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SOLIDIFIED NORMALLY LIQUID HYDROCARBONS

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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 inflammable type and preferably of the combustible fuel type. One example, for instance, is 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 similar lighter while the fuel is at normal temperature.

One method of solidifying normally liquid hydrocarbons comprises the formation in situ in the hydrocarbon to be solidified of a voluminous gel of a metallic soap substantially insoluble or limitedly soluble in said hydrocarbon. This is accomplished 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 is preferably one of acid neutralization. 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. The viscosity of the mix and the particle size of the suspended saponification agent should be so coordinated at the beginning of the quiescent reaction stage that no appreciable segregation of the particles of saponification agent occurs during that stage. 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 agitated and is preferably substantially maintained at that temperature until gel formation has proceeded to a point at which the desired viscosity is obtained. 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. Completion of the solidification while the mix is substantially quiescent is of importance as disturbance by agitation during at least the last stages of congelation is detrimental to the desired characteristics and particularly to the homogeneity of the solidified product.

The reaction stage at which the desired viscosity and thus stability of suspension of saponification agent obtains, as described in the foregoing procedure, is relatively transient and makes storage of the mix pending solidification at any desired subsequent time, as for instance in fuel containers, impossible. In fact the reactivity of the mix in the stable suspension stage is often such that the same will proceed the solidification so rapidly that difficulties in handling or filling into containers may be experienced.

I have discovered that there is a certain differential reactivity with respect to the saponification agents in accordance with the invention between on the one hand fatty acids of the type saponifiable to yield voluminous metallic soaps, and on the other hand, abietic acid or rosin. Whereas the fatty acids in accordance with the invention are saponifiable to a satisfactory degree with relative speed at normal or slightly raised temperatures, abietic acid and rosin undergo saponification only very slowly at these temperatures. Small amounts of alcohol, however, will expedite the saponification reaction of rosin or abietic acid to a point where the same

is substantially equivalent to that of the fatty acids. Although the reactivity of the fatty acids is also enhanced by small amounts of alcohol this is to a much greater extent the case with rosin or abietic acid.

In accordance with the invention I prepare what may be termed a stable basic solidifiable hydrocarbon mix. This is accomplished by dissolving a mixture of a suitable fatty acid such as stearic acid, and rosin in the hydrocarbon to be solidified and then dispersing therein the saponification agent, as for example a finely divided sodium methylate or sodium hydroxide. If the proportion of fatty acid, as, for instance, stearic acid, present in the solution is so adjusted that it is just sufficient to bring the gel formation to a point where no stratification or segregation of dispersed saponification agent is observed upon discontinuance of agitation, only this gel will be formed and the rosin present, due to the difficulty with which the same is saponifiable under the conditions present in the solution will not react. The fatty soap gel thus formed may thereby be coordinated with the particle size of the suspended saponification agent to impart to the mix a viscosity sufficient to substantially maintain the suspension of saponification agent while the mix is quiescent. The resulting mix can be handled substantially as a liquid and in that condition is stable for a comparatively long period of time without complete and firm solidification. It is then only necessary for the purpose of completing the solidification, i. e., to complete the saponification of the unreacted rosin in the mix to add a relatively small amount of alcohol, whereupon the reaction will proceed in the manner hereinbefore stated. In many instances, the rosin saponification reaction proceeds more rapidly at least in the initial stages while at a slightly raised temperature as is the case when saponifying the fatty acid. For the purpose, therefore, of procuring ultimate solidification such as in suitable containers for distribution or use, I prefer to add the alcohol to the aliphatic acid soap mix, fill the resulting product into the containers, such as fuel containers, while raising the temperature of the mix either just preceding the container filling operation or while the product is in the containers to the temperature of expedited reaction.

Instead of dispersing the saponification agent in a mixture of a fatty acid and rosin, it is possible and sometimes of advantage to first disperse the saponification agent in a solution of the fatty acid alone. The rosin may then be added after completed saponification of the fatty acid either as such or in the form of a solution in a portion of the hydrocarbon to be solidified to obtain the substantially stable basic solidifiable hydrocarbon mix in accordance with the invention.

The procedure in accordance with the invention is for instance exemplified in the following example:

Example I

.6% of stearic acid and 5.5% of rosin was dissolved in a petroleum hydrocarbon cut of boiling range of 145 to 210° F. 1.3% of sodium methylate (calculated as crystal alcohol free) preferably produced by evaporating to dryness a mixture of equal parts by weight of substantially anhydrous sodium hydroxide and anhydrous methyl alcohol was thereupon added to the stearic acid and rosin containing hydrocarbon. The reaction mass was heated for a short period of time maintaining the temperature at approximately 40° C. with 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 hydrocarbon solution in finely pulverized dry form and kept in fine suspension therein by means of agitation. The resulting product containing the sodium stearate gel and containing unreacted saponification agent and unsaponified rosin is substantially stable and constitutes a product that may be completely solidified at any subsequent time. Such solidification was accomplished by adding thereto .9% of methyl alcohol, heating to approximately 40° C. and leaving the same substantially quiescent for completion of the solidification reaction.

The following example is furnished by way of illustrating an alternative procedure in accordance with the invention.

Example II

38 parts by weight of finely pulverized sodium hydroxide are covered with 50 parts by volume of a hydrocarbon cut identical with that described in connection with Example I. The mix is thoroughly ground while adding from time to time additional hydrocarbon up to a total of 100 parts by volume. The thusly obtained hydrocarbon dispersed sodium hydroxide is then extended with and dispersed in 1,000 parts by volume of hydrocarbon. 25 parts by weight of stearic acid are melted and dissolved in 100 parts by volume of hydrocarbon whereupon this solution is added to the sodium hydroxide hydrocarbon suspension prepared as above recited. The saponification reaction is almost immediate, resulting in the formation of a gel which imparts to the hydrocarbon a viscosity sufficient to maintain the unreacted sodium hydroxide particles in suspension. 175 parts by weight of molten rosin are dissolved in 2800 parts by volume of hydrocarbon whereupon the rosin solution is added to the sodium stearate soap gel with agitation and continuing the agitation for approximately five minutes. There is then added to the well agitated mix about 25 to 40 and preferably 30 parts by volume of methyl alcohol and the agitation continued for another one to two minutes. The mix becomes increasingly more viscous as the rosin saponification proceeds. The alcohol is preferably added slowly so as to prevent localized reaction. If desired, the alcohol may be added in solution in a portion of the hydrocarbon. During the last stages of the saponification reaction, the reaction mix is permitted to remain quiescent. After discontinuance of the agitation the relatively viscous mix is poured into containers in which solidification proceeds rapidly being satisfactorily completed in approximately fifteen minutes.

Satisfactory gel formation, i. e., gel formation yielding a satisfactory solidified product, can be easily checked by the bright yellow color which the reaction mix finally assumes at or near the end of the saponification reaction. If the color of the reaction mix is green or greenish, the final product will not be satisfactory in that segregation between the soap and the hydrocarbon to be solidified occurs.

The fatty acid in accordance with my invention, is preferably one carrying at least one carboxyl group in aliphatic chain linkage, of pref-

erably at least 12 carbon atoms in said chain. Fatty acids useful in accordance with the invention 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 proportions. Commercial products of this type are, for instance, coconut oil fatty acids, peanut oil fatty acids, palm oil fatty acids and the like. Within the preferred embodiment of my invention, however, I use stearic acid.

The saponification agent in accordance with my invention may be any agent capable of neutralizing the aliphatic acids, i. e., fatty acids and abietic acid or rosin, present in the hydrocarbon solution. Good results are preferably obtained with sodium saponification agents, such as, for instance, sodium hydroxide, sodium alcoholates, particularly sodium methylate and the like.

I prefer to suspend the saponification agent in the hydrocarbon in substantially anhydrous pulverulent finely dispersed form by either dispersing the dry saponification agent as such in the hydrocarbon solution of the fatty acid and rosin or by first preparing a fine dispersion of such saponification agent in substantially dry form in a part of the total hydrocarbon ultimately to be solidified and mixing such dispersion with the other part of such hydrocarbon in which the fatty acid and rosin have been dissolved. In many cases it is of advantage and desirable to expedite the reaction by passing the mix through a colloid mill or other device for procuring finest dispersion. A colloid mill or similar device may be also of advantage to procure finest dispersion in the case where preliminary dispersion of the saponification agent in a hydrocarbon is prepared.

When using alcoholates in accordance with the invention they 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 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 amount of reagents used within the practical application of my invention should be preferably so adjusted that the fatty acid and rosin in aggregate are present in the hydrocarbon solution in an amount sufficient to solidify substantially all of the hydrocarbon present with the soap gel formed. As a general rule, 4 to 10% in the aggregate of fatty acid and rosin will accomplish this result. Of this aggregate I prefer to use 5% to 15% fatty acid.

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.

The alcohol to be used in accordance with the invention for bringing the rosin saponification to the desired completion is preferably a primary aliphatic alcohol. The amount of alcohol to be used may vary with the particular alcohol used and depends inter alia upon considerations of solubility. I prefer to use methyl or ethyl alcohol. In most cases from 0.5% to 1.5% of added alcohol will bring the rosin saponification to the point of desired gel formation.

The alcohol need not necessarily be present in free form and will effect the rosin saponification reaction even when present in the form of crystal alcohol. It is sometimes of advantage however in the latter case to have a very small amount of free alcohol present to initiate the reaction thereby liberating further amounts of alcohol. Crystal alcohol content should therefore be taken into consideration. The total amount of free alcohol ultimately present in the product however should not appreciably exceed 3% by weight of the hydrocarbon as otherwise the characteristic of the products notably that of non-melting when heated or burning, may be deleteriously effected.

The products obtained in accordance with the invention are substantially homogeneous and firm, can be cut with a knife and handled as ordinary solids. The products will not liquify and will burn without melting. The products are further characterized by the fact that the 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 contained in the products in accordance with the invention in solidified form may be recovered by separation with the aid of suitable solvent extraction. In such case the extracting solvent is preferably one in which the metallic soap is preferentially soluble and in which the hydrocarbon material in the solidified product is but limitedly soluble or substantially insoluble. In most instances the latter type recovery of liquid 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 containing alcohol, the hydrocarbon and the metallic soap. The solidified products are 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 hydrocarbons.

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 in-

creasingly 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 equivalents wherein I have endeavored to claim broadly all inherent novelty.

I claim:

1. Method for solidifying a normally liquid inflammable hydrocarbon which comprises reacting a solution in said hydrocarbon of at least one member selected from a first group consisting of stearic acid, palmitic acid, oleic acid, coconut oil fatty acids, peanut oil fatty acids, and palm oil fatty acids, with a saponification agent of the group consisting of sodium hydroxide and sodium alcoholates, suspended with agitation in said solution in substantially dry pulverulent form, of the type reactable with said first group member to form a voluminous metallic soap gel from limitedly soluble to insoluble in said hydrocarbon, to thereby impart to said hydrocarbon a predetermined viscosity, thereafter reacting, in the presence of alcohol, at least one member, selected from a second group consisting of abietic acid and rosin, dissolved in said hydrocarbon, with a saponification agent of the group consisting of sodium hydroxide and sodium alcoholates, suspended in said hydrocarbon in substantially dry pulverulent form, of the type reactable with said second group member to form a voluminous metallic soap gel from limitedly soluble to insoluble in said hydrocarbon, to thereby solidify said hydrocarbon, and permitting the reaction mix to remain substantially quiescent during at least the last stages of the reaction, said viscosity being so coordinated to the particle size of saponification agent as to substantially maintain the same in suspension while the mix is quiescent, agitation being discontinued not earlier than the point at which said coordinated viscosity is present, said alcohol being present in amount not appreciably in excess of 3% by weight of the hydrocarbon.

2. Method for solidifying a normally liquid inflammable hydrocarbon which comprises preparing with agitation a suspension of a saponification agent in substantially dry pulverulent form and in excess of saponifying amount, in a solution in said hydrocarbon of at least one member selected from a first group consisting of stearic acid, palmitic acid, oleic acid, coconut oil fatty acids, peanut oil fatty acids, and palm oil fatty acids, said saponification agent being composed of at least one member selected from the group consisting of sodium hydroxide and sodium alcoholates of the type reactable with said first group member to thereby form a voluminous metallic soap gel from limitedly soluble to insoluble in said hydrocarbon, forming by saponification sufficient metallic soap to impart to the reaction mix a viscosity so coordinated with the particle size of unreacted suspended saponification agent as to substantially maintain the same in suspension while the mix is quiescent, agitation being discontinued not earlier than the point at which said coordinated viscosity is present, thereafter reacting, in the presence of alcohol, at least one member, selected from a second group consisting of abietic acid and rosin, dissolved in said hydrocarbon, with the unreacted portion of said saponification agent to thereby solidify said hydrocarbon, and permitting the reaction mix to remain substantially quiescent during at least the last stages of the reaction, said alcohol being present in amount not appreciably in excess of 3% by weight of the hydrocarbon.

3. Method for solidifying a normally liquid inflammable hydrocarbon which comprises preparing with agitation a suspension of sodium hydroxide in substantially dry pulverulent form in a solution in said hydrocarbon of stearic acid, said sodium hydroxide being present in excess of saponifying amounts, forming sufficient sodium stearate to impart to the reaction mix a viscosity so coordinated with the particle size of unreacted sodium hydroxide as to substantially maintain the same in suspension while the mix is quiescent, agitation being discontinued not earlier than the point at which said coordinated viscosity is present, thereafter reacting, in the presence of an aliphatic alcohol of not in excess of two carbon atoms, rosin dissolved in said hydrocarbon to thereby solidify said hydrocarbon, and permitting the reaction mix to remain substantially quiescent during at least the last stages of the reaction, said alcohol being present in amount not appreciably in excess of 3% by weight of the hydrocarbon.

4. Method according to claim 3 in which said stearic acid is present from 5 to 15% of the total stearic acid and rosin used and in which said alcohol is methyl alcohol in amount between 0.25 and 1.5% by weight of the hydrocarbon.

5. Method for solidifying a normally liquid inflammable hydrocarbon which comprises preparing with agitation a suspension of a saponification agent of the group consisting of sodium hydroxide and sodium alcoholates in substantially dry pulverulent form in a solution of a mixture of organic acids in said hydrocarbon, said mixture comprising at least one member selected from a first group consisting of stearic acid, palmitic acid, oleic acid, coconut oil fatty acids, peanut oil fatty acids, and palm oil fatty acids and at least one member selected from a second group consisting of abietic acid and rosin, said saponification agent being of the type reactable with said aliphatic acids to thereby form a voluminous metallic soap gel from limitedly soluble to insoluble in said hydrocarbon, saponifying said first group member, thereby forming sufficient metallic soap to impart to the reaction mix a viscosity so coordinated to the particle size of saponification agent as to substantially maintain said saponification agent in suspension while the mix is quiescent, agitation being discontinued not earlier than the point at which said coordinated viscosity is present, and thereafter saponifying said second group member in the presence of alcohol while said mix is substantially quiescent during at least the last stages of the reaction, said alcohol being present in amount not appreciably in excess of 3% by weight of the hydrocarbon.

6. Method in accordance with claim 5 in which said first group member is stearic acid and in which said second group member is rosin.

7. Method in accordance with claim 5 in which said first group member is stearic acid present from 5% to 15% of the total acids present and in which said second group member is rosin.

8. In a method for solidifying a normally liquid inflammable hydrocarbon the steps comprising preparing with agitation a suspension of a saponification agent of the group consisting of sodium hydroxide and sodium alcoholates in substantially dry pulverulent form in a solution of a mixture of organic acids in said hydrocarbon, said mixture comprising at least one member selected from a first group consisting of stearic acid, palmitic acid, oleic acid, coconut oil fatty acids, peanut oil fatty acids, and palm oil fatty acids, and at least one member selected from a second group consisting of abietic acid and rosin, said saponification agent being of the type reactable with said organic acids to thereby form a voluminous metallic soap gel from limitedly soluble to insoluble in said hydrocarbon and being present in at least stoichiometric amounts with respect to the total organic acids, and saponifying said first group member, thereby forming sufficient metallic soap to impart to the reaction mix a viscosity so coordinated to the particle size of saponification agent as to substantially maintain said saponification agent in suspension while the mix is quiescent, agitation being discontinued not earlier than the point at which the said coordinated viscosity is present.

9. The steps in accordance with claim 8 in which said first group member is stearic acid and in which said second group member is rosin.

10. The steps in accordance with claim 8 in which said first group member is stearic acid present from 5% to 15% of the total organic acids present and in which said second group member is rosin.

11. A normally liquid inflammable hydrocarbon product, solidifiable by saponification, which comprises predominating amounts of a normally liquid inflammable hydrocarbon, at least one voluminous metallic soap, selected from a first group consisting of the sodium salts of stearic acid, palmitic acid, oleic acid, coconut oil fatty acids, peanut oil fatty acids, and palm oil fatty acids, dispersed through said hydrocarbon and from limitedly soluble to insoluble therein, at least one member selected from a second group, consisting of unsaponified abietic acid and rosin, dissolved in said hydrocarbon, and unreacted saponification agent of the group consisting of sodium hydroxide and sodium alcoholates, said saponification agent being suspended in substantially dry pulverulent form in said hydrocarbon and being so coordinated in particle size to the viscosity imparted to said hydrocarbon by said first group member as to be substantially held in suspension thereby, the amounts of said second group member and of said saponification agent being sufficient upon reaction to substantially solidify the hydrocarbon present.

12. A normally liquid inflammable hydrocarbon product solidifiable by saponification, in accordance with claim 11 in which said first group member is sodium stearate and in which said second group member is rosin.

13. A normally liquid inflammable hydrocarbon product, solidifiable by saponification, in accordance with claim 11 in which said first group member is sodium stearate, in which said second group member is rosin and in which said saponification agent is at least one member selected from the group consisting of sodium hydroxide and sodium methylate, and said sodium stearate being present from 5% to 15% of the total sodium stearate and rosin.

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