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SOLIDIFIED NORMALLY LIQUID HYDROCARBONS

Albert Joseph Laliberte, Naugatuck, Conn., assignor to Safety-Fuel Incorporated, West Cheshire, Conn., a corporation of Connecticut

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This invention relates to new and useful improvements in solidified normally liquid hydrocarbons.

The normally liquid hydrocarbons in accordance with the invention are of the combustible type and preferably of the combustible fuel type. One example is, for instance, a petroleum distillate. Another example is a mixture of hydrocarbons of the benzene series. Although such normally liquid hydrocarbons as are 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 prefer a petroleum distillate of closer boiling point. Also benzol or a light coal tar distillate consisting predominantly of benzol homologues may be used. The normally liquid hydrocarbons in accordance with my invention are preferably for ordinary use readily inflammable and preferentially then possess a flash point not substantially above normal temperature so that combustion may be started by means of a match or a 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 solidified is created, in situ, in such hydrocarbon by reacting a hydrocarbon solution of a suitable organic compound, saponifiable to yield a voluminous metallic soap, with a suitable saponification agent suspended in the hydrocarbon solution in substantially dry pulverulent form, and permitting the reaction to proceed in at least the last stages thereof while the reaction mix is in substantially quiescent condition.

The saponification reaction may be either one of acid neutralization or of double decomposition. The suspension of saponification agent must be maintained substantially stable during at least the quiescent stage of the reaction, i. e., no appreciable segregation of suspended particles should occur upon discontinuance of agitation. This may be accomplished by the formation of a portion of the soap gel to a point at which the viscosity imparted to the mix by the gel is sufficient to substantially maintain the particles in suspension while the mix is substantially quiescent and in the limiting case by suspension of particles of saponification agent of such fineness that the same remains suspended substantially without presence of soap gel. In any case however viscosity of the mix and particle size of suspended saponification agent must be so coordinated at the beginning of the quiescent reaction stage that no appreciable segregation of particles of saponification agent occurs during that stage. Except in the limiting case referred to agitation of the mix should be resorted to until the desired point of viscosity in the mix is obtained.

In some cases it is of advantage to initiate or expedite the saponification reaction by heating the hydrocarbon solution containing the reactants for a short period of time to a temperature of above normal or, alternatively, procure the mixing of the reactants at such temperature. Depending upon the reactants used the temperature requirements may vary. In some cases a temperature of about 40° C. may suffice while in other cases materially higher temperatures must be resorted to. The reaction mix is preferably agitated and the reaction temperature substantially maintained until gel formation therein has proceeded to the desired point of viscosity. Heating and agitation may then be discontinued and the reaction will proceed while the mix is substantially quiescent at a more or less rapid pace. The fact that it is possible to utilize agitation within the first part of the procedure is of advantage in accordance with the invention as it permits the saponification agent to be mechanically suspended throughout the first stage of the reaction. Once gel formation of the type mentioned is obtained, the mass may be introduced into fuel containers in which it will thereafter solidify itself. Completion of the solidification while the mix is substantially quiescent is of prime importance as the disturbance by agitation of the reaction mass during at least the last stages of the congelation is detrimental to the desired characteristics and particularly to the homogeneity of the solidified product.

The organic compound of the afore-mentioned type is preferably a rosin acid or rosin acid salt, or, alternatively a compound of the aliphatic acid or acid salt series, carrying at least one carboxyl or carboxyl metal group, in aliphatic chain linkage, the aliphatic chain 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-mentioned type and nature. If the same is an organic acid, the saponification reaction is one of neutralization of the acid with the saponification 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 invention are, for instance, stearic acid, oleic acid, palmitic acid, abietic acid and the like. In many instances the commercial forms of these acids may be used, such as, for instance, rosin, or, the products obtained by the splitting of fats and containing a mixture of palmitic, stearic, and oleic acids in varying proportions. 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 rosin or stearic acid or a mixture thereof. 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 metal 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.

In some cases, I prefer to suspend the saponification agent in accordance with the invention in substantially anhydrous pulverulent finely dispersed form in the hydrocarbon solution containing the organic acid with the use of a colloid mill or other device for procuring finest dispersion. It is also sometimes of advantage and desirable to initiate or expedite the saponification reaction by passing the reaction mix through such dispersion device. In many instances it may be also of advantage to add to the hydrocarbon solution of the organic compound, in accordance with the invention, the saponification agent in the form of a fine suspension in the hydrocarbon and preferably with vigorous agitation of the mix while adding the suspension. For best results it is also in this case desirable to utilize a colloid mill or other dispersion device in making the hydrocarbon dispersion of the saponification agent.

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 equ molecular proportions of alcohol and hydroxid

The amount of reagents used within the pra tical application of my invention should be pre erably so adjusted that the organic compour and hydrocarbon are present in a ratio sufficier to solidify substantially all of the hydrocarbo present with the soap gel formed. As a gener rule 4% to 10% of the organic compound wi accomplish this result. The saponification ager should be present in amount sufficient to accom plish the saponification, which as a rule, require in excess of stoichiometric amounts. When usin alcoholates containing crystal alcohol, car should be taken that the alcohol content is con sidered in calculating the required amount c saponification agent. The following is a prac tical example in accordance with the inventio given by way of illustration but not of limita tion.

Example I

A petroleum hydrocarbon cut of a boilin range of 145° to 210° F. was used. 5% of steari acid was dissolved in this hydrocarbon. 1.25% of sodium methylate (calculated as crystal al cohol free) produced by evaporation to drynes a mixture of approximately equal parts by weigh of anhydrous sodium hydroxide and anhydrou methyl alcohol, was thereupon added to the hydrocarbon solution of the stearic acid. The reaction mass was heated for a short period o time and the temperature maintained at approximately 40° C. with agitation until ge formation had proceeded to a point where nc 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 the agitation. Upon gel formation as described the reaction mass was poured into fuel containers in which it solidified without any further manipulation. Solidification proceeded very rapidly, being substantially accomplished within a period of 15 to 20 minutes.

In certain instances where the reaction seems to be delayed or to proceed with difficulty, even through the mass is heated to the reaction temperature, a comparatively small amount of alcohol, say from 0.5% to 1.5% based on the hydrocarbon will initiate or expedite the reaction. Such addition of alcohol is particularly beneficial in the case of rosin and allied compounds. A procedure of this type is, for instance, set forth by way of illustration in the following example:

Example II

6.0% of rosin was dissolved in the same petroleum hydrocarbon cut as used in Example I. 1.2% of sodium methylate and 0.9% of alcohol were added to the solution whereupon the reaction mixture was treated in the same manner as described in Example I.

In accordance with my invention and as a further embodiment thereof I find it sometimes of advantage to use a mixture of aliphatic acids and preferably a mixture of stearic acid and rosin. The resulting stearate and resinate containing product possesses in many respects characteristics superior to those possessed by products containing the stearate or resinate alone. Inter alia the stearate and resinate product has a much more uniform consistency and superior homogeneity. Furthermore the burning charac-

teristics are improved. Whereas, for instance, a resinate product leaves a more or less loose sandy residue after its combustion, the residue of the stearate containing resinate product comprises more or less compact isolated residual agglomerations.

In the practical operation of my method I find it sometimes of advantage to carry the saponification reaction only to the point of gel formation at which the desired viscosity necessary for maintaining particle suspension, prevails in the hydrocarbon mix. 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. In such cases, agitation should be used to insure proper suspension of saponification agent at least until the aggregate of the gel formed is sufficient to impart to the mix the desired degree of 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. Thus when preparing, in accordance with the invention, a solidified product containing a mixture of organic acid soaps, such as a stearate-resinate product, the particular procedure of adding the organic compounds in successive portions may be conveniently used. The following example illustrates one mode of operation utilizing the two-phase saponification reaction:

Example III

800 parts by weight of naphtha containing dissolved therein 1.25% by weight of stearic acid and 1.88% by weight methyl alcohol were provided with 1.5% by weight of substantially anhydrous pulverulent sodium hydroxide dispersed in the solution. The sodium hydroxide suspension was maintained with agitation until the completion of sodium stearate gel formation. The particle size of the sodium hydroxide in suspension was such that the sodium stearate gel formed sufficed to maintain the unreacted sodium hydroxide particles in suspension. Agitation was carried out with the aid of a ball mill which at the same time served to produce the desired fine particle size of the hydroxide. Use of the ball mill also aided in the stearate saponification reaction which took place at normal temperatures. To the substantially stable naphtha and sodium stearate mix, containing unreacted sodium hydroxide in substantially stable suspension, 800 parts by weight of naphtha, containing dissolved therein 8.75% by weight of rosin, were added. Upon thoroughly mixing the reaction mix was left quiescent and solidification proceeded rapidly with the formation of sodium resinate gel.

The alcohol present in the foregoing example was added to permit the rosin saponification without the necessity of resorting to higher temperatures. The alcohol also acts to some extent as a reaction booster for the stearate gel formation.

For best results, I prefer a stearate and resinate containing product containing from 5% to 20% and preferably 10% to 15% by weight of stearate calculated on the aggregate amount of metallic soap present.

The products obtained in accordance with the invention are substantially homogeneous and can be cut with a knife and handled as ordinary solids. The products will not liquify when subject to raised temperatures and will burn without melting. 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 manipulations, distillations, 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 hydrocarbon is but limitedly soluble or substantially insoluble. In most cases, the latter type recovery of hydrocarbon material may be procured by slushing the solidified products, made in accordance with the invention, with water.

The products in accordance with the invention are further characterized by a considerable density and represent essentially a substantially solid system predominantly composed of the hydrocarbon material and the metallic soap. 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 the particular organic compound or acid used in the saponification reaction may sometimes yield a product of a more or less heavy viscous molasses-like structure. This condition may be for instance encountered when using oleic acid. Though the resulting products are satisfactory for most purposes and will not melt but on the contrary will become increasingly more solid when heated it is as a general rule particularly for shipping and handling purposes desirable to obtain greater solidity of the compound. In most cases the lack in desired solidity 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 high degree of solidity. By a proper proportioning of such organic compound or acid mixture any desired intermediate solidity 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 or rosin.

The foregoing description is furnished 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 equiv-

alents wherein I have endeavored to claim broadly all inherent novelty.

I claim:

1. Method for solidifying normally liquid inflammable hydrocarbons which comprises reacting a solution, in said hydrocarbon, of at least one organic acid, saponifiable to produce a voluminous metallic soap gel substantially insoluble in said hydrocarbon, with a saponification agent, suspended with agitation in said hydrocarbon in substantially dry pulverulent form, of the type reactable with said compound to thereby form said soap gel and comprising at least one member selected from the group consisting of sodium hydroxide and sodium alcoholates, and permitting the materials to remain substantially quiescent during at least the last stages of the reaction ,the viscosity of the mix and the particle size of the said saponification agent being so coordinated as to substantially maintain said saponification agent in suspension during at least said last stages, agitation being discontinued not earlier than the point at which said coordinated viscosity is present, said organic acid being at least one member selected from the group consisting of rosin acids and aliphatic acids, the latter carrying at least one carboxyl group in aliphatic chain linkage of at least twelve carbon atoms in said chain.

2. Method for solidifying normally liquid inflammable hydrocarbons which comprises reacting a solution in said hydrocarbon, of at least one organic acid, saponifiable to produce a voluminous metallic soap gel substantially insoluble in said hydrocarbon, with a saponification agent, suspended in said hydrocarbon in substantially dry pulverulent form, of the type reactable with said acid to thereby form said soap gel and comprising at least one member selected from the group consisting of sodium hydroxide and sodium alcoholates, agitating the mix at least until the viscosity imparted thereto by a portion of the soap gel formed is sufficient to maintain the saponification agent in suspension while said mix is quiescent, discontinuing agitation and permitting the mix to remain substantially quiescent during at least the last stages of the reaction, said organic acid being at least one member chosen from the group consisting of rosin acids and aliphatic acids, the latter carrying at least one carboxyl group in aliphatic chain linkage of at least twelve carbon atoms in such chain.

3. Method in accordance with claim 2 in which said saponification agent is sodium methylate.

4. Method in accordance with claim 2 in which said organic acid is rosin acid.

5. Method in accordance with claim 2 in which said organic acid is stearic acid.

6. Method for solidifying normally liquid inflammable hydrocarbons which comprises reacting a solution, in said hydrocarbon, of at least one portion of at least one organic acid, saponifiable to produce a voluminous metallic soap gel substantially insoluble in said liquid material, with an excess of saponification agent suspended with agitation in said hydrocarbon in substantially dry pulverulent form, of the type reactable with said acid to thereby form said soap gel and comprising at least one member selected from the group consisting of sodium hydroxide and sodium alcoholates, thereafter reacting in the resulting hydrocarbon mix at least one second portion of at least one such organic acid with unreacted suspended saponification agent, and permitting the materials to remain substantially quiescent during at least the last stages of the second reaction, the viscosity of the mix and the particle size of said saponification agent being so coordinated as to substantially maintain said saponification agent in suspension during at least said last stages, agitation being discontinued not earlier than the point at which said coordinated viscosity is present, said organic acid being at least one member selected from the group consisting of rosin, and aliphatic acids, the latter carrying at least one carboxyl group in aliphatic chain linkage of at least twelve carbon atoms in such chain.

ALBERT JOSEPH LALIBERTE.