcohol, ethyl alcohol, and the like, I prefer to obtain alcoholate formation by adding to a strong and concentrated alcohol, a suitable solid anhydrous metal hydroxide, such as sodium hydroxide with subsequent evaporation of excess alcohol. When proceeding in this manner, I prefer to use an alcohol concentration of in excess of 90% and preferably in excess of 95% and preferably equimolecular proportions of alcohol and hydroxide.

The dispersing or peptizing agent that I may use may be any one or combination of agents and preferably organic agents of this type, well-known in the art, substantially soluble in the hydrocarbon to be solidified, such as petroleum mahogany sulphonate, triethanolamine, and products of like character and nature. The amount of dispersing or peptizing agent to be added depends inter alia upon the reactants used and the fineness of dispersion desired.

The amount of reagents used within the practical application of my invention should be preferably so adjusted that the organic compound and hydrocarbon are present in a ratio sufficient to solidify substantially all of the hydrocarbon present with the soap gel formed. As a general rule 4% to 10% of the organic compound will accomplish this result. The saponification agent should be present in amount sufficient to accomplish the saponification, which as a rule, requires in excess of stoichiometric amounts. When using alcoholates containing crystal alcohol, care

should be taken that the alcohol content is considered in calculating the required amount of saponification agent. A satisfactory solidified product contains approximately 4 to 11% (calculated on the hydrocarbon present) of metallic soap gel.

The following is a practical example in accordance with the invention given by way of illustration but not of limitation.

Example I

A petroleum hydrocarbon cut of a boiling range of 145° to 210° F. was used. 6.25% of stearic acid was dissolved in this hydrocarbon. 1.55% of sodium methylate (calculated as crystal alcohol free) produced by evaporation to dryness a mixture of approximately equal parts by weight of anhydrous sodium hydroxide and anhydrous methyl alcohol, was thereupon added to the hydrocarbon solution of the stearic acid. The reaction mass was substantially maintained at a temperature of approximately 40° C. with vigorous agitation until gel formation had proceeded to a point where no stratification or segregation of saponification agent occurred upon interruption of the agitation. The sodium methylate was added to the organic acid hydrocarbon solution in finely pulverized dry form and kept in fine suspension therein by means of agitation. Vigorous agitation was used throughout the reaction until the completion thereof. The resulting product was a heavily viscous homogeneous mass of a sticky pourable nature. The same burned without increase in fluidity.

In certain instances where the reaction seems to be delayed or to proceed with difficulty even though the mass is heated to the reaction temperature, a small amount of alcohol from 0.5% to 1.5% will initiate or expedite the reaction. The presence of alcohol is further beneficial in that the final product containing small amounts of alcohol, but not exceeding about 3%, is characterized by a firmer structure.

In the practical operation of my method, I find it sometimes of advantage to carry the saponification reaction only to a point at which gel formation in the reaction mass has proceeded to a point at which the viscosity imparted to the mass by the gel formed is sufficient to substantially maintain the particles of unreacted saponification agent in suspension.

This may be achieved, for instance, by preparing a suspension of the entire amount of saponification agent required in a hydrocarbon solution of only a portion of the organic compound. The amount of such organic compound is then preferably so selected as to be just sufficient to yield by saponification, the gel formation necessary for the desired degree of viscosity. The solution obtained in this manner contains unreacted saponification agent held in suspension by the soap gel formed and further amounts of organic compounds may then be added to the solution at any subsequent time for further reaction and solidification. It is however also possible and special circumstances may make it desirable, to use in this multiple step saponification procedure an initial amount of organic compound less than that required for soap gel formation to the point of desired viscosity.

When using this procedure of successively reacting portions of organic compounds, the organic compounds for each portion may be either the same compounds or different compounds as desired.

I claim:

1. Method for solidifying a normally liquid inflammable hydrocarbon which comprises reacting a solution, in said hydrocarbon, of at least one organic fatty acid, saponifiable to produce a voluminous metallic soap gel from limitedly soluble to insoluble in said hydrocarbon, with a saponification agent, suspended in said hydrocarbon in substantially dry pulverulent form, and comprising at least one member selected from the group consisting of sodium hydroxide and sodium alcoholates, the temperature of reaction being such that soap gel precipitates continuously substantially as formed, and agitating the mix throughout the saponification reaction to assure finest comminution of soap gel formed, said organic acid carrying at least one carboxyl group in aliphatic chain linkage of at least twelve carbon atoms in such chain.

2. Method according to claim 1 in which from 4 to 10% of fatty acid calculated upon the total amount of hydrocarbon present is reacted with said saponification agent.

3. Method for solidifying a normally liquid inflammable hydrocarbon which comprises reacting a 4% to 10% solution, in said hydrocarbon, of stearic acid with sodium hydroxide suspended in said hydrocarbon in substantially dry pulverulent form and agitating the mix throughout the saponification reaction to assure finest comminution of the sodium stearate gel formed.

4. Method for solidifying a normally liquid inflammable hydrocarbon which comprises preparing a suspension of sodium hydroxide in a first portion of said hydrocarbon, reacting said suspension with a stearic acid solution in a second portion of said hydrocarbon, said stearic acid being present from 4% to 10% of the total amount of hydrocarbon, and agitating the mix throughout the saponification reaction to assure finest comminution of sodium stearate gel formed.

5. Method for solidifying a normally liquid inflammable hydrocarbon which comprises reacting, in the presence of an aliphatic alcohol of not more than 5 carbon atoms, an organic fatty acid solution in said hydrocarbon with sodium hydroxide, suspended in said hydrocarbon in substantially dry pulverulent form, and agitating the mix throughout the saponification reaction to assure finest comminution of soap gel formed, said alcohol being present in amount not substantially in excess of about 3% of the hydrocarbon, said organic acid being saponifiable to produce a voluminous metallic soap gel from limitedly soluble to insoluble in said hydrocarbon, carrying at least one carboxyl group in aliphatic chain linkage, of at least 12 carbon atoms in such chain and being present in said solution from 4% to 10% of the total amount of hydrocarbon added.

6. Method for solidifying a normally liquid in-

flammable hydrocarbon which comprises reacting, in the presence of methyl alcohol, a stearic acid solution in said hydrocarbon with sodium hydroxide, suspended in said hydrocarbon in substantially dry pulverulent form, and agitating the mix throughout the saponification reaction to assure finest comminution of sodium stearate gel formed, said methyl alcohol being present in amount not substantially in excess of 3% of the hydrocarbon present in the final product.

7. A solidified hydrocarbon material which comprises a hydrocarbon gel of from syrupy viscous to petrolatum like consistency predominantly composed of a normally liquid inflammable hydrocarbon and 4 to 11% of a voluminous sodium fatty acid soap from limitedly soluble to insoluble in said hydrocarbon, said soap having an organic acid radical carrying at least one carboxyl group in aliphatic chain linkage of at least 12 carbon atoms in such chain, said gel having a bulk specific gravity substantially equivalent to the total weight of the components divided by the total volume of the components, being characterized by substantial freedom from melting when burning and being prepared to include precipitation of hydrocarbon fatty acid soap gel by reaction of free fatty acid, dissolved in said hydrocarbon, with solid, pulverulent saponification agent of the group consisting of sodium hydroxide and sodium alcoholates at a temperature assuring precipitation of soap gel continuously as formed and agitation substantially throughout the saponification reaction.

8. A solidified hydrocarbon material which comprises a hydrocarbon gel of substantially petrolatum like consistency predominantly composed of a normally liquid inflammable hydrocarbon and 4 to 11% of sodium stearate, said gel having a bulk specific gravity substantially equivalent to the total weight of the components divided by the total volume of the components, being characterized by substantial freedom from melting when burning and being prepared to include precipitation of hydrocarbon sodium stearate gel by reaction of free stearic acid, dissolved in said hydrocarbon, with solid, pulverulent saponification agent of the group consisting of sodium hydroxide and sodium alcoholates at a temperature assuring precipitation of stearate gel continuously as formed and agitation substantially throughout the saponification reaction.

9. A solidified hydrocarbon material in accordance with claim 8 in which said hydrocarbon gel contains not in excess of 3% of methyl alcohol based on the hydrocarbon present.

10. A solidified hydrocarbon material in accordance with claim 8 in which said hydrocarbon gel contains a pyrotechnical compound.

ALBERT JOSEPH LALIBERTE.

In the following example, an alternative procedure obtaining a stearic acid soap in accordance with the invention is illustrated.

Example II

A dispersion of substantially anhydrous NaOH in naphtha was prepared by finely grinding three parts by weight of NaOH with 21 parts by weight of naphtha and adding the resulting dispersion including 28 parts by weight of naphtha washings to 91 parts by weight of naphtha. 15 parts by weight of stearic acid were melted and added to 140 parts by weight of naphtha. The stearic acid naphtha solution was added slowly to the well agitated dispersion of sodium hydroxide in naphtha. Reaction took place immediately and stirring was continued for approximately twenty minutes at which time reaction was substantially complete. The reaction mass constituted a syrupy sticky mass that could be poured and which adhered tenaciously to any surface with which it was contacted or against which it was thrown. The product burned without decrease in viscosity.

In the following example an illustration is given of the preparation of a solidified hydrocarbon material in accordance with the invention using a dispersing or peptizing agent.

Example III

The procedure in this example is the same as that utilized in Example II. In this case, three parts by weight of mahogany sulphonate were added to a suspension of 5 parts by weight of NaOH in 140 parts by weight of gasoline. A solution of 25 parts by weight of stearic acid in 140 parts by weight of gasoline was slowly added to the vigorously stirred NaOH dispersion and the agitation continued until completion of the reaction. The product formed in this case possessed a consistency similar to that of petrolatum. The product could not be poured and when in contact with or thrown against a surface, adhered tenaciously thereto. The product upon heating or burning did not liquefy.

The consistency of the products in accordance with my invention may be varied or modified by changes in the reactants used so as to procure lesser or greater soap formation. Thus, for instance, when using a stearate soap as solidification agent higher amounts of stearic acid and NaOH, as seen from Example III, will produce solidified products more nearly approaching petrolatum like consistency.

In accordance with my invention and as a still further embodiment thereof, I have discovered that it is possible to incorporate pyrotechnical agents and compositions into the solidified hydrocarbons substantially without materially affecting the characteristics of these products particularly with respect to liquefaction when heating or burning. These products may comprise any one or more of the known pyrotechnical agents or compositions including incendiary agents or compositions well known in the art. In the preparation of these products, I find it of advantage to finely disperse the pyrotechnical or incendiary agent in the hydrocarbon suspension of the saponification agent. Care should be taken however that the incendiary or pyrotechnical agent is so selected that it will not react with either the organic compound or saponification agent so as to impair the saponification reaction. Thus, for instance, dispersions of mixtures of chlorate with

magnesium powder exhibit a thermite effect when ignited. These products are as a rule characterized by intermittent flaring.

The products obtained in accordance with the invention are characterized by a high degree of homogeneity and are of a consistency varying from pourable syrupy viscous to substantially non-pourable petrolatum-like consistency. The products possessing the consistency similar to or approaching that of petrolatum can be handled as ordinary solids. The products in accordance with the invention will not liquefy or materially decrease in viscosity, as the case may be, when subject to raised temperatures such as when burning the products. The products further distinguish themselves by a relatively high degree of stickiness, i. e., they adhere tenaciously to most surfaces with which they come into contact. This is particularly true of the products of petrolatum like consistency. The products are further characterized by the fact that the normally liquid hydrocarbon material which they contain may be recovered in substantially unadulterated form by the application of pressure, centrifugal manipulation, distillation or the like. Alternatively, the hydrocarbon material may be recovered from the products solidified in accordance with the invention by separation with the aid of suitable solvent extraction. In such case, the extracting solvent is preferably one in which the metallic soap is substantially soluble and the hydrocarbon but limitedly soluble or substantially insoluble.

The products in accordance with the invention are characterized by a considerable density. The solidified products are thus substantially free from voids and have a bulk specific gravity, i. e., specific gravity of the entire product, equivalent to at least the specific gravity of the normally liquid hydrocarbon component and preferably a bulk specific gravity approximately equivalent to the total weight of the components divided by the total volume of the components. By reason of their density and characteristics of structure, the solidified products contain a high volume percentage of hydrocarbon material.

In the preparation of solidified products as hereinabove set forth, a particular organic compound or acid used in the saponification reaction may sometimes yield a product of an undesirably low viscosity. This condition may be for instance encountered when using oleic acid. Though the resulting products are satisfactory for most purposes and will not materially increase in fluidity or decrease in viscosity when heated, it is, as a general rule, particularly for shipping and handling purposes, desirable to obtain a more highly viscous consistency of the compound. In most cases the lack in desired high consistency can be remedied by using the particular organic compound or acid in question together with an organic compound or acid of the type yielding solidified products of a more satisfactory degree of consistency. By a proper proportioning of such organic compound or acid mixture, desired intermediate consistencies can be procured. For example, where oleic acid is to be used in the saponification reaction it is preferred to use a mixture of oleic acid with stearic acid.

The foregoing description is by way of illustration and not of limitation and it is, therefore, my intention that the invention be limited only by the appended claims or their equivalents, in which I have endeavored to claim broadly all inherent novelty.

CERTIFICATE OF CORRECTION.

Patent No. 2,385,818.

October 2, 1945.

ALBERT JOSEPH LALIBERTE.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, first column, line 29, claim 3, after the word "form" insert --, the temperature of reaction being such that sodium stearate gel precipitates continuously substantially as formed,--; line 39, claim 4, and second column, line 5, claim 6, after the comma and before "and agitating" insert --the temperature of reaction being such that sodium stearate gel precipitates continuously substantially as formed,--; same page, first column, line 48, claim 5, after the comma and before "and agitating" insert --the temperature of reaction being such that soap gel precipitates continuously substantially as formed,--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of January, A. D. 1946.

Leslie Frazer

(Seal)

First Assistant Commissioner of Patents.